Aroyl Peroxides. Part 7.[1] The Effects of Additives on the Thermolysis of Aroyl Peroxides in Arenes and the Elimination of Possible Complications in the Measurement of Partial Rate Factors for Phenylation

By **Roger Bolton, Bryce N. Dailly, Kazuko Hirakubo, Kong Hung Lee,** and **Gareth H. Williams,*** Department of Chemistry, Bedford College, Regents Park, London NW1 4NS

Competitive homolytic arylation of arenes has been carried out under conditions in which biaryl formation is maximised. Improved yields of biaryl were obtained with *o*-chloroanil, nitro- and nitroso-compounds, and transition metal salts; nitrosobenzene, pentafluoronitrosobenzene, copper(II) benzoate, and iron(III) benzoate caused nearly theoretical yields of biaryl and aroic acid. Partial rate factors, measured under such conditions, are free from uncertainties arising from the selective removal of σ-complexes by side-processes such as dimerisation. The possibility that arenes form complexes with aryl radicals or their precursors as a necessary part of the selection process between substrate molecules was not confirmed in studies of the application of the additivity principle and of the multiplication rule, and of variation in the relative concentration of the two competing arenes. The absence of any discrepancies indicates that the measured partial rate factors are not influenced by such putative complex formation. The mechanism of action of these catalysts has been investigated.

THE reactions of aroyl peroxides with arenes to give biaryls by homolytic arylation have been widely used for the synthesis of biaryls and also for the measurement of partial rate factors for arylation.[2] The usefulness of these reactions for both purposes is, however, seriously impaired by their tendency, in some instances, to give considerable amounts of high-boiling, resinous products consisting mainly of derivatives of isomeric tetrahydroquaterphenyls resulting from dimerisation of the σ-complexes formed by addition of aryl radicals to the substrate nucleus [reactions (1) and (2)].[3] In such reactions only a relatively small proportion of the σ-complexes gives biaryls by the chain-transfer reaction (3).[4] Reactions in which the substrate Ar'H is, for example, benzene, alkylbenzenes, fluorobenzene, and chlorobenzene proceed thus. However, in a few other substrates (*e.g.* bromobenzene and nitrobenzene) reaction (2) is largely superseded by (4) whereby biaryls are formed in much higher yield, and residue formation is minimised. Chain termination by (2) leads to 1.5-order induced decomposition whereas (4) leads to a first-order induced decomposition. Partial rate factors obtained from biaryl yields in reactions of the latter type are much less subject to possible errors arising from different rates of dimerisation and hence selective removal of the various σ-complexes which lead to biaryls.

$$\mathrm{Ar\cdot} + \mathrm{Ar'H} \longrightarrow [\mathrm{ArAr'H}]\cdot \quad (\sigma\cdot) \qquad (1)$$

$$2[\mathrm{ArAr'H}]\cdot \longrightarrow \text{dimers} \qquad (2)$$

$$[\mathrm{ArAr'H}]\cdot + (\mathrm{ArCO{\cdot}O})_2 \longrightarrow \mathrm{ArAr'} + \mathrm{ArCO_2H} + \mathrm{ArCO{\cdot}O\cdot} \qquad (3)$$

$$[\mathrm{ArAr'H}]\cdot + \mathrm{ArCO{\cdot}O\cdot} \longrightarrow \mathrm{ArAr'} + \mathrm{ArCO_2H} \qquad (4)$$

Reaction (2) can be suppressed, and (4), or its equivalents, promoted, by small amounts of certain additives in reactions in which (2) is the chief mode of chain-termination. These additives include nitroso- and nitroarenes,[5,6] and transition metal salts.[7,8] Oxidising agents, such as gaseous oxygen [9] and quinones [10] have also been reported to increase biaryl yields. We now report the results of a comprehensive survey of the effects of a number of additives on the reactions of aroyl peroxides with benzene a typical substrate in which reaction (2) is the main chain-termination process.[4a]

The results relating to the reaction of benzoyl peroxide with benzene are given in Table 1. All are averages of the results of at least two duplicate reactions, agreement between which was close.

o-*Chloranil*.—Dihydrobiphenyls are formed to the extent of 0.02 mol per mol peroxide in the reaction in the absence of additives, by disproportionation of σ-complexes (5), and can be oxidised to biaryls by *o*-chloranil added *after* the completion of the decomposition of the peroxide. The greater increase in biaryl yield when *o*-chloranil was present during the decomposition indicates that it also oxidises σ-complexes to biaryls. It is, however, not particularly efficient in increasing biaryl yields.

$$2[\mathrm{ArAr'H}]\cdot \longrightarrow \mathrm{ArAr'} + \mathrm{ArAr'H_2} \qquad (5)$$

Nitrosoarenes.—Nitrosobenzene and *m*-dinitrobenzene have long been known to be efficient additives and the mechanism of their action is understood.[6] Pentafluoronitrosobenzene appears to be even more efficient, and probably acts by an analogous mechanism. In both cases only small amounts are required.

Transition Metal Salts.—This survey confirms previous conclusions relating to copper(II) benzoate and cobalt naphthenate,[8] and leads to several generalisations.

(1) Copper(II) aroates, and iron(III) benzoate are the most efficient and convenient additives.

TABLE 1

Yields (mol per mol peroxide) of products of reactions of benzoyl peroxide (0.083 mol dm^{-3}) with benzene in the presence of additives (80°)

Additive (g per g peroxide)	Biphenyl	Benzoic acid	Residue [a]
None	0.381	0.276	0.422
o-Chloranil (1.0) [b]	0.561	0.490	
o-Chloranil (1.0)	0.660		
Nitrosobenzene (0.02)	0.869	0.955	
Pentafluoronitrosobenzene (0.02)	0.995	0.926	
m-Dinitrobenzene (0.2)	1.036	0.926	
Copper(II) benzoate (0.3)	0.800	0.797	0.114
Copper(II) benzoate (0.5)	0.825	0.806	
Copper(II) *p*-toluoate (0.5)	0.615	0.669	
Copper(II) *p*-chlorobenzoate (0.5)	0.949	0.885	
Copper(II) *p*-nitrobenzoate (0.5)	0.812	0.805	
Iron(III) benzoate (0.06)	0.653	0.707	0.226
Iron(III) benzoate (0.24)	0.797	0.867	0.117
Iron(III) benzoate (0.33)	0.842	0.907	0.100
Iron(III) benzoate (0.41)	0.943	0.966	0.077
Iron(III) benzoate (1.50)	0.932	0.954	0.024
Nickel(II) benzoate (0.3)	0.631	0.438	0.257
Ammonium benzoate (0.5)	0.354	0.258	0.424
Iron(III) acetate (0.2)	0.396	0.408	0.299
Copper(II) acetate (0.2)	0.737	0.737	0.105
Chromium(III) acetate (0.22)	0.635	0.298	0.279
Manganese(III) acetate (0.25)	0.363	0.299	0.378
Copper(II) naphthenate (1.0)	0.341		0.400
Cobalt(II) naphthenate (1.0)	0.522		0.417
Iron(III) chloride (0.32)	0.010	1.17	0.065
Iron(III) chloride (0.08)	0.14	1.04	0.05
Iron(III) chloride (0.03)	0.80	0.85	0.12
Copper(II) chloride (0.4)	0.652	0.953	0.151
Copper(I) chloride (0.4)	0.642	0.336	0.239
Nickel(II) chloride (0.4)	0.443	0.281	0.380
Copper(II) nitrate (0.43)	0.790	0.486	0.136
Oxygen	0.320	0.232	

[a] Calculated as tetrahydroquaterphenyl. [b] Added after completion of decomposition of peroxide.

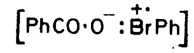
(2) Of the copper salts, the *p*-chlorobenzoate is the most efficient, being a little better than the benzoate, although this small advantage may be offset by the readier availability of the benzoate.

(3) Iron(III) benzoate is particularly effective as well as being convenient to use. It is more soluble in arenes than copper(II) benzoate although deposition of a form of iron(III) benzoate occurred during the reaction. Indeed many of the reactions with metal salts were not homogeneous, a fact which militates against adequate kinetic investigations of them.

(4) The effectiveness of iron(III) benzoate increases with its concentration, up to a maximum at *ca.* 0.5 mol per mol of the peroxide. Addition of dried commercial iron(III) benzoate, or iron(III) benzoate prepared as described below, in about this amount is therefore recommended as the best and most convenient general procedure for obtaining high yields of biaryls in this reaction.

(5) Salts other than aroates are less effective, and no advantage therefore accrues from their use. Iron(III) chloride is anomalous in drastically reducing the biaryl yield with a concomitant increase in the yield of benzoic acid. The reason for this is not clear, but presumably involves some reaction or association of benzoyloxyl radicals with the salt which inhibits their decarboxylation. The effect of iron(III) chloride in very low concentration is, however, different, since in these reactions the yields of both biphenyl and benzoic acid are substantially increased. It must be presumed that such concentrations are too low for this reaction or association to occur, and that the iron(III) salt aids the oxidation of σ-complexes to biaryls in a similar manner to iron(III) benzoate.

Mechanism of Transition Metal Catalysis.—In those substrates such as bromobenzene in which (4) rather than (2) is the main termination reaction, it has been suggested [4b] that the stationary concentration of benzoyloxyl radicals is increased by the formation of charge-transfer complexes of them with the substrate (I). The



$$[\mathrm{PhCO{\cdot}O^{-}:\overset{+\cdot}{Br}Ph}]$$

(I)

rate of (4) is therefore increased to such an extent that σ-complexes react thus, rather than by dimerisation. In substrates such as benzene or chlorobenzene, on the other hand, such complexes, if they are formed at all, are less stable, and hence the concentration of benzoyloxyl radicals is not increased sufficiently to render (4) more rapid than (2). The rates of these two processes are therefore rather finely balanced and it is relatively easy for that of (4) to be increased by electron transfer processes involving metals. Representing the metal as its ion (although in solvents such as arenes this is obviously an oversimplification), the stoicheiometry of such processes can be indicated by reactions such as (7)—(9) for iron(III) benzoate. This scheme is stoicheiometrically equivalent to (4), iron(III) being regenerated in (8). The

$$[\mathrm{ArAr'H}]^{\cdot} + \mathrm{Fe^{3+}} \longrightarrow \mathrm{ArAr'} + \mathrm{H^{+}} + \mathrm{Fe^{2+}} \qquad (7)$$

$$\mathrm{ArCO{\cdot}O{\cdot}} + \mathrm{Fe^{2+}} \longrightarrow \mathrm{ArCO{\cdot}O^{-}} + \mathrm{Fe^{3+}} \qquad (8)$$

$$\mathrm{ArCO{\cdot}O^{-}} + \mathrm{H^{+}} \longrightarrow \mathrm{ArCO_2H} \qquad (9)$$

regeneration of the metal in its higher valency state is required since quantities of the metal salts equimolar with that of the peroxide are not required to give almost theoretical yields of biaryls and benzoic acid. The reaction with copper(II) salts probably proceeds by similar oxidation and proton-loss by the σ-complex as in (7), rather than by the mechanism suggested by Hey *et al.*[8]

The rate constant for the reaction in benzene containing iron(III) benzoate in the presence of the radical-scavenger galvinoxyl to suppress all radical-induced reactions of the peroxide at 80.0° ($2.10 \pm 0.1 \times 10^{-5}$ s^{-1} over a four-fold range of peroxide concentrations and a four-fold range of catalyst : peroxide ratios) is comparable with that for the reaction in the absence of any additive at 78° (1.67×10^{-5} s^{-1}).[4a] Thus iron(III) benzoate has no significant influence on the rate of unimolecular decomposition, as is required by the mechanism suggested. Approximate measurements of the *total* rate of decomposition of the peroxide, in the presence of iron(III) benzoate, however, show that it is considerably faster than the uncatalysed reaction (k_{tot} *ca.* 14 × 10^{-5} s^{-1}) and that the rate shows little variation over the peroxide concentration range 0.04—0.165 mol dm^{-3} (Table 2).

TABLE 2

First-order rate constants for the decomposition of benzoyl peroxide in benzene in the presence of iron(III) benzoate (80°) ([catalyst]/[peroxide] 0.5)

[Peroxide]/mol dm^{-3}	$10^5 k_{\text{tot}}$/s^{-1}
0.165	13.4
0.0823	13.8
0.0412	13.9
0.0164	14.7
0.0083	17.4

The rate constant for the uncatalysed reaction is lower and varies linearly with the square root of the peroxide concentration, indicating a 1.5-order induced reaction.[4a] The induced decomposition in the catalysed reaction, which is approximately first-order, thus cannot be terminated by (2) and the kinetics are consistent with termination by (4) or its stoicheiometric equivalent (7)—(9). The observed increase in the rate constant at very low peroxide concentrations, and the observation that the approximately first-order reactions whose rates are given in Table 2 were preceded by faster reactions in the early stages of the decompositions, however, indicate that further complexities probably exist in the detailed manner in which metal benzoates participate in the induced decomposition.

TABLE 3

Yields (mol per mol peroxide) of products of reactions of aroyl peroxides with benzene in the presence and absence of iron(III) benzoate (0.018 mol dm^{-3}) (80°)

Peroxide (mol dm^{-3})	Iron(III) benzoate	Product yields (mol per mol peroxide)		
		Biaryl	Aroic acid	Residue [a]
o-Chlorobenzoyl (0.064)	—	0.284	0.484	0.477
o-Chlorobenzoyl (0.064)	+	0.938	0.858	0.042
m-Chlorobenzoyl (0.064)	—	0.450	0.473	0.320
m-Chlorobenzoyl (0.064)	+	0.865	0.808	0.028
p-Chlorobenzoyl (0.064)	—	0.447	0.423	0.424
p-Chlorobenzoyl (0.064)	+	0.804	0.853	0.041
o-Toluoyl (0.074)	—	0.367	0.537	0.331
o-Toluoyl (0.074)	+	0.817	0.752	0.065
p-Toluoyl (0.074)	—	0.522	0.350	0.355
p-Toluoyl (0.074)	+	0.734	0.910	0.022

[a] Calculated as appropriate tetrahydroquaterphenyl derivative.

Other Aroyl Peroxides.—Iron(III) benzoate is equally effective in the reactions of several other aroyl peroxides with benzene (Table 3). Its use therefore provides an improved general method for the synthesis of biaryls.

Oxygen.—There are two reports in the literature of the use of a stream of gaseous oxygen to bring about marked increases in the yields of biaryls and benzoic acid in the reactions of benzoyl peroxide with arenes.[9] We have, however, not been able to repeat this finding in a number of experiments under various conditions.

Partial Rate Factors for Phenylation.—The best hitherto available results are collected in two reviews.[2,9] There are two important potential complications which can arise in measurements of partial rate factors, namely (*a*) the possibility that the intermediate σ-complexes may be removed to different extents by various side reactions and (*b*) that radicals and/or their precursors may form complexes, of greater stability than the radicals or their precursors, with the arenes in a stage which precedes σ-complex formation.

The most important side reaction in (*a*) is combination of σ-complexes, which can lead to erroneous values of both relative rates of arylation (${}^{\mathrm{PhX}}_{\mathrm{PhH}}K$, PhH = 1) and of isomer distributions, from which partial rate factors are derived.

If (*b*) occurs, the intermolecular selection among different arenes by radicals (leading to relative rates as measured in competitive reactions) is affected by the relative stabilities of any complexes which may be formed, as well as by the reactivities of the arenes in the addition of the radicals to their nuclei to give the σ-complexes. Intramolecular selection within a single arene (isomer distributions) should be affected to a lesser extent, if at all. Complex formation of this kind would be expected to be most prevalent when wide differences exist between the polarities of the arene and the radical or its precursors. This has been considered to be the cause of discrepancies in partial rate factors for the pentafluorophenylation of arenes [11] and the phenylation of polyfluoroarenes.[12] In both these systems polarity differences are of such a magnitude as to render complex formation likely. Indeed stable complexes of arenes with polyfluoroarenes are well known.

We now report results bearing on the influence of both these complications upon the phenylation of arenes with benzoyl peroxide.

Reactions with Single Substrates.—Measurements of partial rate factors which are free from complication (*a*) can be made provided that all the experiments are conducted under conditions conducive to the quantitative or near-quantitative conversion of σ-complexes into biaryls. The results in Table 4 show that high-yield conditions can be realised in reactions of benzoyl peroxide with arenes by the use of iron(III) benzoate, generally the most efficient and least complicated of the additives. Similar results, which agreed well with those in Table 4,

TABLE 4

Effects of additives on reactions of benzoyl peroxide (1 g) with arenes (50 cm^3) (80°)

Arene	Additive [a]	Benzoic acid (mol per mol peroxide)	Biaryl (mol per mol (peroxide)	Isomer (%)		
				o	*m*	*p*
Chlorobenzene	None	0.339	0.402	54.6	27.2	18.2
	DNB	0.791	0.754	52.6	28.6	18.8
	PhNO	0.809	0.843	56.1	25.9	18.0
	Ph$_F$NO	0.707	0.805	58.2	24.4	17.4
	CuB	0.805	0.713	57.3	25.4	17.3
	FeB	0.973	0.945	58.0	23.9	18.1
Bromobenzene	None	0.954	0.745	54.2	30.4	15.4
	DNB	0.885	0.850	54.8	29.7	15.5
	PhNO	1.083	0.793	54.9	29.3	15.8
	Ph$_F$NO	0.841	0.824	54.0	29.8	16.2
	CuB	0.949	0.748	58.3	27.8	13.9
	FeB	0.983	0.962	54.3	29.4	16.3
Fluorobenzene	None	0.250	0.623	48.2	51.8 [b]	
	CuB	0.864	0.892	52.8	47.2 [b]	
	FeB	0.843	0.829	54.4	45.6 [b]	
p-Dichlorobenzene	None		0.664			
	CuB		0.888			
	FeB		0.974			
1,3,5-Trichlorobenzene	None		0.866			
	FeB		0.956			
Methyl benzoate	None	0.251	0.627	48.1	19.9	32.0
	CuB	0.799	0.801	56.6	16.3	27.1
	FeB	0.725	0.774	53.4	16.5	30.1
Benzophenone	None		0.844	40.0	21.1	38.9
	CuB		0.884	50.1	17.6	32.3
	FeB		0.987	47.7	18.6	33.7
Benzonitrile	None		0.723	52.3	17.4	30.3
	CuB		0.783	57.0	15.2	27.8
	FeB		0.834	57.6	15.7	26.7

[a] DNB = *m*-dinitrobenzene (0.18 g); PhNO = nitrobenzene (0.02 g); Ph$_F$NO = pentafluoronitrosobenzene (0.02 g); CuB = copper(II) benzoate (0.05 g); FeB = iron(III) benzoate (0.5 g). [b] *meta* + *para*.

were obtained with the nitro-compounds and with copper(II) benzoate.

In most cases, the isomer percentages obtained in the presence of additives differ somewhat from those obtained in their absence, although the differences are not of such a magnitude as to alter the broad pattern of homolytic phenylation of these arenes which has emerged from previous measurements. In these cases, the values obtained from the high-yield reactions show that the *ortho*-isomer is formed a little more abundantly than previously found, with a corresponding decrease in the relative yields of the *meta*- and *para*-isomers. It would appear, therefore, that in uncatalysed reactions the dimerisation of the σ-complexes leading to *ortho*-substitution is disproportionately rapid. This effect is, however, usually small.

Resolution of the gas chromatographic peaks due to 3- and 4-fluorobiphenyl is difficult, and we therefore measured combined yields of these products. The observed decrease in the proportion of the *ortho*-isomer when the phenylation is carried out in the presence of *m*-dinitrobenzene may be due to the reduction of nitro-compounds to nitroso-compounds which is thought to be the first of the sequence of steps whereby they influence the total reaction.[6] The effective catalyst for the dehydrogenation of the σ-complexes is thought to be the nitroso-compound. If nitro-groups are reduced more rapidly by the *ortho*- than by the *meta*- and *para*-σ-complexes, a decrease in the observed relative yield of 2-chlorobiphenyl would be expected. For this reason there must remain some doubt concerning the reliability of results obtained from reactions catalysed by nitro-compounds. The other catalysts are not subject to this uncertainty.

The phenylation of alkylbenzenes is complicated by concomitant hydrogen abstraction from the side-chain, giving benzyl-type radicals which dimerise to give derivatives of bibenzyl, *e.g.* (10) and (11).[13-16] Yields in

$$\mathrm{PhCH_3 + R\cdot \longrightarrow RH + PhCH_2\cdot} \qquad (10)$$

$$\mathrm{2PhCH_2\cdot \longrightarrow PhCH_2CH_2Ph} \qquad (11)$$

$(\mathrm{R\cdot = Ph\cdot\ or\ PhCO{\cdot}O\cdot})$

the phenylation of toluene (Table 5) are improved substantially by metal benzoates, but the proportions of the various products arising from side-chain and nuclear attack are only slightly affected, apart from a small increase in the proportion of 2-methylbiphenyl similar to those observed with other arenes and probably arising from the same cause. The proportion of side-chain attack is higher than that previously reported (13%).[13] It is likely that this discrepancy arises from the use in this work of a different and more reliable analytical method (g.l.c.). Slight differences between the isomer proportions now reported and those reported by previous workers for the uncatalysed reaction probably have a similar origin.

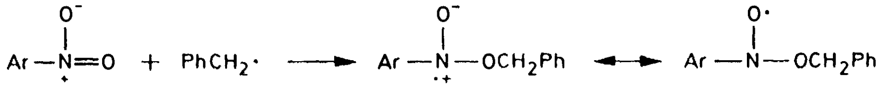
m-Dinitrobenzene is a rather inefficient catalyst in this reaction. It gives rise, however, to a marked *decrease* in

TABLE 5

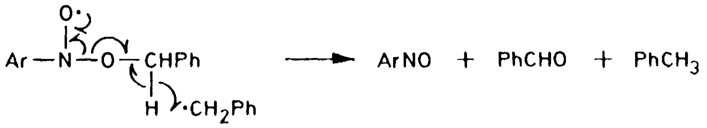
Effect of additives on reactions of benzoyl peroxide (1.5 g) with toluene (75 cm^3) (80°)

Additive (g)	Methylbiphenyls (mol per mol peroxide) *A*	Bibenzyl (mol per mol peroxide) *B*	*A* + *B*	% Side-chain attack	Isomer (%) *o*	Isomer (%) *m*	Isomer (%) *p*
None	0.382	0.119	0.501	23.8	61.6	24.5	13.9
DNB (0.2)	0.526	0.038	0.564	6.8	62.5	24.0	13.5
FeB (0.4)	0.576	0.170	0.746	22.7	63.9	20.1	16.0
CuB (0.4)	0.582	0.180	0.762	21.2	65.4	20.2	14.4

the yield of bibenzyl (to 6.8% side-chain attack with 0.2 g additive), as has been reported previously.[9] This probably arises from the consumption of benzyl radicals in reactions (12) and (13),[17] which result in reduction by benzyl radicals of the nitro-groups to nitroso-groups. The relative inefficiency of *m*-dinitrobenzene in increasing biaryl yields in this reaction is not unexpected. The accepted mechanism of the 'nitro-group effect' of increasing biaryls yields[6] involves dehydrogenation of σ-complexes by a stable diarylnitroxide [reaction (14)]. However, with an alkylbenzene (which, as the substrate, is present in high concentration) (14) may be superseded by (15), so that the nitroxide is no longer so effective in dehydrogenating the σ-complexes.



$$\mathrm{Ar{-}\underset{+}{\overset{O^-}{\overset{|}{N}}}{=}O + PhCH_2\cdot \longrightarrow Ar{-}\underset{\cdot +}{\overset{O^-}{\overset{|}{N}}}{-}OCH_2Ph \longleftrightarrow Ar{-}\overset{O\cdot}{\overset{|}{N}}{-}OCH_2Ph} \qquad (12)$$



$$\mathrm{Ar{-}\overset{O\cdot}{\overset{|}{N}}{-}O{-}\underset{\underset{H}{|}}{C}HPh \quad \cdot CH_2Ph \longrightarrow ArNO + PhCHO + PhCH_3} \qquad (13)$$

$$\mathrm{Ar\underset{\underset{Ph}{|}}{N}{-}O\cdot + PhC_6H_5CH_3\cdot \longrightarrow Ar\underset{\underset{Ph}{|}}{N}{-}OH + PhC_6H_4CH_3} \qquad (14)$$

$$\mathrm{Ar\underset{\underset{Ph}{|}}{N}{-}O\cdot + PhCH_3 \longrightarrow Ar\underset{\underset{Ph}{|}}{N}{-}OH + PhCH_2\cdot} \qquad (15)$$

The reaction of benzoyl peroxide with anisole has been reported to give unusually high yields (*ca.* 20%) of methoxyphenyl benzoates, arising from addition of benzoyloxyl radicals to the nucleus, and dehydrogenation of the resulting σ-complexes.[18] It therefore appeared necessary to take account of this benzoyloxylation in our investigation of the influence of additives on the stoicheiometry of this reaction. These results are given in Table 6, and show that in the uncatalysed reaction, methoxyphenyl benzoates are not formed in such high yields, but are in better agreement with a later report.[19] This reaction does, however, display several unusual features. First, the high yields of benzoic acid formed are notable. It has been suggested[20] that benzoyloxyl radicals abstract hydrogen from the side-chain, and products which may arise from this process have been detected.[19] Benzoic acid might also arise from reaction (16)[21] the phenol being formed by the well known free-radical dealkylation of anisole.[22,23] Both these processes are additional sources of benzoic acid, which depend upon the presence of the methoxy-group in the substrate.

Secondly, contrary to a previous report,[9] we find that the yield of methoxybiphenyls is not increased if a stream of oxygen is passed through the reaction mixture during the whole period of the decomposition of the peroxide. On the contrary, a decrease in this yield occurs, while the yield of esters is greatly increased.

TABLE 6

Effect of additives on reactions of benzoyl peroxide (1.09) with anisole (50 cm^3) (80°)

	Methoxybiphenyls				Methoxyphenyl benzoates				
Additive (g)	Yield (mol per mol peroxide) *A*	Isomer (%) *o*	Isomer (%) *m*	Isomer (%) *p*	Yield (mol per mol peroxide) *B*	Isomer (%) *o*	Isomer (%) *p*	*A* + *B*	Benzoic acid (mol per mol peroxide)
None	0.412	73.7	11.8	14.5	0.037	71.5	28.5	0.449	1.176
Oxygen	0.168				0.286			0.454	1.289
CuB (0.25)	0.453	70.2	19.3	10.5	0.365	69.0	31.0	0.818	1.043
FeB (0.45)	0.518	70.3	18.1	11.6	0.126	60.7	39.3	0.644	0.949
DNB (0.58)	0.367				0.085			0.454	1.213
$\mathrm{Ph_FNO}$ (0.01)	0.395				0.050			0.445	

Such increases in the ester yields are also brought about by the metal benzoates, but in this case, the biaryl yields are also increased. The metal benzoates are obviously capable of promoting the dehydrogenation of σ-complexes leading to phenylation, and therefore presumably, also of those leading to benzoyloxylation. The addition of aroyloxyl radicals to arenes is known to be reversible,[24] in contrast to the addition of phenyl radicals, which has been shown by Atkinson *et al.*[25] to be irreversible at 80°, although the opposite view has also been expressed.[26] It is therefore to be expected that acceleration of the dehydrogenation of the σ-complexes for benzoyloxylation should lead to an increase in the ester yield by inhibiting the retrogression of the initial addition (17). This effect is particularly noticeable with anisole because of the prevalence of benzoyloxylation with this substrate. It is likely that this process is unusually favoured because benzoyloxyl radicals become associated with the electron-rich methoxy-groups by the formation of a charge-transfer complex [reaction (18)]. The increase in the yield of the esters in the presence of oxygen probably arises from autoxidation of σ′·. The expected parallel increase in the biaryl yield which would arise from autoxidation of the σ-complexes for phenylation (σ·) is, however, not realised, and the observed decrease may result from scavenging of phenyl radicals by oxygen.

$$\mathrm{PhOH + (PhCO{\cdot}O)_2 \longrightarrow PhO{\cdot} + PhCO_2H + PhCO{\cdot}O{\cdot}} \qquad (16)$$

$$\mathrm{PhCO{\cdot}O{\cdot} + C_6H_5OMe \rightleftharpoons PhCO{\cdot}OC_6H_5OMe{\cdot} \xrightarrow{(-H\cdot)} PhCO{\cdot}OC_6H_4OMe} \qquad (17)$$

$$\mathrm{Ph{-}\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}Me + {\cdot}O{\cdot}CO{\cdot}Ph \rightleftharpoons \left[Ph{-}\overset{\cdot+}{\underset{\cdot\cdot}{O}}Me\ :\overset{-}{\underset{\cdot\cdot}{O}}{\cdot}CO{\cdot}Ph\right]} \qquad (18)$$

Nitroso- and nitro-compounds are not efficient additives with this substrate, possibly because of scavenging of the electrophilic nitroxide radicals by anisole as by toluene. High-yield conditions appear to be best achieved with the metal benzoates, and their effects on the distribution of the isomeric methoxybiphenyls and methoxyphenyl benzoates are given in Table 6. Unusually large amounts of the *ortho*-isomers are formed in the uncatalysed phenylation and benzoyloxylation reactions, possibly because the benzoyloxyl radicals exist largely in the form of their complexes with the methoxy-groups of anisole (18). If decarboxylation occurs in such complexes, phenyl radicals must be formed in close proximity to the *ortho*-positions, which may consequently display enhanced reactivity in phenylation, as well as in benzoyloxylation. The isomer percentages for both reactions are changed when metal benzoates are added but in contrast to the corresponding results for the other arenes (Tables 4 and 5), the relative yields of the *ortho*-isomers are reduced. The metal salts appear to inhibit the formation of the complexes which lead to enhanced *ortho*-reactivity, perhaps by themselves becoming associated with benzoyloxyl radicals. Benzoyloxylation of anisole apparently takes place only in the *ortho*- and *para*-positions, thus clearly illustrating the known electrophilicity of the benzoyloxyl radicals.[27] Again the apparent reactivity of the *ortho*-position is reduced by the metal benzoates, as would be expected if the metal salts inhibit the formation of complexes of benzoyloxyl radicals with methoxy-groups.

Reactions with Mixed Substrates.—Table 7 gives the results of experiments in which equimolar mixtures of benzene and other arenes were allowed to react with benzoyl peroxide in the presence and absence of iron(III) benzoate [and copper(II) benzoate in the case of anisole].

TABLE 7

Reactions of benzoyl peroxide (1 g) with equimolar mixtures (50 cm³) of benzene and arenes (ArH) in the presence and absence of additives (80°)

ArH	Additive (g)	PhAr (mol per mol peroxide)	Biphenyl (mol per mol peroxide)	Bibenzyl (mol per mol peroxide)	Methoxyphenyl benzoates (mol per mol peroxide)	Total binuclear products (mol per mol peroxide)	$^{\mathrm{ArH}}_{\mathrm{PhH}}K$	Isomers (%) in biaryls			Partial rate factors for phenylation		
								o	*m*	*p*	*o*	*m*	*p*
Chlorobenzene	None	0.305	0.268			0.573	1.14	54.6	27.2	18.2	1.9	0.9	1.2
	FeB (0.5)	0.510	0.356			0.866	1.43	57.6	26.1	17.3	2.5	1.1	1.5
Bromobenzene	None	0.441	0.300			0.741	1.47	54.2	30.5	15.3	2.4	1.35	1.35
	FeB (0.5)	0.548	0.359			0.907	1.53	54.5	29.5	16.0	2.3	1.35	1.5
Fluorobenzene	None	0.321	0.297			0.619	1.08	48.2	51.8 [a]		1.5	1.1	1.2
	FeB (0.5)	0.441	0.359			0.800	1.23	55.0	45.0 [a]		2.0	1.1	1.1
p-Dichlorobenzene	None	0.470	0.286			0.756	1.65						
	FeB (0.5)	0.635	0.321			0.956	1.98						
1,3,5-Trichlorobenzene	None	0.780	0.157			0.937	4.99						
	FeB (0.5)	0.766	0.158			0.924	4.86						
Methyl benzoate	None	0.555	0.294			0.849	1.89	48.1	19.8	32.1	2.7	1.1	3.6
	FeB (0.5)	0.620	0.306			0.926	2.03	53.6	16.5	29.9	3.3	1.0	3.6
Benzophenone	None	0.571	0.130			0.701	4.39	40.1	21.1	38.8	2.65	1.4	5.1
	FeB (0.5)	0.633	0.159			0.792	3.97	47.8	18.6	33.6	2.85	1.1	4.0
Benzonitrile	None	0.580	0.302			0.882	1.92	52.3	17.4	30.3	3.0	1.0	3.5
	FeB (0.5)	0.692	0.380			1.072	1.82	57.1	15.6	27.3	3.1	0.85	3.0
Toluene	None	0.294	0.165	0.062		0.521	1.81	62.6	24.0	13.4	3.4	1.3	1.5
	FeB (0.5)	0.445	0.272	0.055		0.772	1.64	60.9	21.6	17.5	3.0	1.1	1.7
Anisole	None	0.376	0.116		0.050	0.544	3.18	75.8	11.0	13.2	7.2	1.05	2.5
	FeB (0.5)	0.395	0.214		0.089	0.698	1.78	70.1	16.6	13.3	3.7	0.9	1.3
	CuB (0.06)	0.567	0.272		0.167	1.007	2.08	68.8	20.1	11.1	4.3	1.3	1.4

[a] *m* + *p*.

It is clear from the yields of the various biaryls that the results obtained with additives are much less subject to uncertainty. The differences between the results obtained with and without the additive are sometimes considerable, *e.g.* in chlorobenzene, where the yields are low in the uncatalysed reaction. In bromobenzene, which gives good yields of bromobiphenyls even without additives, the differences are smaller. The isomer distributions observed in competitive reactions are very close to those obtained from the reactions with single substrates (Table 4). Those in Table 7 were used in calculating partial rate factors. The partial rate factors for fluorobenzene given in Table 7 were calculated using the *meta* : *para* ratio (1.98 : 1) given by Lewis and Williams [28] who measured it by an i.r. spectrographic method. Any error entailed in this procedure is likely to be very small. While the bibenzyl formed from toluene must be estimated in order to assess the total yield, it does not enter into the calculation of the relative rate and partial rate factors for attack at the nuclear positions.

In the reactions with anisole, the presence of both iron(III) and copper(II) benzoate causes a large reduction in the apparent relative rate of phenylation of anisole. This is due partly to the fact that the catalysts increase the yield of biphenyl more than they do that of the methoxybiphenyls, since the yield of these products is already fairly high in the absence of additives (*cf.* Table 6). Secondly, if in the uncatalysed reaction complexes are formed between benzoyloxyl radicals and methoxy-groups, it is not unreasonable that the reactivity of anisole to phenyl radicals formed by the decarboxylation of these complexed benzoyloxyl radicals should appear to be unusually high. This relative rate should be reduced to its true value, if as was suggested earlier, the additives prevent this complex-formation, so that in their presence, the phenyl radicals are free, and are not formed in close proximity to anisole molecules. Copper(II) benzoate appears to be the better additive in these reactions, almost all the phenyl groups from the peroxide being accounted for as known products. Therefore the partial rate factors obtained from these experiments are thought to be the most reliable. The concentration of the additives appears to have little effect on these parameters, within the range investigated. Indeed very small amounts of copper(II) benzoate are effective in increasing the yields to a point at which the combined yield of all the simple products is close to its theoretical maximum.

Tests for Complex Formation.—Since conditions have been established for the measurement of partial rate factors free from the uncertainty arising from possible selective removal of σ-complexes, these factors can confidently be used to investigate the effects of possible complex formation between the substrates and the radicals or their precursors [complication (*b*)]. The following tests can be applied and should reveal complex formation, if it exists in these reactions, by causing observable discrepancies.

(1) If the measured partial rate factors reflect the activation energies of the various reactions of addition of *free* phenyl radicals to the various sites in the various substrates, the effects of several substituents in a nucleus on these activation energies can be expected to be additive. If, on the other hand, complexes are formed, the partial rate factors must also be partly dependent upon the relative stabilities of these complexes, and the effects of several substituents on these stabilities would not be expected to be additive. Thus breakdown of the 'additivity principle' is expected if complexes are formed.

(2) The relative rates of phenylation of the three possible pairs taken from three substrates A, B, and C should, in the absence of complications, be related by the 'multiplication rule' (19). If complexes are formed, and their relative stabilities are solvent-dependent (as

$$ {}^{\mathrm{A}}_{\mathrm{C}}K = {}^{\mathrm{A}}_{\mathrm{B}}K\,{}^{\mathrm{B}}_{\mathrm{C}}K \qquad (19) $$

they probably are), this rule would be expected to break down.

(3) If the above conditions prevail, measured relative rates would be expected to vary with the relative proportions of the competing substrates in the mixture, due allowance having been made for the unequal concentrations of the substrates. No such variation should be observed if the phenyl radicals are free, and select freely between the substrates.

Tests (1) and (2) have been applied to pentafluorophenylation of arenes, and to phenyldefluorination of polyfluoroarenes, where complex formation is likely.[11,12] Large discrepancies were revealed, and were taken as evidence for complex formation. We now report the application of all three tests to the phenylation of simple arenes.

Additivity Principle.—Table 8 gives the results of measurements of relative rates of phenylation of *p*-dichlorobenzene and 1,3,5-trichlorobenzene by means of competitive reactions with equimolar mixtures of each of these substrates with benzene in the presence and absence of additives. The measured relative rates are compared with relative rates calculated using the additivity principle from measured partial rate factors for the phenylation of chlorobenzene under the same conditions in each case (Table 7). The results indicate that large discrepancies exist between the observed and calculated relative rates, both derived from uncatalysed reactions,

TABLE 8

Reactions of benzoyl peroxide (1 g) with equimolar mixtures (50 cm^3) of benzene and *p*-dichlorobenzene or 1,3,5-trichlorobenzene (ArH) in the presence or absence of additives (0.5 g) (80°)

ArH	Additive	${}^{\mathrm{ArH}}_{\mathrm{PhH}}K$	${}^{\mathrm{ArH}}_{\mathrm{PhH}}K_{\mathrm{calc.}}$
p-Dichlorobenzene	None	1.65	1.15
	FeB	1.98	1.76
	CuB	2.13	2.01
1,3,5-Trichlorobenzene	None	4.99	2.15
	FeB	4.86	4.48

in some of which, particularly those with benzene and chlorobenzene (Table 7), yields were low. However, when all the parameters were derived from catalysed, high-yield reactions, such discrepancies as are revealed are small, and are likely to be within experimental error. The discrepancies in the uncatalysed reactions are therefore due to the inaccuracy of measurements made under these conditions. These experiments therefore do not provide any evidence for complex formation in these systems.

TABLE 9

Comparison of measured and calculated relative rates of phenylation of arenes in the presence and absence of additives (80°)

Arene (ArH)	' Intermediate ' arene	Additive	${}^{\mathrm{ArH}}_{\mathrm{PhH}}K_{\mathrm{obs}}$	${}^{\mathrm{ArH}}_{\mathrm{PhH}}K_{\mathrm{calc.}}$
Chlorobenzene	*p*-Dichlorobenzene	None	1.14	1.57
		CuB	1.51	1.51
		FeB	1.43	1.43
	1,3,5-Trichlorobenzene	None	1.14	1.40
		FeB	1.43	1.46
Bromobenzene	*p*-Dichlorobenzene	None	1.47	1.01
		CuB	1.46	1.53
		FeB	1.46	1.39
Anisole	Toluene	None	3.18	2.95
		FeB	1.79	2.14
		CuB	1.92	1.99 [a]

[a] ${}^{\mathrm{PhMe}}_{\mathrm{PhH}}K$ with iron(II) benzoate as catalyst used in the calculation.

Multiplication Rule.—Relative rates of phenylation of several pairs of arenes (chlorobenzene–*p*-dichlorobenzene, chlorobenzene–1,3,5-trichlorobenzene, bromobenzene–*p*-dichlorobenzene, and anisole–toluene) have been measured by means of competitive experiments using equimolar mixtures of these arenes in the presence and absence of additives, and have been used to calculate relative rates of phenylation of monosubstituted benzenes (benzene = 1) using the multiplication rule in the form ${}^{\mathrm{A}}_{\mathrm{PhH}}K = {}^{\mathrm{A}}_{\mathrm{B}}K\,{}^{\mathrm{B}}_{\mathrm{PhH}}K$. These calculated relative rates are compared with directly measured values in Table 9. There are substantial differences between the observed and calculated values for chlorobenzene and bromobenzene from reactions in which no catalysts were used, but the agreement is much better if results from catalysed reactions only are used. For anisole, the observed and calculated values agreed quite well even for uncatalysed reactions, although this agreement may be fortuitous. However, it is clear from the comparisons in Table 9 that once errors arising from σ-complex dimerisation are eliminated by the use of additives, the discrepancies become so small as not to provide evidence for complex formation. The discrepancies reported by Davies *et al.*[29] in experiments of this type with *p*-dichlorobenzene as the intermediate arene may have arisen because the competitive experiments were conducted without the use of additives to increase biaryl yields.

Variation of Relative Proportions of Arenes.—Relative rates measured directly in competitive experiments with mixtures of benzene and several arenes in different relative concentrations, with additives, are reported in Table 10. It is clear from these results that the differences observed are small and unsystematic. They are probably within experimental error, and the results do not therefore support the hypothesis that complexes are formed.

Thus tests for complex-formation have been applied in reactions of phenyl radicals with benzene, chlorobenzene, *p*-dichlorobenzene, 1,3,5-trichlorobenzene, bromobenzene, toluene, and anisole. None of these tests has provided any convincing evidence for the formation of complexes of the substrates with the phenyl radical or its precursors, in sharp contrast to previous results with polyfluorinated radicals or substrates. It is concluded that differences of polar character between phenyl radicals and these simple arenes are not of such a magnitude as to conduce to complex formation to an extent sufficient to have any significant effect on partial rate factors for phenylation of these arenes.

TABLE 10

Effect of variation of relative substrate concentrations on measured relative rates of phenylation of arenes (ArH) (80°)

ArH	Molar ratio ArH : PhH	Additive	${}^{\mathrm{ArH}}_{\mathrm{PhH}}K$
Chlorobenzene	2 : 1	FeB	1.39
	3 : 2	FeB	1.43
	1 : 1	FeB	1.43
	2 : 3	FeB	1.32
	1 : 2	FeB	1.31
Toluene	3 : 1	FeB	1.44
	1 : 1	FeB	1.55
	1 : 3	FeB	1.54
Anisole	2.8 : 1	CuB	1.69
	1 : 1	CuB	1.62
	1 : 3	CuB	1.72
Anisole	1.8 : 1	FeB	1.78
	1 : 1	FeB	1.81
	1 : 3	FeB	1.67
	1 : 5	FeB	1.70

Partial rate factors obtained from experiments in which iron(III) benzoate ensures the formation of high yields of biaryls are self-consistent, and unaffected by selective loss of σ-complexes by dimerisation. These factors, which are given in Table 7, being substantially uninfluenced by complications (*a*) and (*b*) are probably therefore the most reliable so far reported and can be regarded as valid indices of the reactivities of the various nuclear sites in these arenes to addition of phenyl radicals. For anisole, copper(II) benzoate catalysed reactions were used, because these reactions consistently gave higher yields than those with this arene and iron(III) benzoate. The unusually high values of F_{o}, but not F_{p}, for anisole is easily understood in terms of the postulate made earlier that benzoyloxyl radicals are associated closely with the methoxy-groups. The partial rate factors for methyl benzoate, benzonitrile, and benzophenone, all of which contain a multiple bond conjugated with the aromatic nucleus, display activation of both *ortho-* and *para*-positions. This activation is thought to arise from the ability of these conjugated groups to contribute to the delocalisation of the unpaired electron in the σ-complexes for *ortho-* and *para*-substitution, thus increasing the stability of these, and hence increasing the reactivities of the *ortho-* and *para*-positions in these arenes. The *meta*-positions are unaffected since no such delocalisation is possible in the σ-complex for *meta*-substitution.[30] In this respect the behaviour of these arenes is akin to that of nitrobenzene and biphenyl, which have the same structural feature. The remaining partial rate factors in Table 7 do not differ greatly from those previously reported,[2] and do not necessitate any drastic revision of previous views concerning this reaction. For the reasons already stated, however, they are probably more reliable than the earlier results.

EXPERIMENTAL

AnalaR benzene was desulphurised with concentrated sulphuric acid, washed, dried, and fractionally distilled. Commercially available solids were crystallised to constant m.p. Liquids, including arenes other than benzene, were dried and fractionally distilled. Their purity was monitored by g.l.c.

Peroxides.—Commercial benzoyl peroxide was purified as described by Hey and Walker.[31] *o*-Chlorobenzoyl peroxide was prepared by the general method described by Price and Krebs,[32] m.p. 100° (lit., 95°,[33] 102—103° [34]). *m*-Chlorobenzoyl peroxide, m.p. 122° (lit., 123°,[33] 122—123° [34]), and *p*-chlorobenzoyl peroxide, m.p. 138° (lit., 138° [31,35]), were prepared by the general method described by Hey and Walker.[31] *o*-Toluoyl peroxide was prepared by Price and Krebs' general method,[32] m.p. 53° (lit., 52.5—53.5° [33]). *p*-Toluoyl peroxide was prepared by the method of Swain *et al.*,[36] m.p. 137° decomp.) [lit., 136—137° (decomp.),[36] 136° (decomp.) [37]].

Additives.—*o*-Chloranil was conveniently prepared as described by Hey *et al.*[38] Pentafluoronitrosobenzene was commercial material (Bristol Organics Ltd). Copper(II) benzoate was made by heating ethanolic solutions of the aroic acid and copper(II) acetate. The copper(II) aroates which precipitated from the solutions at 0° were filtered off, washed, and dried to constant weight. Iron(III) benzoate was either dried commercial material or was prepared by mixing equimolar aqueous solutions of iron(III) chloride and sodium benzoate. The precipitated iron(III) benzoate was filtered off, washed, and dried. Other metal salts were dried commercial specimens.

Reference Compounds.—Halogenobiphenyls (except 2- and 4-fluorobiphenyl) were prepared by three methods: (*a*) by heating a solution of the appropriate halogenoaniline and pentyl nitrite in benzene;[39] (*b*) by the Sandmeyer reaction from the appropriate aminobiphenyl; and (*c*) by decomposition of the appropriate halogenbenzoyl peroxide in benzene.

All the halogenobiphenyls used are known and their m.p.s or b.p.s conformed closely to those recorded in the literature.[40] Method (*a*) is recommended as a suitable general procedure, which was also used for the preparation of the methylbiphenyls.

2-Phenylbenzophenone, m.p. 86° (lit.,[40] 90°), was prepared by treatment of the Grignard reagent derived from 2-iodobiphenyl with benzaldehyde in benzene and subsequent oxidation of the product.

3-Phenylbenzophenone, m.p. 79° (lit.,[40] 79°), was prepared by refluxing the Grignard reagent derived from 3-bromobiphenyl with benzonitrile in ether. The resulting ketimine was hydrolysed to give the ketone by refluxing with hot aqueous hydrochloric acid. The ketone was obtained by fractional distillation *in vacuo*, b.p. 264—267° at 25 mmHg, and crystallised from light petroleum.

4-Phenylbenzophenone, m.p. 102° (lit.,[41] 104—105°), was prepared by the Friedel–Crafts reaction of benzoyl chloride with biphenyl in benzene in the presence of aluminium chloride.

2-, 3-, and 4-methoxycarbonylbiphenyl were prepared by Saltiel and Curtis' method,[42] m.p.s 114, 160, and 118° respectively (lit.,[42] 114—115, 160—161, and 117—118°, respectively).

The 2-, m.p. 33°, 3-, m.p. 44°, and 4-, m.p. 86°, cyanobiphenyls were prepared by refluxing solutions of the corresponding bromobiphenyls (16 g) and copper(I) cyanide (7.8 g) in dimethylformamide (10.5 cm^3) for 6 h. The resulting mixtures were poured into a solution of hydrated iron(III) chloride in concentrated hydrochloric acid (14 cm^3) and water (8.3 cm^3). After the mixture had been maintained at 60—70° for 20 min and cooled, the separated organic layer was steam distilled. Extraction with ether, removal of ether from the dried ($MgSO_4$) extracts, and distillation *in vacuo* gave the cyanobiphenyls (lit., m.p.s: 2-, 30—32; 3-, 43—45; 4-, 85—86° [43]).

2-Methoxybiphenyl, m.p. 29° (lit.,[44] 29°), was prepared by methylation of 2-hydroxybiphenyl (B.D.H.) with dimethyl sulphate in aqueous alkali. 3-Methoxybiphenyl, b.p. 130—134° at 0.1 mmHg (lit.,[45] 136—138° at 2 mmHg) was isolated from the reaction of *m*-anisidine and pentyl nitrite with benzene at 80°,[39] and the 4-isomer by methylation of 4-hydroxybiphenyl with dimethyl sulphate, m.p. 84° (lit.,[40] 85°).

o- and *p*-methoxyphenyl benzoate were prepared by benzoylation of the corresponding phenols, m.p.s 57—58 and 73—74°, respectively (lit., 58 [40] and 75° [46] respectively).

Biphenyl (B.D.H.), bibenzyl (B.D.H.), and 2- and 4-fluorobiphenyl (Koch-Light) were crystallised from aqueous ethanol, m.p.s 71, 52, 74, and 74°, respectively (lit.,[40] 71, 52, 73.5, and 74.2°, respectively).

Reactions of Aroyl Peroxides with Single and Mixed Arenes.—Solutions of the peroxide in the arene or mixture of arenes (50 or 100 cm^3) containing the appropriate additive, when such was used, were maintained at 80° under nitrogen for 72 h when decomposition of the peroxide was complete. After addition of the internal standard for g.l.c. analysis and filtration, if necessary, to remove metal salts, the cold solutions were extracted with aqueous sodium hydrogencarbonate (6 × 20 cm^3), to remove the aroic acid, which was quantitatively recovered from the aqueous extracts by acidification and repeated extraction with dichloromethane.

TABLE 11

Chromatography of reaction products

Arene(s)	Instrument [a]	Internal standard	Column [b]	Temperature (°C)
Chlorobenzene	1	Diphenylmethane	A	170
Chlorobenzene–benzene	1	Diphenylmethane	A	170
Bromobenzene	1	Diphenylmethane	A	200
Bromobenzene–benzene	1	Diphenylmethane	A	200
Fluorobenzene	1	Pentamethylbenzene	B	160
Fluorobenzene–benzene	1	Pentamethylbenzene	B	160
Toluene	1	Pentamethylbenzene	A	150
Toluene	1	Pentamethylbenzene	D	130
Toluene–benzene	1	Pentamethylbenzene	A	150
Toluene–benzene	1	Pentamethylbenzene	D	130
Toluene–benzene	1	Pentamethylbenzene	C	200
Anisole	2	Pentamethylbenzene	A	200
Anisole–benzene	2	Pentamethylbenzene	A	200
Anisole–toluene	2	Pentamethylbenzene	D	130
p-Dichlorobenzene	1	Bibenzyl	C	200
p-Dichlorobenzene–benzene	1	Bibenzyl	C	200
p-Dichlorobenzene–chlorobenzene	1	Diphenylmethane	A	170
p-Dichlorobenzene–chlorobenzene	1	Bibenzyl	C	200
p-Dichlorobenzene–bromobenzene	1	Diphenylmethane	A	200
p-Dichlorobenzene–bromobenzene	1	Bibenzyl	C	200
1,3,5-Trichlorobenzene	1	Bibenzyl	C	200
1,3,5-Trichlorobenzene–benzene	1	Bibenzyl	C	200
1,3,5-Trichlorobenzene–chlorobenzene	1	Diphenylmethane	A	170
1,3,5-Trichlorobenzene–chlorobenzene	1	Bibenzyl	C	280
Methyl benzoate	1	Bibenzyl	B	200
Methyl benzoate–benzoate	1	Bibenzyl	B	200
Benzonitrile	2	Bibenzyl	A	180
Benzonitrile–benzene	2	Bibenzyl	A	180
Benzophenone	2	Triphenylmethane	A	200
Benzophenone–benzene	2	Triphenylmethane	A	200

[a] Instrument 1, Perkin-Elmer F21D; instrument 2, Pye 104. [b] A = 8 ft × $\frac{1}{8}$ in O.D., packed with 15% Apiezon L grease on 100—120 mesh Celite (Embacel). B = 8 ft × $\frac{3}{8}$ in O.D., packed with 20% Apiezon L grease on 100—120 mesh Celite. C = 8 ft × $\frac{3}{8}$ in O.D., packed with 20% Carbowax on 100—120 mesh Celite. D = 8 ft × $\frac{1}{8}$in O.D., packed with 15% silicone elastomer E301 on 100—120 mesh Celite. E = 8 ft × $\frac{1}{8}$ in O.D., packed with 20% silicone elastomer E301 on 100—120 mesh Celite.

In the reactions with metal aroates, after filtration and before extraction with sodium hydrogencarbonate, the solutions were shaken with 50% aqueous orthophosphoric acid to hydrolyse the metal salts. The acid extracts, and water washings of the organic phase, were rejected. Allowance was made for the quantity of aroic acid formed by the hydrolysis of the salts in calculating the yield of aroic acids formed in the reactions themselves. Solvent was removed from the dried ($MgSO_4$) organic layers using a rotary evaporator or by fractional distillation. The solvent removed was monitored by g.l.c. analysis to ensure that it contained no biaryls. In some reactions esters formed in the reactions were hydrolysed by refluxing for 6 h with ethanolic potassium hydroxide (20 cm^3 of 10% solution). While still warm, the mixture was extracted with benzene (2 × 20 cm^3); these extracts were re-extracted twice with dilute aqueous potassium hydroxide. Benzene was removed from the washed and dried organic portion. The biaryls in the residue were then estimated by g.l.c. analysis as described below. The presence of the esters was later found not to affect the analysis for biaryls, and in later reactions, including those from which partial rate factors were obtained, this stage was omitted. Results of duplicate experiments agreed to within 2%.

In the uncatalysed decomposition of benzoyl peroxide in benzene, dihydrobiphenyls were estimated by Gill and Williams' method.[4a]

Analysis of Mixtures of Biaryls.—Reaction products were identified by comparison of their retention times with those of authentic specimens under identical conditions using at least two column packings of different polarities. After the identification, the detector was calibrated for quantitative analysis by the method of internal standardisation. Standard solutions were made up containing each reaction product in turn with the appropriate internal standard. A number of such solutions covering a wide range of relative concentrations was prepared for each component. Each such solution was analysed three times by g.l.c. using the appropriate conditions as given in Table 11. In all cases the carrier gas was nitrogen at 1 kPa cm^{-2} except for the toluene–benzene product on column packing C, when it was 1.5 kPa cm^{-2}.

Good agreement was always obtained between duplicate analyses and the mean heights for the components relative to the standard were used to plot calibration curves for all of the products. In some cases peak areas were also plotted similarly, and gave identical results in the analyses. No particular advantage accrued from the use of peak areas, provided a sufficiently wide range of relative concentrations was used in the construction of the calibration graphs based on peak heights. The calibration graphs were used to determine the concentrations of the various components in the product mixtures, by reference to the internal standard in each case. The accuracy of the method was checked by the analysis of appropriate synthetic mixtures of known concentration. It was possible to analyse these mixtures to within 2%. Special procedures, as detailed below, had to be used in certain cases, particularly when resolution of components was difficult or incomplete.

Chlorobenzene and Mixtures containing Chlorobenzenes.—Since 3- and 4-chlorobiphenyl were not completely resolved even under the best conditions (Table 11), correction factors were applied. Calibration curves were constructed for each isomer individually with diphenylmethane as standard. A number of solutions was also made up, each containing the same concentration of diphenylmethane with both 3- and 4-

chlorobiophenyl in different concentrations relative to each other. Values of the known mole ratio of each isomer relative to diphenylmethane in these solutions were then plotted against the values of these relative mole ratios obtained by the use of the individual calibration curves for each isomer. The slopes of the straight lines so obtained gave correction factors which were applied to the relative mole ratios obtained directly from the individual calibration curves. In the reactions with chlorobenzene–*p*-dichlorobenzene mixtures the yields of the chlorobiphenyls were obtained by using column A and diphenylmethane as described above for the chlorobenzene reactions, and the yields of 2,5-dichlorobiphenyl by using column C with bibenzyl as internal standard (*cf.* Table 11). A similar procedure was employed for the products of the reactions with chlorobenzene–1,3,5-trichlorobenzene mixtures.

Bromobenzene–p-*Dichlorobenzene Mixtures*.—The yields of the bromobiphenyls were obtained using column A and diphenylmethane as in reactions with bromobenzene alone, and the yields of 2,5-dichlorobiphenyl using column C with bibenzyl as internal standard (*cf.* Table 11).

Fluorobenzene and Mixtures containing Fluorobenzenes.—While biphenyl and 2-fluorobiphenyl were well resolved from one another and from other components, 3- and 4-fluorobiphenyl could not be separated on any of the columns. Calibration curves for biphenyl and 2- and 4-fluorobiphenyl against pentamethylbenzene were therefore constructed. Analysis of synthetic mixtures containing all three isomeric fluorobiphenyls showed that an accurate estimate of the sum of their contents of 3- and 4-fluorobiphenyl could be obtained by the use of the calibration curve for 4-fluorobiphenyl (*cf.* Tables 4 and 7).

Toluene and Mixtures containing Toluene.—With column A, bibenzyl could not be separated from 4-methylbiphenyl, and this combined peak overlapped slightly that due to 3-methylbiphenyl. The other components were well resolved. With column D, bibenzyl and 2-methylbiphenyl were well resolved, but 3- and 4-methylbiphenyl emerged as a single peak. Calibrations with both of these columns for each component separately, and the use of standard solutions containing pentamethylbenzene with different relative amounts of 3- and 4-methylbiphenyl (column A), as described above for 3- and 4-chlorobiphenyls allowed a complete analysis to be made. This was accurate to within 2% for bibenzyl and 2-methylbiphenyl, and 3% for the 3- and 4-isomers, as indicated by the analysis of synthetic mixtures of known composition, made up from authentic specimens of the several components. The products of reactions with benzene–toluene mixtures contained biphenyl as well as the above components. Biphenyl and 2-methylbiphenyl were not resolved on columns A and D. An additional analysis using column C (*cf.* Table 11) on which these components were well resolved, was therefore necessary to obtain the relative yields of biphenyl in these reactions.

Anisole and Mixtures containing Anisole.—After reaction the neutral fractions containing biaryls and methoxyphenyl benzoates were not concentrated, but were analysed directly by g.l.c. Column A did not completely resolve the 3- and 4-methoxybiphenyls, and correction factors obtained as described above for 3- and 4-chlorobiphenyl were applied. The esters were well resolved, and their yields were obtained by the use of appropriate calibration curves. No corrections were necessary. A small unidentified peak emerged immediately before (but well resolved from) that due to 2-methoxyphenyl benzoate in the reactions in the absence of metal benzoates. In the analysis of the binuclear products of the reactions with mixtures of anisole and toluene, the yields of bibenzyl, 2-methylbiphenyl, and 3- and 4-methylbiphenyls together were obtained using column D as described above for the reactions with toluene. The yields of the methoxybiphenyls were obtained with the same column. The yields of esters in these products were not determined.

Kinetics.—The rate of the unimolecular decomposition of benzoyl peroxide in benzene was measured spectrophotometrically, and the total rate of decomposition titrimetrically as described by Gill and Williams.[4a]

We thank the S.R.C. for a grant to B. N. D. and Bedford College for a grant to K. H.

[0/650 *Received*, 1*st May*, 1980]

REFERENCES

[1] Part 6, Y. Rees and G. H. Williams, *J. Chem. Soc., Perkin Trans. 1*, 1974, 2266.

[2] G. H. Williams, Chem. Soc. Special Publication No. 24, 1970, p. 25; M. J. Perkins, ' Free Radicals,' ed. J. K. Kochi, Wiley, New York, 1973, vol. II, p. 231.

[3] B. M. Lynch and K. H. Pausacker, *Aust. J. Chem.*, 1957, **10**, 40; D. F. De Tar and R. A. J. Long, *J. Am. Chem. Soc.*, 1958, **80**, 4842; G. A. Razuvaev, B. G. Zateev, and G. G. Petukhov, *Proc. Acad. Sci. USSR*, 1960, **130**, 366; D. H. Hey, M. J. Perkins, and G. H. Williams, *J. Chem. Soc.*, 1963, 5604; D. F. De Tar, R. A. J. Long, J. Rendleman, J. Bradley, and P. Duncan, *J. Am. Chem. Soc.*, 1967, **89**, 4051.

[4] G. B. Gill and G. H. Williams, *J. Chem. Soc.*, 1965, (*a*) 995; (*b*) 7127.

[5] D. H. Hey, M. J. Perkins, and G. H. Williams, *Chem. Ind.* (*London*), 1963, 83; G. B. Gill and G. H. Williams, *J. Chem. Soc. B*, 1966, 880.

[6] G. R. Chalfont, D. H. Hey, K. S. Y. Liang, and M. J. Perkins, *Chem. Commun.*, 1967, 367; *J. Chem. Soc. B*, 1971, 233.

[7] M. S. Kharasch and A. Fono, *J. Org. Chem.*, 1958, **23**, 324; 1959, **24**, 72; M. S. Kharasch and G. Sosnovsky, *J. Am. Chem. Soc.*, 1958, **80**, 756; M. S. Kharasch, G. Sosnovsky, and N. C. Yang, *ibid.*, 1959, **81**, 5819; G. Sosnovsky and N. C. Yang, *J. Org. Chem.*, 1960, **25**, 899.

[8] D. H. Hey, K. S. Y. Liang, and M. J. Perkins, *Tetrahedron Lett.*, 1967, 1477.

[9] M. Eberhardt and E. K. Eliel, *J. Org. Chem.*, 1962, **27**, 2289; R. T. Morrison, J. Cazes, N. Samkoff, and C. H. Howe, *J. Am. Chem. Soc.*, 1962, **84**, 4152.

[10] C. D. Hall, *Chem. Ind.* (*London*), 1965, 384.

[11] R. Bolton, J. P. B. Sandall, and G. H. Williams, *J. Chem. Res.*, 1977 (S), 24, (M), 373.

[12] R. Bolton, J. P. B. Sandall, and G. H. Williams, *J. Fluorine Chem.*, 1974, **4**, 355.

[13] R. L. Dannley and B. Zaremsky, *J. Am. Chem. Soc.*, 1955, **77**, 1588.

[14] D. H. Hey, B. W. Pengilly, and G. H. Williams, *J. Chem. Soc.*, 1956, 1463.

[15] F. F. Gadallah and R. M. Elofson, *J. Org. Chem.*, 1969, **34**, 3335.

[16] M. J. Perkins, Ph.D. Thesis, London, 1962.

[17] R. A. Jackson and W. A. Waters, *J. Chem. Soc.*, 1960, 1653.

[18] B. M. Lynch and R. B. Moore, *Can. J. Chem.*, 1960, **40**, 1461.

[19] R. A. McClelland, R. O. C. Norman, and C. B. Thomas, *J. Chem. Soc., Perkin Trans. 1*, 1972, 562.

[20] D. R. Augood and G. H. Williams, *Chem. Rev.*, 1957, **57**, 123.

[21] J. J. Batten and M. F. R. Mulcahy, *J. Chem. Soc.*, 1956, 2948; J. J. Batten, *ibid.*, p. 2959.

[22] B. R. Cowley, R. O. C. Norman, and W. A. Waters, *J. Chem. Soc.*, 1959, 1799.

[23] M. S. Kharasch and R. L. Huang, *J. Org. Chem.*, 1952, **17**, 669.

[24] T. Nakata, K. Tokumaru, and O. Simamura, *Tetrahedron Lett.*, 1967, 3303; M. E. Kurz and P. Kovacic, *J. Org. Chem.*, 1968, **33**, 1950; *J. Am. Chem. Soc.*, 1966, **88**, 2068; P. Kovacic, C. G. Reid, and M. J. Brittain, *J. Org. Chem.*, 1970, **35**, 2152.

[25] D. J. Atkinson, M. J. Perkins, and P. Ward, *J. Chem. Soc. C*, 1971, 3240.

[26] M. Kobayashi, H. Minito, and N. Kobori, *Bull. Chem. Soc. Jpn.*, 1969, **42**, 2738; R. Henriquez, A. R. Morgan, P. Mulholland, D. C. Nonhebel, and G. G. Smith, *J. Chem. Soc., Chem. Commun.*, 1974, 987; R. Henriquez and D. C. Nonhebel, *Tetrahedron Lett.*, 1975, **44**, 3855, 3857.

[27] M. E. Kurz and M. Pellegrini, *J. Org. Chem.*, 1970, **35**, 990.

[28] P. Lewis and G. H. Williams, *J. Chem. Soc. B*, 1969, 120.

[29] D. I. Davies, D. H. Hey, and B. Summers, *J. Chem. Soc. C*, 1971, 2681.

[30] G. H. Williams, *Chem. Ind. (London)*, 1961, 1286.

[31] D. H. Hey and E. W. Walker, *J. Chem. Soc.*, 1948, 2213.

[32] C. C. Price and E. Krebs, *Org. Synth.*, 1943, **23**, 65.

[33] A. T. Blomquist and A. J. Buselli, *J. Am. Chem. Soc.*, 1951, **73**, 3883.

[34] D. H. Hey, S. Orman, and G. H. Williams, *J. Chem. Soc.*, 1965, 101.

[35] Chang Shih, D. H. Hey, and G. H. Williams, *J. Chem. Soc.*, 1958, 1885.

[36] C. G. Swain, W. H. Stockmayer, and J. T. Clarke, *J. Am. Chem. Soc.*, 1950, **72**, 5426.

[37] J. K. Hambling, D. H. Hey, S. Orman, and G. H. Williams, *J. Chem. Soc.*, 1961, 3108.

[38] D. H. Hey, M. J. Perkins, and G. H. Williams, *J. Chem. Soc.*, 1963, 5604.

[39] J. I. G. Cadogan, *J. Chem. Soc.*, 1962, 4257.

[40] I. M. Heilbron and H. M. Bunbury, ' Dictionary of Organic Compounds,' Eyre and Spottiswoode, London, 1965, 4th edn.

[41] R. J. Orr and H. L. Williams, *J. Phys. Chem.*, 1953, **57**, 925.

[42] J. Saltiel and H. Curtis, *J. Am. Chem. Soc.*, 1971, **93**, 2056.

[43] R. L. Dannley and E. C. Gregg, *J. Am. Chem. Soc.*, 1954, **76**, 2997.

[44] R. A. Friedel, M. Orchin, and L. Reggel, *J. Am. Chem. Soc.*, 1948, **70**, 199.

[45] G. Wittig and G. Fuhrmann, *Ber.*, 1940, **73**, 1197.

[46] K. Nakazawa and S. Bata, *J. Pharm. Soc. Jpn.*, 1955, **75**, 378.