AROYLOXYLATION IN AROMATIC SYSTEMS

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

by

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July, 1985

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To

My husband, Rusli bin Abd. Ghani,

and children,

Norehan, Muhammad Ridzwan, and Muhamad Amin.

ACKNOWLEDGEMENT

I would firstly like to thank my supervisor, Dr. Roger Bolton for his help and constant support throughout this project. He was always there when needed to discuss the problems that I encountered, and drawing upon his vast knowledge of the subject always had an answer.

I should also like to thank Mr. Don Parkinson for the ^{19}F-n.m.r spectra which he ran, Miss H.S. Mohran for her help in operating the g.l.c and h.p.l.c instruments, and all my colleagues in the Chemistry Department who helped make my time there a very enjoyable experience.

Finally, I should like to thank Professor G.H. Williams for suggesting the research topic, and Jabatan Perkhidmatan Awam Malaysia (JPM) and Universiti Malaya for the financial support which made all this possible.

July, 1985 N.A

ABSTRACT

The thermal decomposition of benzoyl peroxide in anisole at 80° gave 10.8 mol% methoxyphenyl benzoate, with an *ortho*:*para* ratio of 3:2. The inclusion of copper(II) benzoate in acetonitrile increased the yield to about 20 mol%. The yield and isomer distribution of methoxyphenyl benzoate varied significantly with the temperature, and depended also upon the anisole:benzoyl peroxide:copper(II) benzoate ratio, and were influenced by deuterium at the *ortho*- or *para*- position.

Kinetic analysis, using galvinoxyl, showed that copper(II) benzoate slightly increased the rate of the primary homolysis of benzoyl peroxide at 60-75°, but the rate was slower than in the uncatalysed decomposition at 80-82°.

Visible spectroscopic analysis showed that benzoyl peroxide reacted with copper(II) benzoate in acetonitrile to form a new species with a maximum absorption at 388 nm ($\varepsilon_{max} \sim 256\ 000\ M^{-1}cm^{-1}$). The rate of its formation was proportional to the concentration of benzoyl peroxide, and increased with temperature. The preformed species could not oxygenate anisole effectively.

The investigation was extended to halogenated anisoles, which gave high yields of methoxyphenyl benzoate, and to the polynuclear systems, naphthalene and methylnaphthalenes.

The thermal decomposition of benzoyl peroxide in anisole was investigated in the presence of other additives, such as copper(II) chloride, copper(II) bromide, iodine, N-bromosuccinimide, bromine, and tin(IV) chloride, in acetonitrile.

As another method of oxygenation, the benzoyl peroxide initiated reaction of halogenated aromatic compounds with acetate ions gave results which agreed with previous literature reports. This reaction could not be extended to anisole and highly fluorinated aromatic compounds.

Perbenzoic acid was found to be an ineffective reagent for oxygenation of aromatic compounds, even in the presence of additives.

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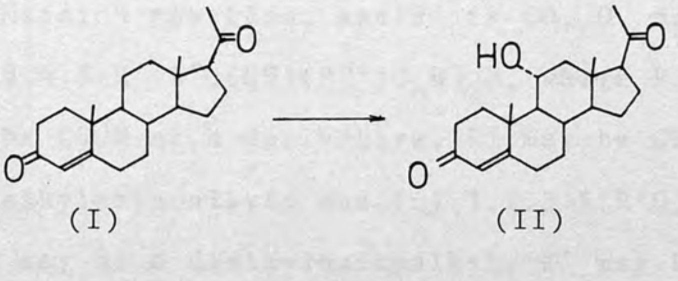
1. INTRODUCTION.

1.1. Oxygenation of organic compounds [@].

The direct production of phenols from aromatic hydrocarbons has long been a desirable synthetic goal, both in the laboratory and commercially, but there was no useful general method available.

Presently, the technique of microbial hydroxylation [1] is extensively applied in the production of steroids on a commercial scale. The technique uses micro-organisms (either bacteria or fungi) to introduce an -OH group into an organic molecule by performing a direct conversion of C-H to C-OH with defined regio- and stereo- specificity. For example, in 1950, Murray and Peterson discovered that fungus Rhizopus arrhizus was able to convert progesterone (I) to 11 α-hydroxyprogesterone (II) in high isolable yield at 27° [2] (Scheme 1).



Scheme 1

[@] The term "oxygenation" refers to the reaction, RH $\longrightarrow$ ROH, in general, regardless of the mechanism or the number of steps involved.

The use of isolated enzymes or enzyme preparations for hydroxylation on a synthetic scale is not widespread because of their instability and the difficulty involved in separation.

R. Breslow <u>et</u> <u>al</u>. [3] have carried out an extensive program of research aimed at mimicking the selectivity of enzyme reactions with some degree of success. The target of the program called "Biomimetic control of chemical selectivity" was the development of "remote oxidation" or "remote functionalisation" reactions. The aim was to achieve selective reactions at arbitrarily large distances from any functional group of the substrate, the distance being determined by the geometry of a complexed reagent, catalyst, or template. Their research was mainly centred on steroid systems, and generally involved free-radical processes.

In medicinal chemistry, organic compounds of the general formulas (a) $[3,5,4\text{-}R_2(OH)C_6H_2]_2R'$ and $1,2,3\text{-}R(OH)(COOH)\text{-}C_{10}H_5$, where R represents dialkylaminoalkyl groups introduced by the Mannich reaction, and R' is CO, O, or SO_2;
(b) $[2,3,4,5\text{-}R'(R'')(OH)(R''')C_6H]_2R$, where R may be S or CH_2, R' may be COOH or a derivative, R" may be CH_3, and R"' may be a dialkylaminoalkyl; and (c) $1,2,3\text{-}R(R'O)(R''OC)C_{10}H_5$, where R may be a dialkylaminoalkyl, R' may be an acetoxy, and R" may be a dialkylaminoalkyl or another substituted amino group; have been synthesized as possible anti-cancer agents [4]. These compounds have shown relatively low acute and chronic toxicities and have been effective against

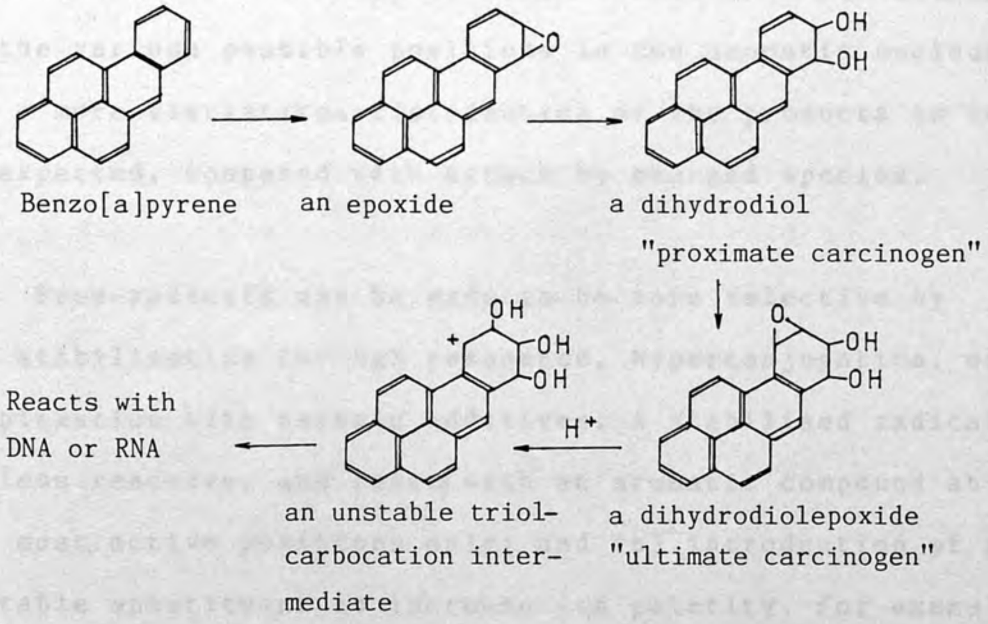
Rous chicken sarcoma and other animal neoplasms. The application of direct hydroxylation methods to the syntheses of such compounds has not yet been made.

1.1.1. Homolytic versus heterolytic method of oxygenation.

A heterolytic oxygenation of an unactivated aromatic hydrocarbon would normally proceed through several tedious and lengthy steps. The oxygenation of substituted aromatic compounds by this method is greatly governed by the polarity of the substituent and oxygenating agent. On the other hand, a homolytic oxygenating method involving a suitable highly reactive oxy-radical under ideal conditions can be made synthetically useful. In general, it has been shown that all substituents, regardless of their polarity, activate the aromatic nucleus towards free radical attack at the ortho- and para- positions [5]. A homolytic oxygenation method was found helpful as a probe for understanding the complex processes of biological oxidation [6] and carcinogenesis of polynuclear aromatic compounds [7].

One of the intriguing features of the biological oxidation of aromatic compounds [6] was the observation that they can be attacked at positions which are different from those affected by the majority of the oxidising or substituting agents in regular laboratory use. It was tentatively suggested that the biological oxidation, which is essentially a hydroxylation, was due to hydroxy, or similar, free radicals. For example, the metabolic oxidation of anthracene produced 1,2-dihydro-1,2-dihydroxyanthracene [8] which was ascribed to an initial process of free radical addition.

The homolytic method of oxygenation was found generally useful for predicting carcinogenicity of polynuclear aromatic compounds [7]. It is known that there are certain points of correspondence between the chemical reactivity of the hydrocarbons in substitution and their carcinogenic activity. It was suggested that the administered carcinogen may undergo some form of substitution reaction, possibly akin to a hydroxylation, and that this contributes an important step in a complicated chain of events leading eventually to carcinogenesis. It is now thought that the chemical transformations leading to the induction of tumorigenesis are enzyme-assisted [9] (Scheme 2).



Scheme 2

The elucidation of the chemical events caused by chemical carcinogens in the body is essential for the effective prevention and treatment of cancer.

The problems normally encountered in homolytic aromatic substitution reactions are (a) low yield of the desired product; (b) low selectivity between the available sites of attack; and (c) high yield of tarry residue. These problems arise because the attacking entity is a highly reactive free radical. Its reaction normally involves complicating side-reactions such as dimerisation and disproportionation.

1.2. Isomer distribution in homolytic aromatic substitution.

Homolytic aromatic substitution reactions are generally very fast with low energies of activation. The highly reactive neutral free radical is less selective in its attack at the various possible positions in the aromatic nucleus, and a more statistical distribution of the products is to be expected, compared with attack by charged species.

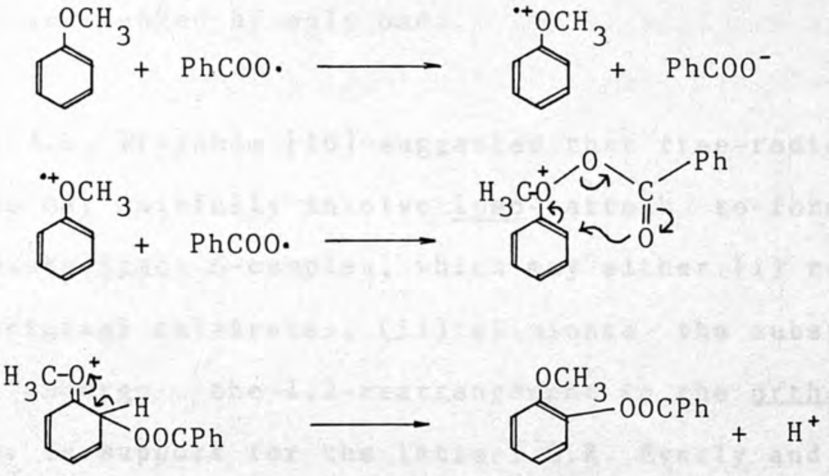
Free-radicals may be made to be more selective by (a) stabilisation through resonance, hyperconjugation, or complexation with certain additives. A stabilised radical is less reactive, and reacts with an aromatic compound at its most active positions only; and (b) introduction of a suitable substituent to increase its polarity. For example, 4-nitrophenyl radical is more electrophilic than phenyl radical [10]. In this case, the isomer distribution is greatly influenced by the substituent on the aromatic ring. The position of attack is where the odd electron may be delocalised by the substituent to lead to a more stable intermediate σ-complex.

In general, a high o:p ratio is obtained in all free-radical aromatic substitution reactions. Several explanations were given :-

(a) Waters [11] claimed that all free-radicals are essentially electrophilic. The attack occurs at the position of highest electron density, which is normally at the substituent. An ortho- attack subsequently happens due to close proximity.

(b) Rondestvedt and Blanchard [12] offered an explanation based on the inductive effect of the substituent. They suggested that in the formation of a π-complex as a precursor of σ-complex, the radical tends to become associated at the site of highest electron density. For a substituent with a negative inductive effect such as a nitro group, the site of highest electron density is at the substituent. The π-complex thus formed rearranged to the ortho- σ-complex. For a substituent with a positive inductive effect such as a methyl group, the site of highest electron density is at the ortho- position.

(c) Lynch and Moore [13] suggested that a charge-transfer complexation between the radical and substituent, followed by a cyclic rearrangement to the <u>ortho</u>- position, was to account for the extensive <u>ortho</u>- benzoyloxylation in anisole (Scheme 3).

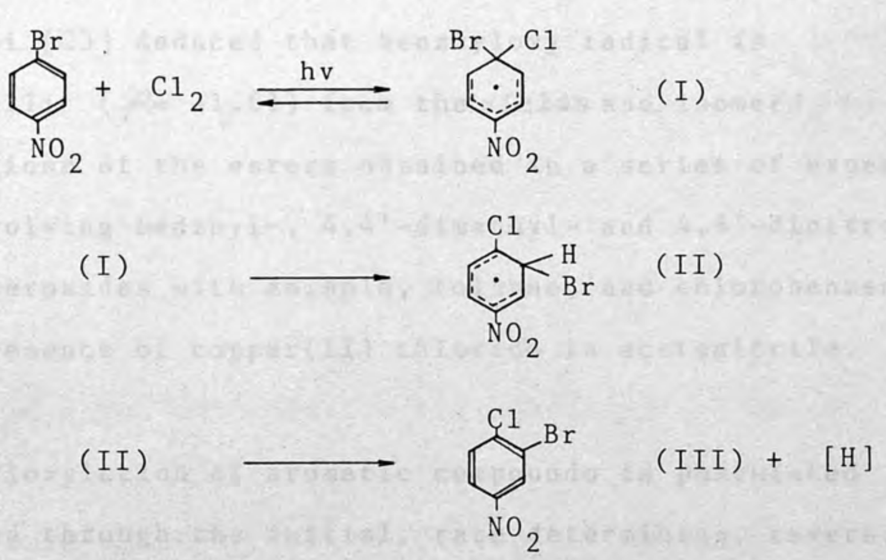


<u>Scheme 3</u>

The reduced incidence of <u>ortho</u>- attack in anisole in the presence of copper(II) benzoate (<u>o</u>:<u>p</u> ratio, 2.2 ; compared to 2.5 in its absence) [14] seemed to support the above postulate. It was assumed that the additive prevents the formation of complex between the radical and the aromatic compound, perhaps by associating itself with the radical.

(d) Bolton, Sandall, and Williams [15] suggested that σ-intermediates are better stabilised by <u>ortho</u>- substituents than by <u>para</u>- substituents. This was deduced from the observation that the o:p ratios of phenylation products in benzene derivatives, C_6H_5X, were commonly greater than two and directly opposite in pentafluorobenzene (o:p ratio, 1.4); in reactions with benzoyl peroxide. It was argued that this arose because the C-4 position in pentafluorobenzene is flanked by two _ortho_- fluorine atoms, whereas the C-2 position is flanked by only one.

(e) J.G. Traynham [16] suggested that free-radical reactions may initially involve _ipso_- attack to form the intermediate _ipso_- σ-complex, which may either (i) revert to the original substrates, (ii) eliminate the substituent, or (iii) undergo the 1,2-rearrangement to the _ortho_- position. In support for the latter, C.R. Everly and J.G. Traynham [17] found 2-bromo-4-nitrochlorobenzene (III) amongst the products from the light-catalysed chlorination of 4-bromonitrobenzene which is consistent only with the 1,2-rearrangement of the initially formed _ipso_- cyclohexadienyl radical (I) (Scheme 4).



Scheme 4

1.3 Aroyloxylation of aromatic compounds.

Aroyl peroxide decomposes either photochemically or thermally in aromatic compounds to effect mainly arylation, with aroyloxylation as a minor side-reaction. The amount of ester produced depends on the aromatic compound and experimental conditions. For example, Gill and Williams reported 2 mol% phenyl benzoate from benzene at 78° [18] and 6 mol% chlorophenyl benzoate from chlorobenzene at 80.2° [19] in the reactions with benzoyl peroxide. Higher yields of esters were reported from (a) reactive aromatic compounds such as polynuclears [20] and aromatic ethers [13]; (b) reactions in the presence of additives [14,21]; and (c) reactions at low temperatures.

McBride's recent investigation of the structure of benzoyloxy radical by EPR spectroscopy in a crystalline matrix at low temperature [22] showed that the unpaired electron is in an orbital of sigma-symmetry. Kurz and Pellegrini [23] deduced that benzoyloxy radical is electrophilic ($\rho = -1.61$) from the yields and isomer distributions of the esters obtained in a series of experiments involving benzoyl-, 4,4'-dimethyl- and 4,4'-dinitrobenzoyl-peroxides with anisole, toluene, and chlorobenzene, in the presence of copper(II) chloride in acetonitrile.

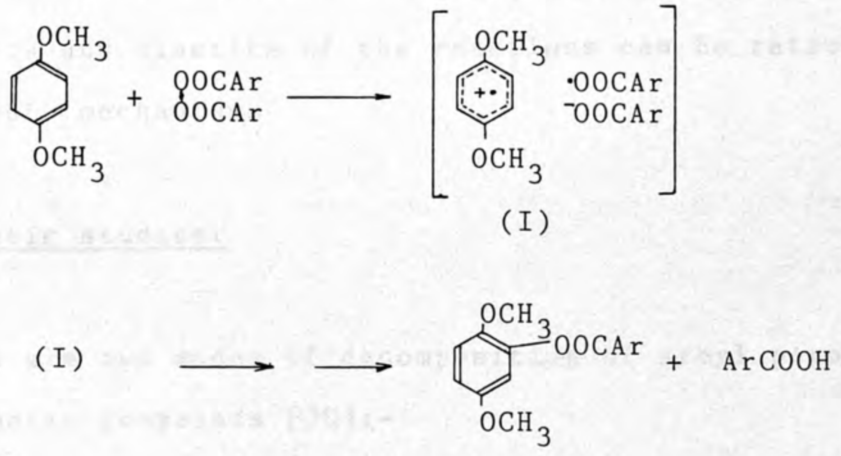
Aroyloxylation of aromatic compounds is postulated to proceed through the initial, rate-determining, reversible addition [24] of free, resonance-stabilised [25] aroyloxy radical to the aromatic nucleus to form the intermediate aroyloxycyclohexadienyl radical, $\sigma\cdot$. This is either oxidised to aryl aroate, or undergoes side-reactions such as fragmentation, dimerisation, or disproportionation. Competitively, the aroyloxy radical decarboxylates to aryl radical, which undergoes a similar, but irreversible, addition-elimination sequence through the intermediate arylcyclohexadienyl radical, $\sigma\cdot'$, which is oxidised to biaryl. The by-products formed in significant amounts are carbon dioxide, aroic acid, and high boiling residues consisting mainly of isomeric tetrahydroquarteraryls. The mechanism of the reaction is well documented [10] (Scheme 5).

$$
\begin{array}{lll}
(\mathrm{ArCOO})_2 & \longrightarrow & 2\ \mathrm{ArCOO}\cdot \\
\mathrm{ArCOO}\cdot & \longrightarrow & \mathrm{Ar}\cdot + \mathrm{CO_2} \\
\mathrm{ArCOO}\cdot + \mathrm{Ar'H} & \rightleftharpoons & \mathrm{ArCOOAr'H}\cdot \quad (\sigma\cdot) \\
\mathrm{Ar}\cdot + \mathrm{Ar'H} & \longrightarrow & \mathrm{ArAr'H}\cdot \quad (\sigma\cdot') \\
(\mathrm{ArCOO})_2 + \sigma\cdot & \longrightarrow & \mathrm{ArCOOAr'} + \mathrm{ArCOOH} + \mathrm{ArCOO}\cdot \\
(\mathrm{ArCOO})_2 + \sigma\cdot' & \longrightarrow & \mathrm{ArAr'} + \mathrm{ArCOOH} + \mathrm{ArCOO}\cdot \\
2\sigma\cdot,\ 2\sigma\cdot',\ \sigma\cdot + \sigma\cdot' & \longrightarrow & \text{dimerisation or disproportionation.}
\end{array}
$$

Scheme 5

The physical evidence for the reversibility of aroyloxylation reaction has been obtained by carbon-13 CIDNP studies which indicates that the addition of perfluorobenzoyloxy radical in the photolysis of perfluorobenzoyl peroxide in chlorobenzene is reversible [26].

Walling and Zhao [27] have suggested an electron-transfer mechanism (ET) to account for the high yield of ester (about 50%) and acid (>100%) in the decomposition of aroyl peroxides in electron-rich aromatic compounds, such as 1,4-dimethoxybenzene (Scheme 6).



Scheme 6

An alternative to the ET mechanism suggested was the S_N2 mechanism, the bimolecular nucleophilic substitution on peroxidic oxygen. The ET mechanism was favoured by the above workers since the decomposition of benzoyl peroxide at 80° was faster (a) in polar solvents (k, acetonitrile, $5.1\times10^{-5}s^{-1}$; benzene, $2.7\times10^{-5}s^{-1}$); (b) in the presence of electron-withdrawing group on the peroxide (k, 4,4'-dimethoxybenzoyl peroxide, $8.4\times10^{-5}s^{-1}$; benzoyl peroxide,

$2.7\text{x}10^{-5}\text{s}^{-1}$); and (c) with increased electron-density of aromatic compounds (k, 1,4-dimethoxybenzene, $3.9\text{x}10^{-5}\text{s}^{-1}$; 2,5-dimethyl-1,4-dimethoxybenzene, $700\text{x}10^{-5}\text{s}^{-1}$, in acetonitrile). The above reaction serves as an example of molecule – induced decomposition of benzoyl peroxide

There are several reports in the literature on the reaction of benzoyl peroxide with nucleophiles which was postulated to involve either ET or S_N2 mechanism [28,29]. It is difficult to determine which one predominates since the products and kinetics of the reactions can be rationalised by both mechanisms

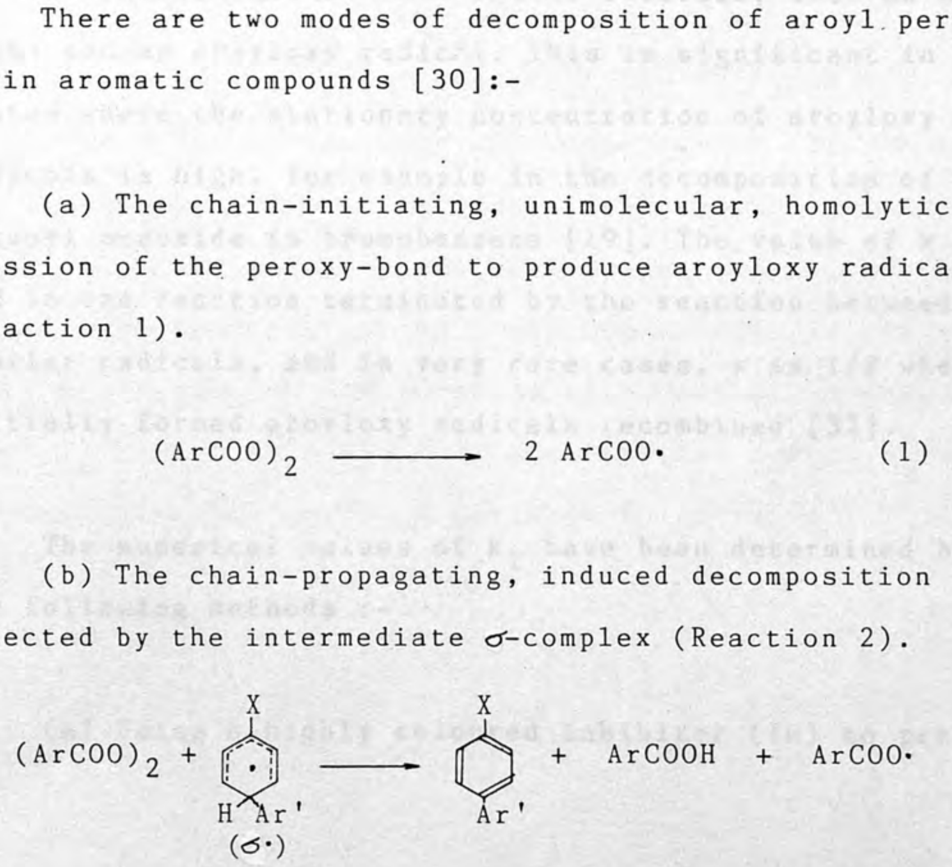
1.3.1 Kinetic studies.

There are two modes of decomposition of aroyl peroxide in aromatic compounds [30]:-

(a) The chain-initiating, unimolecular, homolytic scission of the peroxy-bond to produce aroyloxy radicals (Reaction 1).

$$(\text{ArCOO})_2 \longrightarrow 2\ \text{ArCOO}\cdot \qquad (1)$$

(b) The chain-propagating, induced decomposition effected by the intermediate σ-complex (Reaction 2).



(2)

The introduction of an electron-attracting substituent in the peroxide was shown to result in its increased susceptibility to induced decomposition [31].

The overall decomposition kinetics are the sum of the spontaneous homolysis (Reaction 1) and radical-induced decomposition (Reaction 2) (Equation 1), where k_1 and k_i are the specific rate constants of the primary homolysis and radical-induced decomposition, respectively.

$$-\frac{d[P]}{dt} = k_1[P] + k_i[P]^x \qquad (1)$$

The value of x is determined by the mode of the chain-termination reaction. It is 1.0 if the chain is terminated by the reaction between two unlike radicals, such as a sigma and an aroyloxy radical. This is significant in a system where the stationary concentration of aroyloxy radicals is high, for example in the decomposition of benzoyl peroxide in bromobenzene [19]. The value of x is 3/2 in the reaction terminated by the reaction between two similar radicals, and in very rare cases, x is 1/2 when the initially formed aroyloxy radicals recombined [32].

The numerical values of k_1 have been determined by the following methods :-

(a) Using a highly coloured inhibitor (In) to prevent the induced decomposition (Reaction 3).

$$(ArCOO)_2 \xrightarrow{k_1} 2\ ArCOO\cdot \qquad (1)$$

$$ArCOO\cdot + In \longrightarrow ArCOO\text{-}In \qquad (3)$$

The rate of the disappearance of the inhibitor is followed spectrometrically, and is given by Equation 2.

$$\begin{aligned} -\frac{d[In]}{dt} &= 2k_1[(ArCOO)_2] \qquad (2) \\ &= \text{constant, at high initial concentration of peroxide.} \end{aligned}$$

The general first-order rate constant is (Equation 3) :-

$$k_1 t = \ln\ [\ a/(a-x)] \qquad (3)$$

The stoichiometry of the inhibited decomposition of the peroxide indicates that the concentration of the inhibitor reacted at time t is equal to 2x. If the optical density of the solution is A_o at time t_o, and A_t at time t, then the fraction of the inhibitor reacted is $[(A_o-A_t)/A_o]$ and the fraction of the peroxide which had decomposed is given by Equation 4; where j is a constant and equal to the initial molar ratio of peroxide to inhibitor.

$$1/2j\ [(A_o-A_t)/A_o] = x/a \qquad (4)$$

The first-order rate constant for the inhibited decomposition is given by Equation 5.

$$k_1t = \ln \left[\frac{2jA_o}{A_o(2j-1) + A_t}\right] \qquad (5)$$

Janzen, Evans, and Nishi [33] have listed values of k_1 for benzoyl peroxide at different temperatures obtained by them and other workers, using inhibitors such as galvinoxyl and N-(t-butyl)-α-phenylnitrone (PBN), in benzene (Table 1).

Table 1 The rate constant, k_1, for the thermal decomposition of benzoyl peroxide in benzene.

T/°C	$k_1/10^{-5}s^{-1}$
44.0	0.01
54.9	0.09
60.0	0.19
65.6	0.32
71.0	0.60
75.8	1.19
78.0	1.67
80.0	3.28

The activation energy, E_A, for the primary homolysis of benzoyl peroxide in benzene calculated from Table 1 is

32.8 kcalmol^{-1} (137 kJmol^{-1}).

Nozaki and Bartlett [30] obtained a value of 33.3 kcalmol^{-1} (139 kJmol^{-1}), and Janzen et al. [33] obtained a value of 30.4 kcalmol^{-1} (127 kJmol^{-1}) by using the electron-spin resonance spin trapping method, for the primary homolysis of benzoyl peroxide.

Suehiro et al. [34] discovered that stable free-radicals, such as triphenylmethyl ($Ph_3C\cdot$), were able to cause induced decomposition of benzoyl peroxide (Scheme 7).

$$Ph_3C\text{-}CPh_3 \rightleftharpoons 2\,Ph_3C\cdot$$

$$(PhCOO)_2 + Ph_3C\cdot \longrightarrow Ph_3C\text{-}OOCPh + PhCOO\cdot$$

Scheme 7

Janzen et al. [33] suggested that an induced decomposition of benzoyl peroxide by galvinoxyl which produces additional benzoyloxy radicals was a likely possibility; to account for the faster production of benzoyloxy radical than expected in its presence.

(b) From rate equation (Equation 1).

$$-\frac{d[P]}{dt} = k_1[P] + k_i[P]^x \qquad (1)$$

or,

$$k_t = k_1 + k_i[P]^{(x-1)} \qquad (6)$$

where k_t (Equation 6) is the observed first-order rate constant. A plot of k_t against $[P]^{(x-1)}$ gives k_1 at the point of intersection of zero peroxide concentration.

Using this method, Gill and Williams [18] obtained a k_1 value of $1.88x10^{-5}s^{-1}$ for benzoyl peroxide at 78° in benzene; and Vidal, Court, and Bonnier [28] obtained a value of $4.0x10^{-5}s^{-1}$ at 80° in benzene, which agreed with their value of $3.9x10^{-5}s^{-1}$ obtained in the presence of PBN as an inhibitor.

1.3.2 Isotope effect.

Saltiel and Curtis [24] showed that the formation of phenyl benzoate in the photolysis of benzoyl peroxide in benzene-benzene-d_6 mixture in oxygen at 30° showed a large apparent deuterium effect, in contrast to the smaller effect for biphenyl formation, under the same condition. At $1.5x10^{3}$M oxygen concentration, the isotopic composition of phenyl benzoate was 84.2%, and pentadeuterophenyl benzoate, 14.6%, as determined by mass spectrometry. The apparent isotope effect for benzoyloxylation reaction was attributed to the reversible formation of $\sigma\cdot$, and preferential extrusion of H over D.

Eliel, Meyerson, Welvart, and Wilen [35] showed that the isotopic composition of the recovered substrates from the thermal decomposition of a variety of peroxides in a mixture of benzene-benzene-d_6 at 78° was unchanged, signifying that there was no selective consumption of undeuterated compound.

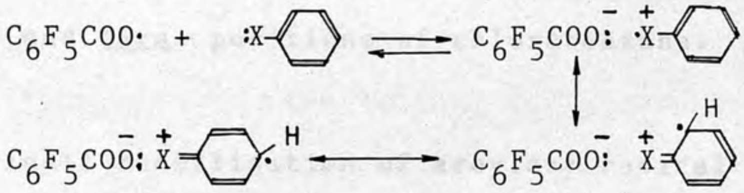
Kurz and Pellegrini [23] suggested that the lack of kinetic isotope effect in benzoyloxylation reaction in the presence of certain additives, such as copper(II) chloride was due to the efficient oxidation of σ•, thus suppressing its reversal and other side-reactions.

1.3.3. Promoting aroyloxylation reaction in aromatic compounds.

1.3.3.1. Stabilisation of aroyloxy radical.

Aroyloxy radical is thermally unstable. It decarboxylates spontaneously at high temperatures to form the highly reactive aryl radical. Barnett and Vaughan [36] showed that at 0.08M benzoyl peroxide in benzene, the amount of carbon dioxide increased from 72 to 156 mol% as the temperature was increased from 55° to 80°. More direct evidence was found by Kurz and Kovacic [37] who obtained 75 and 56 mol% methoxyphenyl benzoate from the copper(II) chloride catalysed decomposition of benzoyl peroxide in anisole at 60° and 80°, respectively.

Certain aromatic compounds are able to promote aroyloxylation reactions by stabilising the aroyloxy radical through the formation of a charge-transfer complex. The complex formation is more pronounced in the case of a highly electrophilic oxy-radical and an easily oxidised aromatic compound. M.W. Coleman [32] obtained high yields of phenyl pentafluorobenzoate (88 and 77 mol%) from the decomposition of perfluorobenzoyl peroxide in bromo- and chloro- benzenes, respectively, at 80°. It was suggested that the initially formed perfluorobenzoyloxy radical was stabilised by one-electron transfer from the aromatic compound (Scheme 8).



Scheme 8

The higher yield of ester in bromo- than chlorobenzene was due to the more extensive charge-transfer from the more electropositive and polarisable bromine substituent. In comparison, the above reaction in fluorobenzene gave 65 mol% phenyl pentafluorobenzoate [32]. It was argued that the lower yield of the ester was because the highly electronegative fluorine substituent could not stabilise perfluorobenzoyloxy radical by a charge-transfer process.

It is noteworthy that the resultant complex between perfluorobenzoyloxy radical and the halobenzene mainly collapsed to form the intermediate σ-complex at C-1, and subsequently eliminated the halogen to give the unsubstituted ester. It was supposed that the highly electrophilic perfluorobenzoyloxy radical attacked the position of greatest electron density at C-1.

Kaptein, Freeman, and Hill [26] found from carbon-13 CIDNP study that perfluorobenzoyloxy radical formed in the photolysis of perfluorobenzoyl peroxide predominantly add to the <u>ortho</u>- and <u>para</u>- positions of chlorobenzene.

The intrinsic stabilisation of aroyloxy radical through the presence of an electron-donating group in its aromatic ring was shown not to have a great influence on the yields of esters in certain aromatic compounds. Kurz and Pellegrini [23] showed that the copper(II) chloride catalysed decomposition of 4,4'-dinitrobenzoyl-, benzoyl-, and 4,4'-dimethylbenzoyl- peroxides in toluene at 60° gave 47, 41, and 38 mol% tolyl aroates, respectively.

The thermal decomposition of benzoyl peroxide in aromatic compound in the presence of iodine was found to give an almost quantitative yield of aryl benzoate and benzoic acid. The only other product detected in significant amount was iodoarene. For example, Kovacic, Reid, and Brittain [38] obtained 60 mol% tolyl benzoate by decomposing benzoyl peroxide in toluene in the presence of a small amount of iodine. In a similar experiment, Hashimoto, Koike, and Yamamoto [39] obtained between 72-9 mol% tolyl benzoate, compared to only 3 mol% when iodine was excluded. Hammond [40] also reported aryl benzoate and benzoic acid as the main products in this type of reaction. Several different mechanisms were suggested by these workers :-

(a) Iodine-catalysed, non-radical reaction.

Hammond [40] observed that the relative amounts of ester and acid formed were considerably influenced by the iodine concentration. While the yield of acid increased steadily with increasing iodine concentration, the yield of ester passed through a maximum. The following mechanism was proposed (Scheme 9).

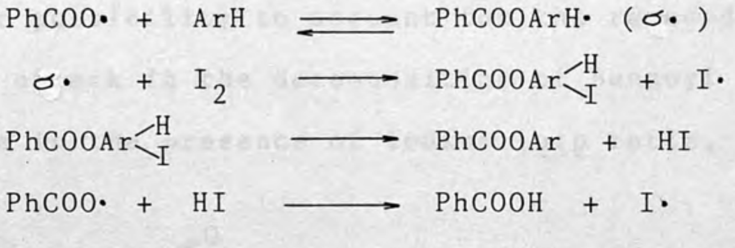
$$
\begin{array}{lcl}
(\mathrm{PhCOO})_2 & \xrightarrow{\qquad} & 2\ \mathrm{PhCOO\cdot} \\
\mathrm{PhCOO\cdot} + \mathrm{I}_2 & \xrightarrow{\qquad} & \mathrm{PhCOOI} + \mathrm{I\cdot} \\
\mathrm{PhCOO\cdot} + \mathrm{I}_2 & \xrightarrow{\qquad} & \mathrm{PhI} + \mathrm{CO}_2 + \mathrm{I\cdot} \\
 & \xrightarrow{\qquad} & \mathrm{PhI} + \mathrm{CO}_2 \\
\mathrm{PhCOOI} & \xrightarrow{\mathrm{ArH,\ I_2}} & \mathrm{PhCOOAr} + \mathrm{HI} \\
 & \xrightarrow{\mathrm{ArH,\ 2I_2}} & \mathrm{PhCOOH} + \mathrm{ArI} \\
2\ \mathrm{I\cdot} & \xrightarrow{\qquad} & \mathrm{I}_2 \\
\mathrm{PhCOOI} + \mathrm{HI} & \xrightarrow{\qquad} & \mathrm{PhCOOH} + \mathrm{I}_2
\end{array}
$$

Scheme 9

At high concentration of iodine, the benzoyloxy radical formed in the primary process was converted to the unstable benzoyl hypoiodite which reacted rapidly with the aromatic compound in an iodine-catalysed, non-radical reaction.

(b) Scavenging of σ· by iodine, followed by loss of hydrogen iodide.

Hashimoto, Koike, and Yamamoto [39] deduced that the oxidising agent was not a polar intermediate, but a benzoyloxy radical, from the observation that (i) the rate of benzoyloxylation of a number of monosubstituted benzenoid compounds (relative to benzene) in the reaction was of the same order as in the absence of iodine; (ii) the similar isomer distribution obtained with and without iodine; and (iii) the yield of phenyl 4-substituted benzoate from the decomposition of 4,4'-disubstituted benzoyl peroxides in benzene at 80° in the presence of iodine was $OCH_3:CH_3:H:Cl:Br = 86.5:84.0:75.3:94.6:95.0\%$. The mechanism suggested is shown in Scheme 10.



$$\begin{aligned}
&\mathrm{PhCOO\cdot} + \mathrm{ArH} \rightleftharpoons \mathrm{PhCOOArH\cdot}\ (\sigma\cdot)\\
&\sigma\cdot + \mathrm{I_2} \longrightarrow \mathrm{PhCOOAr}{<}\begin{smallmatrix}\mathrm{H}\\ \mathrm{I}\end{smallmatrix} + \mathrm{I\cdot}\\
&\mathrm{PhCOOAr}{<}\begin{smallmatrix}\mathrm{H}\\ \mathrm{I}\end{smallmatrix} \longrightarrow \mathrm{PhCOOAr} + \mathrm{HI}\\
&\mathrm{PhCOO\cdot} + \mathrm{HI} \longrightarrow \mathrm{PhCOOH} + \mathrm{I\cdot}
\end{aligned}$$

Scheme 10

(c) Stabilisation of benzoyloxy radical and oxidation of $\sigma\cdot$ by iodine.

Kovacic, Reid, and Brittain [38] suggested a mechanism very similar to the copper(II) chloride catalysed decomposition of benzoyl peroxide in aromatic compound [37] from the similar isomer distribution observed with and without iodine in the reactions with toluene (Scheme 11).

$$\begin{aligned}
&(PhCOO)_2 && \longrightarrow && 2\ PhCOO\cdot \\
&PhCOO\cdot + I_2 && \rightleftharpoons && PhCOOI + I\cdot \\
&PhCOO\cdot + ArH && \rightleftharpoons && PhCOOArH\cdot\ (\sigma\cdot) \\
&\sigma\cdot + I\cdot && \longrightarrow && PhCOOAr + HI \\
&PhCOOI + HI && \longrightarrow && PhCOOH + I_2
\end{aligned}$$

Scheme 11

(d) Formation of a bulky radical moiety.

Kovacic, Reid, and Brittain [38] also suggested an involvement of a bulky attacking species, such as in Figure 1, as another possibility to account for the reduced occurence of <u>ortho</u>- attack in the decomposition of benzoyl peroxide in anisole in the presence of iodine (<u>o</u>:<u>p</u> ratio, 47:53).

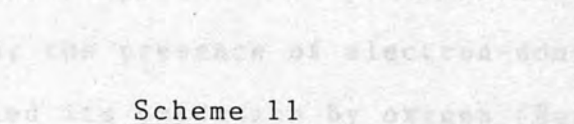
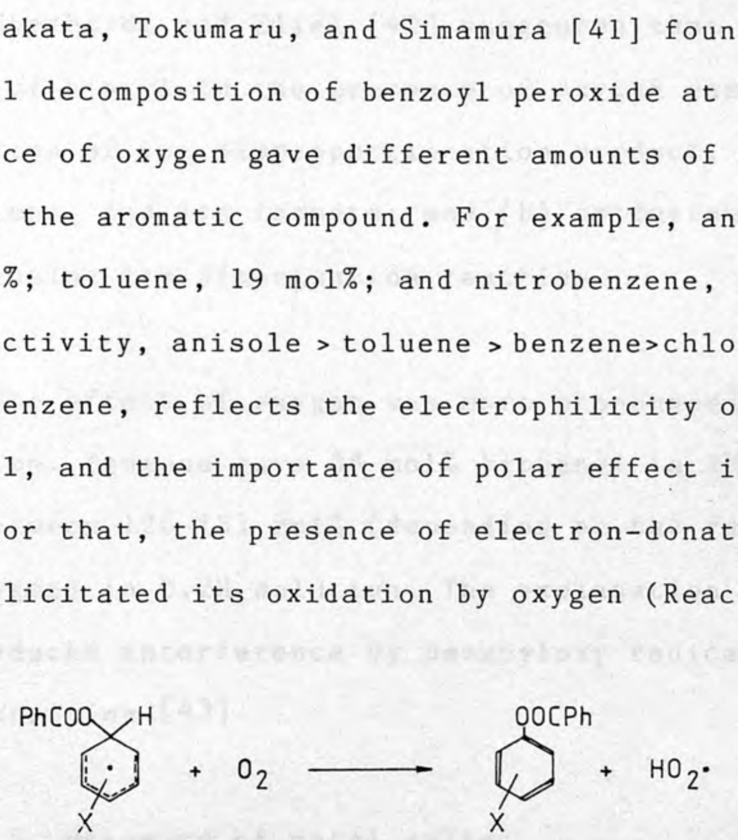


Figure 1

It was argued that the less reactive radical moiety was able to effect the oxygenation of anisole because of the high reactivity of the compound towards substitution.

1.3.3.2. Presence of oxygen.

Nakata, Tokumaru, and Simamura [41] found that the thermal decomposition of benzoyl peroxide at 79° in the presence of oxygen gave different amounts of ester, depending on the aromatic compound. For example, anisole gave 33 mol%; toluene, 19 mol%; and nitrobenzene, none. The order of reactivity, anisole > toluene > benzene>chlorobenzene> nitrobenzene, reflects the electrophilicity of benzoyloxy radical, and the importance of polar effect in the formation of $\sigma\cdot$;or that, the presence of electron-donating substituent in $\sigma\cdot$ falicitated its oxidation by oxygen (Reaction 4).



(4)

It was also shown that the yield of ester in the presence of oxygen depended on the temperature. Benzene gave 6 and 18 mol% phenyl benzoate at 80° and 62°,respectively. The explanations given were the increased concentration of dissolved oxygen at the lower temperature and the reduced rate of decarboxylation of benzoyloxy radical.

In a similar experiment, Morrison, Cazes, Samkoff, and Howe [42] showed that bubbling of oxygen at a rate of 15-20 mlmin^{-1} at 80° gave high yields of biaryls instead. For example, anisole gave 73 mol% methoxybiphenyl in the presence of oxygen compared to 50 mol% in its absence.

Eberhardt and Eliel [43] suggested that the higher yield of biaryl in the presence of oxygen was due to (a) oxidation of the disproportionation product, arylcyclohexa-1,4-diene, and its isomers; and (b) oxidation of $\sigma\cdot$, thus suppressing its dimerisation reaction.

The effect of oxygen was more pronounced in dilute solution. Benzene gave 38 mol% biphenyl in 2M solution, and between 126-151 mol% (depending on the rate of bubbling in oxygen) in 0.2M solution. The explanation offered was the reduced interference by benzoyloxy radical at the lower concentration [43].

1.3.3.3. Presence of metal salts.

It is well established that copper salts drastically alter the pathways of peroxide reactions. Kurz and Kovacic [37] obtained 56 mol% methoxyphenyl benzoate from the copper(II) chloride catalysed decomposition of benzoyl peroxide in anisole at 80° in acetonitrile solvent, compared to none when the catalyst was omitted.

Kochi [44] formulated the role of copper salts in the peroxide decomposition reactions as involving a series of redox steps :-(a) reduction of the peroxide by copper(I) to oxy-radical and copper(II); (b) chain-transfer between oxy-radical and aromatic compounds; and (c) copper(II) oxidation of the intermediate radical formed in (b). The modified mechanism for the decomposition of aroyl peroxide is given in Scheme 12.

$$\begin{array}{lll}
(\mathrm{ArCOO})_2 + \mathrm{Cu^{I}X} & \longrightarrow & \mathrm{ArCOOCu^{II}X} + \mathrm{ArCOO}\cdot \\
\mathrm{ArCOO}\cdot \quad + \mathrm{Ar'H} & \rightleftharpoons & \mathrm{ArCOOAr'H}\cdot\ (\sigma\cdot) \\
\quad \sigma\cdot \quad + \mathrm{Cu^{II}X_2} & \longrightarrow & \mathrm{ArCOOAr'} \quad + \mathrm{Cu^{I}X} + \mathrm{HX} \\
\mathrm{ArCOOCu^{II}X} + \mathrm{HX} & \longrightarrow & \mathrm{ArCOOH} + \mathrm{Cu^{II}X_2}
\end{array}$$

Scheme 12

In a kinetic study of copper(II) chloride catalysed decomposition of diisopropyl peroxydicarbonate (peroxide: catalyst mol ratio, 6.7:1) in toluene (40 ml) with acetonitrile (300 ml) as the solvent at 50°, Kurz and Kovacic [45] found that the peroxide decomposed at a rate of $6.45\times10^{-3}\,\mathrm{min}^{-1}$ in the uncatalysed reaction, and $6.6\times10^{-2}\,\mathrm{min}^{-1}$ in the catalysed, calculated on a pseudo-first order basis. The rate was fastest when copper(I) chloride was used instead, but tapered off after about 30% of the peroxide had decomposed. It was suggested that this was because the mixed copper(II) salt, $\mathrm{ArCOOCu^{II}X}$, could not oxidise the σ-complex. The experiment with the peroxide and copper(II) chloride (no toluene) was more complex in its kinetic; the initial rate was slightly faster than the uncatalysed decomposition, but not as rapid as the catalysed in the presence of toluene. The observation indicates the importance of the aromatic compound in the propagation step.

Bolton, Dailly, Hirakubo, Lee, and Williams [14] showed that the rate constant for the unimolecular decomposition of benzoyl peroxide in neat benzene in the presence of iron(III) benzoate at 80°, using galvinoxyl, was $2.1\times10^{-5}s^{-1}$ which was comparable to $1.67\times10^{-5}s^{-1}$ at 78° in the absence of the additive.

The mechanisms for the oxidation of the intermediate radical were proposed by Kochi [44], and by Kochi and Subramanian [46] as ligand transfer (LT) or electron transfer (ET).

In the LT mechanism, the redox process is accomplished through a transition state involving a bridged ligand (Scheme 13).

$$R\cdot + Cu^{II}X \rightarrow [R\cdot X\text{-}Cu^{II} \longleftrightarrow R\text{-}XCu^{I}] \rightarrow RX + Cu^{I}$$

Scheme 13

The process is sensitive to the nature of the bridging ligand, but not to the substituent in the radical fragment.

The halide, especially the bromide and chloride, of the metal ions are effective bridging ligands.

The ET mechanism involves a transfer of an electron from the radical to the copper(II) salt. It results in a transition state with a high degree of carbonium ion character (Scheme 14).

$$R\cdot + Cu^{II}Y \longrightarrow [R^{+}YCu^{I} \longleftrightarrow R.YCu^{II}] \longrightarrow \text{products} + Cu^{I}$$

Scheme 14

This process is hindered by the presence of an electron withdrawing substituent in the radical fragment.

Both LT and ET processes are extremely rapid. They represent extreme situations in redox processes. In most cases, the transition state of the redox reactions can be suitably represented as a resonance hybrid between LT and ET contributions; the importance of each depends on the nature of the radical, ligand, and metal ion.

From a study of the copper(II) chloride catalysed decomposition of benzoyl peroxide labelled with oxygen-18 in the carbonyl oxygens, in 1,4-dimethylbenzene, Reid and Kovacic [25] obtained 2,5-dimethylphenyl benzoate containing oxygen-18 equally partitioned between the carbonyl and ether oxygen of the ester group. From this, and the similarity of orientation observed in a similar experiment without the catalyst, they suggested that the attacking entity was either a free, resonance-stabilised benzoyloxy radical, or the benzoyloxy radical was present complexed with copper(II) chloride, such that the oxygen parity was maintained (Figure 2).

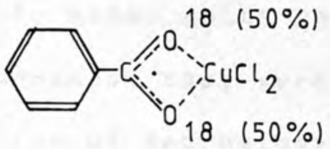


Figure 2

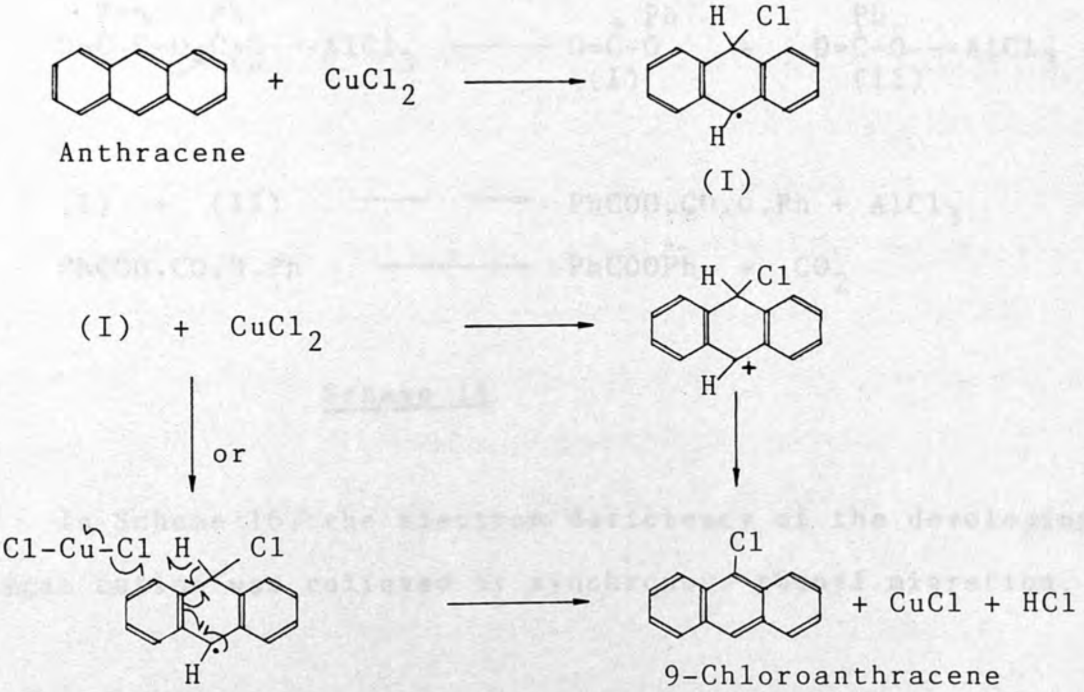
From the copper(II) salts catalysed decompositon of diisopropyl peroxydicarbonate in toluene, Kurz and Kovacic [21] showed that the copper(II) salts which are good ligand transfer agents, such as the halides, serve best as oxidation catalysts; while copper(II) acetate and benzoate were virtually ineffective.

Kurz and Kovacic [45] found that the optimum mol ratio for high yield of ester in the copper(II) chloride catalysed decomposition of diisopropyl peroxydicarbonate in toluene was aromatic:peroxide:catalyst, 17.3:1:0.3. It was found that (i) there was a marked steady decline in the extent of aromatic oxygenation as the mol ratio of aromatic compound to peroxide was reduced from the 17.3 level; and (ii) the amount of oxygenation product decreased substantially as the catalyst:peroxide ratio was reduced below the 0.3 level, while only small increases were noted above this level.

Hey, Liang, and Perkins [47], and Bolton, Dailly, Hirakubo, Lee, and Williams [14] obtained improved yields of biaryls from benzene and chlorobenzene in the presence of iron(III) benzoate, copper(II) benzoate, and other additives, in the absence of acetonitrile. It was suggested that since the metal salts were not very soluble in the aromatic compounds, they were inadequate to intercept a high proportion of benzoyloxy or $\sigma^{\cdot}$, which therefore decarboxylated [47].

The use of metal halides as good oxidising catalysts are complicated by their ability to act as good halogenating agents. Nonhebel [48a] found that anthracene was converted to 9-chloroanthracene in 79-98% yield, by refluxing it with copper(II) chloride for one minute under heterogeneous condition; in a non-polar solvent, such as chlorobenzene or carbon tetrachloride. The reaction was postulated as proceeding by the homolytic decomposition of a π-complex between copper(II) halide and aromatic hydrocarbon, based on two arguments (i) the reaction appeared to take place with aromatic compounds which might be expected to form a π-complex fairly readily; and (ii) the reaction with toluene produced bibenzyl. The mechanism suggested is given in Scheme 15 [48b].

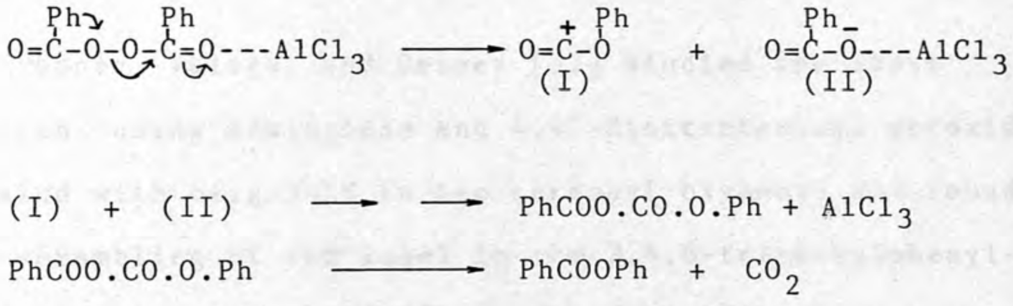
Kovacic and Brace [49], and Ware and Borchert [50] found similar halogenating abilities of iron(III) chloride and copper(II) chloride. They suggested a polar mechanism from (i) the order of reactivity of aromatic compound, toluene > 2-chlorotoluene > chlorobenzene > 1,2-dichlorobenzene> 1,4-dichlorobenzene, which is the same for a typical electrophilic aromatic substitution; (ii) the selectively *para*-orientation; (iii) the solvent effect. Solvents such as dimethylformamide, in which the catalyst is soluble, gave lower yield of halogenated product because of its interaction with the solvent ; and (iv) the catalytic effect. It was found that when aluminium chloride was added to the warm reaction mixture of anthracene and copper(II) chloride in nitrobenzene, a vigorous reaction ensued and 9,10-dichloroanthracene was formed more rapidly and in good yield [50].



Scheme 15

1.3.3.4. Presence of Lewis acid.

The use of a Lewis acid catalyst such as aluminium chloride was shown by Edward, Chang, and Samad [51] to result in the heterolysis of the peroxide linkage. The products formed depended on the aromatic compounds. Benzoyl peroxide decomposed in benzene in the presence of aluminium chloride at 0-50° to give about 28 mol% phenyl benzoate, and between 29-74 mol% carbon dioxide. Since phenyl benzoate was also isolated from reactions in solvents such as dichloromethane, toluene, and nitrobenzene, the mechanism proposed [51] for its formation was that given in Scheme 16.



$$O{=}\overset{Ph}{C}{-}O{-}O{-}\overset{Ph}{C}{=}O{-}{-}{-}AlCl_3 \longrightarrow \underset{(I)}{O{=}\overset{+}{C}{-}\overset{Ph}{O}} + \underset{(II)}{O{=}\overset{Ph\,-}{C}{-}O{-}{-}{-}AlCl_3}$$

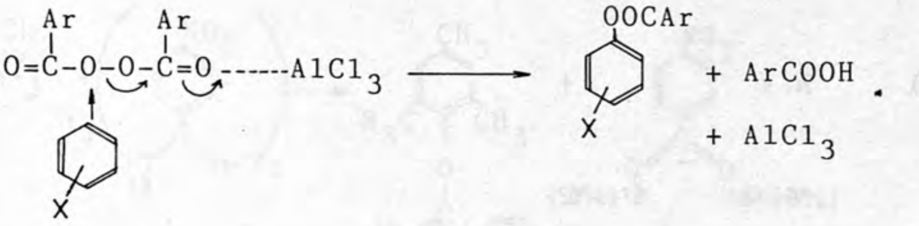
$$(I) + (II) \longrightarrow \longrightarrow PhCOO.CO.O.Ph + AlCl_3$$

$$PhCOO.CO.O.Ph \longrightarrow PhCOOPh + CO_2$$

Scheme 16

In Scheme 16, the electron deficiency of the developing oxygen cation was relieved by synchronous phenyl migration.

In reactive aromatic compounds such as anisole, and a peroxide which was deactivated towards aryl migration such as 4,4'-dinitrobenzoyl peroxide, 28 mol% methoxyphenyl 4-nitrobenzoate with an o:p ratio of 0.33, and 57 mol% 4-nitrobenzoic acid were obtained by Edward *et al.* [51]. The orientation of the substitution product was in accord with an electrophilic attack on the aromatic nucleus, and resembled the Friedel-Crafts substitution (Reaction 5).

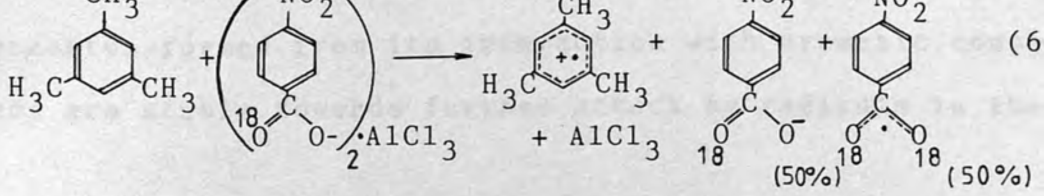


(5)

The synchronous electron-donation from an external nucleus was only possible with highly reactive aromatic compounds.

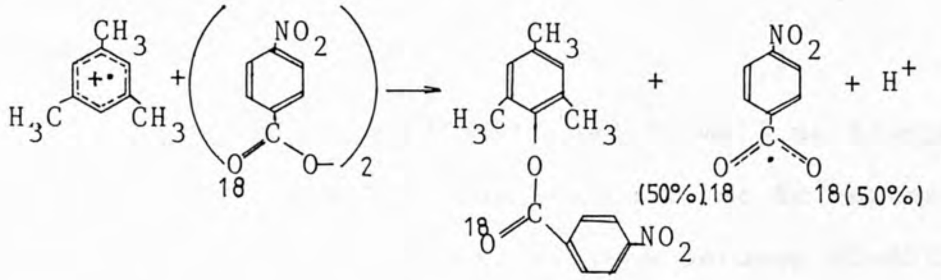
Denney, Valega, and Denney [52] studied the above reaction using mesitylene and 4,4'-dinitrobenzoyl peroxide labelled with oxygen-18 in the carbonyl oxygens; and found some scrambling of the label in the 2,4,6-trimethylphenyl-4-nitrobenzoate obtained. The partial equilibration was shown not to be due to some sort of reversible dissociation of the peroxide. The result suggested the possibility of two competing reaction paths, such as follows :-

(a) Attack by 4-nitrobenzoyloxy radical, possibly formed as in Reaction 6, resulting in scrambling of the label in the product.



(6)

(b) Induced decomposition of the peroxide by mesityl radical cation, resulting in specifically labelled ester (Reaction 7).



(7)

The use of this reaction as a method for direct introduction of an oxy-group onto aromatic nucleus was seriously limited by the absence of a suitable solvent. For example, Edward et al.[51] found that naphthalene dissolved in nitrobenzene or nitromethane gave only gummy and intractable tars in the reaction with 4,4'-dinitrobenzoyl peroxide in the presence of aluminium chloride at 8-10°. Similarly, 1,3-dimethoxybenzene gave only intractable product when dichloromethane was used as the solvent.

1.4. Reaction of benzoyl peroxide with aromatic compounds.

Benzoyl peroxide has been chosen as an ideal oxygenating agent because (i) it is a relatively stable, non-hazardous compound, which can be obtained in a crystalline form of high purity (>99%); (ii) it reacts at a reasonable rate at convenient temperatures (60-80°); and (iii) the benzoates formed from its interaction with aromatic compounds are stable towards further attack by radicals in the reaction medium, and easily isolated from other by-products by simple hydrolysis.

1.4.1. Anisole.

Lynch and Moore [13] obtained 20 mol% methoxyphenol by hydrolysing mixtures from reactions at 80° after 30-50 hours. The isomer distributions were between 65-82% _ortho_- and 18-35% _para_-. It was suggested that the large variations in the isomer distributions obtained were probably due to the occurence of some preferential oxidation of 4-methoxyphenol during hydrolysis.

McClelland, Norman, and Thomas [53] obtained 4 mol% methoxyphenyl benzoate (_o_:_p_ ratio, 52:48) from a reaction at 80° for 60 hours under a nitrogen atmosphere. Methoxybiphenyl (45 mol%), phenoxymethylanisole (11 mol%), and phenoxymethyl benzoate (3 mol%), were also obtained. The addition of benzoic acid increased the yield of methoxyphenyl benzoate to 8 mol%.

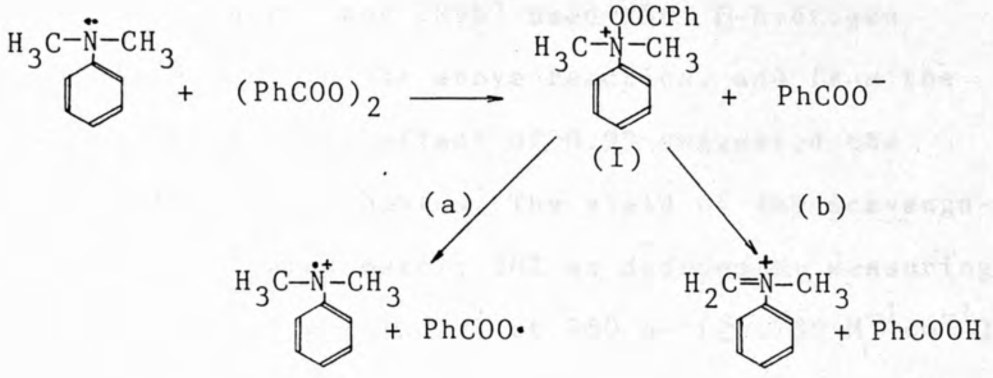
Kovacic, Reid, and Brittain [38] obtained 87 mol% methoxyphenyl benzoate (_o_:_p_ ratio, 47:53) from a reaction at 90±2° for 20 hours in the presence of iodine. It was suggested that iodine effectively reduced the extent of decarboxylation of benzoyloxy radical, even at the high temperature.

Nakata, Tokumaru, and Simamura [41] obtained 33 mol% methoxyphenyl benzoate (*o*:*p* ratio, 33:67) in the presence of oxygen at 79°, which is in agreement with 28.6 mol% obtained at 80° by Bolton *et al*. [14].

Good yields of methoxyphenyl benzoate were also obtained in the presence of metal salts. Bolton *et al*. [14] obtained 36.5 mol% (*o*:*p* ratio, 69:31) in the presence of copper(II) benzoate at 80°; but the yield was only 12.6 mol% in the presence of iron(III) benzoate (*o*:*p* ratio, 61:39). Kurz and Kovacic [37] obtained 75 mol% (*o*:*p* ratio, 68:32) at 60°, and 56 mol% (*o*:*p* ratio, 67:33) at 80°, in the presence of copper(II) chloride dissolved in acetonitrile. They also reported that the ester was not formed in the absence of the catalyst at 80°.

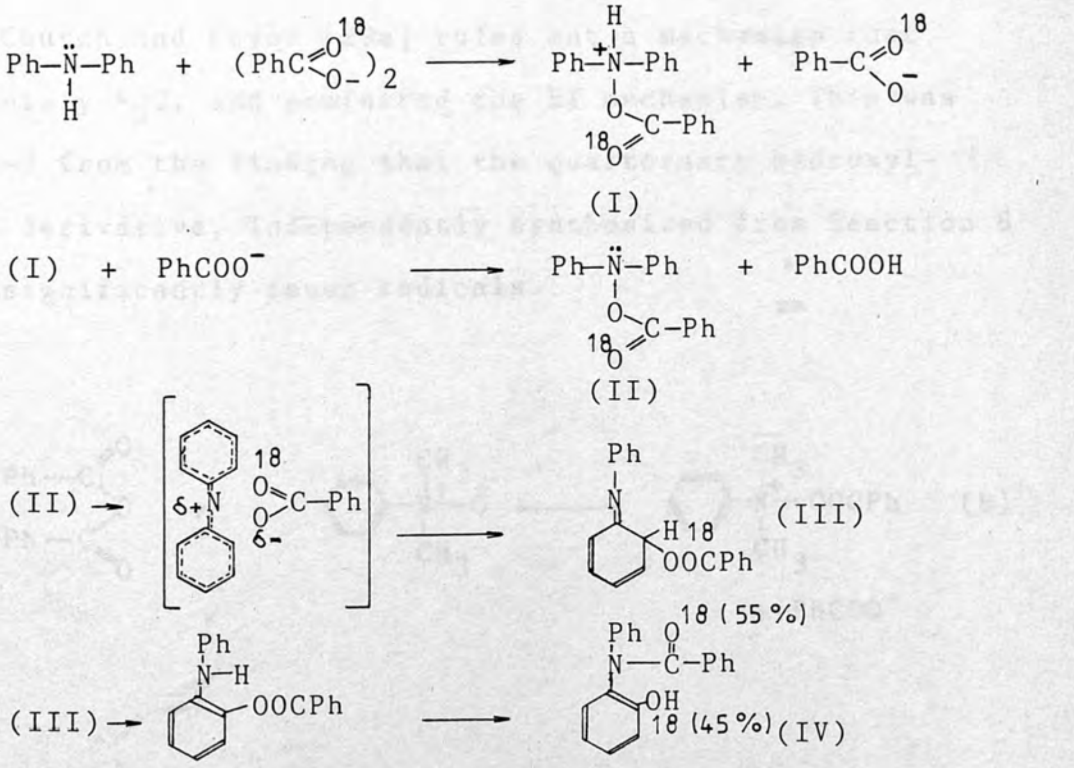
1.4.2. Aromatic amines.

The decomposition of benzoyl peroxide in dimethylaniline at 0° gave mainly benzoic acid in an almost quantitative yield, methylaniline, and formaldehyde, plus smaller amounts of 4-dimethylaminophenyl benzoate and 4,4'-di-(dimethylamino)diphenylmethane [95]. Walling and Indictor [54] suggested a mechanism involving a rate-controlling nucleophilic attack of the peroxide by dimethylaniline to form an unstable intermediate (I) which decomposed by competing radical (path a) and non-radical (path b) forming processes (Scheme 17).



Scheme 17

Denney and Denney [55] supported the S_N2 mechanism from a study of a reaction between benzoyl peroxide labelled with oxygen-18 in the carbonyl positions, and diphenylamine. N-Phenyl-N-2-hydroxyphenylbenzamide (IV) which was obtained contained oxygen-18 partially scrambled as shown in Scheme 18.

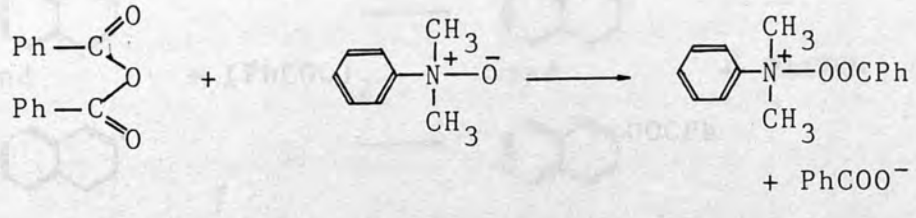


Scheme 18

Pryor and Hendrickson [29b] used the β-hydrogen kinetic isotope test in the above reaction, and from the observed inverse isotope effect of 0.93 suggested the dominance of the S_N2 mechanism. The yield of the scavengable radicals was approximately 20% as deduced by measuring the disappearence of galvinoxyl at 750 nm (ε ,760 $M^{-1}cm^{-1}$).

Graham and Mesrobian [56] suggested an initial formation of the quarternary hydroxylamine derivative which subsequently decomposed to give radical products, from (i) spectrophotometric evidence which indicated that the primary step occured through the reversible formation of a molecular complex between the amine and benzoyl peroxide, and (ii) the reaction could initiate polymerisation. It was observed that carbon dioxide was not evolved in the reaction.

Church and Pryor [29a] ruled out a mechanism that was solely S_N2, and preferred the ET mechanism. This was deduced from the finding that the quarternary hydroxylamine derivative, independently synthesized from Reaction 8 gave significantly fewer radicals.

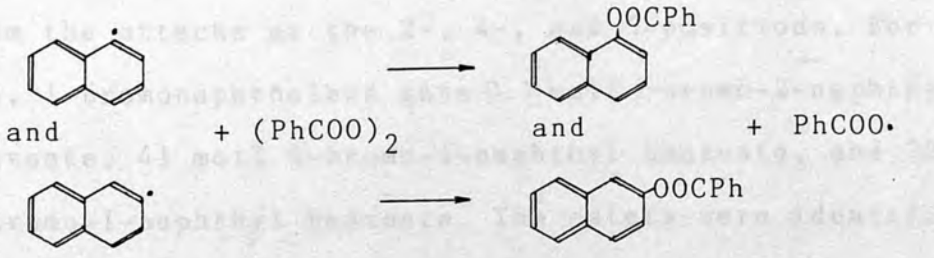


(8)

1.4.3. Polynuclear aromatic hydrocarbons.

Davies, Hey, and Williams [20a] decomposed benzoyl peroxide in naphthalene at 85° for 72 hours, and 100° for 24 hours, and obtained 32 and 24 mol% naphthols, respectively, after hydrolysing the reaction mixtures. The isomer distribution was 72.9% 1- and 27.1% 2-. The other reaction products were 20.3 mol% phenylnaphthalene, 28.9 mol% binaphthyl, and 119 mol% benzoic acid, obtained from a reaction at 85°.

The formation of binaphthyl meant that another path by which benzoyloxy radicals might have reacted was hydrogen abstraction from naphthalene to form naphthyl radical and benzoic acid. The possibility that phenyl radical was involved in this reaction was discounted on two reasons :-
(i) benzene was not formed in a detectable amount; and
(ii) binaphthyl was not formed from radical sources such as phenylazotriphenylmethane. From this, naphthyl benzoate might be formed in the induced decomposition of benzoyl peroxide by naphthyl radical (Reaction 9).



(9)

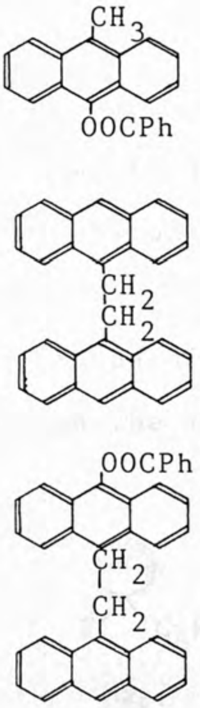
The lower yield of naphthyl benzoate at the higher temperature was possibly due to (i) increased decarboxylation of benzoyloxy radical; and/or (ii) reduced incidence of induced decomposition.

Lynch and Pausacker [20b] obtained between 18-28 mol% naphthol (1-:2- ratio, 88:12) from a similar reaction at 100° for 4-19 hours.

Boyland and Sims [57] could not isolate any naphthyl benzoate from a reaction of benzoyl peroxide with naphthalene in chlorobenzene at 80° for 30 hours, but found that the free naphthol could be isolated by (i) chromatographic separation of the reaction products; and (ii) hydrolysis of the resinous fraction from the chromatography column. It was discovered that authentic 1- and 2- naphthyl benzoates, when chromatographed under their experimental conditions, were partially hydrolysed to the free naphthol.

Dannley and Gippin [58] decomposed benzoyl peroxide in 1-substituted naphthalenes (chloro-, bromo-, and nitro-) at 70±2° for 72 hours, and obtained benzoates resulting from the attacks at the 2-, 4-, and 5-positions. For example, 1-bromonaphthalene gave 0.7 mol% 1-bromo-2-naphthyl benzoate, 41 mol% 4-bromo-1-naphthyl benzoate, and 20 mol% 5-bromo-1-naphthyl benzoate. The esters were identified as the naphthols after purification on alumina column.

Roitt and Waters [6] showed that benzoyloxy radicals attacked the exposed <u>meso</u>- positions of anthracene, 1,2-benzanthracene, and 3,4-benzopyrene, in reactions at 80° in chlorobenzene. Anthracene gave 15 mol% 9-benzoyloxyanthracene; and 3,4-benzopyrene gave 33 mol% 5-benzoyloxy-3,4-benzopyrene. Phenanthrene and chrysene were inert in this reaction. 9-Methylanthracene was very reactive towards benzoyloxy radicals, giving mainly the products shown in Figure 3.



9-benzoyloxy-10-methylanthracene

1,2-bis(9-anthracenyl)ethane

10-[2-(9'-anthracenyl)ethyl]-9-anthracenyl benzoate

<u>Figure 3</u>

The relative order of reactivities indicated in this reaction, 9-methylanthracene > 3,4-benzopyrene ≫ anthracene, 1,2-benzanthracene > 1,2:5,6-dibenzanthracene > phenanthrene, chrysene, follows their order of carcinogenic potency [7].

1.4.4. Fluoroaromatic compounds.

The decomposition of benzoyl peroxide in fluoroaromatic compounds gave mainly phenylation products arising from displacement of hydrogen and fluorine. In most cases, the process of aryldehydrogenation predominates over aryldefluorination. For example, Bolton, Sandall, and Williams [59] obtained 9.1 mol% 2-fluorobiphenyl, and 42.5 mol% 2,3-difluorobiphenyl, from 1,2-difluorobenzene at 80°.

The mechanism by which fluorine was removed from the corresponding $\sigma^{\cdot}_{F}$ -intermediate involves the formation of hydrogen bond with benzoic acid, formed from the oxidation of $\sigma^{\cdot}_{H}$ by benzoyl peroxide [59].

In hexafluorobenzene, the intermediate $\sigma^{\cdot}_{H}$ was formed through the 1,2-rearrangement of $\sigma^{\cdot}_{F}$ (Reaction 10) [60].

($\sigma^{\cdot}_{F}$) ($\sigma^{\cdot}_{H}$)

(10)

Oldham, Williams, and Wilson [61] obtained between 65-92 mol% pentafluorobiphenyl from hexafluorobenzene in a reaction at 80° for 72 hours; and Bolton, Coleman, and Williams [60] identified 5-10 mol% 2,2',3,4,5,6-hexafluorobiphenyl as one of the reaction products in the above reaction at 78.2° for 72 hours. The benzoyloxylation products were not obtained.

Allen, Bolton, and Williams [62] obtained low yields of aryl benzoates from polyfluoroaromatic compounds at 80°. 1,2,4,5-Tetrafluorobenzene gave 7.0 mol% 2,4,5-trifluorophenyl benzoate. The presence of trichloroacetic acid increased the yield to 21.0 mol%. It was found that iron(III) benzoate increased the yield of dehydrogenation products; while trichloroacetic acid, defluorination products of the corresponding σ-complexes.

Coleman [32] argued that metal salts such as iron(III) benzoate could not oxidise $\sigma^{\bullet}_{F}$ because (i) the strength of C-F bond, and (ii) the improbability of fluorine to leave as fluorinium cation, $F^{\oplus}$.

1.5. Other methods of aroyloxylation.

1.5.1. The $S_{ON}2$ reaction.

The oxidatively-initiated bimolecular nucleophilic substitution reaction ($S_{ON}2$) is a member of the family of electron-transfer chain (ETC) promoted processes, which includes the well-established reductively initiated unimolecular nucleophilic substitution reaction ($S_{RN}1$) [73].

The general form of the $S_{ON}2$ reaction is given in Scheme 19.

$$\begin{array}{llll}
RX - e & \longrightarrow & [RX]^{+\bullet} & (1) \\
[RX]^{+\bullet} + Nu^{-} & \longrightarrow & [RXNu]^{\bullet} & (2) \\
[RXNu]^{\bullet} & \longrightarrow & [RNu]^{+\bullet} + X^{-} & (3) \\
[RNu]^{+\bullet} + RX & \longrightarrow & RNu + [RX]^{+\bullet} & (4)
\end{array}$$

Scheme 19

The initiation step is a one-electron oxidation of an aromatic compound to form a radical cation (Step 1). This may be achieved anodically or by using oxidising agents such as Cu(III) [63]. The radical cation undergoes an ipso-addition of a nucleophile to form an intermediate σ-complex (Step 2), which eliminates X^{-} (Step 3) to form a new radical cation. The chain-transfer reaction (Step 4) involves the transfer of an electron from the aromatic compound to the new radical cation.

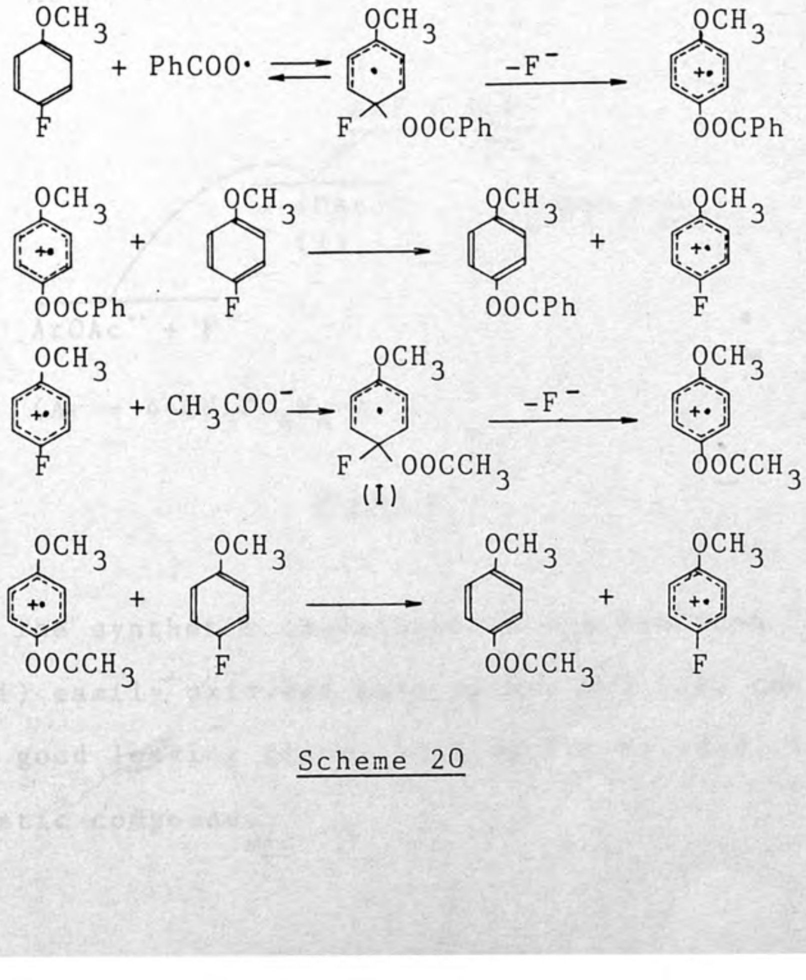
Since the mechanism involves three intermediate radicals, namely, $[RX]^{+\bullet}$, $[RXNu]^{\bullet}$, and $[RNu]^{+\bullet}$, the generation of any one of these will provide an entry into the propagation cycle. For example, Eberson and Jönsson [64] decomposed benzoyl peroxide in 4-fluoroanisole in a mixture of acetic acid and potassium acetate at 78° for 20 hours, and obtained 4-methoxyphenyl acetate and the corresponding benzoate as shown in Table 2.

Table 2 The yield (mol%) of 4-methoxyphenyl acetate and 4-methoxyphenyl benzoate from 4-fluoroanisole in $S_{ON}2$ reactions @.

$(PhCOO)_2$/mmol	acetate	benzoate
0.25	41	16
0.5	65	20
1.0	88	12
2.0	54	10

@, [4-Fluoroanisole]= 1M, glacial acetic acid, [KOAc]= 0.5M.

The mechanism proposed is given in Scheme 20.



Scheme 20

5-Fluoro-2-methoxybiphenyl and the corresponding benzoate were also formed in 9-14 mol% yields. The total yield in excess of 100 mol% (based on the peroxide) demonstrates the catalytic nature of the reaction. It was found that the yield of 4-methoxyphenyl acetate reduced to 10 mol% when potassium acetate was omitted, but the yield of the benzoate was not affected.

Eberson, Jönsson, and Wistrand [65] deduced from a thermodynamic treatment that the formation of (I) is exothermic, and the loss of fluoride from (I) is favoured over loss of acetate (Figure 4).

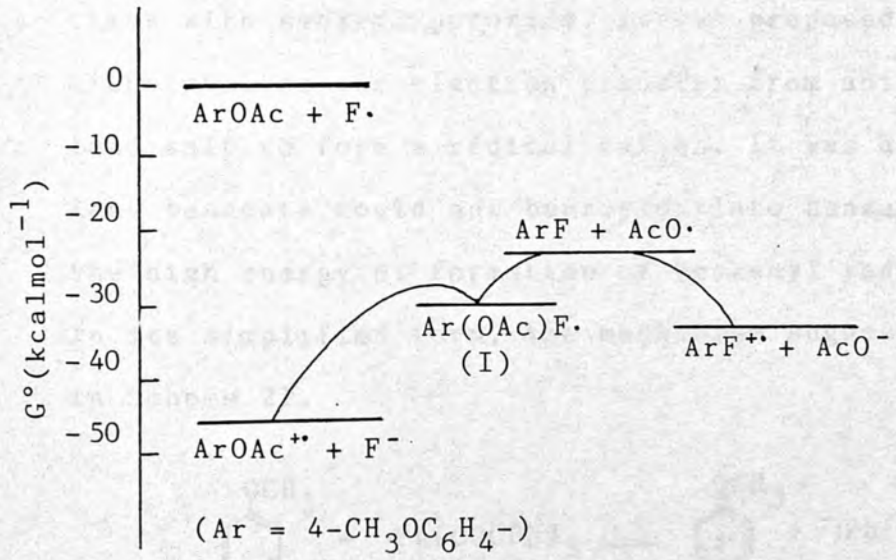
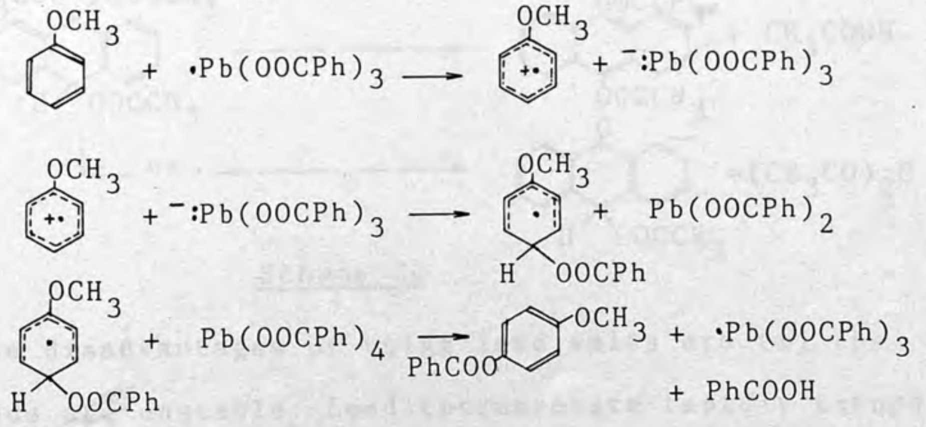


Figure 4

The synthetic usefulness of the reaction is limited to (i) easily oxidised substrates, and (ii) the presence of a good leaving group, such as the halides, in the aromatic compound.

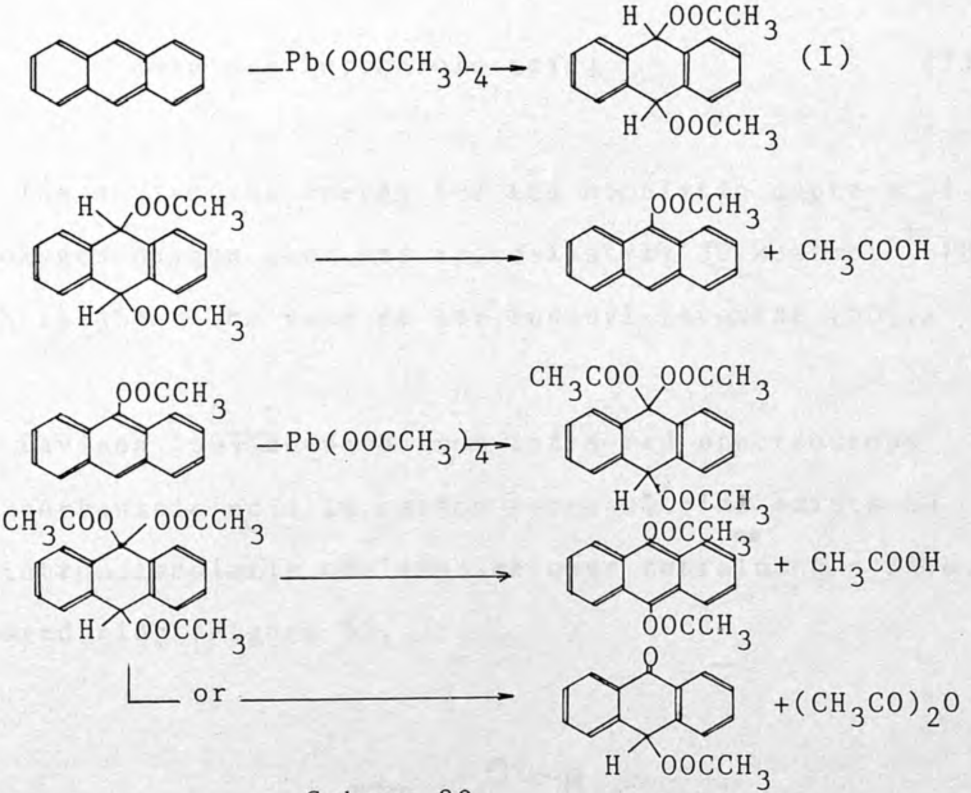
1.5.2. Lead(IV) salts.

McClelland, Norman, and Thomas [53,66] obtained 12 mol% methoxyphenyl acetate (o:p ratio, 41:59), and 73 mol% methoxyphenyl benzoate (o:p ratio, 31:69) from reactions of anisole with lead tetraacetate and lead tetrabenzoate at 80° for 10-20 minutes, under a nitrogen atmosphere, and in the presence of a catalytic amount of diisopropyl peroxydicarbonate as a radical source. The yield was based on the assumption that one mol of the product was equivalent to one mol of lead salt. From the rate of benzoyloxylation of anisole with lead tetrabenzoate, which exceeds 1000 times that of benzene, when compared with only about 8 times with benzoyl peroxide, it was proposed that the reaction involves one-electron transfer from anisole to the lead salt to form a radical cation. It was assumed that lead benzoate could not benzoyloxylate benzene because of the high energy of formation of benzenyl radical cation. In its simplified form, the mechanism suggested is outlined in Scheme 21.



Scheme 21

Fieser and Hershberg [7] reported greater than 90% monoacetoxy product from a reaction between lead tetraacetate and 3,4-benzopyrene in a mixture of acetic acid and benzene at room temperature. Fieser and Putnam [67] obtained 9-acetoxyanthracene and anthraquinone from a complex mixture of products from a reaction of anthracene at 50-55° with the above reagent. From the isolation of *cis*- and *trans*- 9,10-diacetoxy-9,10-dihydroanthracene (I) from the above reaction mixture, Fieser and Putnam [67] suggested a mechanism involving an initial addition of two acetoxy groups without the elimination of hydrogens (Scheme 22).



Scheme 22

The disadvantages of using lead salts are (i) the compounds are unstable. Lead tetraacetate rapidly turned brown due to the formation of lead dioxide on exposure to the atmosphere; and (ii) they are cumulative poisons. They can be absorbed through the skin from solutions.

1.5.3. Perbenzoic acid.

Cohen and Edwards [68] found that a solution of perbenzoic acid in benzene produced free radicals. In a study using free radical scavenger, α,α-diphenyl-β-picrylhydrazyl (DPPH), it was found that the rate of the decomposition of perbenzoic acid followed a first-order kinetic form (Equation 7).

$$\text{Rate} = k[\text{Perbenzoic acid}] \qquad (7)$$

The activation energy for the homolytic rupture of the oxygen-oxygen bond was approximately 30 kcalmol^{-1} [68], which is about the same as for benzoyl peroxide [30].

Davison [69] deduced from infra-red spectroscopy that perbenzoic acid in carbon tetrachloride exists as the intramolecularly chelated monomer containing a five-membered ring (Figure 5).

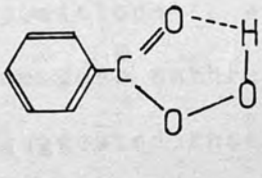


Figure 5

Cohen and Edwards [68] suggested that this structure prevails in non-polar solvents, such as benzene. It was found that the free-radical cleavage does not occur to any significant extent in 1-butanol. It was suggested that in this solvent, perbenzoic acid formed hydrogen-bonds with the solvent molecules, such that the electrons are displaced towards the oxygen attached to carbon (Figure 6).

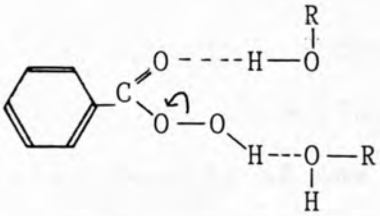


Figure 6

Eckhardt [70] decomposed perbenzoic acid in various polynuclear aromatic compounds in chloroform at 4°, and found that only the carcinogenic hydrocarbons such as methylcholanthrene, 3,4-benzopyrene, and 1,2-benzanthracene reacted. Naphthalene and phenanthrene were inert in this reaction.

Roitt and Waters [71] decomposed perbenzoic acid in the presence of similar carcinogenic hydrocarbons as Eckhardt, in chloroform at 0°, and found that oxidation occured at the meso- positions to give complex mixtures of products. Anthracene gave anthraquinone, and possibly, anthraquinol. It was suggested that perbenzoic acid is an electrophilic reagent which tend to provide electropositively polarised hydroxyl fragments, rather than the "neutral" hydroxyl radical (Reaction 11).

$$\mathrm{PhCO\overset{\curvearrowleft}{O}{-}OH} \quad + \quad \mathrm{H\overset{\curvearrowright}{-}Ar} \longrightarrow \mathrm{PhCOOH} \quad + \quad \mathrm{ArOH} \qquad (11)$$

Swern [72] suggested that the peroxide oxygen in peracids is electrophilic, and readily released in the presence of a nucleophilic group, such as a double bond. It was found that the reaction rate was increased when electron-releasing group was attached to, or in close proximity, to the double bond. This is because of the increased electron density of the ethylenic system, which resulted in an increase in the nucleophilic properties of the double bond. Similarly, the rate was decreased when electron-attracting group was present because of a decrease in the nucleophilic properties of the double bond.

Kurz and Kovacic [37] reacted perbenzoic acid in toluene in the presence of copper(II) chloride in acetonitrile at 60° for 3 hours, and obtained 109 mol% benzoic acid, 13 mol% benzyl chloride, and 3 mol% benzaldehyde. The nuclear substitution products were not detected. The yield of benzoic acid increased to 114 mol% when the catalyst was omitted.

These results suggest that perbenzoic acid cannot be used as an oxygenation reagent in aromatic compounds.

2. EXPERIMENTAL

2.1. Instruments.

2.1.1. Gas-liquid chromatography was done on a Pye-Unicam series 104 or 204 machine, with a flame ionisation detector; and connected to a 308 LDC computing integrator.

2.1.2. High-performance liquid chromatography was done on a VA Varian 5000 liquid chromatograph.

2.1.3. Visible spectroscopy was done on a Perkin-Elmer 551S UV-Vis double-beam spectrophotometer.

2.1.4. ^{1}H-N.m.r spectroscopy was recorded on a Hitachi Perkin-Elmer, R-24B, 60 MHz machine.

2.1.5. ^{19}F-N.m.r spectroscopy was recorded on a Jeol FX-90Q multinuclear Fourier transform instrument, operating at 84.26 MHz.

2.1.6. Infra-red spectroscopy was recorded on a Perkin-Elmer 197 spectrometer.

2.1.7. Molecular weight was determined on a vapour pressure Mechrolab osmometer, model 301.

2.2. Methods of analysis.

Unless otherwise stated, the analytical procedures were as follows :-

2.2.1. Gas-liquid chromatography.

Gas-liquid chromatography was done using a 5ft.x 1/8 in. o.d. glass column packed with 10% Apiezon L on 80-100 mesh celite, at 200°, and nitrogen at a pressure of 2.75 kgcm^{-2} as the carrier gas.

2.2.1.1. Qualitative analysis.

The reaction products were identified by comparing their relative retention times with those of authentic compounds (R_t= 1.0 for internal standard) under identical conditions (Table 3).

2.2.1.2. Quantitative analysis.

After the identification of the reaction products, 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 a chosen internal standard. A number of such solutions covering a wide range of relative concentrations was prepared

Table 3 Relative retention times data for g.l.c analysis.

Compound	Rel. R_t
Pentamethylbenzene (internal standard)	1.0
2-Methoxybiphenyl	2.3
4-Methoxybiphenyl	4.0
2,3,4,5,6-Pentafluorobiphenyl	0.7
2,3,5,6-Tetrafluoro-4-methoxybiphenyl	1.8
2-Methoxyphenyl acetate	0.6
4-Methoxyphenyl acetate	0.8
2,3,5,6-Tetrafluoro-4-methoxyphenyl acetate	0.4
4-Dimethylaminophenyl acetate	1.7
1-Naphthyl acetate	0.3 *
2-Methoxyphenyl benzoate	6.5
4-Methoxyphenyl benzoate	10.0
2,3,5,6-Tetrafluoro-4-methoxyphenyl benzoate	3.5
Pentafluorophenyl benzoate	1.3
1-Naphthyl benzoate	2.8 *
2-Naphthyl benzoate	3.4 *

*, Relative to 4-methoxyphenyl benzoate at 240°.

for each component. Each such solution was analysed three times by g.l.c.

The following methods were used to determine the concentrations of the various components in the reaction mixtures :-

(a) Using calibration graph.

An average peak area ratio, determined by multiplying the peak height with the width at half the peak height, for the component relative to the internal standard was used to plot the calibration curve for all the products. This was used to determine the concentration of the various components in the reaction mixture, by reference to the internal standard in each case.

(b) Using 308 LDC computing integrator.

The 308 LDC computing integrator was calibrated with the standard solutions above. The integrator response was found to be accurate to within 92-95%.

2.2.2. High-performance liquid chromatography.

High-performance liquid chromatography was done using a 250mm x 4.5mm Spherisorb S5 nitrile column (serial number E0198 ; batch number 19/235) at 235 nm. A solution of 40% acetonitrile and 60% deionised water was used as the eluant with a flow-rate of 1.5 $\mathrm{mlmin^{-1}}$ at 25° and 92 atmosphere.

The qualitative and quantitative analyses were as for g.l.c (2.2.1).

Table 4 Relative retention times data for h.p.l.c analysis.

Compound	Rel. R_t
4-Methoxyphenyl benzoate (internal standard)	1.00
4-Methyl-1-naphthyl benzoate	1.28
1-Methyl-2-naphthyl benzoate	1.27
2,3-Dimethyl-1-naphthyl benzoate	1.43

2.2.3. ^{19}F-N.m.r spectroscopy.

2.2.3.1. Qualitative analysis.

The chemical shifts (δ_F in ppm upfield from $CFCl_3$; $CDCl_3$ solvent) were compared with those calculated by assuming the additivity of substituent effects ($\Delta\delta_{o\text{-}OCH_3}$,-4.4; $\Delta\delta_{m\text{-}OCH_3}$,+2.0;$\Delta\delta_{p\text{-}OCH_3}$,+1.7) upon the chemical shifts of compounds listed in Table 5.

2.2.3.2. Quantitative analysis.

The chemical shifts obtained were assigned to each fluorine in the isomeric mixture with reference to the calculated values, and the integrals used to calculate the percentage composition of each isomer (Appendix 1) [74].

Table 5 ^{19}F-N.m.r data for C_6F_5X.

X	δ_F/ ppm			Ref.
	2-	3-	4-	
F	162.9	162.9	162.9	[75]
OCH_3	158.5	164.9	164.6	[75]
OH	163.6	170.9	165.6	*
$OOCCH_3$	154.0	164.1	159.6	[76]
OOCPh	152.9	162.8	158.4	*
C_6H_5	143.9	163.2	156.8	[74]
C_6F_5	138.1	161.1	150.5	*
Octafluoro-naphthalene	146.01 (1-)		154.7 (2-)	*

*, Authentic compounds.

2.2.4. ^{1}H-N.m.r spectroscopy.

^{1}H-N.m.r spectroscopy was used in qualitative analyses. The integrations, multiplicities, and chemical shifts (upfield of TMS in ppm ; $CDCl_3$ solvent) were used to confirm the structure of authentic compounds.

2.2.5. Molecular weight.

The vapour pressure Mechrolab osmometer was calibrated with standard solutions of benzil in benzene.

2.3. Purification of organic reagents.

2.3.1. Acetonitrile (Aldrich) was treated with activated 4A molecular sieves for one week. Calcium hydride was added, portionwise, to the partially dried solvent until the evolution of hydrogen had ceased. The liquid was decanted from the solid residue and fractionally distilled through a 30-cm Vigreux fractionating column, collecting the middle cut. B.p. 82°/760 mmHg; lit. 81.6° [77].

2.3.2. Anisole (Koch-Light) was fractionally distilled through a 30-cm Vigreux fractionating column, taking the middle cut. B.p. 154°/760 mmHg; lit. 155° [77].

2.3.3. Benzoyl peroxide (BDH) containing 30% water was dissolved in the minimum quantity of warm chloroform. The solution was poured into a separating funnel and the aqueous layer rejected. The chloroform solution was rapidly filtered through a Buchner funnel into two volumes of ice-cold methanol, with stirring. The fine white precipitate was collected on the Buchner funnel and dried in a vacuum desiccator over calcium chloride. M.p. 107-8°; lit. 106-8° [77].

2.3.4. 2-Fluoro-, 4-fluoro-, 4-chloro-, and pentafluoroanisoles, hexafluorobenzene, 1-fluoronaphthalene, and octafluoronaphthalene (Aldrich) were used directly.

2.3.5. Naphthalene (Griffin and George) was purified by washing its ethereal solution with sodium bicarbonate solution (3 times). The solid obtained when ether was removed was recrystallised from ethanol. M.p. 79.5-80°; lit. 80.5 [77].

2.3.6. 1-Methylnaphthalene was vacuum-distilled. B.p. 114-5°/15 mmHg; lit. 110°/12 mmHg [77].

2.4. Preparation of organic reagents.

2.4.1. Copper(II) benzoate [14].

Copper(II) acetate, $CuO.Cu(OOCCH_3)_2.6H_2O$ (6.0 g ; 16 mmol) was dissolved in ethanol by heating and stirring. It was filtered to removed undissolved solid. A solution of benzoic acid (7.5 g ; 0.06 mol) in ethanol was added to the hot copper acetate solution until precipitation commenced. The green precipitate was filtered and washed with hot ethanol. It was dried in the oven (100°). Yield 6.25 g (63.9%).Visible spectroscopy (1-cm silica cells; MeCN as reference) gave λ_{max} = 690 nm (ε_{max} = 1094 $M^{-1}cm^{-1}$). The molecular weight in benzene was 1222 ; molecular formula, $Cu_4(OOCPh)_8$ (required, 1223). IR (Nujol; NaCl plates) gave

ν = 680 (s), 720 (m), 1400 (m), 1560 (m), and 1610 (m) cm^{-1}.

2.4.2. 2-Deuteroanisole [78].

Magnesium turnings (2.0 g ; 0.083 mol) were covered with anhydrous diethyl ether (25 ml) in a 500-ml three-necked round-bottomed flask fitted with a double-surface reflux condenser, a sealed stirrer unit, and a 100-ml dropping funnel. Calcium chloride guard-tubes were placed on the condenser and dropping funnel.

1-Bromopropane (11.0 g ; 0.089 mol) was dissolved in anhydrous diethyl ether (75 ml); 20 ml of the solution was added to the magnesium turnings. The reaction was initiated by grinding the magnesium surface with a glass rod. Once the reaction had started, the rest of the solution was added with vigorous stirring at such a rate that kept the ether gently refluxing. The mixture was further heated for thirty minutes, and cooled. The ether was removed. Anisole (20.0 g ; 0.18 mol) was added. The mixture was gently heated under reflux at 120° (oil-bath) for four hours, during which white fumes were given off.

The 2-anisyl magnesium bromide formed above was dissolved in anhydrous diethyl ether (100 ml). Deuterium oxide (7 ml ; 0.39 mol) was slowly added with vigorous stirring. The solution was treated with a mixture of ammonium chloride (37 g) and ice (150 g). The ether layer was separated and washed three times with distilled water, dried ($MgSO_4$), filtered, and the ether removed.

2-Deuteroanisole was obtained by fractional distillation. Yield 10.7 g (75% pure). B.p. 151-2°/760 mmHg. ^{1}H-N.m.r gave δ_H = 3.6 (s ; 3H), and 6.7-7.3 (m ; 4.25H).

2.4.3. 4-Deuteroanisole.

The apparatus was set up as in (2.4.2).

Magnesium turnings (6.0 g ; 0.25 mol) were covered with anhydrous diethyl ether (25 ml). 4-Bromoanisole (46.75 g ; 0.25 mol) was dissolved in anhydrous diethyl ether (100 ml); 20 ml of the solution was added to the magnesium, and the reaction initiated as before. Once the reaction had started, the rest of 4-bromoanisole solution was added with stirring at such a rate that kept the ether gently refluxing. The mixture was further heated for an hour on a water-bath, and cooled. Deuterium oxide (4.5 ml ; 0.25 mol) was cautiously added with vigorous stirring.

The solution was treated with a mixture of ammonium chloride (25 g) and ice (100 g). The ether layer was separated, washed three times with distilled water, dried ($MgSO_4$), filtered, and the ether removed.

4-Deuteroanisole was obtained by fractional distillation. Yield 10.0 g (60% pure). B.p. 153-4°/760 mmHg. ^{1}H-N.m.r gave δ_H = 3.65 (s ; 3H), and 6.9 (m ; 4.4H)

2.4.4. 4-Methoxynonafluorobiphenyl.

4-Methoxynonafluorobiphenyl was initially donated by Dr. R. Bolton. G.l.c analysis showed two main peaks at R_t = 180 and 568 s. These were shown to correspond to 4-methoxynonafluorobiphenyl, prepared by the same method as for 2,3,5,6-tetrafluoro-4-methoxybiphenyl from 2,3,4,5,6-pentafluorobiphenyl [79] (2.5.3) ; and 4,4'-dimethoxyoctafluorobiphenyl, respectively.

Decafluorobiphenyl (1.0 g ; 3.0 mmol) was added to a solution of sodium (0.06 g ; 2.6 mmol) in dry methanol (15 ml). The mixture was heated under reflux for four hours. Water was added when cooled, and the product extracted with ether. The residue when ether was removed was recrystallised from ethanol. Yield 0.55 g (61.1%). M.p. 41-2° ; lit. 50-1° [80]. ^{1}H-N.m.r gave δ_H = 4.15 (s). G.l.c showed two peaks at R_t = 171 (87%) and 444 s (13%). ^{19}F-N.m.r gave δ_F = 138.5 (s), 140.7 (s), 150.9 (t), 152.1 (t), 158.1(t) and 161.8 (5 peaks). δ_F calculated for 4-methoxynonafluorobiphenyl were 138.1 ($F_{2'},F_{6'}$), 140.1 (F_2,F_6), 150.5 ($F_{4'}$), 156.7 (F_3,F_5), and 161.1 ($F_{3'},F_{5'}$).

2.4.5. 4,4'-Dimethoxyoctafluorobiphenyl [81].

Sodium (1.17 g ; 0.05 mol) was dissolved in methanol (15 ml). The excess of solvent was removed.

Decafluorobiphenyl (6.0 g ; 0.018 mol) and dimethyl sulphoxide (25 ml) were added, and the mixture heated under reflux for four hours. The white solid formed was extracted with diethyl ether, and the extract washed with distilled water (3 times), and the ether removed. The oily residue was recrystallised from ethanol. Yield 1.35 g (21.0%). M.p. 83-4° ; lit. 83-4.5 [82]. ^{19}F-N.m.r gave δ_F = 140.4 (d) and 158.0 (d) ; J= 19.53 Hz. δ_F calculated for 4,4'-dimethoxyoctafluorobiphenyl were 140.1 (F_2,F_6,$F_{2'}$,$F_{6'}$) and 156.7 (F_3,F_5,$F_{3'}$,$F_{5'}$). G.l.c showed one main peak at R_t = 444 (>97%), and smaller peaks at 168, 270, 720, and 804 s.

2.4.6. N,N -Dimethyl-4-fluoroaniline was prepared by the same method as for N,N -dimethylaniline from aniline [83].

4-Fluoroaniline (13.75 ml), purified by vacuum-distillation (b.p. 88-9°/24 mmHg ; lit. 187°/757 mmHg [77]), and trimethylphosphate (11.5 ml) were gently heated in a 500-ml round-bottomed flask fitted with a water condenser until a vigorous reaction commenced. The heating was stopped. When two layers were seen, the heating was continued under gentle reflux for two hours. Sodium hydroxide solution (12.5 g in 50 ml water) was cautiously added to the cooled solution (50°), and the mixture refluxed for one hour. It was poured into a large beaker and left to cool to room temperature. The oily layer of amine was poured out from the solid residue. The residue was washed with water and extracted with ether. The ether extract was added to the liquid amine, dried ($MgSO_4$), filtered, and the ether removed. The residue was treated with an equal amount of acetic anhydride and left to stand overnight. Concentrated hydrochloric acid (10 ml in 15 ml water) was carefully added and the solution extracted with ether. Sodium hydroxide solution (25%) was cautiously added to the acidic mixture until the oily product separated. This was extracted with ether, dried ($MgSO_4$), filtered, and the ether removed. The product was distilled under reduced pressure using an air condenser. Yield 7.76 g. B.p. 84-6°/14 mmHg ; lit. 78-9.5°/ 16 mmHg. M.p. 29-30° ; lit. 25° [77]. ^{1}H-N.m.r (EM-360 Varian Anaspect) gave δ_H = 2.96 (s ; 6H), and 7.0 (m ; 4H). ^{19}F-N.m.r gave δ_F = 129.28 ; lit. 129.9 [84]. δ_F for 4-fluoroaniline was 127.25 ; lit. 127.23 [84]. H.p.l.c showed one peak at R_t = 7.4 minutes.

2.4.7. Galvinoxyl. (2,6-Di-t-butyl-α-(3,5-di-t-butyl-4-oxo-2,5-cyclohexa-2,5-dienylidene)-4-tolyloxy radical) [32].

2,6-Di-t-butylphenol (21.0 g ; 0.1 mol) and formaldehyde (37% ; 15 ml) were dissolved in absolute ethanol (50 ml) and nitrogen was passed through the solution. An aqueous solution of sodium hydroxide (8 g ; 15 ml) was slowly added, and the mixture gently heated for 20 minutes.

The yellow solid formed on cooling was washed with dilute acetic acid until neutral to litmus, and then filtered. It was recrystallised from ethanol. Yield of 4,4'-dihydroxy-3,5,3',5'-tetra-t-butyldiphenylmethane, 8.0 g (35.7%). M.p. 154° ; lit. 154° [85]. ^{1}H-N.m.r gave δ_H = 1.37 (s ; 36H), 3.72 (s ; 2H), 4.87 (s ; 2H), and 6.85 (s ; 4H). UV-Vis spectroscopy (Perkin-Elmer 124 ; 1-cm silica cells ; MeCN as reference) gave λ_{max} = 292 (ε_{max} = 124 $M^{-1}cm^{-1}$) and 390 nm (ε_{max} = 87 $M^{-1}cm^{-1}$).

The yellow solid obtained (5.0 g ; 11.7 mmol) was dissolved in sodium-dried ether (70 ml) and stirred with drierite (1 g) and lead dioxide (11 g) for 12 hours at room temperature under a stream of nitrogen in blackened apparatus. After this time, the solid residue was removed by quick filtration on the Buchner funnel. The ether extract was further charged with drierite (1 g) and lead dioxide (7 g) for another 6 hours. After removal of the solid residue as before, the ether was removed on a rotary-film evaporator. The solid obtained was recrystallised from deoxygenated light petroleum (b.p. 80-100°) to give 1.25 g (25.4%) small violet needles, m.p. 154° ; lit. 153-4 [32]. Visible spectroscopy (Perkin-Elmer 124 ; 1-cm silica cells ; deoxygenated ethanol as reference) gave λ_{max} = 428 nm (ε_{max} = 116 000 $M^{-1}cm^{-1}$) ; lit. 431 nm (ε_{max} = 154 000 $M^{-1}cm^{-1}$) [18].

2.4.8. Perbenzoic acid [86].

Sodium (2.1 g ; 0.09 mol) was dissolved in "super-dry" methanol (40 ml) in a conical flask with moderate cooling, and the resulting solution cooled to -5° in a freezing mixture.

Recrystallised benzoyl peroxide (20.0 g ; 0.083 mol) was dissolved in chloroform (80 ml), and cooled to 0°. This was immediately added to the sodium methoxide solution, with shaking and cooling, at such a rate that the temperature did not rise above 0°. The mixture was kept for 4-5 minutes in the ice-salt bath with continous shaking.The "milky" solution was transferred to a separating funnel. Water (200 ml) containing much chopped ice was added to extract sodium perbenzoate. The chloroform layer was separated, and the aqueous layer extracted with cold chloroform (2x40 ml).

Cold sulphuric acid (90 ml ; 0.5 M) was added to the aqueous layer. Perbenzoic acid was extracted from the solution using cold chloroform (3x40 ml), and the extract washed with cold water (2x20 ml), dried (Na_2SO_4), and concentrated on a rotary-film evaporator.

The residual chloroform was removed under reduced pressure while passing in carbon dioxide through a capillary tube. The solid residue was dried in a vacuum-desiccator over calcium chloride. It was kept in the dark at 0°. Yield 9.8 g (86.0%). M.p. 38-9° ; lit. 41-3° [77].

2.4.9. Perfluorobenzoic acid.

Perfluorobenzonitrile (20.0 g ; 0.1 mol) was heated for one hour at 100-30° with concentrated sulphuric acid (18 ml) to give a homogeneous mixture and then cooled to 90°. Water (24 ml) was added over two hours at 80-90° with cooling. The flask was refluxed for six hours, and cooled to about 35°. Dichloromethane (30 ml) was added, and stirred until the precipitate dissolved. The organic layer was collected. The aqueous layer was extracted with dichloromethane (2x25 ml), and the combined extract dried ($CaCl_2$), filtered, and most of the solvent removed. The solid was collected and dried in a vacuum-desiccator over calcium chloride. Yield 16.3 g (76.9%). M.p. 100-2° ; lit. 99-101° [87].

2.5. Preparation of authentic compounds.

2.5.1. 2-Methoxybiphenyl [14].

2-Hydroxybiphenyl (8.5 g ; 0.05 mol) was dissolved in sodium hydroxide solution (30 ml ; 7%) by heating and stirring. Dimethyl sulphate (5 ml) was added to the solution in a round-bottomed flask, and warmed at 70-80° for one hour, and cooled. The oily product was extracted with diethyl ether, and the extract washed with dilute sodium hydroxide solution, dried ($MgSO_4$), filtered, and the ether removed.

2-Methoxybiphenyl was distilled under reduced pressure. Yield 4.3 g (46.7%). B.p. 155°/13 mmHg ; lit. 159-60°/18 mmHg [77].

2.5.2. 4-Methoxybiphenyl [14].

4-Methoxybiphenyl was similarly prepared from 4-hydroxybiphenyl (8.5 g ; 0.05 mol) as in (2.5.1).

The solid product was filtered off under suction and washed with dilute sodium hydroxide solution. It was recrystallised from methylated spirit. Yield 3.7 g (40.0%). M.p. 88-9° ; lit. 91-2° [77].

2.5.3. 2,3,5,6-Tetrafluoro-4-methoxybiphenyl [79].

Sodium (0.7 g ; 0.03 mol) was placed in a dry round-bottomed flask fitted with a reflux condenser and cooled in ice-water. "Super-dry" methanol (15 ml) was added all at once.

2,3,4,5,6-Pentafluorobiphenyl (1.0 g ; 4.0 mmol) was added, and the mixture heated under reflux for one hour.

The solid formed was extracted with petroleum ether (b.p. 30-40°) and the ether removed. It was recrystallised from ethanol. M.p. 55-7° ; lit. 63-4° [79]. ^{1}H-N.m.r gave δ_H = 4.07 (s ; 3H) and 7.28 (s ; 5H). ^{19}F-N.m.r (Perkin-Elmer R-12B ; 56.4 MHz ; $CFCl_3$) gave δ_F = 143.4 (d ; 2F) and 156.5 (d ; 2F). δ_F calculated, 145.9 (F_2,F_6) and 158.8 (F_3,F_5). G.l.c showed three peaks at R_t= 486 (>99%), 780, and 924 s.

2.5.4. 2-Methoxyphenyl acetate [88].

2-Methoxyphenol (11.0 ml ; 0.1 mol) was dissolved in sodium hydroxide solution (50 ml ; 3M) in a 250-ml conical flask. Ice (100 g) and acetic anhydride (15 ml ; 0.16 mol) were added. The flask was stoppered and shaken vigorously for 5 minutes. The product was extracted with diethyl ether (4x20 ml), and the extract washed with dilute sodium hydroxide solution, dried ($MgSO_4$), filtered, and the ether removed. The product was distilled under reduced pressure. Yield 11.35 g (68.4%). B.p. 124°/14 mmHg ; lit. 123-4°/13 mmHg [88].

2.5.5. 4-Methoxyphenyl acetate was similarly prepared from 4-methoxyphenol (12.4 g ; 0.1 mol) as in (2.5.4).

The oily product crystallised upon scratching and was recrystallised from dilute ethanol. Yield 8.52 g (51.3%). M.p. 32-3° ; lit. 30-2° [88].

2.5.6. 1-Naphthyl acetate was similarly prepared from 1-naphthol (7.2 g ; 0.05 mol) as in (2.5.4). Yield 2.38 g ; (25.6%).M.p. 44-4.5° ; lit. 43-6° [77].

2.5.7. 2-Methoxyphenyl benzoate

2-Methoxyphenol (6.0 ml ; 0.05 mol) was dissolved in sodium hydroxide solution (70 ml ; 10%) in a 500-ml round-bottomed flask. Benzoyl chloride (9.0 ml ; 0.08 mol) was added and the flask stoppered and shaken vigorously until the smell of benzoyl chloride was gone (15 min). The solid was recrystallised from methylated spirit. Yield 4.75 g (41.7%).M.p. 58-9° ; lit. 58-9.5° [37].

2.5.8. 4-Methoxyphenyl-, 1- and 2-naphthyl- benzoates were similarly prepared from 4-methoxyphenol, 1- and 2- naphthols, respectively, as in (2.5.7).

The m.p. of 4-methoxyphenyl benzoate was 87-8° ; lit. 85.5-7° [37] ; 1-naphthyl benzoate, 53-4° ; lit. 55° [20a] ; and 2-naphthyl benzoate, 103-4° ; lit. 106° [20a].

2.5.9. Pentafluorophenyl benzoate [89]

Hexafluorobenzene (5.0 g ; 27 mmol) was heated under reflux with potassium hydroxide pellets (3.8 g ; 0.07 mol) in t-butanol (50 ml) for one hour, and cooled. Water (100 ml) was added, and t-butanol distilled off. The residual aqueous solution was filtered and extracted with ether (2x25 ml). The aqueous layer was acidified with hydrochloric acid (5M), and the oil which separated was extracted with ether (4x25 ml). The extract was washed with water, dried ($MgSO_4$), filtered, and the ether removed.

Pentafluorophenol was obtained by distillation under reduced pressure. Yield 3.65 g (73.5%).B.p. 49°/13 mmHg ; lit. 143°/760 mmHg [89]. ^{19}F-N.m.r gave δ_F = 163.6 (F_2,F_6 ; J, 24.4 Hz), 165.6 (F_4 ; J, 19.5 Hz), and 170.9 (F_3,F_5 ; J, 19.5, 24.4 Hz).

Pentafluorophenol (0.5 g ; 2.6 mmol) was shaken with benzoyl chloride (0.5 ml ; 4.3 mmol) in pyridine (5 ml) in a stoppered round-bottomed flask for one hour. The solid formed was extracted with ether. The extract was washed successively with water and sodium hydrogen carbonate solution, dried ($MgSO_4$), filtered, and the ether removed. The residue was recrystallised from ethanol. Yield 0.3 g ; (37.8%). M.p.74-5° ; lit. 74-5° [89]. ^{19}F-N.m.r gave δ_F=152.9 (F_2,F_6 ; J, 19.5 Hz), 158.4 (F_4 ; J, 24.4 Hz), and 162.8 (F_3,F_5 ; J, 19.5, 24.4 Hz). G.l.c showed one peak at R_t= 596 s.

2.5.10. 2,4,5,6-Tetrafluoro-3-methoxyphenol was prepared from pentafluoroanisole (5.38 g ; 27 mmol) as in (2.5.9). Yield 4.64 g (87.7%).B.p. 93°/12 mmHg ; lit. 99-100°/15 mmHg [90]. G.l.c (155°) showed three peaks at R_t = 221 (28%), 296 (71.6%), and 429 s (0.4%). ^{1}H-N.m.r gave δ_H = 3.85 (s ; 3H) and 6.9 (s ; 1H). ^{19}F-N.m.r gave δ_F = 159.1 (s), 159.7 (d), 164.4 (d), 165.0 (d), 165.7 (t), and 170.8 (t). δ_F calculated for 3,4,5,6-tetrafluoro-2-methoxyphenol, 165.6 (F_6), 166.5 (F_3), 167.6 (F_4), and 172.6 (F_5) (27%); 2,4,5,6-tetrafluoro-3-methoxyphenol, 159.2 (F_2), 161.2 (F_4), 165.3 (F_6) and 172.9 (F_5) (71%); and 2,3,5,6-tetrafluoro-4-methoxyphenol, 165.6 (F_2,F_6) and 166.5 (F_3,F_5) (2%). IR (liquid ; NaCl plates) showed the characteritic broad absorption band at ν = 3400 cm^{-1} due to the -OH group.

2.5.11. 2,4,5,6-Tetrafluoro-3-methoxyphenyl acetate was prepared by the same method as for pentafluorophenyl trifluoroacetate from pentafluorophenol and trifluoroacetyl chloride [91].

2,4,5,6-Tetrafluoro-3-methoxyphenol (1.0 g ; 5.0 mmol) was condensed with acetyl chloride (5.0 ml ; 70 mmol) at -28° (CCl_4/dry ice) for 2½ hours. The mixture was left to warm to room temperature, and the excess acetyl chloride distilled off. The remaining liquid was extracted with ether, and the extract washed successively with water and saturated sodium hydrogen carbonate solution. It was dried ($MgSO_4$), filtered, and the ether removed. The liquid was distilled under reduced pressure. B.p. 94-5°/11 mmHg. G.l.c showed three peaks at R_t= 84 and 96 (~80% for both), and 105 s (~20%). ^{1}H-N.m.r gave δ_H = 2.18 (s ; 3H) and 3.85 (s ; 3H).

^{19}F-N.m.r gave δ_F = 148.9, 154.1, 154.7, 155.1, 157.9, 158.7, 159.5, 160.3, 164.7, 165.7, and 170.6. δ_F calculated for 3,4,5,6-tetrafluoro-2-methoxyphenyl acetate, 156.0 (F_6), 159.7 (F_3), 161.6 (F_4), and 165.8 (F_5) (28%) ; 2,4,5,6-tetrafluoro-3-methoxyphenyl acetate, 149.6 (F_2), 155.2 (F_4) 155.7 (F_6), and 166.1 (F_5) (34%) ; 2,3,5,6-tetrafluoro-4-methoxyphenyl acetate, 156.0 (F_2,F_6) and 159.7 (F_3,F_5) (17%) ; and the unreacted isomeric tetrafluoromethoxyphenols (21%).

<u>2.5.12. 2,4,5,6-Tetrafluoro-3-methoxyphenyl benzoate</u> was prepared from 2,4,5,6-tetrafluoro-3-methoxyphenol (0.5 g ; 2.6 mmol) as in (2.5.9). Yield 0.41 g (52.0%).M.p. 112-4°. G.l.c showed three peaks at R_t= 690 (32%), 846 (27%), and 924 s (41%). ^{19}F-N.m.r; δ_F = 139.6 (d), 148.5 (s), 149.8 (d), 152.8 (d), 154.4 (five peaks), 157.7(t), 158.6 (t), 160.0 (t), and 164.3 (four peaks). δ_F calculated for 3,4,5,6-tetrafluoro-2-methoxyphenyl benzoate, 154.9 (F_6), 158.4 (F_3), 160.4 (F_4), and 164.5 (F_5) (39%) ; 2,4,5,6-tetrafluoro-3-methoxyphenyl benzoate, 148.5 (F_2), 154.0 (F_4), 154.6 (F_6), and 164.8 (F_5) (19.5%), and 2,3,5,6-tetrafluoro-4-methoxyphenyl benzoate, 154.9 (F_2,F_6) and 158.4 (F_3,F_5) (41.5%).

2.5.13. 2-Heptafluoronaphthyl benzoate.

2-Heptafluoronaphthol was prepared from octafluoronaphthalene (3.67 g ; 13.5 mmol) as in (2.5.9). The liquid obtained by vacuum-distillation, b.p. 146°/19 mmHg, solidified to a white solid, m.p. 115-9° ; lit. 116-20° [92]. ^{19}F-N.m.r gave δ_F = 147.9, 148.4 (4F), 152.67 (1F), 156.67 (1F), and 158.0 (1F). δ_F calculated, by assuming the additivity of substituent effect ($\Delta\delta_{o\text{-}OH}$, + 0.7) upon the chemical shifts of octafluoronaphthalene (Table 5), 146.01 (F_4,F_5,F_8), 146.7 (F_1), 154.7 (F_6,F_7), and 155.4 (F_3).

2-Heptafluoronaphthyl benzoate was obtained from 2-heptafluoronaphthol as a white solid. Yield 0.27 g (39.6%). M.p. 132-3°; lit. 134° [92] ^{19}F-N.m.r gave δ_F = 134.5 (1F), 146.1 (4F), 153.8 (1F), and 154.9 (1F). δ_F calculated by assuming the additivity of substituent effect ($\Delta\delta_{o\text{-}OOCPh}$, - 10.0) upon the chemical shifts of octafluoronaphthalene (Table 5), 136.01 (F_1), 144.7 (F_3), 146.01 (F_4,F_5,F_8), and 154.7 (F_6,F_7).

<u>2.5.14. 4-Dimethylaminophenol</u> was prepared by the same method as for 3-dimethylaminophenol from 3-aminophenol [93].

4-Aminophenol (10.9 g ; 0.1 mol) was added ,portionwise, over a period of 1½ hours, to dimethyl sulphate (23.7 g ; 0.19 mol) in a round-bottomed flask and stirred using a magnetic stirring bar. The flask was then fitted with a reflux condenser and heated on a water-bath for two hours, and cooled. It was poured into ice-water (80 ml), forming a pink solution. Solid sodium carbonate was slowly added until the mixture was alkaline, and the product extracted with ether (5x25 ml).

Hydrochloric acid (5M) was added to the ether extract until all the black liquid separated. This was removed and made alkaline with sodium carbonate solution (10%). The product was extracted with ether, dried ($MgSO_4$), filtered, and the ether removed. The black liquid obtained was vacuum-distilled to give a viscous pale yellow liquid. Yield 2.23 g (16.3%). B.p. 164-5°/19 mmHg ; lit. 165°/30 mmHg [77]. The liquid solidified to a black solid on standing. ^{1}H-N.m.r gave δ_H = 2.84 (s ; 6H), 3.75 (s ; 1H), and 6.65 (m ; 4H). G.l.c (240°) showed one main peak at R_t =124 s (89.8%).

2.5.15. <u>4-Dimethylaminophenyl acetate</u> was prepared from 4-dimethylaminophenol (1.0 g ; 7.3 mmol) as in (2.5.4). Yield 0.83 g (63.5%). M.p. 75-7°, from petroleum ether (b.p. 30-40°) ; lit. 77-8° [94]. ^{1}H-N.m.r gave δ_H = 2.18 (s ; 3H), 2.82 (s ; 6H), and 6.5-6.95 (m ; 4H). H.p.l.c showed one peak at R_t = 5.7 minutes.

2.5.16. <u>4-Dimethylaminophenyl benzoate</u> was prepared from 4-dimethylaminophenol as in (2.5.7). The solid product was recrystallised from petroleum ether (b.p. 30-40°). M.p. 154.5-5° ; lit. 158° [95]. ^{1}H-N.m.r gave δ_H = 2.85 (s ; 6H), and 6.51-8.11 (m ; 9H). H.p.l.c showed one peak at R_t = 10.3 minutes.

2.5.17. 4-Methyl-1-naphthyl benzoate.

2.5.17.1. From 1-Methylnaphthalene [83].

1-Methylnaphthalene (10.0 g ; 0.07 mol) was dissolved in glacial acetic acid (50 ml) by gentle warming, and cooled in ice-water. Concentrated nitric acid (10 ml) was slowly added with shaking. The mixture was warmed to 80° for one minute, and then poured into cold water (500 ml) with vigorous stirring. It was boiled for thirty minutes and cooled. The oily semi-solid formed was recrystallised from aqueous ethanol to give 4.3 g (33.0%) small brown needles of 4-methyl-1-nitronaphthalene, m.p. 57-9°. The unreacted 1-methylnaphthalene was removed by column chromatography (neutral alumina ; petroleum ether, b.p. 40-60°). The yellow band in the column was eluated with benzene to give small yellow needles, m.p. 64.5-5° ; lit. 71-2° [96]. ^{1}H-N.m.r gave δ_H = 2.75 (s ; 3H) and 7.3-8.3 (m ; 6H).

4-Methyl-1-nitronaphthalene (4.0 g ; 0.02 mol) was reduced by warming its ethanolic solution with tin (8 g) and concentrated hydrochloric acid (40 ml). After 10 min., the mixture was heated under reflux for 30 min., and cooled. It was made alkaline with sodium hydroxide solution (30%), and extracted with ether (5 times). The ether extract was washed with water (3 times), and dried ($MgSO_4$). 4-Methyl-

1-naphthylamine was obtained as a dark viscous liquid when ether was removed. Yield 2.3 g (73.2%). It was distilled under reduced pressure to give a pale yellow viscous oil, b.p. 178-80°/16 mmHg ; lit. 176°/12 mmHg [77].

4-Methyl-1-naphthylamine (2.3 g ; 15.0 mmol) was diazotised by dissolving in concentrated sulphuric acid (10 ml solution of 55 ml concentrated sulphuric acid in 75 ml water), and cooled in ice-salt mixture to 0°. Sodium nitrite solution (1.8 g in 4 ml water) was added dropwise with stirring to the cold solution while keeping the temperature below 5°, until a test drop gave an immediate black colouration on potassium iodide-starch paper. The mixture was stirred for a further 10 minutes and then left to warm to room temperature. It was warmed to 50-5° with stirring until the evolution of nitrogen had ceased. 4-Methyl-1-naphthol was obtained by steam-distillation.

4-Methyl-1-naphthol was benzoylated with benzoyl chloride (2.5.7) to give 4-methyl-1-naphthyl benzoate. Yield 0.09 g (2.3%). M.p. 76-7° ; lit. 81-2° [77] from ethanol. ^{1}H-N.m.r gave $\delta_H = 2.65$ (s ; 3H) and 7.23-8.3 (m ; 11H). H.p.l.c showed peaks at $R_t = 278$ (74.6%), and 294 (25.4%) s.

2.5.17.2. From 1-naphthol.

(a) 1-Methoxynaphthalene [83].

1-Naphthol (36.0 g ; 0.25 mol) was dissolved in sodium hydroxide solution (10.5 g in 150 ml) in a two-necked round-bottomed flask fitted with a reflux condenser and a dropping funnel, each fitted with a calcium chloride guard-tube. The mixture was stirred with a magnetic stirring bar, and the temperature kept at 10°. Dimethyl sulphate (24 ml) was added, dropwise, while stirring. The mixture was warmed on a water-bath for one hour at 70-80°, and cooled. The liquid product was extracted with ether, washed with sodium hydroxide solution (10%), and then with water. It was dried ($MgSO_4$), and the ether removed. 1-Methoxynaphthalene was obtained by distillation under reduced pressure. Yield 21.0 g (53.2%). B.p. 146-7°/18 mmHg ; lit. 135°/10 mmHg [77]. ^{1}H-N.m.r gave δ_H = 3.76 (s ; 3H), and 5.91-8.21 (m ; 7H).

(b) 4-Methoxy-1-naphthylaldehyde [97].

Dimethylformamide (11 ml) was cooled (ice-bath) in a two-necked round-bottomed flask equipped with a reflux condenser and a dropping funnel, each carrying a calcium chloride guard-tube. Phosphorus oxychloride (13.8 ml) was added to the solution, dropwise, from the dropping funnel.

1-Methoxynaphthalene (20.0 g ; 0.126 mol) was added, portionwise, with stirring. The reaction mixture was heated for three hours on a water-bath. It was poured into crushed ice (50 g) in a beaker. Saturated sodium acetate solution was added until the pH was between 6-8, with stirring. The product was extracted with benzene, and the extract washed with dilute hydrochloric acid, then with sodium carbonate solution, and finally with water. It was dried ($MgSO_4$), and the benzene removed. The liquid product was vacuum-distilled. Yield 17.65 g (75.3%).B.p. 169-70°/17 mmHg and 212-3°/17 mmHg ; lit. 204-5° /15 mmHg [97]. ^{1}H-N.m.r gave δ_H = 4.0 (s ; 3H), 6.72-8.3 (m ; 6H), and 9.2 (d ; 1H).

(c) 4-Methoxy-1-methylnaphthalene.

4-Methoxy-1-naphthylaldehyde (17.0 g ; 0.09 mol) , hydrazine hydrate (8.6 g ; 98%), and diethylene glycol (80.4 ml) was heated at 100° for five minutes, and cooled in ice-water. Potassium hydroxide pellets (6.7 g ; 0.12 mol) was carefully added, and the flask heated under reflux until the evolution of nitrogen had ceased (about one hour). Water was added to the cooled mixture and the product extracted with ether, dried ($MgSO_4$), and the ether removed to give a pale yellow oil. Yield 9.6 (62.0%).B.p. 158-60°/ 18 mmHg and 162°/18 mmHg ; lit. 154-5°/15 mmHg [97].

(d) 4-Methyl-1-naphthyl benzoate.

4-Methoxy-1-methylnaphthalene (1.0 g ; 5.8 mmol) and pyridine hydrochloride (3.0 g ; 0.026 mol), prepared by passing dry hydrogen chloride gas into dry pyridine, was heated at 240° (electric heating mantle) for 30 minutes. Water was added to the cooled product, and then extracted with ether, dried ($MgSO_4$), and the ether removed to give 4-methyl-1-naphthol.

4-Methyl-1-naphthol was benzoylated with benzoyl chloride as in (2.5.7) to give 4-methyl-1-naphthyl benzoate. Yield 0.89 g (58.4%).M.p. 75-6° ; lit. 81-2° [77]. ^{1}H-N.m.r gave δ_H = 2.65 (s ; 3H) and 7.25-8.35 (m ; 11H). H.p.l.c showed one peak at R_t = 280 s.

2.5.18. 1-Methyl-2-naphthyl benzoate [97].

2-Methoxy-1-naphthylaldehyde was prepared from 2-methoxynaphthalene (40.0 g ; 0.25 mol) as in (2.5.17.2b). Yield 29.15 g (62.7%). M.p. 79-81° ; lit. 73-5° [77]. ^{1}H-N.m.r gave δ_H = 3.95 (s ; 3H), 7.0-7.9 (m ; 6H), and 9.0-9.2 (d ; 1H).

2-Methoxy-1-methylnaphthalene was obtained from 2-methoxy-1-naphthylaldehyde (20.0 g ; 0.11 mol) as in (2.5.17.2c). Yield 13.29 g (70.2%).M.p. 37-8° ; lit. 41° [97]. ^{1}H-N.m.r gave δ_H = 2.46 (s ; 3H), 3.85 (s ; 3H), and 6.95-7.8 (m ; 6H).

2-Methoxy-1-methylnaphthalene (0.5 g ; 2.9 mmol) was converted to 1-methyl-2-naphthol as in (2.5.17.2d). It was benzoylated to give 1-methyl-2-naphthyl benzoate. Yield 0.5 g (65.6%). M.p. 112-4° ; lit. 117° [77]. ^{1}H-N.m.r gave δ_H = 2.5 (s ; 3H), and 7.2-8.25 (m ; 11H). H.p.l.c showed one peak at R_t = 276 s.

2.5.19. 2,3-Dimethyl-1-naphthyl benzoate.

2,3-Dimethylnaphthalene (10.0 g ; 64.0 mmol) was nitrated as in (2.5.17.1) to give 2,3-dimethyl-1-nitronaphthalene. Yield 7.9 g (61.4%). M.p. 109-10° ; lit. 110-10.5° [98]. ^{1}H-N.m.r gave δ_H = 2.38, 2.5 (s ; 6H), and 7.2-7.7 (m ; 5H).

2,3-Dimethyl-1-nitronaphthalene (6.0 g ; 0.03 mol) was reduced to 2,3-dimethyl-1-naphthylamine. Yield 2.15 g (41.9%).

2,3-Dimethyl-1-naphthol (0.6 g ; 29.8%) was obtained as a red solid, m.p. 112-3°, from the diazotisation of 2,3-dimethyl-1-naphthylamine (2.0 g ; 11.7 mmol). ^{1}H-N.m.r gave δ_H =2.35, 2.45 (s ; 6H), 5.15(s ; 1H), and 7.3-7.5 (m ; 5H).

2,3-Dimethyl-1-naphthyl benzoate (0.17 g ; 35.4%) was obtained as a pale yellow solid, m.p. 118-20°, from 2,3-dimethyl-1-naphthol (0.3 g ; 1.74 mmol). ^{1}H-N.m.r gave δ_H = 2.2, 2.4 (s ; 6H), and 7.2-8.2 (m ; 10H). H.p.l.c showed one peak at R_t = 282 s.

2.6. The decomposition of benzoyl peroxide in aromatic compounds.

2.6.1. Procedure.

The aromatic compound (50 ml) was introduced into a 250-ml round-bottomed flask fitted with a reflux condenser, and immersed in an oil-bath set at the stated temperature. It was deaerated by dropping pieces of solid carbon dioxide from the top of the condenser.

In the experiment with an additive, an accurately known weight was dissolved in acetonitrile (50 ml), and added to the aromatic compound.

When the temperature equilibration had been achieved, an exactly known weight of benzoyl peroxide (1 g) was added. The flask was shaken thoroughly, and the reaction left to proceed for a fixed time.

A known amount of internal standard (pentamethylbenzene for the reaction of anisole or its derivatives ; and 4-methoxyphenyl benzoate for naphthalene or its derivatives) was added before work-up.

2.6.2. Work-up.

2.6.2.1. The uncatalysed decomposition.

The content of the flask was poured into a separating funnel. The acidic part was extracted with saturated hydrogen carbonate solution (6x20 ml), and discarded.

2.6.2.2. The catalysed decomposition.

The content of the flask was shaken with (i) 50% aqueous *ortho*- phosphoric acid for the reaction with copper(II) benzoate until the colour changed from green to brown ; (ii) hydrochloric acid (5M) for the reaction with copper(II) chloride or bromide until the colour changed from black to brown ; or (iii) aqueous sodium thiosulphate solution (0.1M) for the reaction with iodine, until the colour of iodine disappeared.

The organic layer was washed with water until the washings were neutral to litmus. The acidic part was extracted as above (2.6.2.1).

The organic layer was dried ($MgSO_4$), filtered, and the solvent removed under reduced pressure.

The reaction mixture was analysed by g.l.c for the reaction of anisole, its derivatives, and naphthalene ; and h.p.l.c for the reaction of methylnaphthalenes.

The yield was expressed as 100 mol of product per mol of peroxide (mol%).

2.6.3. Results.

Table 6 The decomposition of benzoyl peroxide in anisole$^{@}$

$Cu_4(OOCPh)_8$	T°/t(hr)	Mol%				
		phenylation			benzoyloxylation	
		o-	m-	p-	o-	p-
none	80°/72hr	25.1	5.9	4.9	5.2	3.5
		-	7.9	5.7	6.8	5.3
		-	7.2	6.7	5.1	3.8
		-	8.0	4.6	7.1	6.3
present	80°/20hr	22.6	8.0	4.4	13.4	3.2
	80°/72hr	32.5	9.3	5.4	16.1	3.6
		30.6	16.8	6.4	14.8	2.4
present	60°/20hr	18.7	8.9	4.1	5.3	5.1
	60°/48hr	21.3	6.5	3.8	5.5	7.8
	60°/72hr	17.4	5.7	3.4	7.5	11.9
		-	8.4	4.6	8.5	15.9
		15.5	-	2.8	6.6	16.9

@, Anisole:$(PhCOO)_2$:$Cu_4(OOCPh)_8$ ~ 100:1:0.01 ;
-, not determined.

Table 7 The copper(II) benzoate catalysed decomposition of benzoyl peroxide in anisole under different experimental conditions for 72 hours.

T°	Mol ratio *	Methoxyphenyl benzoate	
		mol%	*o*:*p* ratio
55°	22.6:1.0:0.1 **	8.4	36:64
	99.8:1.0:0.035	8.3	33:67
	119.6:1.0:0.04	11.6	25:75
60°	13.0:1.0:0.15 **	9.0	33:67
	94.6:1.0:0.15	16.7	30:70
	113.4:1.0:0.005	20.7	48:52
	115.2:1.0:0.015	19.4	39:61
	159.9:1.0:0.37	23.5	28:72
	175.0:1.0:0.46	23.1	28:72
	472.6:1.0:0.42	19.5	24:76
80°	21.6:1.0:0.15 **	3.8	52:48
	92.0:1.0:0.14	11.0	52:48
	105.3:1.0:0.01	4.2	85:15
	109.2:1.0:0.015	11.7	82:18
	110.4:1.0:0.01	17.2	86:14
	267.3:1.0:0.08	15.1	60:40
	306.8:1.0:0.01	3.2	59:41
	317.2:1.0:0.005	7.4	52:48

(Continued)...

Table 7 (Continuation).

T°	Mol ratio *	Methoxyphenyl benzoate	
		mol%	*o*:*p* ratio
80°	337.5:1.0:0075	16.4	62:38
	590.2:1.0:0.02	4.3	68:32
82°	21.8:1.0:0.15 **	2.1	62:38
	75.6:1.0:0.025	2.0	-
	92.8:1.0:0.03	1.8	-

*, Anisole:$(PhCOO)_2$:$Cu_4(OOCPh)_8$; **, "optimum" condition [45] ; -, greater than 99% *ortho*-.

A graphical method was used in order to find the "optimum" condition for the yield of benzoyloxylation product in this system (Appendix 2).

The shaded areas in Appendix 2 gave the corresponding mol ratios for high yield (ca. 20 mol%) of methoxyphenylbenzoate, in favour of the *para*- isomer at 60°, and *ortho*-isomer at 80°. The combination of these gave :-

Anisole:$(PhCOO)_2$:$Cu_4(OOCPh)_8$ = 160:1:0.1 at 60°

and 110:1:0.015 at 80°

Table 8 The copper(II) benzoate catalysed decomposition of benzoyl peroxide in deuteroanisole at 60°[@]

Compound	Time (hr)	Mol%				
		phenylation			benzoyloxylation	
		o-	*m*-	*p*-	*o*-	*p*-
2-Deutero-anisole	20	24.3	74.1	4.1	4.8	13.4
	72	9.2	82.1	1.0	4.1	12.8
		6.1	79.1	1.1	4.3	8.3
4-Deutero-anisole	20	3.6	0.7	1.2	3.0	-
	48	2.4	0.7	1.1	1.7	2.5
	72	3.9	0.9	1.0	2.3	4.8
		4.8	1.3	1.0	2.7	3.7
		4.4	-	-	3.6	3.1
		4.5	-	-	2.6	4.3

@, Aromatic:peroxide:copper(II) mol ratio ~ 100:1:0.1 ;
-, not determined.

Table 9 The copper(II) benzoate catalysed decomposition of benzoyl peroxide in haloaromatic compounds $^{@}$

Compound	Expt.	Mol%			
		phenylation	benzoyloxylation		
			o-	p-	o:p ratio
2-Fluoro-anisole	1	1.3	42.6	-	
	2	0.4	38.6	-	
	3 *	2.1	52.9	-	
4-Fluoro-anisole	1	9.0	-	142.0	
	2	-	8.2	126.1	6:94
	3 **	-	4.8	26.9	15:85
	4 ***	...	15.0	...	
4-Chloro-anisole	1	-	12.4	22.3	36:64
	2	-	12.0	21.3	36:64
Pentafluoroanisole	1	20.7	...	64.2	
Hexafluoro-benzene	1	...	0.03		
	2 *	...	-		

@, Aromatic:peroxide:catalyst mol ratio ∼ 100:1:0.05, 60°, 72 hours ; *, at 80° ; **, uncatalysed decomposition ; ***, copper(II) chloride, 20 hours ; -, not detected ; ..., not determined.

Table 10 The copper(II) benzoate catalysed decomposition of benzoyl peroxide in naphthalene for 72 hours.

Mol ratio *	T°	1-Naphthyl benzoate (mol%)
4.0:1.0:0.009	60°	6.4
3.5:1.0:0.005		2.4
3.8:1.0:0.005		4.1
3.7:1.0:0.03		3.5
13.9:1.0:0.12		3.2
24.1:1.0:none	80°	2.0
19.5:1.0:0.13		13.0
22.9:1.0:0.16 **	82°	11.6
30.4:1.0:0.23 **		7.4
23.0:1.0:0.19	82°	18.6
2.0:1.0:0.05 ***	60°	3.6
2.5:1.0:0.05 ***	80°	1.8
4.5:1.0:none ‡	60°	3.4
4.5:1.0:0.006 ‡		3.4
1.9:1.0:0.29 ‡‡	60°	trace

*, $C_{10}H_8:(PhCOO)_2:Cu_4(OOCPh)_8$; **, 24 hours ; ***, $C_{10}H_8$ dissolved in chlorobenzene ; ‡, iodine was included ; ‡‡, $CuCl_2$, 20 hours.

Table 11 The copper(II) benzoate catalysed decomposition of benzoyl peroxide in naphthalene derivatives @

Compound	T°	Product (mol%)
1-Methylnaphthalene	60°	4-Methyl-1-naphthyl benzoate (0.7) 1-Methyl-2-naphthyl benzoate (nil)
	80°	4-Methyl-1-naphthyl benzoate (3.4) 1-Methyl-2-naphthyl benzoate (nil)
2,3-Dimethylnaphthalene	80°	2,3-Dimethyl-1-naphthyl benzoate (0.03)
1-Chloronaphthalene	80°	1-Naphthyl benzoate (trace)
Octafluoronaphthalene	80°	2-Heptafluoronaphthyl benzoate (trace) *

@, Aromatic compound ~1 g , peroxide:catalyst mol ratio ~126:1 , 72 hours ; *, by g.l.c

Table 12 The decomposition of benzoyl peroxide in anisole in the presence of additives at 60° @

Additive	Mol%			
	phenylation	benzoyloxylation		
		o-	*p*-	*o*:*p* ratio
none	22.2	4.0	6.6	38:62
N-Bromosuccinimide (0.01 mol)	12.8	2.3	5.8	28:72
$CuBr_2$ (0.01 mol)	nil	14.5	9.3	61:39
Br_2 (0.02 mol)	nil	nil	nil	-
I_2 (0.15 mmol)	8.9	14.5	44.1	25:75
$CuCl_2$ *	trace trace	42.9 31.2 **	23.0 17.8 **	65:35 64:36
$CuCl_2$-I_2 ‡	2.9	30.6	24.6	55:45
$Cu_4(OOCPh)_8$-I_2 ‡	7.5	12.4	25.3	33:67
$SnCl_4$ (2.2 mmol)	4.1	0.9	1.1	45:55

@, Anisole:$(PhCOO)_2$ ~80:1, 72 hours ; *, anisole:$(PhCOO)_2$:$CuCl_2$=20:1:1.5 , 20 hours ; **, 80°; ‡ , see (3.4).

2.6.4. The stability of 2- and 4- methoxyphenyl benzoates under the experimental and analytical conditions.

2-Methoxyphenyl benzoate (21.0 mmol) and 4-methoxyphenyl benzoate (29 mmol) were dissolved in toluene, and allowed to react with benzoyl peroxide in the presence of copper(II) benzoate at 80° for 72 hours as above (2.6.1). Analysis by g.l.c after work-up indicated the presence of 2-methoxyphenyl benzoate (19.8 mmol), and 4-methoxyphenyl benzoate (34.1 mmol).

2.6.5. The relative reactivity of anisole to naphthalene in the copper(II) benzoate catalysed decomposition of benzoyl peroxide at 80°.

Copper(II) benzoate (0.21 mmol) in acetonitrile (20 ml) was added to a mixture of anisole (0.01 mol) and naphthalene (0.01 mol) in a 100-ml round-bottomed flask at 80°. Benzoyl peroxide (0.48 mmol) was added, and the reaction left to proceed for 72 hours. The reaction was worked-up as in (2.6.2). G.l.c analysis (240°) showed the relative areas of 4-methoxyphenyl benzoate to 1-naphthyl benzoate equal to 0.92.

Under the above experimental conditions, the extent of phenylation and <u>ortho</u>- benzoyloxylation of anisole were very small.

2.6.6. The effect of copper(II) catalysts in the decomposition of benzoyl peroxide in anisole.

Benzoyl peroxide (0.98 g ; 4.1 mmol) was dissolved in anisole (20.0 ml ; 0.18 mol) in a 50-ml volumetric flask. The volume was made 50.0 ml with acetonitrile. The mixture was deoxygenated, and then heated at 60° in a 100-ml round-bottomed flask for 24 hours, and cooled. It was divided into five equal parts, and each further treated as in Table 13 . The work-up was as in (2.6.2).

Table 13 The decomposition of benzoyl peroxide in anisole in the presence of copper(II) catalyst [@]

Mixture/Experimental conditions	Mol%			
	phenylation	benzoyloxylation		
		o-	*p*-	*o*:*p* ratio
(I)	16.9	2.4	1.6	60:40
(I)/60°,72hr *	22.2	4.0	6.6	38:62
(I)/60°,72hr, $Cu_4(OOCPh)_8$	13.3	2.8	5.1	35:65
(I)/80°,72hr	15.1	2.2	3.1	42:58
(I)/80°,72hr, $Cu_4(OOCPh)_8$	16.2	1.6	2.4	40:60
(I)/60°,72hr,$CuCl_2$	5.4	17.1	11.0	61:39

@, Anisole:peroxide:catalyst mol ratio ~ 44.5:1:1 ;
(I), Anisole-$(PhCOO)_2$,60°,24hr ; *, separate run

2.7. Kinetic investigations.

2.7.1. The decomposition of benzoyl peroxide in anisole-acetonitrile in the presence of galvinoxyl.

Anisole (10.0 ml) and acetonitrile (200.0 ml) were degassed by initially shaking under reduced pressure at the water-pump, and then on the ultra-sonic bath for 30 minutes. The flask was fitted with a reflux condenser and further deoxygenated by dropping several pieces of solid carbon dioxide from the top of the condenser.

Galvinoxyl (8.0 mg ; 1.90×10^{-5} mol) was added to the above mixture. An aliquot (20.0 ml) was pipetted into a 100-ml three-necked round-bottomed flask equipped with a reflux condenser, a thermometer which dipped into the solution, and a suba-seal. The flask was immersed in a thermostatically-controlled oil-bath set at the stated temperature.

When the thermometer reading had become constant, an exactly known weight of benzoyl peroxide (0.05-0.1 g) was added. The flask was thoroughly shaken, and the time noted. At a known time interval, an aliquot (1.0 ml) was withdrawn using a 5.0-ml syringe pierced through the suba-seal, and discharged into a cold test-tube (ice-water) containing deoxygenated ethanol (5.0 ml). The test tube was shaken and left to warm to room temperature.

Copper(II) benzoate (0.12 g ; 9.8×10^{-5} mol) was added to the remaining anisole-acetonitrile mixture (120 ml) for the reaction with the additive.

The absorbance reading was taken at 428 nm, with deoxygenated ethanol as the reference at 25.1°.

A plot of absorbance, A, against time, t, was made for each experiment, and a value of the initial absorbance, A_o, at time, t_o, was obtained from it. Another plot of $\ln [A_t + A_o(2j - 1)]$, where A_t was the absorbance at time, t, and j, the mol ratio of benzoyl peroxide to galvinoxyl, against t was made. The value of k_1 was obtained from the slope (Equation 5). The activation energy for the reaction was calculated from the slope ($= -E_A/R$) of $\ln k_1$ against T^{-1} (K^{-1}) (Figure 7).

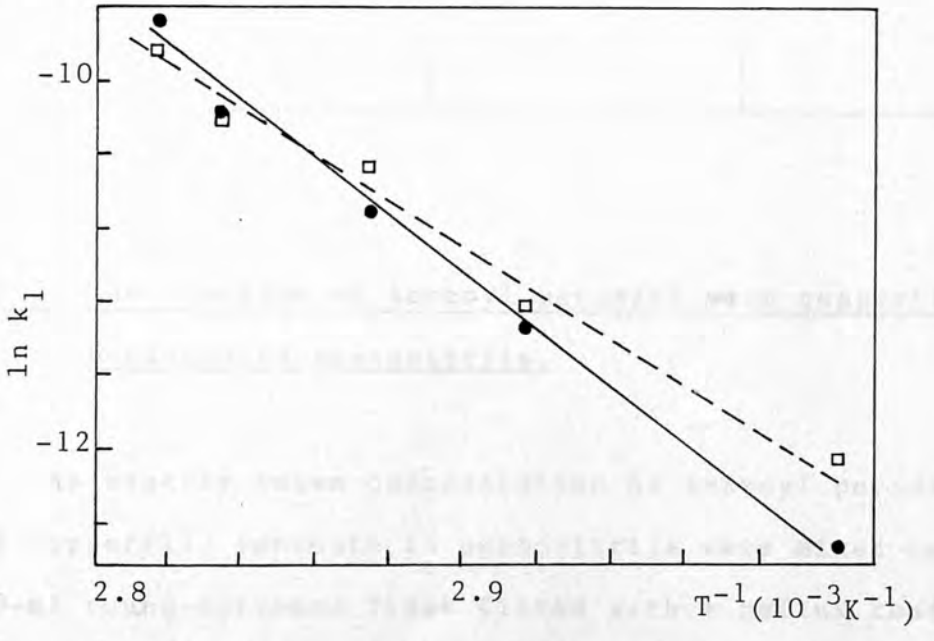


Figure 7 The decomposition of benzoyl peroxide in anisole in the presence of galvinoxyl ; ● ,uncatalysed ; □ , copper(II) benzoate catalysed.

Table 14 The rate constant, k_1, and activation energy, E_A, for the decomposition of benzoyl peroxide in anisole-acetonitrile in the presence of galvinoxyl.

T°	$Cu_4(OOCPh)_8$	$k_1/10^{-6}s^{-1}$	$E_A/kJmol^{-1}$
60°	none	3.5	125.0
70°		11.7	
75°		22.5	
80°		38.9	
82°		62.5	
60°	0.82 mM	5.9	96.3
70°		13.3	
75°		28.3	
80°		37.5	
82°		51.3	

2.7.2. The reaction of benzoyl peroxide with copper(II) benzoate in acetonitrile.

An exactly known concentration of benzoyl peroxide and copper(II) benzoate in acetonitrile were mixed in a 100-ml round-bottomed flask fitted with a reflux condenser and immersed in an oil-bath at the stated temperature. For each experiment, a flask containing benzoyl peroxide in acetonitrile of equivalent concentration was also immersed at the same temperature at the same time to use as a reference in visible spectroscopic analysis.

At a known time interval, an aliquot (3.0 ml) was withdrawn from each flask into a separate test-tube kept in ice-water. It was left to warm to room temperature.

The absorbance, A, was taken at 388 nm at 25° (Figure 8). A graph of A against time t was made, and a value of A_{∞} deduced from it. The concentration, x, was calculated ($x = A/\varepsilon_{max}.$; $\varepsilon_{max} = 256\ 000\ M^{-1}cm^{-1}$).

The results are tabulated in Appendix 3.

There was no maximum absorption at 388 nm in a control experiment where benzoyl peroxide or copper(II) benzoate was omitted.

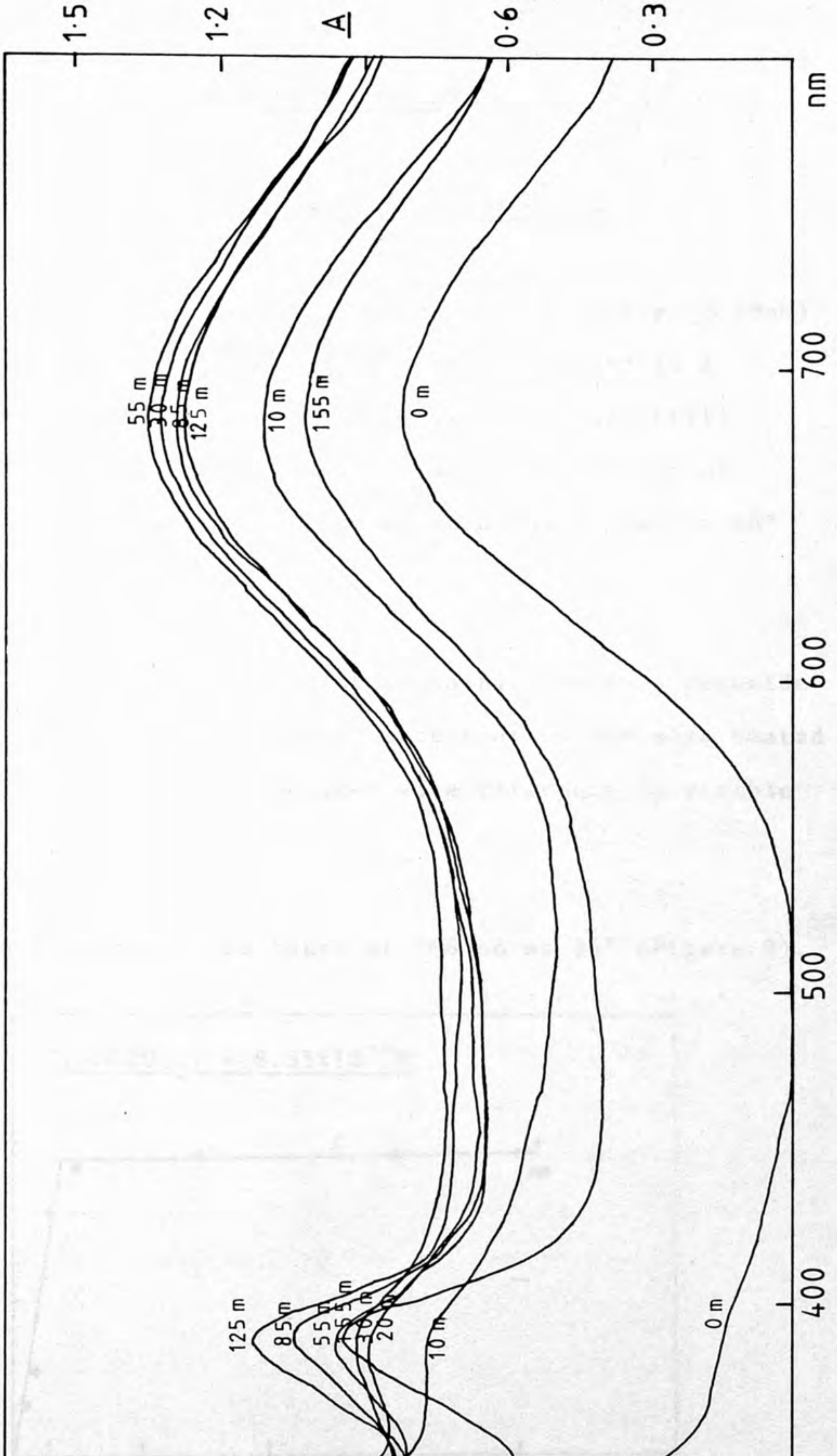


Fig.8. Reaction of benzoyl peroxide with copper(II) benzoate in acetonitrile at 80°

2.8. The chemistry of copper complex.

2.8.1. The molar extinction coefficient, ε_{max}.

An acetonitrile solution of benzoyl peroxide (2.78mM) and copper(II) benzoate (1.24×10^{-5}M) were mixed in a concentration ratio of benzoyl peroxide to copper(II) benzoate from 10 to 10^3, keeping the concentration of benzoyl peroxide constant. The mixture was heated at 60° for 24 hours.

At the same time, a flask containing benzoyl peroxide in acetonitrile of equivalent concentration was also heated at 60° for 24 hours, to be used as a reference in visible spectroscopic analysis.

The absorbance was taken at 388 nm at 25° (Figure 9).

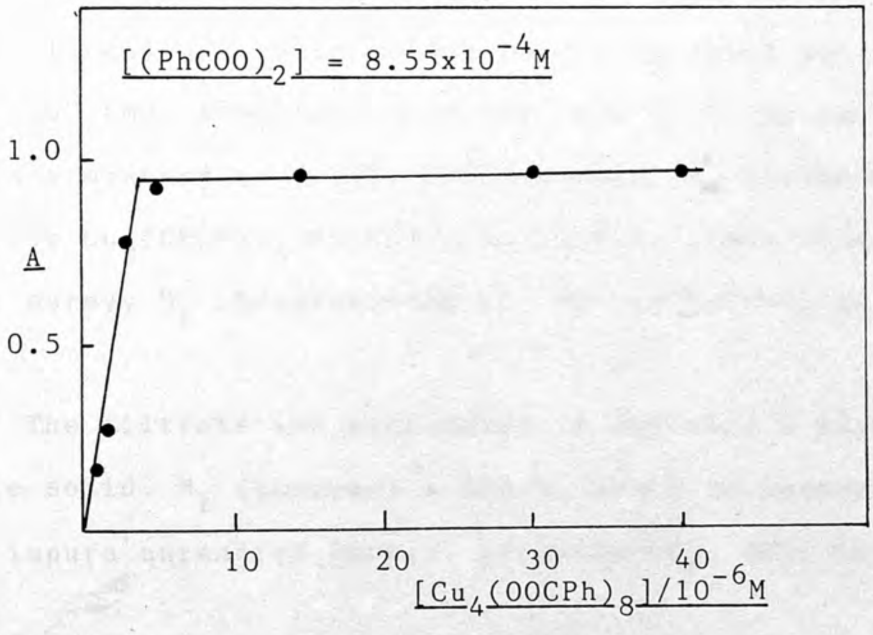


Figure 9

Table 15 The molar extinction coefficient, ε_{max}, of the copper complex.

Concentration/10^{-6}M		A	$\varepsilon_{max}/10^{5}M^{-1}cm^{-1}$	Av. ε_{max}
$(PhCOO)_2$	Cu complex			
855	3.75	0.98	2.61	256 000
1770	7.0	1.75	2.50	

2.8.2. The infra-red spectrum and molecular weight.

Benzoyl peroxide (5.0 g ; 0.021 mol) and copper(II) benzoate (0.5 g ; 0.41 mmol) were heated at 60° for 24 hours in acetonitrile (30 ml). The solvent was removed on a rotary-film evaporator at temperature below 60° to give a gummy green residue which was triturated with warm petroleum ether (b.p. 60-80°) and filtered. IR (Nujol ; NaCl plates) of the petroleum ether-insoluble solid gave ν = 1400 (m), 1580 (w), 1610 (m), and 1700 (m) cm^{-1}. It is a mixture of a pale green powder, M_r (benzene) = 860 (M_r for $Cu_2(OOCPh)_6$ is 853), and a dark green solid (not pure), M_r (benzene)=486 (M_r for $Cu(OOCPh)_4$ is 547.5).

The filtrate was evaporated to dryness. A bluish-white solid, M_r (benzene) = 255.3, which corresponds to the impure unreacted benzoyl peroxide (M_r, 242) was obtained.

A similar experiment at 80° gave a black solid, M_r = 1275, and a black gummy residue. IR (1,3-Hexachlorobutadiene ; NaCl plates) of the black gummy residue showed ν = 1290 (m), 1310 (w), 1420 (m), 1450 (w), and 1700 (s) cm^{-1}

2.8.3. The reaction of copper complex with aromatic compounds.

An exactly known weight of benzoyl peroxide and copper(II) benzoate were dissolved in acetonitrile, and heated at 60° (unless stated otherwise) for 24 hours, and cooled. The aromatic compound was added, and the mixture further heated at 60° (unless stated otherwise) for 48 hours. The reaction mixture was worked-up and analysed as in (2.6). The results are shown in Table 16.

2.8.3.1. The benzoyl peroxide content in the reaction of benzoyl peroxide with copper(II) benzoate at 60° after 24 hours.

Benzoyl peroxide (4.4 mmol) and copper(II) benzoate ($4.3x10^{-6}$mol) were heated at 60° for 24 hours in acetonitrile (20 ml), and cooled. The mixture was transferred into a conical flask, and potassium iodide (1.0 g ; 6.0 mmol) and water (10 ml) were added. The dark brown solution was stirred for 5 minutes in the dark. Water (50 ml) was added, and the content of the flask titrated with solution of sodium thiosulphate (0.18 M ; 22.2 ml). The amount of benzoyl peroxide calculated was 2.02 mol (46 %).

Table 16 The reaction of copper complex with anisole and 4-fluoroanisole at 60°.

Compound	Mol ratio	Mol%	
	$(PhCOO)_2$:Cu(II)	phenylation	benzoyloxylation(*)
Anisole (0.18 mol)	191.6:1	10.5	8.3 (44:56)
	191.6:1	12.1 **	2.7 (46:54) **
	2.2:1 ‡	<1	13.3 (58:42)
	34.0:1 ‡‡	-	2.2 (*ipso*-)
	34.0:1	9.9	7.9 (27:73)
4-Fluoro-anisole (0.05 mol)	34.0:1	-	27.9 (++)

*, *o*:*p* ratio ; **, reaction at 82° ; ‡, in the presence of $CuCl_2$; ‡‡, complex formed at 80° ; (++), 4-methoxyphenyl benzoate.

2.9. Copper(II) benzoate as a benzoyloxylating agent in anisole-2-naphthoyl peroxide-iodine-acetonitrile systems.

Anisole (20.0 ml ; 0.18 mol), copper(II) benzoate (2.6 mmol), and iodine (19.2 mmol) were allowed to react with 2-naphthoyl peroxide in acetonitrile at 60° for 72 hours. The reaction mixture was worked-up as in (2.6).

Analysis by g.l.c indicated the presence of 4-methoxyphenyl benzoate, 0.71 mol% (or 34.5% per mol of copper(II) benzoate) ; and only a trace amount of 2-methoxyphenyl benzoate.

The reaction did not occur in the absence of the peroxide.

2.10. Copper(II) chloride as a chlorinating agent in phenol-benzoyl peroxide-acetonitrile systems.

Phenol (0.94 g ; 0.01 mol) and copper(II) chloride (1.7 g ; 0.01 mol) were dissolved in acetonitrile (50 ml). The mixture was divided into two equal parts. One part was kept at room temperature, while the other was heated at 60° for two days.

Analysis by g.l.c indicated that (i) the reaction at room temperature gave 4-chlorophenol (8.1%). 2-Chlorophenol was not detected ; and (ii) the reaction at 60°

gave 2-chlorophenol (0.7%), and 4-chlorophenol (13.2%).

Benzoyl peroxide (0.1 g ; 0.41 mmol) was added to the reaction mixture at 60°, and further heated at the same temperature for another 24 hours. Analysis by g.l.c indicated the presence of 2-chlorophenol (1.5%), and 4-chlorophenol (82.3%).

2.11. The benzoyl peroxide initiated reaction of aromatic compounds with acetate ions (The $S_{ON}2$ reaction).

2.11.1. Procedure.

The aromatic compound (5.0 ml) was dissolved in glacial acetic acid (5.0 ml) in a small round-bottomed flask fitted with a reflux condenser, and immersed in a constant temperature oil-bath at 78°. Potassium acetate (1.0 g) and acetic anhydride (10 ml) were added.

An exactly known weight of benzoyl peroxide (0.05 g) was added, and the flask shaken thoroughly. The reaction was left to proceed for 20 hours.

An exactly known weight of pentamethylbenzene was added as an internal standard for g.l.c analysis before work-up.

2.11.2. Work-up.

The reaction mixture was neutralised with saturated sodium carbonate solution. The organic part was extracted with ether, and the extract washed with water, dried ($MgSO_4$), filtered, and the ether removed. The solvent was removed by distillation under reduced pressure.

2.11.3. Results.

Table 17 The benzoyl peroxide initiated reaction of aromatic compounds with potassium acetate-acetic acid at 78° @.

Compound	Expt	$(PhCOO)_2$	Mol%			
		mmol	acetate		benzoate	
			o-	p-	o-	p-
Anisole	1 *	0.17	1.5	1.8	2.9	2.1
	2	0.19	2.7	2.5	2.6	1.5
	3	0.53	2.9	2.1	2.3	1.7
	4 **	0.12	1.4	2.1	6.0	4.4
2-Fluoro-anisole	1 *	0.23	20.8	2.2	41.5	-
	2	0.17	167.2	-	131.6	-
	3	0.25	73.5	-	55.2	-
	4	0.30	54.5	3.1	28.4	-

(Continued)....

Table 17 (Continuation).

Compound	Expt	$(PhCOO)_2$	Mol%			
		mmol	acetate		benzoate	
			o-	*p*-	*o*-	*p*-
4-Fluoroanisole	1 *	0.26	-	175.0	-	23.5
	2	0.25	-	135.1	2.3	34.7
	3	0.26	-	298.6	-	27.4
	4	none	-	-	-	-
4-Chloroanisole	1 *	0.15	-	3.5	-	3.7
	2	0.10	-	10.8	-	9.3
	3	0.25	-	8.7	-	3.7
Pentafluoroanisole	1 *	0.16	-	45.5	1.4	4.6
	2	0.20	-	52.8	1.4	1.8
	3 ‡	0.23	-	5.4	0.9	1.6
4-Methoxynonafluorobiphenyl	1	-	-	-	-	-
N,N-Dimethyl-4-fluoroaniline	1 *	0.20	-	58.0	-	(-)
	2	0.43	-	36.3	-	(-)

(Continued)...

Table 17 (Continuation).

Compound	Expt	$(PhCOO)_2$	Mol%			
		mmol	acetate		benzoate	
			o-	p-	o-	p-
1-Fluoronaphthalene	1 *	0.56	27.1	-	17.4	-
	2	0.18	98.6	-	13.6	-
	3	0.39	71.0	-	17.7	-
Octafluoronaphthalene	1	-	-	-	-	-

@, [Aromatic] ~ 2-3 M, [KOAc] = 0.5 M ; *, in the absence of KOAc ; **, 72 hours ; ‡, under reflux ; -, not detected ; (-), not detected by h.p.l.c.

Table 18 The benzoyl peroxide initiated reaction of aromatic compounds with potassium acetate-perfluorobenzoic acid at 78° @.

Compound	Methoxyphenyl-‡/ mol%	
	acetate	benzoate
2-Fluoroanisole *	17.7	19.4
4-Fluoroanisole **	35.6	23.0
4-Chloroanisole *	8.4	3.2

@, [Aromatic] ~ 2-3 M ; [KOAc] = 0.5 M ; *, in glacial acetic acid ; **, in acetic anhydride ; ‡, *ipso*- substitution products.

2.12. The decomposition of perbenzoic acid in anisole and 4-fluoroanisole in the presence of additives at 0-5°

Anisole (20 ml ; 0.18 mol) was placed in a 100-ml round-bottomed flask, and cooled in ice-water. A known amount of the additive (about 2 mmol) was added, and the mixture stirred using a magnetic stirring bar.

Perbenzoic acid (1 g) was dissolved in acetonitrile (25 ml), and added dropwise to anisole.

The course of the reaction was followed on thin-layer chromatographic plates (Polygram SIL G ; $CHCl_3$) until the decomposition of perbenzoic acid was completed (>90% ; 18 hr).

Pentamethylbenzene was added for g.l.c analysis before work-up. Any solid residue was filtered. The work-up was as in (2.6.2).

The procedure was repeated for 4-fluoroanisole (5 ml ; 0.047 mol).

The results are shown in Table 19.

Table 19 The decomposition of perbenzoic acid in anisole and 4-fluoroanisole in the presence of additives.

Compound	Additive	Methoxyphenol		Methoxyphenyl benzoate	
		mol%	*o*:*p* ratio	mol%	*o*:*p* ratio
Anisole	$FeSO_4$	3.3	85:15	0.5	39:61
	$FeSO_4$ *	1.2	98:2	nil	-
	$CuCl_2$	0.3	39:61	3.6	69:31
	$Cu_4(OOCPh)_8$	0.5	73:27	nil	-
	I_2	0.14	100:0	0.9	48:52
4-Fluoro-anisole	$Cu_4(OOCPh)_8$	0.52	62:38	4.1	0:100

*, $FeSO_4$ was dissolved in H_2SO_4 (0.5 M), and MeCN omitted.

2.13. Direct synthesis of 4-methoxyphenyl benzoate from 4-fluoroanisole.

2.13.1. From the copper(II) benzoate catalysed decomposition of benzoyl peroxide.

4-Fluoroanisole (13.4 g ; 0.106 mol) and copper(II) benzoate (0.064 g ; 0.05 mmol) in acetonitrile (4 ml) was placed in a 100-ml round-bottomed flask fitted with a reflux condenser, and immersed in an oil-bath at 60°. The mixture was deaerated by dropping several pieces of solid carbon dioxide from the top of the condenser. The flask was left for 30 minutes for temperature equilibration.

Benzoyl peroxide (0.29 g ; 1.2 mmol) was added to the flask, and shaken thoroughly. The reaction was left to proceed for 72 hours.

The final yellow solution containing a few bluish-green crystals of copper salts was filtered, and a few drops of 50% aqueous *ortho*- phosphoric acid was added to the filtrate. The organic product was taken up in ether, and the extract washed with water (twice), saturated sodium hydrogen carbonate (3 times), and dried ($MgSO_4$). The yellow solution obtained was shown by h.p.l.c to contain four main peaks at R_t = 2.15 (13.9%), 3.6 (28.7%), 5.3 (4-fluoroanisole), and 8.0 minutes (57.4% ; 4-methoxyphenyl benzoate). The unreacted 4-fluoroanisole was removed by vacuum-distillation, b.p. 56-7°/18 mmHg. H.p.l.c showed the presence of a small amount of 4-methoxyphenyl benzoate.

The residue was recrystallised from methylated spirit to give 0.14 g (50.3 mol%) small brown needles, m.p. 87-9° ; mixed m.p. 88-9° ; lit. 88-9°[77]. H.p.l.c gave one peak at R_t= 8.0 minutes, in agreement with authentic compound.

2.13.2. From the benzoyl peroxide initiated reaction with potassium acetate (The $S_{ON}2$ reaction).

4-Fluoroanisole (6.38 g ; 0.05 mol), potassium acetate (2 g), glacial acetic acid (10 ml), and acetic anhydride (20 ml) were introduced into a 100-ml round-bottomed flask fitted with a refluxing water condenser and immersed in an oil-bath at 78°.

Benzoyl peroxide (0.12 g ; 0.5 mmol) was added, and the reaction left to proceed for 20 hours. The mixture was neutralised with sodium carbonate when cooled, and extracted with ether. The ether extract was washed with water (twice), dried ($MgSO_4$), filtered, and the ether removed.

The unreacted 4-fluoroanisole was removed by vacuum-distillation, b.p. 54°/14 mmHg. The purity was checked by g.l.c.

The yellow liquid residue, 0.95 g, was analysed by g.l.c, and was shown to consist of unreacted 4-fluoroanisole (41.8%), 4-methoxyphenyl acetate (47.3% ;0.45 g ; 528 mol%), and 4-methoxyphenyl benzoate (7.2% ; 0.07 g ; 59.8 mol%).

3. DISCUSSION.

3.1. Decomposition of benzoyl peroxide in anisole.

The decomposition of benzoyl peroxide in anisole at 80° for 72 hours gave 9-13 mol% methoxyphenyl benzoate (Table 20), 37.8 mol% methoxybiphenyl (o:m:p ratio, 66:19:15), and approximately 150 mol% benzoic acid. The higher boiling residue was not analysed. The results of other workers are included in Table 20 for comparison.

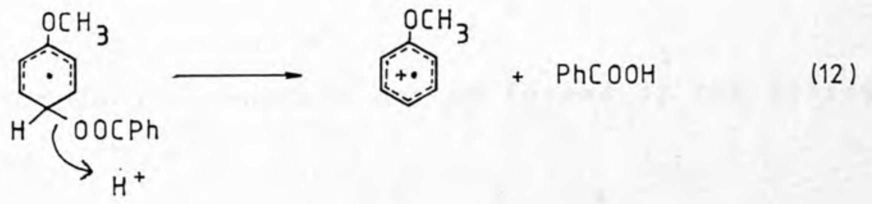
Table 20 The yields and isomer distributions of methoxyphenyl benzoate at 80° for 72 hours.

$[(PhCOO)_2]$/M	Mol%			Isomer distribution		Ref
	o-	p-	total	o-	p-	
0.056	6.8	5.3	12.1	56.2	43.8	This work
0.065	7.1	6.3	13.4	53.0	47.0	
0.083	5.1	3.8	8.9	57.3	42.7	
0.084	5.2	3.5	8.7	59.8	40.2	
0.09	-	-	3.7	71.5	28.5	[14]
0.21	-	-	4.0 *	52.0	48.0	[53]
0.41	-	-	20 **	65-82	18-35	[13]

*, 60 hours ; **, 30 hours and analysed as methoxyphenol

3-Methoxyphenyl benzoate was not detected. This is consistent with previous literature reports. It reflects the electrophilicity of benzoyloxy radical and the directing effect of methoxy-group of anisole.

The small variations in the yields and isomer distributions of methoxyphenyl benzoate, if significant, were probably due to the lower yields of both isomers at higher benzoyl peroxide concentrations. It may be that the prevalence of induced decomposition at the higher concentrations resulted in higher yields of benzoic acid, which may catalyse the fragmentation of σ-complex. Norman and Storey [99] found that in acid condition, benzoyloxy radicals were successfully trapped by aromatic compounds, and then released as benzoic acid in an acid-catalysed fragmentation reaction (Reaction 12).



(12)

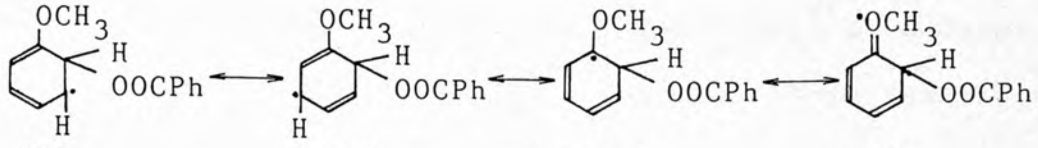
McClelland, Norman, and Thomas [53] suggested that the rate of Reaction 12 was faster with the <u>para</u>-σ-complex from the direction of the change in the <u>ortho</u>-:<u>para</u>- ratio of the product when acid was included.

The isomer distributions obtained in the present work approached the statistical values of 66.7% <u>ortho</u>-

and 33.3% para-, and are in good agreement with that obtained by McClelland, Norman, and Thomas (o:p ratio, 52:48) [53]. It may be inferred from this that the attacking entity is a free, resonance-stabilised, benzoyloxy radical. The suggestion forwarded by Lynch and Moore [13], and by Bolton et al. [14] of a complex formed between benzoyloxy radical and methoxy-oxygen of anisole to account for high yields of the ortho- isomer obtained in their works, is not presently obvious. On steric argument, the ortho- σ-complex is thermodynamically less stable and likely to fragment at a faster rate than the para- σ-complex. Henriquez and Nonhebel [100] suggested that the first step in homolytic aromatic phenylation may be reversible, particularly when the incoming radical enters ortho- to a substituent. This phenomenon ought to be more prominent with the "bulkier" benzoyloxy radicals, and may partly explain the lower than expected yields of the ortho- isomer.

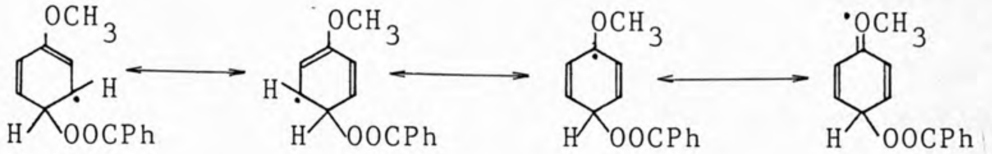
Methoxyphenyl benzoate may be formed by the following mechanisms :-

(a) Benzoyloxy radical adds to the anisole nucleus at either the ortho- or para- position to form the corresponding resonance-stabilised benzoyloxymethoxycyclohexadienyl radical ($\sigma\cdot$) as shown in Figure 10.



(I) (II) (III) (IV)

ortho- σ-complex



(V) (VI) (VII) (VIII)

para- σ-complex

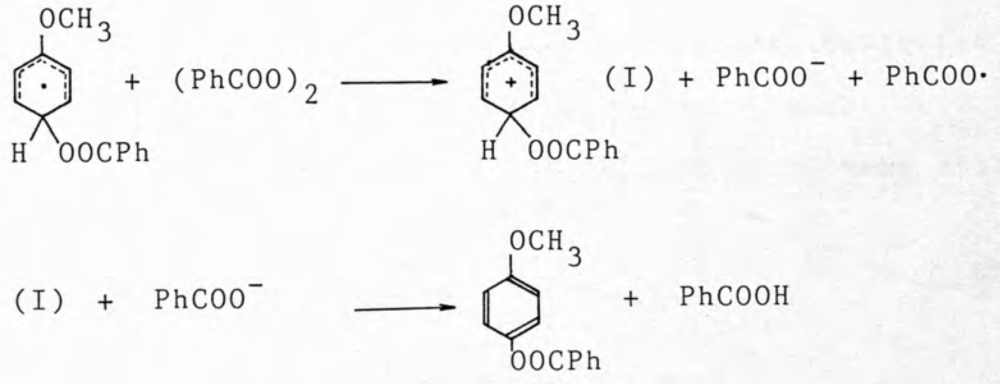
Figure 10

Kurz and Pellegrini [23] suggested that resonance-stabilisation of aroyloxy radical-aromatic adduct (σ·) plays an important role in determining the yields of aroyloxylation products. This was deduced from the better correlation obtained in the plots of the logarithms of the partial rate factors against σ^+ values (rather than σ) to determine the ρ values of $4\text{-}X.C_6H_4COO\cdot$ ($X = NO_2$, H, or CH_3) in the copper(II) chloride catalysed reactions in toluene, anisole, and chlorobenzene.

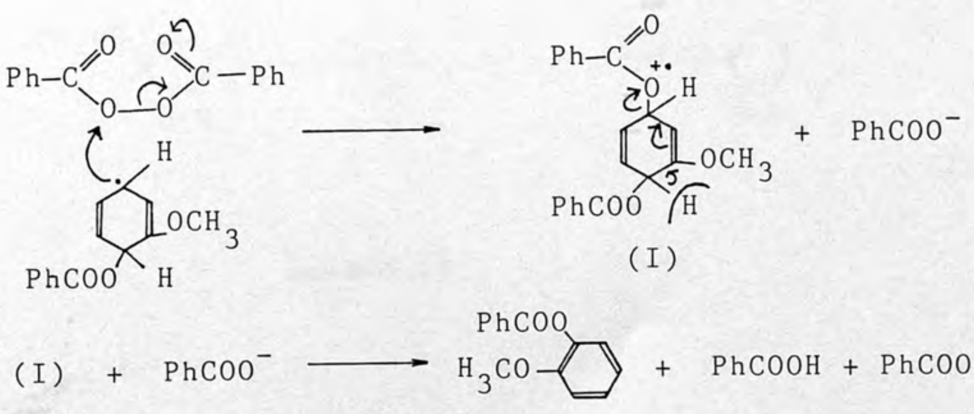
The σ-complex thus formed may undergo four competing reactions (i) fragmentation to the starting materials; (ii) oxidation to methoxyphenyl benzoate by benzoyl peroxide; (iii) disproportionation to methoxyphenyl benzoate and benzoyloxymethoxycyclohexadiene which yield more ester by further oxidation; and (iv) dimerisation. These reactions are shown in Scheme 5.

Methoxyphenyl benzoate is formed in both the propagation (Reaction ii) and termination steps (Reaction iii) [18].

Reaction (ii) corresponds to an induced decomposition of benzoyl peroxide. It may occur by either the ET [19] (Scheme 23) or "S_N2" [28] (Scheme 24) mechanisms.



Scheme 23

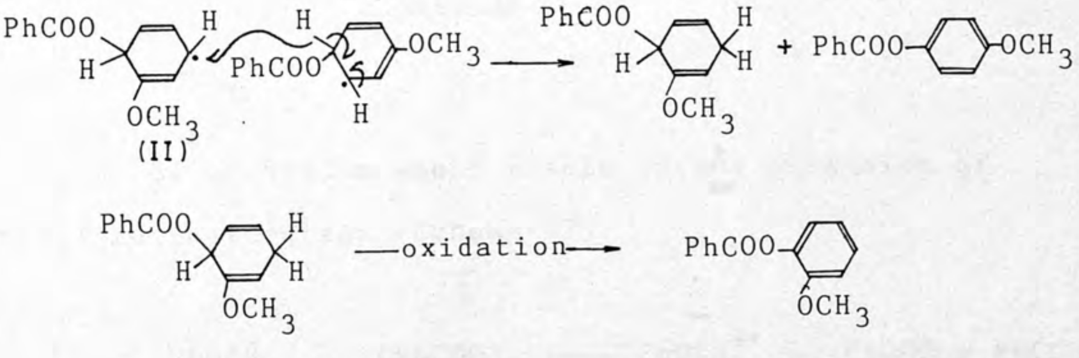


Scheme 24

The "S_N2" mechanism is less likely to be more important in this case because it is subjected to steric hindrance for all the canonical structures (Figure 10) except maybe involving Structure II.

Nozaki and Bartlett [30] found that the induced decomposition of benzoyl peroxide in benzene was a process of lower activation energy (E_A, 105 $kJmol^{-1}$) than the primary homolysis (E_A, 139 $kJmol^{-1}$) and therefore, is less significant at high temperatures.

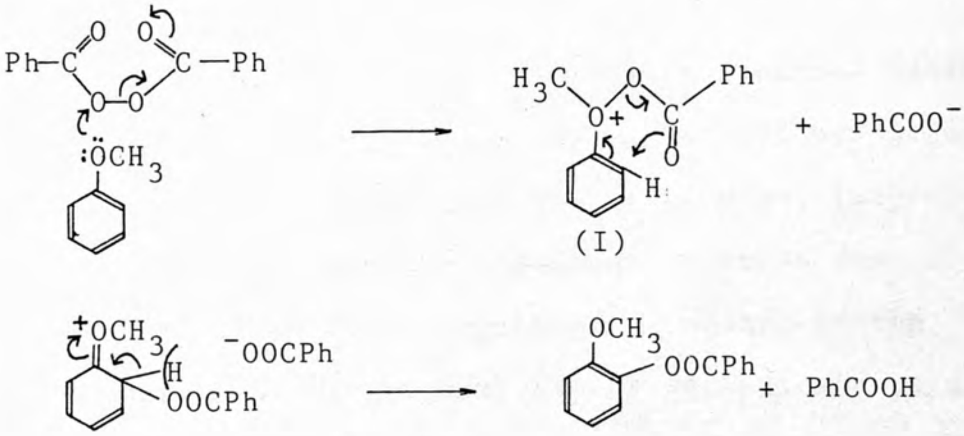
The disproportionation reaction (Reaction iii) requires a close approach of two σ-complexes, and is also subjected to steric hindrance for all the canonical structures (Figure 10) except maybe involving Structure II (Scheme 25).



Scheme 25

(b) Reaction of anisole with benzoyl peroxide by either ET or S_N2 mechanism [27,28].

The S_N2 mechanism (Scheme 26) would result in the formation of (I) as the intermediate, which would be expected to give a high proportion of the <u>ortho</u>- isomer through a cyclic rearrangement, as suggested by Lynch and Moore [13], but is not supported by the present results.



<u>Scheme 26</u>

The ET mechanism would result in the formation of anisyl radical cation (Scheme 27).

$$PhOCH_3 + (PhCOO)_2 \longrightarrow PhOCH_3^{+\cdot} + PhCOO\cdot + PhCOO^-$$

$$PhOCH_3^{+\cdot} + PhCOO\cdot \longrightarrow PhCOO.PhOCH_3^{+} \quad (I)$$

$$(I) + PhCOO^- \longrightarrow PhCOO.C_6H_4.OCH_3 + PhCOOH$$

<u>Scheme 27</u>

McClelland, Norman, and Thomas [53] argued against the formation of anisyl radical cation in the above reaction on two grounds (i) competitive experiment indicated that the rate of benzoyloxylation of anisole by lead tetrabenzoate exceeded 1000 times the rate by benzoyl peroxide, suggesting that the latter reagent was less able to oxidise by one electron acceptance; and (ii) the inclusion of lithium acetate as a foreign nucleophile produced only 0.2 mol% methoxyphenyl acetate.

In conclusion, the low yields of methoxyphenyl benzoate were mainly because of (i) the inability of benzoyl peroxide to act as a good oxidising agent for σ-complex; (ii) the reduced incidence of disproportionation reaction due to steric hindrance, and (iii) the higher tendency of the *ortho*- σ-complex to fragment on steric ground, and *para*- σ-complex by acid catalysis.

It is interesting to note that Kurz and Kovacic [37] did not obtain any methoxyphenyl benzoate from reaction in acetonitrile solvent at 80°.

3.2. The chemistry of copper(II) benzoate.

The molecular weight determined for copper(II) benzoate in benzene was 1222. The infra-red spectrum in Nujol showed absorption bands at 680 (s), 720 (m), 1400 (m), 1560 (m), and 1610 (m) cm^{-1}. The bands at 1400 and 1560 cm^{-1}

correspond to carboxylate anions stretching. There were no ester-type carbonyl bands at 1250 and 1700 cm^{-1}, indicating that all the oxygens were equivalent [101]. From these, it may be suggested that the molecular formula of copper(II) benzoate is $Cu_4(OOCPh)_8$ (M_r, 1223), which is a tetramer of $Cu(OOCPh)_2$. The probable structure is shown in Figure 11.

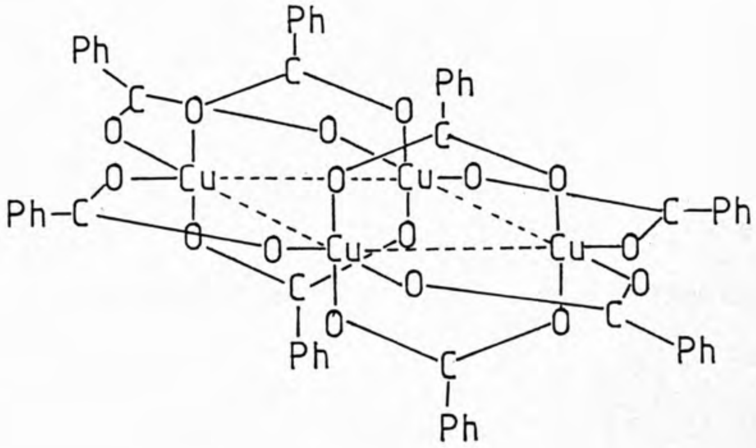


Figure 11. $Cu_4(OOCPh)_8$ (M_r, 1223)

It is noted that three forms of copper(II) benzoate have been prepared; two of which appeared to be polynuclear and one dimeric [102].

The tetramer unit may collapse in acetonitrile solvent. The visible spectrum of copper(II) benzoate in acetonitrile showed an absorption band at 690 nm (ε_{max}, $1.1x10^3 M^{-1} cm^{-1}$), and a weak shoulder at 388 nm, suggesting a copper-copper interaction in a dimeric complex, $Cu_2(OOCPh)_4$ [102]. The structure may be similar to copper(II) acetate (Figure 12).

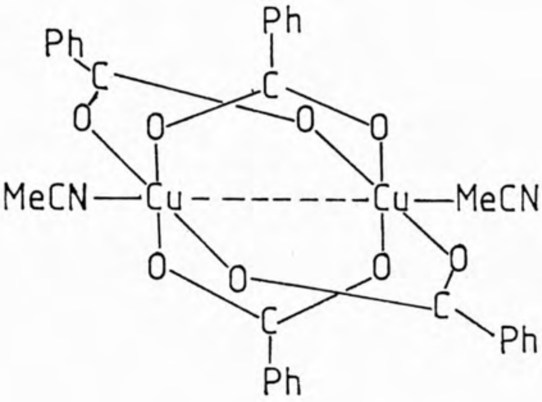


Figure 12. $Cu_2(OOCPh)_4.2\ MeCN$

A monomer-dimer equilibrium may be established in acetonitrile, as was found for the dimeric copper (II) acetate [21].

3.2.1. Interaction of copper(II) benzoate with benzoyl peroxide.

The rate of the primary homolysis of benzoyl peroxide in the presence of copper(II) benzoate in acetonitrile, measured using galvinoxyl as a radical scavenger, was faster at 60-75°, about the same at 80°, and significantly slower at 82°, than in its absence (Table 14).

The activation energy for the primary homolysis of benzoyl peroxide in the presence of copper(II) benzoate was 96 $kJmol^{-1}$, and 125 $kJmol^{-1}$ in its absence. Nozaki and Bartlett [30] and Janzen *et al*. [33] obtained values of 139 and 127 $kJmol^{-1}$, respectively, for the uncatalysed homolysis.

The rate of the primary homolysis of benzoyl peroxide was proportional to the rate of disappearance of galvinoxyl [18]. The faster disappearance of galvinoxyl at 60-75° in the presence of copper(II) benzoate may be due to the faster production of benzoyloxy radicals, whereas the slower rate at 82° was possibly due to the faster consumption of benzoyloxy radicals in side reactions involving copper(II) benzoate.

Benzoyl peroxide was found to react with copper(II) benzoate in acetonitrile to form a new species with a maximum absorption band in the visible spectrum at 388 nm (ε_{max},~256 000 $M^{-1}cm^{-1}$). The absorption band due to copper(II) benzoate at 690 nm was observed to initially increase, and then decrease as the reaction proceeded (Figure 8).

The rate of formation of this species at 60° appears to be dependent upon the concentration of benzoyl peroxide, but not upon the concentration of Cu(II) benzoate (Runs 1-5 ; Appendix 3), and an apparent equilibrium is reached after 20 hours. The position of the equilibrium again seems to be independent of the concentration of copper(II) benzoate. The rate of formation of the species is evidently much slower than that of the thermal decomposition of benzoyl peroxide, but the equilibrium concentration is reached before all peroxide is consumed and so the formation of the species is not stopped by the lack of peroxide.

Various kinetic equations were applied to the rate of formation of the species at different concentrations of peroxide and of copper(II) benzoate. The competitive first- and second- order processes (Reaction 13 and 14) gave no kinetic form which predicted the changes in concentration of the species (I).

$$(\mathrm{PhCOO})_2 \longrightarrow 2\ \mathrm{PhCOO}\cdot \longrightarrow \text{Products} \tag{13}$$

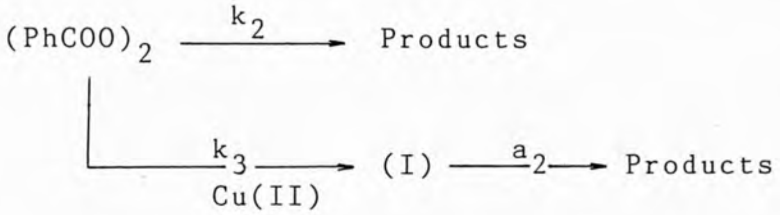
$$(\mathrm{PhCOO})_2 + \mathrm{Cu(II)} \longrightarrow (\mathrm{I}) \tag{14}$$

Equilibrium processes (Reaction 15 and 16) also failed to give good agreement between experimental and calculated concentration of (I).

$$(\mathrm{PhCOO})_2 \xrightleftharpoons{\mathrm{Cu(II)}} (\mathrm{I}) \tag{15}$$

$$(\mathrm{PhCOO})_2 \xrightleftharpoons{\mathrm{Cu(II)}} 2\ (\mathrm{I}) \tag{16}$$

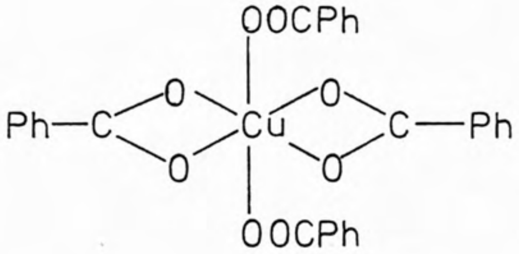
The reaction to give (I) occurs much less quickly than the spontaneous homolysis of benzoyl peroxide, as judged from the rate of destruction of galvinoxyl (k_1, $3.5\mathrm{x}10^{-6}\mathrm{s}^{-1}$, 60°), and the formation of (I) is evidently not the only reason for the increase in this rate by the presence of copper(II) benzoate (k_1, $5.9 \times 10^{-6} s^{-1}$, 60°) although it may exert a catalytic effect upon various chain-processes. The best agreement between theory and experiment came from the application of the consecutive first-order processes, and allowing for the simultaneous loss of peroxide by other routes ($k_2 = k_1$ in the copper(II) benzoate catalysed decomposition of benzoyl peroxide ; Table 14).



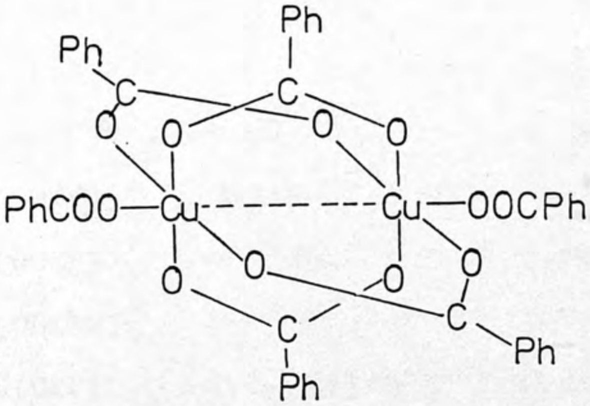
(17)

Values of k_3 and a_2 which reflect the growth profile of (I) are shown in Table 23-26 (Appendix 3). These values were found by iterative computer methods. The ratio of k_3/a_2 was more easily determined, but more than one value of k_3 or a_2 gave satisfactory agreement with experiment; more complex kinetic equations did not.

The reaction between benzoyl peroxide and copper(II) benzoate at 60° gave a green gummy residue when acetonitrile was removed. From this were obtained a dark green solid (M_r, 486) and a pale green powder (M_r, 860). The infrared spectrum showed a new band at 1700 cm^{-1}, indicating the presence of ester-type carbonyl group(s). The visible spectrum of the pale green powder in acetonitrile showed a small shoulder at 410 nm, indicating a copper-copper interaction. Both solids did not have absorption bands at 388 nm. Structure IX and X are tentatively suggested for the dark green solid and pale green powder, respectively.



Structure IX. $Cu(OOCPh)_4$ (M_r, 547.5)



Structure X. $Cu_2(OOCPh)_6$ (M_r, 853)

The reaction at 80° gave a black gummy residue from which was obtained a black solid, M_r 1275. The infra-red and visible spectra were similar to the reaction at 60°. It may correspond to molecular formula $Cu_3(OOCPh)_9$ (M_r,1280) formed in reaction 14 in Scheme 28.

A possible mechanism which is consistent with the observations and products isolated is tentatively suggested in Scheme 28.

$$Cu_2(OOCPh)_4 \rightleftharpoons 2\ {\cdot}Cu(OOCPh)_2 \qquad (1)$$

$$Cu_2(OOCPh)_4 + (PhCOO)_2 \longrightarrow Cu_2(OOCPh)_4^{+\bullet} + PhCOO^- + PhCOO{\cdot} \qquad (2)$$

$$Cu_2(OOCPh)_4^{+\bullet} + PhCOO{\cdot} \longrightarrow Cu_2(OOCPh)_5^{+} \qquad (3)$$

$$Cu_2(OOCPh)_5^{+} + PhCOO^- \longrightarrow Cu_2(OOCPh)_6 \qquad (4)$$

$$Cu_2(OOCPh)_4^{+\bullet} + PhCOO^- \longrightarrow Cu_2(OOCPh)_5^{\bullet} \qquad (5)$$

$$2\ {\bullet}Cu_2(OOCPh)_5 \longrightarrow Cu_4(OOCPh)_{10} \qquad (6)$$

$$2\ {\bullet}Cu_2(OOCPh)_5 \longrightarrow Cu_2(OOCPh)_4 + Cu_2(OOCPh)_6 \qquad (7)$$

$${\bullet}Cu_2(OOCPh)_5 + PhCOO{\cdot} \longrightarrow Cu_2(OOCPh)_6 \qquad (8)$$

$${\cdot}Cu_2(OOCPh)_5 \longrightarrow Cu_2(OOCPh)_4 + PhCOO{\cdot} \qquad (9)$$

$${\cdot}Cu(OOCPh)_2 + (PhCOO)_2 \longrightarrow Cu(OOCPh)_2^{+} + PhCOO^- + PhCOO{\cdot} \qquad (10)$$

$$Cu(OOCPh)_2^{+} + PhCOO^- \longrightarrow Cu(OOCPh)_3 \qquad (11)$$

$$Cu(OOCPh)_2^{+} + PhCOO{\cdot} \longrightarrow Cu(OOCPh)_3^{+\bullet} \qquad (12)$$

$$Cu(OOCPh)_3^{+\bullet} + PhCOO^- \longrightarrow {\cdot}Cu(OOCPh)_4 \qquad (13)$$

$${\cdot}Cu(OOCPh)_4 + {\cdot}Cu_2(OOCPh)_5 \longrightarrow Cu_3(OOCPh)_9 \qquad (14)$$

Scheme 28

The dimeric copper(II) benzoate is expected to persist at 60°, but reactions 10-14 (Scheme 28) may become significant at 80° due to the rupture of copper-copper bonds to form the monomeric copper(II) benzoate.

The intermediacy of copper(III) in the reaction was a likely possibility. Copper(III) complexes are known to absorb in the region 340-400 nm, which is ascribed to the ligand-to-metal charge transfer transition. For example, bis(dihydrogen periodato)cuprate(III) has fairly intense bands at 340 and 421 nm [103]. It was noted that
(a) complexes of copper(II) with soft donor atoms or delocalised π-systems are often readily oxidised to copper(III) by relatively mild oxidants; and (b) copper(III) complexes could slowly oxidise the ligands [103].

Razuvaev and Latyaeva [104] reported that diacyl peroxides were able to oxidise copper to the corresponding copper salts. It may be assumed from this that copper(II) benzoate could be oxidise to copper(III) benzoate by benzoyl peroxide.

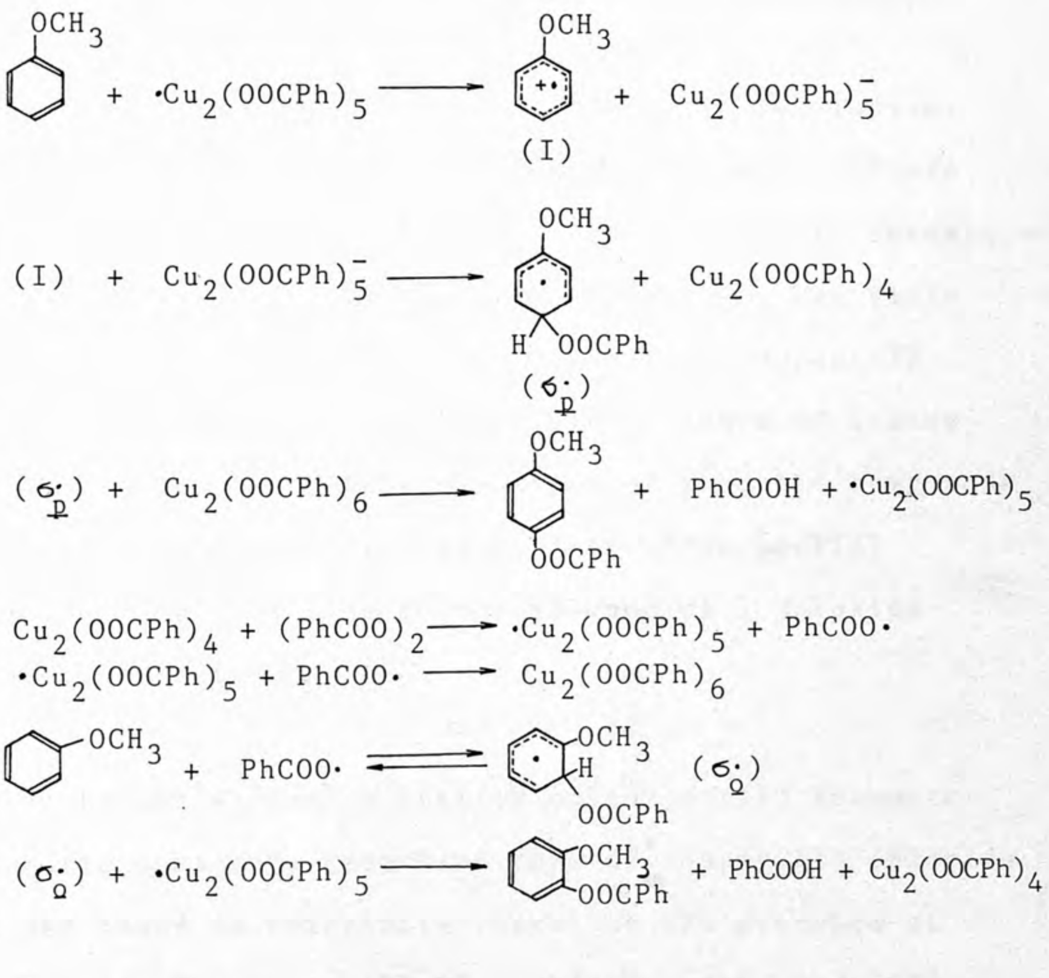
3.2.2. Reaction of "copper(III)" complex mixture with aromatic compounds (Table 16).

The "copper(III)" complex mixture, obtained from a reaction between benzoyl peroxide and copper(II) benzoate in acetonitrile at 60° for 24 hours (peroxide:copper(II) mol ratio, 192:1) reacted with anisole at 60° for 48 hours to give 8.3 mol% methoxyphenyl benzoate (o:p ratio, 44:56), and 10.5 mol% methoxybiphenyl (o:m:p ratio, 50:34:16). A similar reaction at 82° gave 2.7 mol% methoxyphenyl benzoate (o:p ratio, 46:54) and 12.1 mol% methoxybiphenyl (o:m:p ratio, 63:28:9).

At a peroxide:copper(II) mol ratio, 34:1, the above reaction at 60° gave 7.9 mol% methoxyphenyl benzoate (o:p ratio, 27:73) from anisole, and 27.9 mol% 4-methoxyphenyl benzoate from 4-fluoroanisole. The mixture at this ratio when heated at 80° reacted with anisole at 60° to give 2.2 mol% phenyl benzoate as the only product detected by g.l.c.

The "copper(III)" complex mixture (peroxide:copper(II) mol ratio, 2.2:1, 60°) reacted with anisole in the presence of copper(II) chloride at 60° to give 13.3 mol% methoxyphenyl benzoate (o:p ratio, 58:42), and less than 1 mol% methoxybiphenyl. In comparison, the copper(II) chloride catalysed decomposition of benzoyl peroxide in anisole at 60° gave 65.9 mol% methoxyphenyl benzoate (o:p ratio, 65:35) (Table 12). From this, it can be suggested that the reaction in the presence of copper(II) benzoate was not exclusively due to attack by free benzoyloxy radicals. The preferred para- attack suggests two possibilities (a) the reaction involved the participation of a bulky attacking entity; and/or (b) the reaction followed a different mechanism than suggested in Scheme 12.

A mechanism similar to that suggested by McClelland, Norman, and Thomas [53] for the diisopropyl peroxydicarbonate initiated reaction of lead tetrabenzoate with anisole (Scheme 21) may apply to the present system; from the similar isomer distributions of methoxyphenyl benzoate obtained (o:p ratio, 31:69) (Scheme 29).



Scheme 29

The intermediacy of anisyl radical cation in Scheme 29 is made possible by the stronger oxidising capability expected from"copper(III)"complexes. The choice of the species, $\cdot Cu_2(OOCPh)_5$, as the oxidising agent is without any supporting evidence and open to critisisms.

Copper(II) chloride was found to react with benzoyl peroxide in a similar manner (Appendix 3 ; Table 27).

3.2.3. Copper(II) benzoate as a benzoyloxylating agent.

In the presence of 2-naphthoyl peroxide and iodine, copper(II) benzoate in acetonitrile reacted with anisole at 60° for 72 hours to give 34.5% 4-methoxyphenyl benzoate, and a trace amount of the ortho- isomer (2.9). The yield was based on the assumption that one mol of copper(II) benzoate gave one mol of product. The presence of iodine was shown to promote benzoyloxylation of aromatic compounds by benzoyl peroxide [38]. This ability of copper(II) benzoate was not observed in the absence of a peroxide initiator or iodine.

The benzoyloxylating ability of copper(II) benzoate in aromatic compounds resembles that of copper(II) chloride which was found to chlorinate phenol in the presence of benzoyl peroxide to give 82.3% 4-chlorophenol, and 1.5% 2-chlorophenol at 60° (2.10). Nonhebel [48] and Ware and Borchert [50] demonstrated the chlorination of electron-rich aromatic compounds by copper(II) chloride in the absence of a radical initiator.

3.3. Copper(II) benzoate catalysed decomposition of benzoyl peroxide in aromatic compounds.

3.3.1. Anisole.

The copper(II) benzoate catalysed decomposition of benzoyl peroxide in anisole at 80° for 72 hours gave 18.5 mol% methoxyphenyl benzoate (o:p ratio, 84:16), and 50.5 mol% methoxybiphenyl (o:m:p ratio, 62:26:12). Similar reactions at 60° gave 22.4 mol% methoxyphenyl benzoate (o:p ratio, 34:66), and 27.1 mol% methoxybiphenyl (o:m:p ratio, 61:26:13). The other reaction products were not analysed (Table 6).

The formation of methoxyphenyl benzoate was faster at the higher temperature. More than 80% of the total amount of each isomer (o:p ratio, 81:19) was formed in the first 20 hours at 80°, while about 70% of the total *ortho*- and only 40% of the total *para*- isomer yield (o:p ratio, 51:49) were formed after the same time at 60° (Table 6).

Bolton *et al*. [14] obtained 36.5 mol% methoxyphenyl benzoate (o:p ratio, 69:31) from the copper(II) benzoate catalysed decomposition of benzoyl peroxide in neat anisole at 80°.

Kurz and Kovacic [37] obtained 75 and 56 mol% methoxyphenyl benzoate (o:p ratio, 68:32) at 60° and 80°, respectively, from the reaction catalysed by copper(II) chloride in acetonitrile.

The present work gave comparatively lower yields of methoxyphenyl benzoate. This is largely due to the diversionary reaction of benzoyl peroxide with copper(II) benzoate to form an intermediate which could not benzoyloxylate anisole efficiently (3.2).

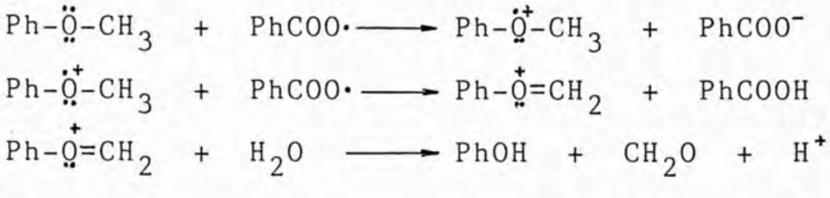
The isomer distributions of methoxyphenyl benzoate were significantly altered with the temperature. The <u>ortho</u>-isomer was being quickly and favourably formed at 80°. It is possible that the copper(II) benzoate catalysed benzoyloxylation at the <u>ortho</u>- position requires a higher activation energy due to steric inhibition, and therefore is more significant at the higher temperature. The <u>para</u>-isomer was being formed in an amount comparable to the uncatalysed decomposition at the same temperature.

At 60°, both isomers were initially formed in about equal amounts. These may arise from contributions of both free benzoyloxy radicals and "copper(III)" complexes. The latter reagents were found to benzoyloxylate anisole exclusively at the <u>para</u>- position (3.2.3). After 48 hours, 60% more of the <u>para</u>- isomer was formed, while the formation of the <u>ortho</u>- isomer had effectively stopped. The increased amount of the <u>para</u>- isomer after this time may be due to reactions involving the "copper(III)" complexes only.

The different effects of copper(II) benzoate at different temperatures were more obvious in reactions using different anisole:peroxide:copper(II) benzoate mol ratio (Table 7).

At 60°, the yields of methoxyphenyl benzoate were not greatly affected by large variations in the peroxide: catalyst mol ratios, but the yields were lower when the anisole:peroxide mol ratio of less than 100:1 was used, while increasing this ratio to about 500:1 did not affect it. In contrast, the isomer distributions were expectedly affected by the anisole:catalyst and peroxide:catalyst mol ratio (Appendix 2 ; a-c). The o:p ratio was (i) about 40:60 at anisole:catalyst mol ratio, $8\text{x}10^3$-$20\text{x}10^3$:1, and peroxide: catalyst,70-100:1 ; and (ii) about 30:70 at anisole:catalyst mol ratio $\leqslant$ 1000:1 and peroxide:catalyst $\leqslant$7:1.

The higher proportions of the para- isomer at higher concentration of copper(II) benzoate support the involvement of copper(II) benzoate in benzoyloxylating at the para-position. The optimum anisole:peroxide:catalyst mol ratio, determined graphically, for a maximum yield of methoxyphenyl benzoate (ca. 20 mol%) in favour of the para- isomer was 160:1:0.1. This is confirmed in an investigation in which a mol ratio of 163.2:1:0.1 gave 25.2 mol% phenol, 14.5 mol% 2-methoxyphenol, and 30.5 mol% 4-methoxyphenol. The yields were determined after alkaline hydrolysis of the reaction mixture. Phenol may be formed from demethoxylation of the high boiling residues during alkaline hydrolysis, or by a free-radical demethylation of anisole as suggested by Lynch and Moore [13] (Scheme 30).



$$\begin{aligned}
&\mathrm{Ph{-}\underset{..}{\overset{..}{O}}{-}CH_3} + \mathrm{PhCOO\cdot} \longrightarrow \mathrm{Ph{-}\underset{..}{\overset{\cdot +}{O}}{-}CH_3} + \mathrm{PhCOO^-}\\
&\mathrm{Ph{-}\underset{..}{\overset{\cdot +}{O}}{-}CH_3} + \mathrm{PhCOO\cdot} \longrightarrow \mathrm{Ph{-}\underset{..}{\overset{+}{O}}{=}CH_2} + \mathrm{PhCOOH}\\
&\mathrm{Ph{-}\underset{..}{\overset{+}{O}}{=}CH_2} + \mathrm{H_2O} \longrightarrow \mathrm{PhOH} + \mathrm{CH_2O} + \mathrm{H^+}
\end{aligned}$$

Scheme 30

At 80°, both the yields and isomer distributions were highly sensitive to small variations in anisole: peroxide:catalyst mol ratios (Appendix 2 ; d-f). The graphically determined optimum mol ratio for a maximum yield of methoxyphenyl benzoate (ca. 20 mol%) in favour of the <u>ortho</u>- isomer was 110:1:0.015, at which a minimum interference by copper(II) benzoate was expected. However, this was not apparent in the product mixture in which a ratio of 107.6:1:0.016 was used; alkaline hydrolysis gave 40.4 mol% phenol, 6.7 mol% 2-methoxyphenol, and 8.4 mol% 4-methoxyphenol.

Another investigation on the effect of copper(II) benzoate in the reaction using high concentrations of copper(II) benzoate was shown in Table 13. The reaction at 60° in the presence of copper(II) benzoate gave lower yield of methoxyphenyl benzoate than the uncatalysed reaction. This was the result of (a) slightly less of the _para_- isomer formed; and (b) the formation of the _ortho_- isomer was almost suppressed. The effect of copper(II) benzoate at 80° was to practically inhibit benzoyloxylation at both the _ortho_- and _para_- positions.

These effect contrasted with the catalytic effect of copper(II) chloride which gave high yields of both the _ortho_- and _para_- isomers, while the isomer distributions were unaffected (Table 13). It is conceivable that copper(II) benzoate was not able to act as oxidising agent for σ-complexes because the bidentate benzoate ligands will resist the tetrahedral configuration associated with copper(I) complexes. In comparison, the oxidation of copper(II) benzoate to copper(III) complex involves no change in configuration [103] (Structure IX and X).

The reaction of 2- and 4-deutero- anisoles with benzoyl peroxide in the presence of copper(II) benzoate at 60° (Table 8) further support the above suggestions.

The reaction with 2-deuteroanisole gave 4.2 mol% 2- and 10.6 mol% 4- methoxyphenyl benzoate after 72 hours; while 4-deuteroanisole gave 2.8 and 4.0 mol%, respectively. These may be compared with 7.5 and 14.9 mol% obtained from anisole. The results are collected in Table 21 for clarity.

Table 21 The yields of methoxyphenyl benzoate in the copper(II) benzoate catalysed decomposition of benzoyl peroxide at 60°.

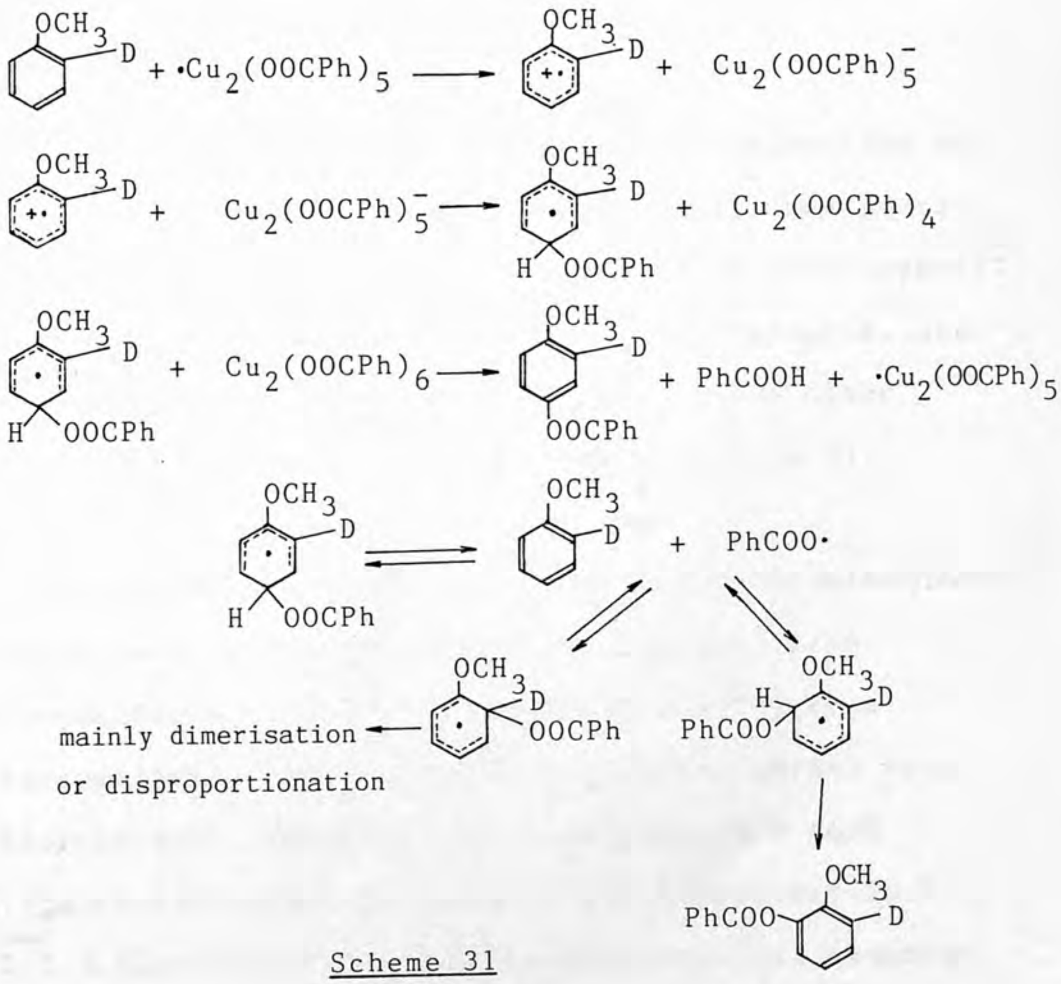
Aromatic compound	Mol%	
	ortho-	*para*-
Anisole	7.5	14.9
2-Deuteroanisole	4.2	10.6
4-Deuteroanisole	2.8	4.0

The isotope effect arose because the σ-complex with deuterium at the tetrahedral carbon was less likely to give the substitution product due to the stronger carbon-deuterium bond [35].

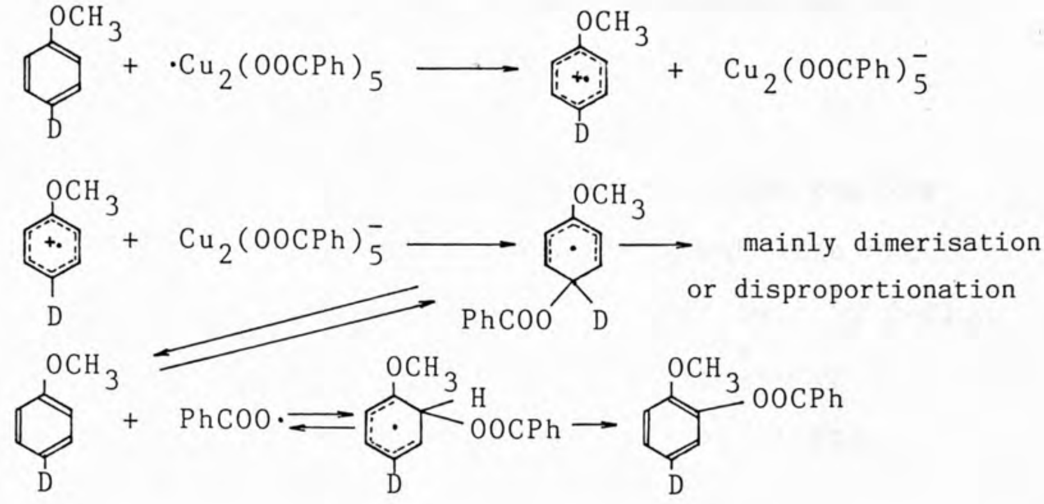
The finding of the deuterium isotope effect confirms the inability of copper(II) benzoate to act as an efficient oxidising agent in the system. Kurz and Kovacic [21] showed that copper(II) acetate and benzoate could not serve as oxidation catalysts in the system diisopropyl peroxydicarbonate-toluene-acetonitrile.

Table 21 shows that (a) the presence of deuterium at one of the *ortho*- positions has approximately halved the yield of the *ortho*- isomer, while the yield of the *para*-

isomer was not affected; and (b) deuterium at the para-position has a deleterious effect on the yield of both isomers. Collectively, these results suggest that the benzoyloxylation reaction may initially occur through the formation of the para- σ-complex which then acted as a source of benzoyloxy radicals for attack at the ortho- positions, or for phenylation reaction. This is not improbable because it was found that "copper(III)" complexes gave exclusively the para- isomer (3.2). Scheme 31 and 32 show how the results for the reactions of 2- and 4-deutero- anisoles, respectively, may be explained.



Scheme 31



Scheme 32

3.3.2. Haloaromatic compounds.

The copper(II) benzoate catalysed decomposition of benzoyl peroxide in 2- and 4-fluoro-, 4-chloro- and pentafluoro- anisoles at 60° gave high yields of methoxyphenyl benzoate arising from displacement of the halogens, and to the exclusion of phenylation products. The other reaction products were not investigated (Table 9).

The yields and isomer distributions of the methoxyphenylbenzoates were 40.6 mol% (exclusively _ortho_-) from 2-fluoroanisole, 134.3 mol% (_o_:_p_ ratio, 6:94) from 4-fluoroanisole, and 34.0 mol% (_o_:_p_ ratio, 36:64) from 4-chloroanisole. Pentafluoroanisole gave 64.2 mol% 2,3,5,6-tetrafluoro-4-methoxyphenyl benzoate and 20.7 mol% 2,3,5,6-tetrafluoro-4-methoxybiphenyl. In contrast, hexafluorobenzene gave only 0.03 mol% pentafluorophenylbenzoate.

The results show that (a) fluorine is more readily displaced than chlorine. This is inconsistent with the strength of carbon-halogen bonds (C-F, 452 kJmol^{-1}; C-Cl, 339 kJmol^{-1}) but follows the order of nucleophilic displacement; and (b) para- fluorine is more readily displaced than ortho- fluorine.

The high yields of esters from reactions of fluoroaromatic compounds with benzoyl peroxide have not been reported before [59,61]. Lewis and Williams [105] found that the kinetic order for the induced decomposition of benzoyl peroxide in fluorobenzene at 80.2° was 3/2, signifying a low stationary concentration of benzoyloxy radical in the system when compared to bromobenzene [19]. It was suggested that fluorine in fluorobenzene could not take part in the formation of charge-transfer complex with benzoyloxy radical due to its high electronegativity.

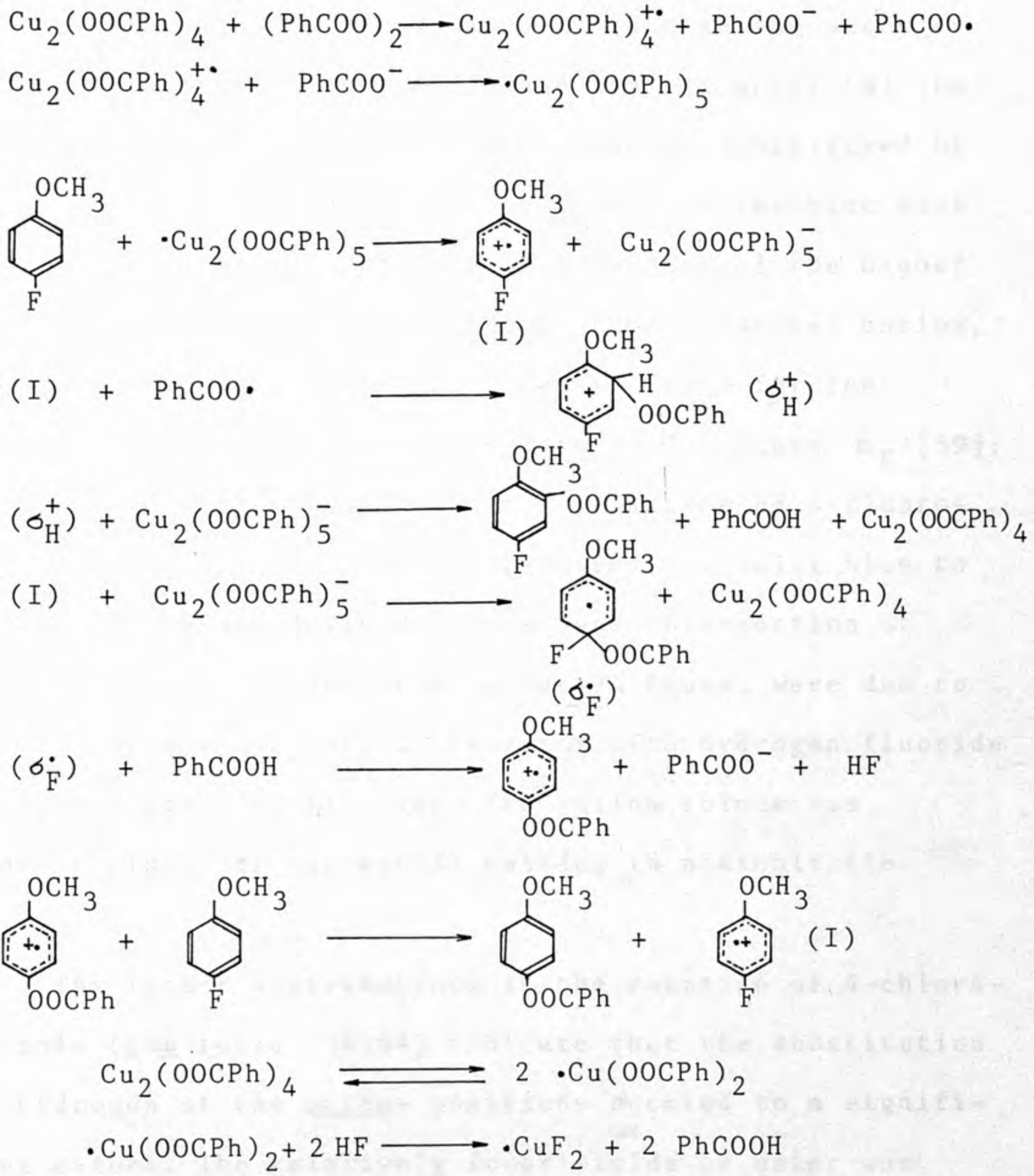
Coleman [32] argued that iron(III) benzoate was not able to oxidise the intermediate σ-complex from hexafluorobenzene because of (a) the strength of carbon-fluorine bond; and (b) the improbability of fluorine to leave as fluorinium cation, F^{+}.

Allen, Bolton, and Williams [62] observed that the effect of iron(III) benzoate in reactions involving polyfluoroarenes was to promote products of aryldehydrogenation of σ-complexes.

The high yields of methoxyphenyl benzoate in the present work must be due to the involvement of copper(II) benzoate in acetonitrile solvent. The uncatalysed decomposition of benzoyl peroxide in 4-fluoroanisole at 60° in acetonitrile gave 32 mol% methoxyphenyl benzoate (o:p ratio, 15:85); while the copper(II) chloride catalysed decomposition gave 15 mol% 5-fluoro-2-methoxyphenyl benzoate as the ortho- susbstitution product, and no 4-methoxyphenyl benzoate (Table 9). This is in contrast with the catalytic effect of copper(II) chloride with anisole (3.4). It can be suggested that the reactions in the presence of copper(II) benzoate followed a different mechanism than was suggested for the copper(II) chloride catalysed reaction [37] (Scheme 36).

The ability of copper(II) benzoate to benzoyloxylate aromatic compounds in the presence of a peroxide was shown in (3.2.3). It is shown in Table 16 that "copper(III)" complex gave higher yields of ester from 4-fluoroanisole (27.9 mol%) than from anisole (7.9 mol%).

Following the arguments in (3.2 and 3.3.1), the following mechanism is tentatively suggested for the copper(II) benzoate catalysed decomposition of benzoyl peroxide in 4-fluoroanisole (Scheme 33).

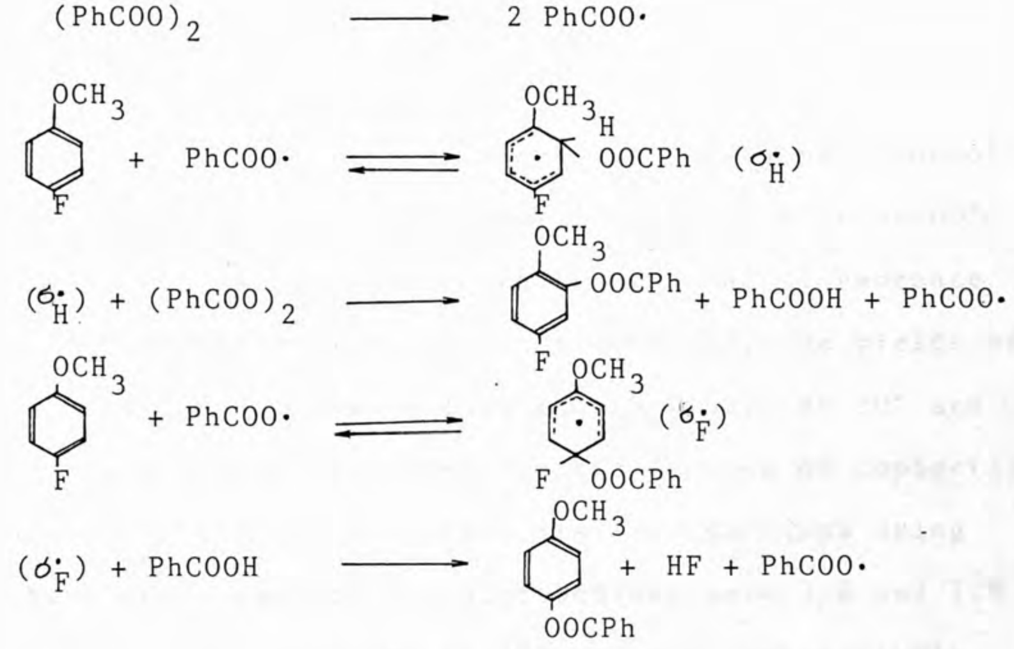


Scheme 33

The mechanism suggested in Scheme 33 resembles the $S_{ON}2$ reaction of aromatic compounds with nucleophiles to be discussed in (3.5). Eberson and Jönsson [63] showed that copper(III) complex of biuret (KCu(biuret)$_2$) can induce the $S_{ON}2$-type behaviour. Scheme 33 explains that (a) the readier displacement of fluorine was due to the stronger hydrogen-bond between fluorine and benzoic acid; (b) the *para*- fluorine is apparently more readily substituted by the bulkier "copper(III)" complex; (c) the reaction with hexafluorobenzene was unsuccessful because of the higher oxidation potential of hexafluorobenzenyl radical cation, and that there was no ready route available for the formation of benzoic acid needed to defluorinate $6^{\cdot}_{F}$ [59]; and (d) the observations that the reactions of 4-fluoro- and pentafluoro- anisoles changed from initially blue to yellow with brown solid deposits, and the reaction of 2-fluoroanisole became brown after 72 hours, were due to the reaction of copper(II) benzoate with hydrogen fluoride to form copper(II) fluoride. The yellow colour was characteristic of copper(II) halides in acetonitrile.

The isomer distributions in the reaction of 4-chloroanisole (*o*:*p* ratio, 36:64) indicate that the substitution of hydrogen at the *ortho*- positions occured to a significant extent. The relatively lower yields of ester was because the weaker hydrogen-bond between chlorine of $6^{\cdot}_{Cl}$ and benzoic acid resulted in relatively slower formation of the radical cation needed to sustain the chain cycle. The reaction mixture was green after 72 hours (similar to the anisole reaction) indicating that copper(II) benzoate was not completely transformed to copper(II) chloride by hydrogen chloride.

In the absence of copper(II) benzoate, the reaction may proceed by the mechanism suggested by Bolton, Sandall, and Williams [59] involving the attack at both the hydrogen- and fluorine- bearing sites (Scheme 34).



Scheme 34

The electrophilic benzoyloxy radicals are more likely to attack the fluorine bearing site because of the higher electron density at the carbon bearing the electronegative fluorine as a result of 4-methoxy substituent. The attack at the hydrogen-bearing sites provided the necessary benzoic acid needed to defluorinate $\sigma^{\cdot}_{F}$ [59].

4-Methoxyphenyl benzoate was isolated in 50.3 mol% yield from the copper(II) benzoate catalysed decomposition of benzoyl peroxide in 4-fluoroanisole (2.13.1). This method is useful on a synthetic scale for the ipso-oxygenation of easily oxidised fluoro- and chloro-aromatic compounds only.

3.3.3. Naphthalene and its derivatives.

The copper(II) benzoate catalysed decomposition of benzoyl peroxide in naphthalene in acetonitrile at 60° gave 3-6 mol% 1-naphthyl benzoate. 2-Naphthyl benzoate and 1-phenylnaphthalene were not detected. The yields of 1-naphthyl benzoate were 13.0 and 18.6 mol% at 80° and 82°, respectively. The yield in the absence of copper(II) benzoate at 80° was 2.0 mol%. Similar reactions using naphthalene dissolved in chlorobenzene gave 3.6 and 1.8 mol% 1-naphthyl benzoate at 60° and 80°, respectively. The reactions gave steam-involatile residues which probably contained binaphthyls, but were not analysed (Table 10).

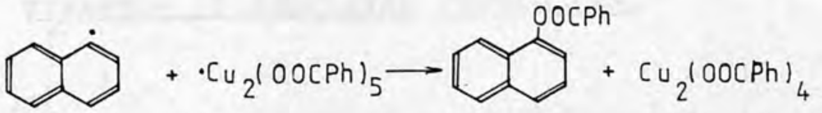
These results are in contrast with those reported by Davies, Hey, and Williams [20a] who obtained 32 mol% naphthol at 85°, and by Lynch and Pausacker [20b] who obtained 18-28 mol% naphthol at 100°, from the uncatalysed reactions in the absence of any solvents.

On the other hand, Boyland and Sims [57] were unable to isolate any naphthyl benzoate from the uncatalysed reaction in chlorobenzene solvent at 80°, although they did obtain free naphthol by chromatographic separation of the reaction mixture.

A competitive experiment using equimolar amounts of anisole and naphthalene indicated that the relative reactivity of anisole to naphthalene in the copper(II) benzoate catalysed reaction at 80° was 0.92 (2.6.5).

The low yields of ester obtained are not surprising from the foregoing discussions (3.3.1). The role of copper(II) benzoate as a benzoyloxylating agent in this system is obvious from the lower yield of ester obtained in its absence.

The increase yields of 1-naphthyl benzoate with temperature is not expected. It may be that the rapid homolysis of benzoyl peroxide at the high temperature gave benzoyloxy radical which abstracted hydrogen from naphthalene at the 1-position to form 1-naphthyl radical [20a]. This may react with the intermediate "copper(III)" complex to give 1-naphthyl benzoate (Reaction 18).



(18)

The decomposition of benzoyl peroxide in naphthalene in the presence of iodine or copper(II) chloride in acetonitrile similarly gave low yields of 1-naphthyl benzoate (Table 10). These additives were found to give high yields of benzoyloxylation products with anisole (Table 12). The low yield in the presence of copper(II) chloride was not due to competitive chlorination reaction, since 1-chloronaphthalene was not detected.

Boyland and Sims [57] suggested that naphthalene is not readily attacked by benzoyloxy radicals because its "free valence number" for the 1-position is close to that of phenanthrene and chrysene. Roitt and Waters [6] found that the latter compounds were unreactive towards benzoyloxy radicals from benzoyl peroxide.

The reactions with 1-methyl-, 2,3-dimethyl-, 1-chloro-, and octafluoro- naphthalenes similarly gave low yields of esters (Table 11).

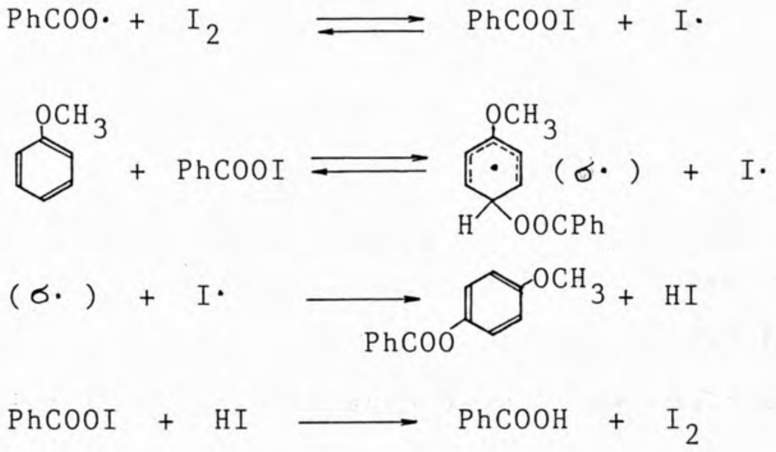
Benzoyloxy radicals probably reacted with naphthalene and its derivatives by hydrogen abstraction as suggested by Davies, Hey, and Williams [20a].

3.4. Decomposition of benzoyl peroxide in anisole in the presence of additives (Table 12).

The decomposition of benzoyl peroxide in anisole in the presence of iodine in acetonitrile at 60° for 72 hours (anisole:peroxide:iodine mol ratio, 90:1:0.08) gave 58.6 mol% methoxyphenyl benzoate (o:p ratio, 25:75), and 8.9 mol% methoxybiphenyl (o:m:p ratio, 52:38:10). The other reaction products were not analysed. Under the same conditions in the absence of the additive was obtained 10.6 mol% methoxyphenyl benzoate (o:p ratio, 38:62), and 22.2 mol% methoxybiphenyl (o:m:p ratio, 60:29:11).

Kovacic, Reid, and Brittain [38] obtained 87 mol% methoxyphenyl benzoate (o:p ratio, 47:53) in a similar reaction at 90±2° for 20 hours, using anisole:peroxide: iodine mol ratio, 12.6:1:0.21. These workers reported that (a) the yield of the ester was independent of aromatic:peroxide mol ratio, but declined significantly when the iodine:peroxide mol ratio of less than 0.2 was used. It was suggested that in less ratio, benzoyloxy radicals were not efficiently trapped, and therefore decarboxylated to phenyl radicals; and (b) solvents such as acetonitrile,1,2-dichlorobenzene, or nitromethane produced a dramatic decrease in the yield of the ester.

The comparatively lower yield of the ester obtained in the present work could not be solely as a result of inefficient trapping of benzoyloxy radicals by iodine because the yield of methoxybiphenyl was lower than in the reaction without the additive. The isomer distribution (o:p ratio, 25:75) suggests that the reaction involved a bulky attacking entity, such as the unstable benzoyl hypoiodite as suggested by Kovacic *et al*. [38] and by Hammond and Soffer [106] (Scheme 35).



Scheme 35

The polar acetonitrile solvent is expected to discourage the homolysis of benzoyl hypoiodite, and stabilise a polar intermediate (Figure 13).

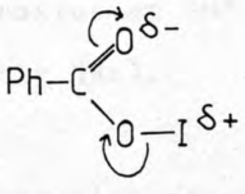


Figure 13

The competitive reaction of this reagent (Figure 13) with anisole to form iodoanisole and benzoic acid

(Reaction 19) may account for the relatively lower yields of ester obtained in acetonitrile. Hammond [40] found that iodoarenes were formed in the decomposition of benzoyl peroxide in benzene and chlorobenzene in the presence of iodine.

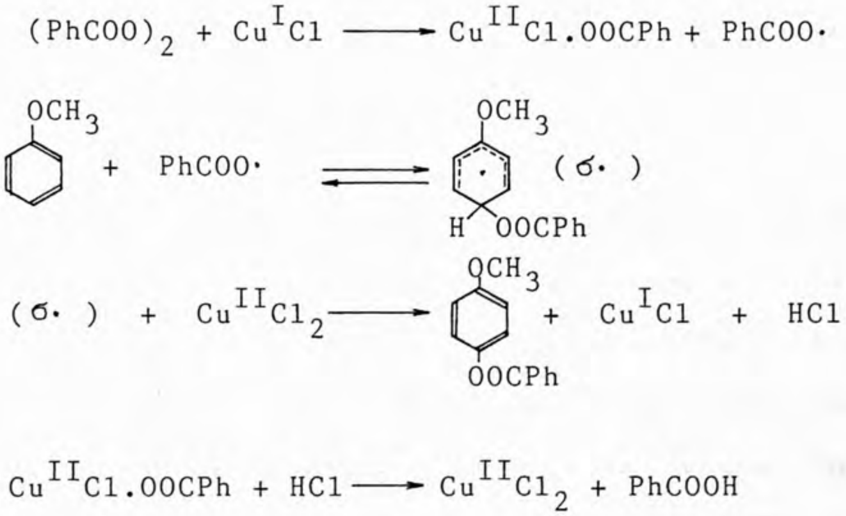
(19)

The mechanism in Scheme 35 suggests the oxidation of σ-complex by iodine atom. It was thought that a better oxidising agent such as bromine could improve the yield of methoxyphenyl benzoate. The reaction performed in the presence of bromine in acetonitrile solution did not give any phenylation or benzoyloxylation products (Table 12). This was because bromine reacted with anisole at room temperature to form a solid product with evolution of acid gas. The solid product formed rapidly reacted with benzoyl peroxide at 60° with more evolution of acid gas (probably HBr).

The above reaction repeated with N-bromosuccinimide (NBS) gave 8.1 mol% methoxyphenyl benzoate (o:p ratio, 28:72) and 12.8 mol% methoxybiphenyl (o:m:p ratio, 62:27:11). The other reaction products were not investigated. The results may be compared with 10.6 mol% methoxyphenyl benzoate (o:p ratio, 38:62) and 22.2 mol% methoxybiphenyl (o:m:p ratio, 60:29:11) obtained in the absence of the additive. The slightly lower yield of methoxyphenyl benzoate in the presence of NBS was because of the lower amount of the ortho- isomer formed, while the yield of the para- isomer was not affected. It can be suggested from this that the attacking entity was a free benzoyloxy radical.

In the presence of benzoyl peroxide, NBS decomposed to bromine atom and succinimidoyl radical. Skell and Day [107] suggested that the dominant chain carrier species in acetonitrile was succinimidoyl radical. Day, Katsaros, Kocher, Scott, and Skell [108] found that succinimidoyl radical was able to substitute aromatic nucleus to give N-arylsuccinimide. It seems likely that the inability of NBS to promote benzoyloxylation of anisole by benzoyl peroxide were due to competitive reactions of bromine, succinimidoyl and benzoyloxy radicals present in the system.

The copper(II) chloride catalysed decomposition of benzoyl peroxide in anisole (anisole:peroxide:catalyst mol ratio, 20:1:1.5) gave 65.9 mol% methoxyphenyl benzoate (o:p ratio, 65:35) at 60°, and 49.0 mol% (o:p ratio, 64:36) at 80°. Kurz and Kovacic [37] obtained 75 mol% (o:p ratio, 68:32) at 60°, and 56 mol% (o:p ratio, 67:33) at 80°; at anisole:peroxide:catalyst mol ratio, 16.8:1:0.3. The mechanism suggested for the reaction is outlined in Scheme 36 [37].



Scheme 36

The large catalyst requirement was due to the inability of $Cu^{II}Cl.OOCPh$ to oxidise σ-complex. Copper(II) chloride was regenerated by metathesis of the mixed copper(II) salt with HCl [21].

Kurz and Kovacic [45] found that in the diisopropyl peroxydicarbonate-toluene-copper(II) chloride-acetonitrile system, the peroxide decomposed at a rate of 6.45×10^{-3} min^{-1} in the uncatalysed reaction, and 6.6×10^{-2} min^{-1} in the catalysed. It was found that the rate was fastest when copper(I) chloride was used instead, in agreement with its function in induced decomposition of the peroxide; but the rate tapered off after about 30% of the peroxide had decomposed, supporting the inability of the mixed copper salt to oxidise σ-complex.

Kochi and Subramanian [46] observed that copper(I) species reacted very rapidly and exothermically with diacyl peroxides at 25°.

In comparison, copper(II) bromide gave only 23.8 mol% methoxyphenyl benzoate (o:p ratio, 61:39). Kurz and Kovacic [21] also observed similar effects of copper(II) bromide in the diisopropyl peroxydicarbonate-toluene-copper(II) bromide-acetonitrile system. They suggested that the reduced ability of copper(II) bromide to catalyse the above reaction was due to the complex equilibria reported to exist in acetonitrile (Scheme 37). This results in the active catalyst being present in low concentration.

$$2\ CuBr_2 \rightleftharpoons Cu(I) + CuBr_3^- + \tfrac{1}{2}\ Br_2$$

$$2\ Cu(II) + 2\ Br^- \rightleftharpoons 2\ Cu(I) + Br_2$$

Scheme 37

The observed effects of the different additives above predict that high yields of methoxyphenyl benzoate may be obtained in a reaction using iodine to trap the benzoyloxy radical , and copper(II) chloride to speed up the rate of the reaction and oxidise the intermediate σ-complex. However, a reaction using a mixture of anisole-benzoyl peroxide-iodine-copper(II) chloride in acetonitrile (mol ratio, 73:1:0.08:0.13) at 60° gave 55.2 mol% methoxyphenyl benzoate (*o*:*p* ratio, 55:45); which is lower than using the additives separately (Table 22).

Table 22 The decomposition of benzoyl peroxide in anisole in the presence of additives at 60°

Additives	Mol%			*o*:*p* ratio
	o-	*p*-	total	
I_2	14.5	44.1	58.6	25:75
$CuCl_2$	42.9	23.0	65.9	65:35
$CuCl_2$-I_2	30.6	24.6	55.2	55:45
$Cu_4(OOCPh)_8$	7.5	14.9	22.4	34:66
$Cu_4(OOCPh)_8$-I_2	12.4	25.3	37.7	33:67

The isomer distribution dismissed the dominant of a bulky attacking entity such as proposed for the iodine catalysed reaction (Scheme 35). The lower yield of methoxyphenyl benzoate suggested that the catalytic ability of copper(II) chloride was reduced by the presence of iodine.

It was observed that the initially red colour due to iodine in the reaction mixture was replaced by green after 72 hours at 60°, suggesting that iodine was consumed in the reaction. In a separate observation, the white solid coagulated from copper(II) chloride solution in acetonitrile after a few minutes at room temperature quickly disappeared on adding a few crystals of iodine. These observations suggest that iodine was diverted from trapping benzoyloxy radical by its reaction with copper(II) chloride, to form a new species with reduced catalytic ability.

A similar reaction using copper(II) benzoate-iodine mixture (anisole:peroxide:iodine:copper(II) mol ratio, 72:1:0.08:0.01) at 60° gave 37.7 mol% methoxyphenyl benzoate (o:p ratio, 33:67), and 7.5 mol% methoxybiphenyl (o:m:p ratio, 54:36:10). The yield of the ester is about 70% higher than using copper(II) benzoate alone, but about 40% lower than using iodine alone. It was observed that iodine was not obviously consumed in the reaction.

The isomer distribution was similar to the copper(II) benzoate reaction. The reaction probably followed the same course (Scheme 29). The main function of iodine was posssibly to oxidise the σ-complex (Scheme 35).

The decomposition of benzoyl peroxide in anisole in the presence of tin(IV) chloride in acetonitrile at 60°

gave only 2 mol% methoxyphenyl benzoate (o:p ratio, 45:55), and 4 mol% methoxybiphenyl (o:m:p ratio, 59:32:11). The reaction mixture was initially bright pink at room temperature, but rapidly became black at 60°. Edward, Chang, and Samad [51] observed a similar effect of aluminium chloride when solvents such as nitrobenzene, nitromethane, or dichloromethane, were used.

3.5. The benzoyl peroxide initiated reactions of aromatic compounds with nucleophiles (The $S_{ON}2$ reaction).

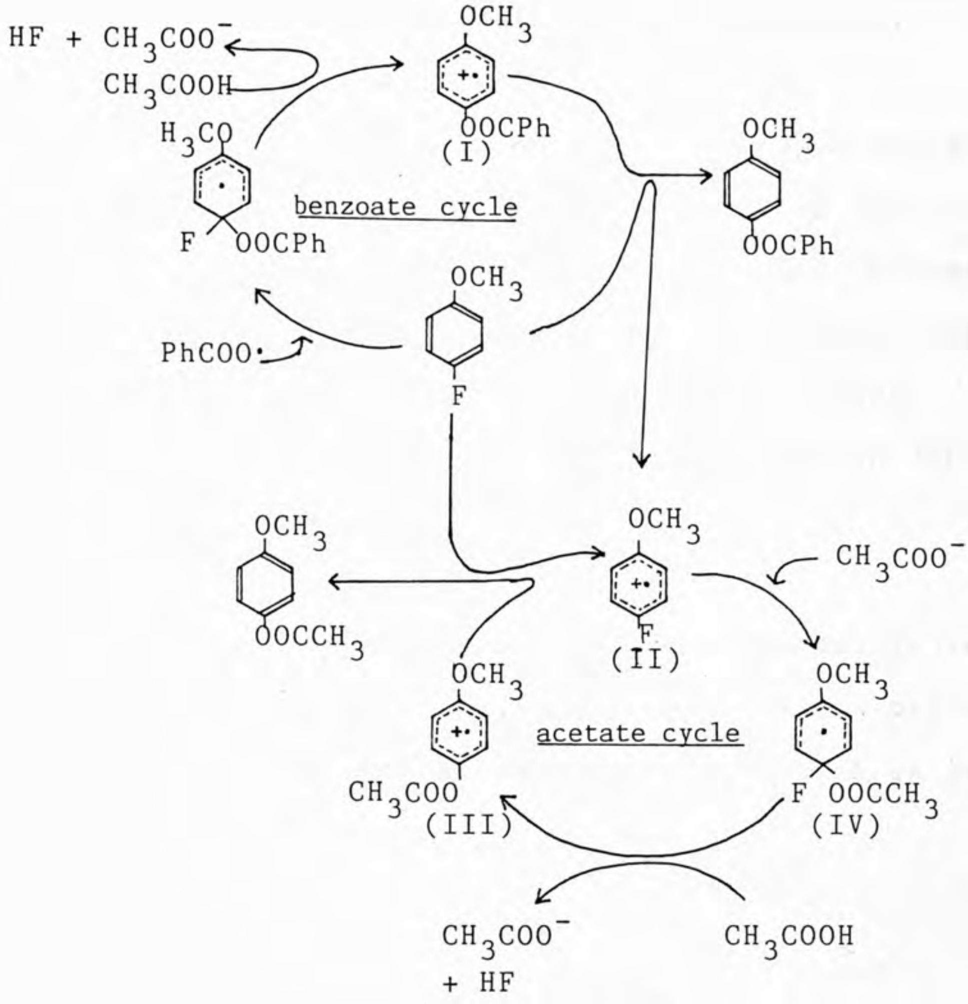
The benzoyl peroxide initiated reactions of 2-fluoro-, 4-fluoro-, and pentafluoro- anisoles, and 1-fluoronaphthalene , with acetate ions gave high yields of defluorinated acetates (50-200 mol%), and benzoates (20-100 mol%). Anisole and 4-chloroanisole gave lower yields of both products (3-10 mol%). N,N-Dimethyl-4-fluoroaniline gave 36.3-58.0 mol% 4-dimethylaminophenyl-acetate; the corresponding benzoate was not detected. The highly fluorinated aromatic compounds, 4-methoxy-nonafluorobiphenyl and octafluoronaphthalene did not react. The reaction could not take place in the absence of the initiator (Table 17).

Table 2 shows the results of similar investigations by Eberson and Jönsson [64] with 4-fluoroanisole. The present work gave higher yields of 4-methoxyphenyl acetate and benzoate; but the ratios of acetate to benzoate were similar at between 3:1 and 10:1.

Eberson and Jönsson [64] suggested the $S_{ON}2$ mechanism; which refers to the oxidatively initiated bimolecular nucleophilic substitution reaction (Scheme 20).

Aromatic compounds normally undergo electrophilic substitution reactions, such as nitration and halogenation. Nucleophilic reagents would be repelled by the electron-clouds above and below the aromatic ring. However, the initiation of the $S_{ON}2$ reaction above proceeded through an initial attack by an electrophilic benzoyloxy radical. In the case where the aromatic ring is deactivated towards electrophilic attack, such as with 4-methoxynonafluorobiphenyl and octafluoronaphthalene, the $S_{ON}2$ reaction could not occur. The aromatic rings in the highly fluorinated compounds are electron-deficient and therefore unreactive towards the electrophilic benzoyloxy radicals.

The benzoyloxy radical is expected to attack the electron-dense fluorine-bearing carbon to form an intermediate σ-complex ($\sigma_F^{\bullet}$). In acid condition, fluorine is easily eliminated from $\sigma_F^{\bullet}$ as the fluoride ion through the formation of strong H-bond with acetic acid, to form the essential intermediate radical cation which enters the chain cycle. Scheme 38 is another version of Scheme 20 to show how the chain-cycle was initiated by benzoyl peroxide for 4-fluoroanisole.

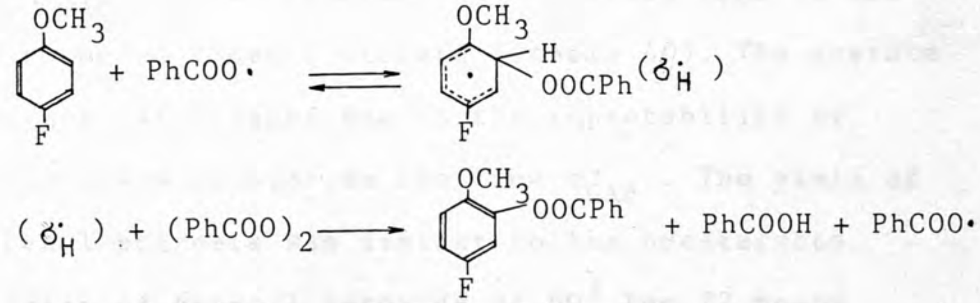


Scheme 38

The success of both the benzoate and acetate cycles depends on (a) the ease of formation of radical cations (I, II, and III). Radical cations (I) and (III) were formed by elimination of fluorine as fluoride from the corresponding σ_F-complexes. The slower elimination of chlorine from δ_{Cl}-complex in the reaction with 4-chloroanisole may account for the lower yields of both 4-methoxyphenyl acetate and benzoate. This is because the hydrogen-bond formed between acetic acid and chlorine of δ_{Cl}-complex is weaker than between fluorine from σ_F-complex;

(b) high concentration of aromatic compounds. Both the benzoate and acetate cycles depend on the conversion of 4-fluoroanisole to the radical cation (II) (Scheme 38). This factor may account for the higher yields of both the acetate and benzoate obtained in the present work ([Aromatic] ~ 2M) compared to that of Eberson and Jönsson [64] ([Aromatic] = 1M);

(c) low concentration of benzoyl peroxide (Table 17). Benzoyl peroxide present in high concentration may undergo side-reactions with the aromatic compounds such as in Scheme 39.



Scheme 39

A similar effect was also observed by Eberson and Jönsson [64] (Table 2).

The success of the acetate cycle depends on (a) the ease of formation of radical cation (II) in chain-transfer reactions involving 4-fluoroanisole and radical cations (I) and (III). Eberson, Jönsson, and Wistrand [65] calculated that this step is slightly endothermic ($\Delta G \leqslant 10$ kcalmol^{-1}), but the formation of (III) and (IV) are exothermic, and the loss of fluoride from (IV) is favoured over that of acetate. The initiation of the acetate cycle is only possible by easily oxidised substrate.

Anisole apparently could not fulfil the above requirement, and therefore gave low yields of methoxyphenylacetate. The acid-catalysed elimination of benzoic acid from σ-complex (Reaction 12) [99] provided the necessary radical cation to form acetoxymethoxycyclohexadienyl radical ($\sigma^{\cdot}_{OAc}$) by its reaction with acetate ion. It was oxidised to methoxyphenyl acetate (Scheme 40). The acetate cycle was not established due to the improbability of hydrogen to leave as hydride ion from $\sigma^{\cdot}_{OAc}$. The yield of methoxyphenyl benzoate was similar to the uncatalysed decomposition of benzoyl peroxide at 80° for 72 hours (Table 6);

$$C_6H_5OCH_3 + PhCOO\cdot \rightleftharpoons PhCOO.C_6H_5OCH_3\cdot\ (\sigma\cdot)$$

$$(\sigma\cdot) + (PhCOO)_2 \longrightarrow PhCOO.C_6H_4OCH_3 + PhCOOH + PhCOO\cdot$$

$$(\sigma\cdot) + CH_3COOH \longrightarrow C_6H_5OCH_3^{+\cdot}\ (I) + PhCOOH + CH_3COO^-$$

$$(I) + CH_3COO^- \longrightarrow CH_3COO.C_6H_5\,OCH_3\cdot\ (\sigma^{\cdot}_{OAc})$$

$$(\sigma^{\cdot}_{OAc}) + (PhCOO)_2 \longrightarrow CH_3COO.C_6H_4OCH_3 + PhCOOH + PhCOO\cdot$$

Scheme 40

(b) the availability of acetate ions. The exclusion of potassium acetate from the reactions resulted in lower yields of the corresponding acetate, while the yields of the benzoate were not affected. This is because the acetate cycle could not be maintained by the weaker nucleophile, acetic acid.

Similarly, the inclusion of perfluorobenzoic acid resulted in low yields of the acetates (Table 18). For example, 4-fluoroanisole gave 23.0 mol% 4-methoxyphenyl benzoate and 35.6 mol% 4-methoxyphenyl acetate. Thus, perfluorobenzoic acid mainly affected the yield of the acetate. This is because it removed the acetate ion as acetic acid by Reaction 20.

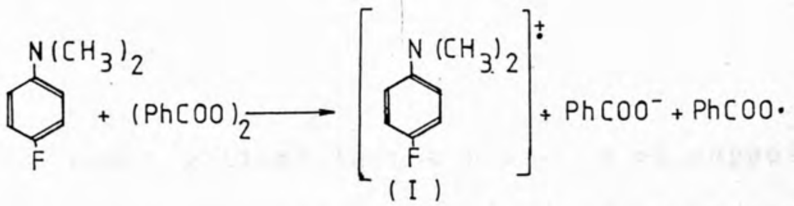
$$C_6F_5COOH + CH_3COO^- \longrightarrow C_6F_5COO^- + CH_3COOH \quad (20)$$

The corresponding methoxyphenyl perfluorobenzoate was not formed in the reactions with 2-fluoro-, 4-fluoro-, and 4-chloro- anisoles (Table 18). Perfluorobenzoate ion is expected to be a weaker nucleophile than acetate due to the presence of five aromatic fluorines.

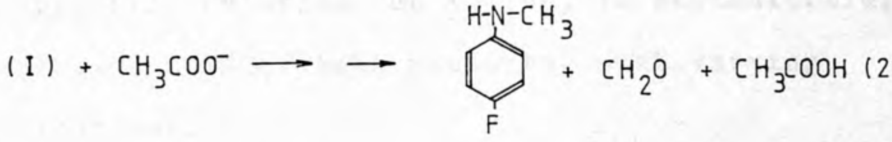
Eberson and Jönsson [64] observed a similar effect in the presence of trifluoroacetic acid in the reaction with 4-fluoroanisole.

N,N-Dimethyl-4-fluoroaniline gave 36.3-58.0 mol% 4-dimethylaminophenyl acetate in the above reaction; the corresponding benzoate was not detected. G.l.c (195°) showed greater than 800 mol% of a compound, R_t = 353 s, which most probably correspond to N-methyl-4-fluoroaniline (Reaction 22).

The above reaction may be initiated differently (Reaction 21).



(21)



(22)

The formation of (I) in Reaction 21 provides a direct entry into the acetate cycle (Scheme 38). Its formation may proceed through the S_N2 or ET mechanism [54-56]. Reactions 21 and 22 may account for the absence of the corresponding benzoate, and the comparatively lower yield of the acetate.

3.6. Decomposition of perbenzoic acid in anisole and 4-fluoroanisole.

The decomposition of perbenzoic acid in anisole in the presence of iron(II) sulphate in acetonitrile at 0-5° gave 3.3 mol% methoxyphenol (o:p ratio, 85:15) and 0.5 mol% methoxyphenyl benzoate (o:p ratio, 39:61). A similar experiment using a sulphuric acid solution of iron(II) sulphate and without acetonitrile solvent gave 1.2 mol% methoxyphenol (mainly ortho-); the corresponding benzoate was not formed.

Similar investigations in the presence of copper(II) benzoate, copper(II) chloride, or iodine, in acetonitrile, gave between 0.1-4 mol% of both products, with varying isomer distributions.

Under the same conditions in the presence of copper(II) benzoate, 4-fluoroanisole gave 0.52 mol% methoxyphenol (o:p ratio, 62:38) and 4.1 mol% 4-methoxyphenyl benzoate.

These results are tabulated in Table 19.

The final reaction mixtures were either deep brown or black for all of the reactions above.

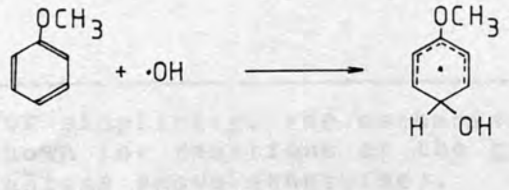
Kurz and Kovacic [37] did not obtain any of the above products in the decomposition of perbenzoic acid in toluene in the presence of copper(II) chloride at 60°. These workers suggested that unsymmetrical peroxides are reduced by copper(I) ion in such a way that the most electron deficient member of the peroxide linkage accepts the electron.

Kurz and Pellegrini [23] found that benzoyloxy radical is appreciably more electron deficient ($\rho = -1.61$) than the hydroxyl radical ($\rho = -0.41$). It can be inferred from this that the chain carrying species in the perbenzoic acid decomposition is the hydroxyl radical, formed in a similar manner to Fenton's reagent [109] (Reaction 23).

$$PhCOO.OH \; + \; M^{n+} \longrightarrow M^{(n+1)+} \; + \; PhCOO^{-} \; + \; \cdot OH \qquad (23)$$

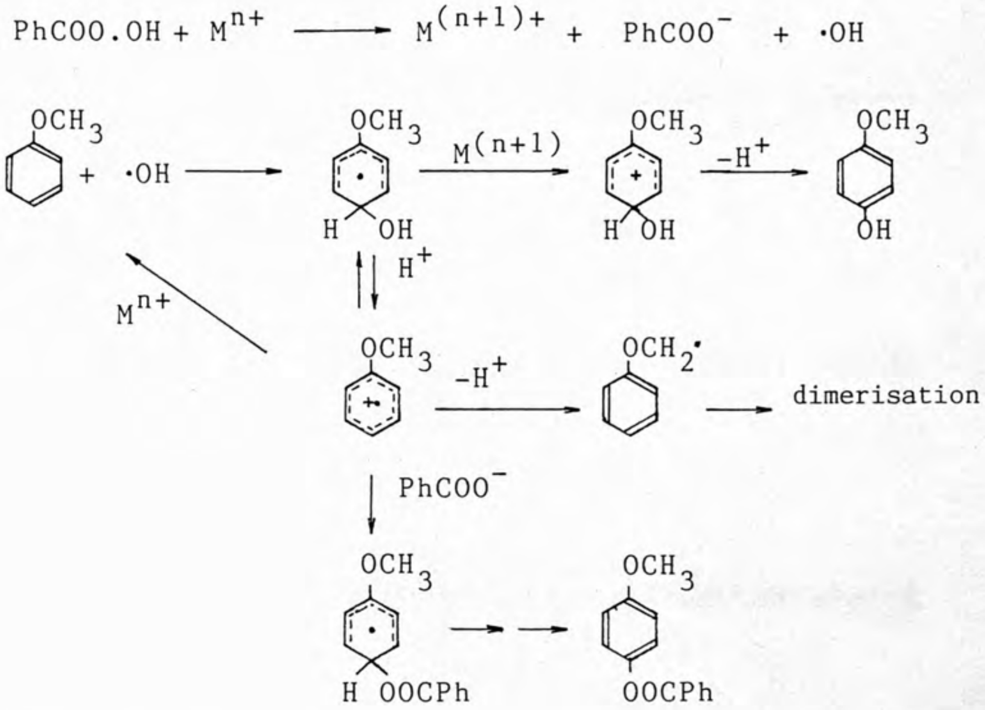
Radiation chemistry results show that hydroxyl radical adds very rapidly to aromatic compound (k, 10^{9}-10^{10} $M^{-1}s^{-1}$). The resulting hydroxycyclohexadienyl radical can be observed directly by UV or ESR spectroscopy [109].

Fendler and Gasowski [110] suggested that hydroxyl radical reacted with anisole to form hydroxymethoxycyclohexadienyl radical (Reaction 24).



(24)

The low yields of both methoxyphenol and methoxyphenyl benzoate obtained in the present work can be explained using the above arguments, and by adopting the scheme suggested by C. Walling [109] (Scheme 41).



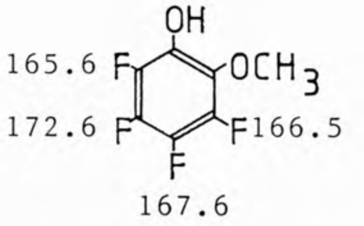
Scheme 41

Methoxyphenol and methoxyphenyl benzoate formed in the initial stages further undergo the same reaction course as anisole, to form a complex mixture of products.

Note: For simplicity, the mechanisms in all Schemes are shown for reactions at the para- positions only (unless shown otherwise).

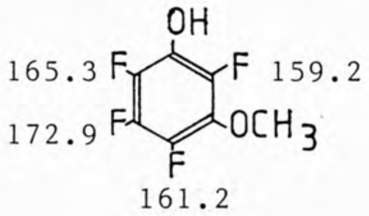
APPENDIX 1 The isomer ratio of tetrafluoromethoxyphenols (2.5.10) from ^{19}F-n.m.r spectrum.

(a) δ_F calculated/ppm from Table 5.



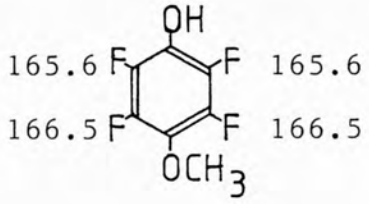
3,4,5,6-Tetrafluoro-2-methoxyphenol

(I)



2,4,5,6-Tetrafluoro-3-methoxyphenol

(II)



2,3,5,6-Tetrafluoro-4-methoxyphenol

(III)

(b) δ_F obtained from ^{19}F-n.m.r spectrum.

δ_F/ppm	m	Assignment	Integration (cm)
159.05	s	F_2(II)	1.3
159.70	d	F_4(II)	5.4
164.40	d	F_6(II), F_6(I), F_2(III), F_6(III)	9.4
164.98	d	F_3(I), F_3 and F_5(III)	
165.65	t	F_4(I)	2.5
170.75	t	F_5(I), F_5 (II)	2.0

(c) Calculation.

(I) = 2.5 cm

(II)= 6.7 cm

(I) + (II) + (III) = 9.4 cm = 100%

$$\frac{(I) + (II) + (III)}{(I)} = 3.76$$

$$3.76\ (I) = 100\%$$

$$\underline{\underline{(I) = 26.6\%}}$$

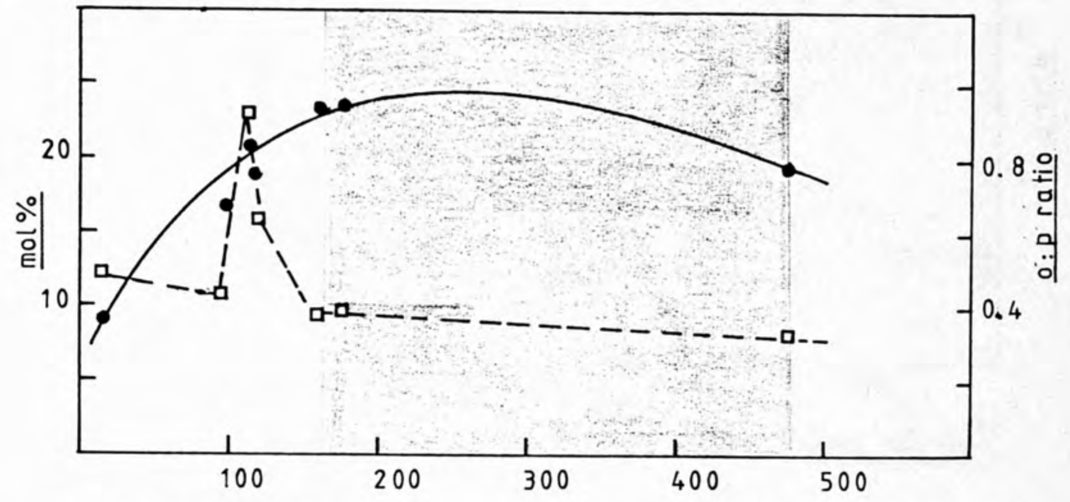
$$\frac{(I) + (II) + (III)}{(II)} = 1.4$$

$$1.4\ (II) = 100\%$$

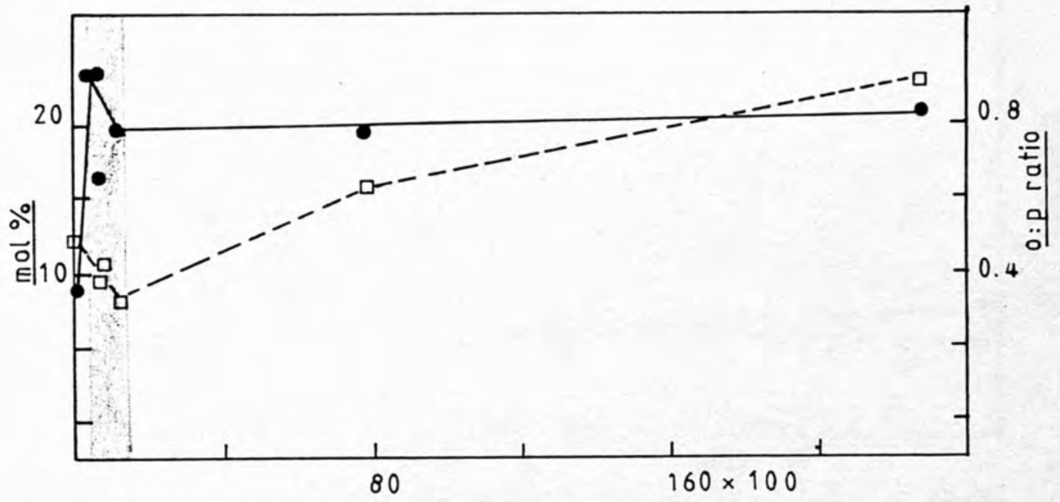
$$\underline{\underline{(II) = 71.4\%}}$$

Therefore, $\underline{\underline{(III) = 2\%}}$

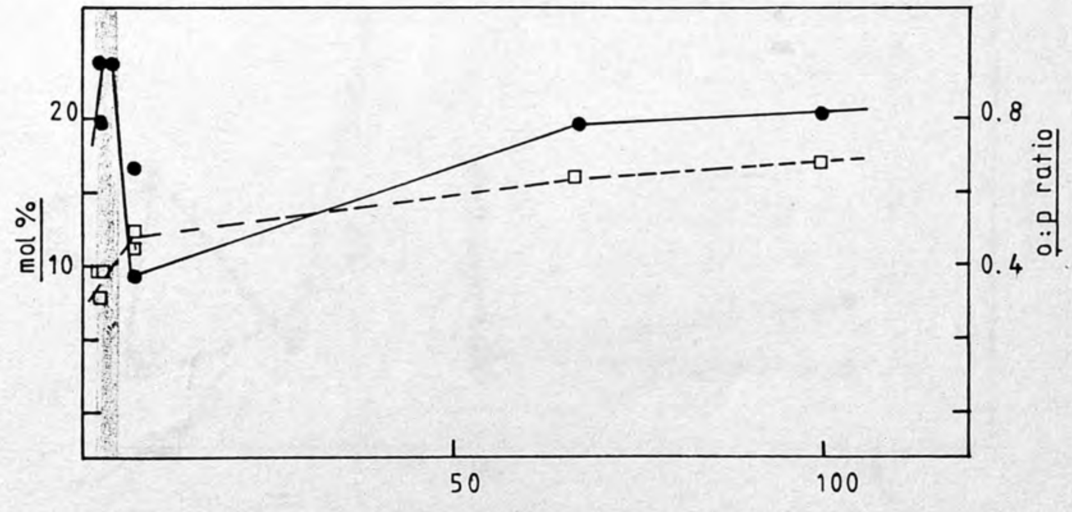
APPENDIX 2 (● , mol% ; □ , o:p ratio).



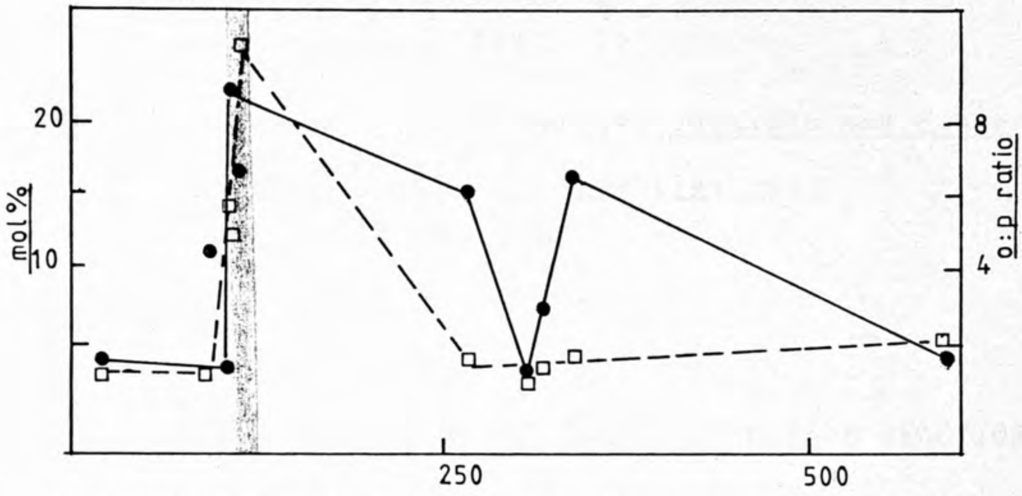
(a) Variation with anisole:peroxide mol ratio at 60°C



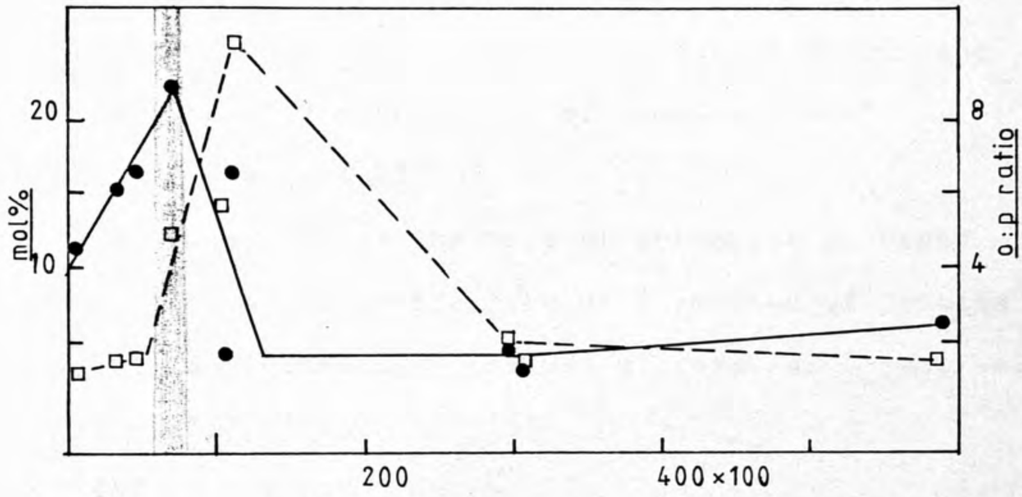
(b) Variation with anisole:catalyst mol ratio at 60°C



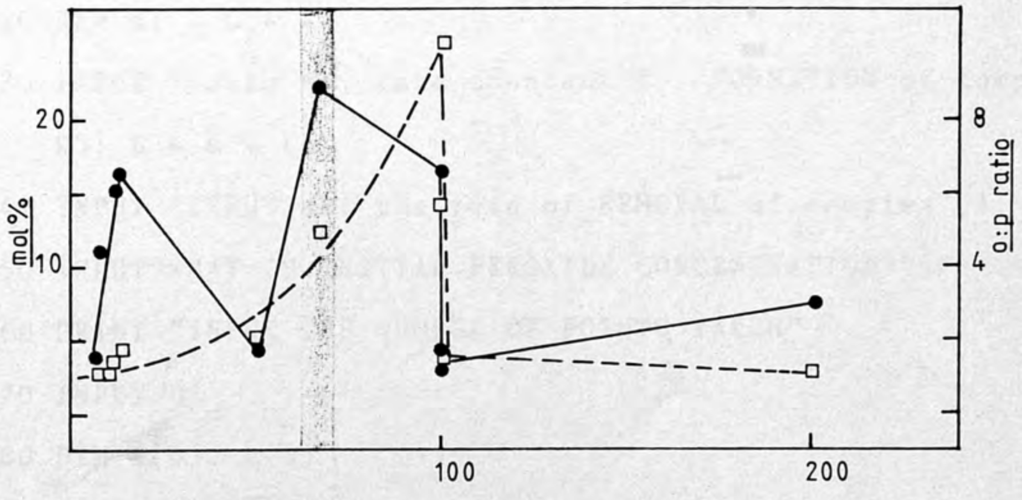
(c) Variation with peroxide:catalyst mol ratio at 60°C



(d) Variation with anisole: peroxide mol ratio at 80°C



(e) Variation with anisole: catalyst mol ratio at 80°C



(f) Variation with peroxide: catalyst mol ratio at 80°C

APPENDIX 3 Reaction between benzoyl peroxide and copper(II) benzoate - kinetic investigation.

(a) Computer program 1

```
 10 REM NORBANI KINETICS - ARE THEY CONSECUTIVE REACTIONS?
 20 CLS
 30PRINT
 40PRINT
 50PRINT
 60 PRINT "If a1 = Rate of decomposition of Bz2O2, and
    a2 = Rate of decomposition of complex, then"
 70 PRINT "a1 = k2 + k3"
 80 PRINT "where k2 is the rate of formation of other
    products and k3 is the rate of formation of complex"
 90 PRINT "So (COMPLEX) = (Bz2O2).a2.(exp -a2.t -exp -a1.t)/
    (a1 - a2)"
100 PRINT
110 INPUT "Guess k2, the rate constant for Bz2O2 decom. to
    give products";L
120 REM a1 = L + k3
130 INPUT "Guess k3, rate constant for FORMATION of complex";
    K3: B = L + K3
140 INPUT "INPUT a2, the rate of REMOVAL of complex";A
150 INPUT"WHAT IS INITIAL PEROXIDE CONCENTRATION?";P
160 PRINT "INPUT THE NUMBER OF POINTS TAKEN"
170 INPUT D
180 DIM K(D), L(D)
```

```
190 PRINT "INPUT TIME OF SAMPLINGS":FOR N = 1 to D: INPUT
    K(N):NEXT N
200 CLS
210 PRINT "a2 =";A:PRINT "k2 = ";L:PRINT "k3 = ";K3:PRINT
    "PEROXIDE CONCENTRATION =";P:PRINT
220 FOR N = 1 to D
230
240 T=K(N)
250 H=A*T:J=EXP(-H)
260 Y=B*T:Z=EXP(-Y)
270 W=J-Z
280 PRINT"CONCENTRATION OF INTERMEDIATE IS"
290 PRINT P*K3*W/(B-A),T;"MINS"
300 NEXT N
310 PRINT
320 PRINT"OTHER CALCULATION?"
330 INPUT C$: IF C$="N" THEN STOP
340 PRINT "SAME RATE CONSTANTS AND PEROXIDE CONCENTRATION?"
350 INPUT D$: IF D$="N" THEN RUN
360 CLS
370 PRINT "a2 =";A:PRINT "k2 = ";L:PRINT "k3 = ";K3:PRINT
    "PEROXIDE CONCENTRATION =";P:PRINT
380 GOTO 160
```

(b) Computer program 2

```
 10 REM NORBANI KINETICS - ARE THEY CONSECUTIVE REACTIONS?
 20 CLS
 30PRINT
 40PRINT
 50PRINT
 60 PRINT "If a1 = Rate of decomposition of Bz2O2, and a2 =
    Rate of decomposition of complex, then"
 70 PRINT "a1 = k2 + k3"
 80 PRINT "where k2 is the rate of formation of other
    products and k3 is the rate of formation of complex"
 90PRINT "So (COMPLEX) = (Bz2O2).a2.(exp -a2.t - exp -a1.t)/
    (a1 - a2)"
100 PRINT
110 INPUT "Guess k2, rate constant for Bz2O2 decom. to
    give products";L
120 REM a1 = L + k3
130 INPUT "Guess k3, rate constant for FORMATION of
    complex";K3: B = L + K3
140 INPUT "INPUT a2, the rate of REMOVAL of complex";A
150 INPUT"WHAT IS THE INITIAL PEROXIDE CONCENTRATION?";P
160 D=9
170 CLS
180 PRINT "a2 =";A:PRINT "k2 = ";L:PRINT "k3 = ";K3:PRINT
    "PEROXIDE CONCENTRATION =";P:PRINT
190 RESTORE
200 FOR N = 1 TO D
```

```
210 READ T
220 H=A*T:J=EXP(-H)
230 Y=B*T;Z=EXP(-Y)
240 W=J-Z
250 PRINT"CONCENTRATION OF INTERMEDIATE IS"
260 PRINT P*K3*W/(B-A),T;"MINS"
270 NEXT N
280 DATA 10,20,80,110,170,230,1440,2000,10000
290 PRINT
300 PRINT"OTHER CALCULATION?"
310 INPUT C$: IF C$="N" THEN STOP
320 CLS
330 PRINT "LAST VALUES WERE a2 =";A:PRINT "k2 = ";L:PRINT
    "k3 = ";K3:PRINT "PEROXIDE CONCENTRATION =";P:PRINT
340 PRINT"SAME CONSTANTS":INPUT D$:IF D$="N" THEN GOTO 110
350 INPUT D$: IF D$="N" THEN RUN
360 INPUT"SAME CONCENTRATION OF PEROXIDE? Y/N";E$:IF E$="N"
    THEN GOTO 150
370 STOP
```

Table 23 Reaction between benzoyl peroxide and copper(II) benzoate at 60°.

(a) $[(PhCOO)_2] = 9.17 \times 10^{-4}M$

Run	$[Cu(II)]/10^{-4}M$	Time/min	10	20	55	85	125	185	1440
1	0.64	A (388 nm)/10^{-2}	1.6	5.6	10.6	16.1	19.6	25.6	113.2
		$x/10^{-8}M$ (found)	6.3	21.9	41.4	62.9	76.6	100.0	442.2
		$x/10^{-8}M$ (calculated) *	6.0	13.0	34.0	52.0	74.0	105.0	-
2	1.27	A (388 nm)/10^{-2}	5.0	7.5	14.5	17.5	21.5	27.5	113.0
		$x/10^{-8}M$ (found)	19.5	29.3	56.6	68.4	84.0	107.4	441.4
3	1.91	A (388 nm)/10^{-2}	12.0	13.5	22.5	27.0	29.5	36.5	113.5
		$x/10^{-8}M$ (found)	46.9	52.7	87.9	105.4	115.2	142.5	443.4
4	2.55	A (388 nm)/10^{-2}	10.0	19.0	23.0	27.0	34.0	42.0	112.5
		$x/10^{-8}M$ (found)	39.1	74.2	89.8	105.5	132.8	164.1	439.5
5	3.18	A (388 nm)/10^{-2}	13.0	21.0	27.0	34.0	34.0	41.0	111.5
		$x/10^{-8}M$ (found)	50.8	82.0	105.5	132.8	132.8	160.2	435.5

Continued.....

(b) $[Cu_4(OOCPh)_8] = 1.59 \times 10^{-4}$M

Run	$[(PhCOO)_2]/10^{-4}$M	Time/min	10	20	80	110	170	230	1440
6	1.83	A (388 nm)/10^{-2}	2.5	3.3	4.6	5.1	6.7	7.8	18.7
		$x/10^{-8}$M (found)	9.8	12.9	17.9	19.9	26.2	30.5	73.0
		$x/10^{-8}$M (calculated)*	1.4	2.8	11.0	15.0	23.0	30.0	
7	3.67	A (388 nm)/10^{-2}	3.0	3.6	5.5	8.1	11.1	11.8	36.7
		$x/10^{-8}$M (found)	11.7	14.1	21.5	31.6	43.4	46.1	143.4
		$x/10^{-8}$M (calculated)*	2.8	5.6	22.0	30.0	46.0	61.0	
8	5.50	A (388 nm)/10^{-2}	1.9	2.8	8.5	13.4	18.4	21.4	57.9
		$x/10^{-8}$M (found)	7.4	10.9	33.2	52.3	71.9	83.6	226.2
		$x/10^{-8}$M (calculated)*	4.2	8.4	33.0	45.0	69.0	91.0	
9	7.34	A (388 nm)/10^{-2}	1.6	2.6	5.4	9.2	13.5	17.9	83.3
		$x/10^{-8}$M (found)	6.3	10.2	21.1	35.9	52.7	69.9	325.4
		$x/10^{-8}$M (calculated)*	5.6	11.2	44.0	60.0	92.0	120.0	
10	9.17	A (388 nm)/10^{-2}	4.4	5.0	10.6	12.3	21.0	26.3	106.4
		$x/10^{-8}$M (found)	17.2	19.5	41.4	48.1	82.0	102.7	415.6
		$x/10^{-8}$M (calculated)*	7.0	14.0	55.0	75.0	114.0	152.0	

*, Calculated using $k_2 = 3.42 \times 10^{-4}$ min^{-1}; $k_3 = 7.7 \times 10^{-6}$min^{-1} ; and $a_2 = (0.2-1) \times 10^{-3}$ min^{-1}

Table 24 Reaction between benzoyl peroxide and copper(II) benzoate at 70°.

$[(PhCOO)_2] = 0.0102\ M\ ;\ [Cu(OOCPh)_2.2H_2O] = 2.71x10^{-4}M$

Time/min	10	20	40	60	80	210	240	275	300	330	360
A (388 nm)/10^{-2}	18.3	29.3	47.0	57.0	50.3	79.5	86.6	95.0	100.4	110.1	116.8
x/10^{-7}M (found)	7.2	11.5	18.4	22.3	19.7	31.1	33.8	37.1	39.2	43.0	45.6
x/10^{-7}M (calculated)*						31.0	33.5	36.3	38.0	40.2	42.1

*,Calculated using $k_2 = 8x10^{-4}min^{-1}$; $k_3 = 1.2x10^{-6}min^{-1}$; and $a_2 = 1x10^{-3}min^{-1}$

Table 25 Reaction between benzoyl peroxide and copper(II) benzoate at 80°.

$[(PhCOO)_2] = 2.65x10^{-3}M\ ;\ [Cu_4(OOCPh)_8] = 1.58x10^{-3}M$

Time/min	10	20	45	75	115	145	175	226	∞
A (388 nm)/10^{-2}	12.0	15.0	18.9	27.0	46.5	18.0	54.0	84.9	87.0
x/10^{-7}M (found)	4.7	5.9	7.4	10.5	18.2	7.0	21.1	33.2	34.0
x/10^{-7}M (calculated)*	2.2	4.2	8.8	13.4	18.1	21.0	22.8	25.3	32.7

*, Calculated using $k_2 = 2.25x10^{-3}min^{-1}$; $k_3 = 8.5x10^{-6}min^{-1}$; and $a_2 = 4x10^{-3}min^{-1}$

Table 26 Reaction between benzoyl peroxide and copper(II) benzoate at 21°

	Light					Dark				
$[(PhCOO)_2]/10^{-3}M$	18.6					3.3				
$[Cu_4(OOCPh)_8]/10^{-3}M$	1.31					0.3				
Time/min	1560	5460	5820	6930	20160	30	1170	1335	2730	14400
A (388 nm)/10^{-2}	19.8	61.8	66.6	79.8	151.0	2.5	7.0	7.3	8.5	32.7
x/10^{-7}M (found)	3.8	24.1	26.0	31.2	58.9	1.0	2.7	2.9	3.3	12.8
x/10^{-7}M (calculated)*	2.8	25.0	26.6	31.5	87.2	0.04	1.4	1.6	3.2	16.2

*, Calculated using $k_2 = 3.42x10^{-6}min^{-1}$ for both light and dark; $k_3 = 2.5x10^{-8}min^{-1}$(light); $k_3 = 3.6x10^{-8}min^{-1}$(dark); $a_2 = 3x10^{-6}min^{-1}$(light); and $a_2 = 4.3x10^{-6}min^{-1}$(dark).

Table 27 Reaction between copper(II) chloride and benzoyl peroxide at 60°.@

$[CuCl_2.2H_2O] = 2.58x10^{-3}M$; $[(PhCOO)_2] = 4.44x10^{-3}M$

Time/min	0	10	20	30	60	120	150	180	210	240	270	1440
A (460 nm)	1.2	1.26	1.26	1.28	1.28	1.40	1.29	1.09	1.056	1.045	1.006	0.402
x/10^{-3}M ‡	1.9	2.12	2.12	2.15	2.15	2.34	2.16	1.82	1.77	1.75	1.69	0.67

@, Colour changed from yellow → brownish → blackish green → pale green (24 hours); ‡, $\varepsilon = 595.7\ M^{-1}cm^{-1}$

Table 28 Reaction between copper(II) benzoate and benzoyl peroxide at 60°.

$[Cu_4(OOCPh)_8] = 1.59 \times 10^{-4}$ M

Run	$[(PhCOO)_2]/10^{-4}$ M	Time/min	0	10	20	30	90	120	180	240	1440
6	1.83	A (690 nm)/10^{-2}	16.5	18.7	20.7	20.0	18.1	16.5	15.0	15.5	11.7
		x/10^{-4}M(found)*	1.5	1.7	1.9	1.8	1.7	1.5	1.4	1.4	1.1
7	3.67	Time/min	0	11	21	31	91	121	181	241	1440
		A (690 nm)/10^{-2}	16.6	19.5	21.0	20.8	18.2	19.2	19.1	16.7	11.7
		x/10^{-4}M(found)*	1.5	1.8	1.9	1.7	1.8	1.7	1.5	1.5	1.1
8	5.50	Time/min	0	12	22	32	92	122	182	242	1440
		A (690 nm)/10^{-2}	16.7	19.8	19.7	19.5	19.0	19.9	20.3	19.3	13.5
		x/10^{-4}M(found)*	1.5	1.8	1.8	1.8	1.7	1.8	1.9	1.8	1.2
9	7.34	Time/min	0	13	23	33	93	123	183	243	1440
		A (690 nm)/10^{-2}	19.7	20.1	20.0	19.2	15.0	15.4	14.1	13.0	13.3
		x/10^{-4}M(found)*	1.8	1.8	1.9	1.8	1.4	1.4	1.3	1.2	1.2

Continued...

Table 28 (Continuation)

Run	$[(PhCOO)_2]/10^{-4}M$	Time/min	0	14	24	34	94	124	184	244	1440
10	9.17	A (690 nm)/10^{-2}	19.0	19.0	21.8	20.7	19.5	18.4	20.6	20.2	16.5
		$x/10^{-4}M$(found)*	1.7	1.7	2.0	1.9	1.8	1.7	1.9	1.9	1.5

*,Calculated using $\varepsilon = 1.1x10^3M^{-1}cm^{-1}$

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