REACTIONS OF ACYL PEROXIDES

by

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INTRODUCTION

The benzoyloxy derivatives of aromatic compounds are generally prepared by benzoylation of the appropriate phenol. However, for many aromatic systems the phenolic forms are unstable relative to their keto tautomers(1) or else are excessively difficult to prepare(2). Thus for example, α - and β - furanol and their benzoates have never been prepared, although α - furanol acetate has been prepared by a two-step procedure from furan(3).

In such cases, preparation of the benzoyloxy derivative by direct substitution of the aromatic compound might be most convenient. Such direct substitution reactions have already been observed in the formation of α - and β - naphthyl benzoates (among other products) from the reaction of napthalene with benzoyloxy radicals from the decomposition of dibenzoyl peroxide at 72°C(4), and in the formation of benzoyloxy derivatives of phenols by reaction with benzoyl peroxide(5), probably by an ionic mechanism(6,7). However, little systematic study has been made of the use of diaroyl peroxides for this purpose. The beginnings of such a study is reported in this thesis. In a historical survey (Chapter I) the reactions of diaroyl peroxides are surveyed in the wider context of a study of such reactions of organic peroxides in general. An attempt has been made to classify reactions involving peroxide fission as homolytic or heterolytic.

In the following chapter is recorded the discussion of the results of investigating the reactions of diaroyl peroxides with aromatic hydrocarbons under Friedel-Crafts conditions, with organomagnesium and organolithium compounds, with aromatic secondary amines, and with phenols.

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CHAPTER I

SURVEY OF REACTIONS OF PEROXIDES

Reactions(1) form and break bonds; and by far the most important kind of bond that they can produce or destroy is the covalent bond.

First it can be formed from electrons supplied one by each of the combining species, that is, by colligation, and broken by the reverse process, homolysis:

$$A\cdot + B\cdot \quad \underset{\text{homolysis}}{\overset{\text{colligation}}{\rightleftharpoons}} \quad A{:}B \qquad (1)$$

In this type of reaction, the species A· and B· are normally odd electron molecules, that is, either odd-electron atoms, such as H· or Cl·, or free radicals, such as HO· or $CH_3\cdot$, where the single dot represents the unpaired electron. Few odd-electron molecules are stable in ordinary conditions, though many can be transiently produced by thermal or photolytic, or other radiative dissociation of a covalent bond. Reactions which form and break covalent bonds by colligation and homolysis are called homolytic reactions. Many such reactions start with a thermal or radiative, or surface-catalysed homolysis. Some appear to be initiated by the mutual homolysis of two bonds to form a stronger bond or bonds.

Secondly, the covalent bond can be formed by co-ordination, and broken by the opposite process, heterolysis:

$$\text{A:} + \text{B} \underset{\text{heterolysis}}{\overset{\text{Co-ordination}}{\rightleftharpoons}} \text{A:B} \qquad (2)$$

In this type of process, the species A: and B are, normally, both even electron molecules: and a high proportion of them are ordinary stable substances. Reactions which form and break bonds by co-ordination and heterolysis are known as heterolytic reactions. Most low-temperature reactions are heterolytic. The simplest affect only one bond; that is, they involve a single co-ordination or a single heterolysis. But many affect two or more bonds, and involve both co-ordination and heterolysis.

The peroxide linkage may break homolytically or heterolytically and in some cases both kinds of cleavage may proceed simultaneously. Although this dual character of the cleavage makes the study of the reactions of peroxides complicated, there are some diagnostic tests(2) for the detection of radical decomposition of peroxide. These are as follows:

(a) <u>vinyl polymerization</u>

When the decomposing compound A:B can initiate polymerization of a vinyl monomer such as ethylene, styrene or methyl methacrylete, the presence of radicals among the primary decomposition products of A:B may be suspected.

(b) effect of solvent on rate of decomposition

When a substance decomposes by means of a heterolytic cleavage, the overall rate of decomposition will bear a definite relation to the acidity or basicity of the solvent and to the dielectric constant of the solvent. The absence of systematic relation between decomposition rate and the above mentioned variables is diagnostic of a homolytic cleavage.

(c) effect of inhibitors

There are certain substances which characteristically inhibit free radical initiated chain reactions. These substances include quinone, hydroquinone and other polyhydroxy derivatives of benzene, primary and secondary aromatic amines, nitrous acid, nitric oxide, iodine, oxygen etc. It should be realized, that not all of these substances act as inhibitors for all radical chain reactions.

(d) primary products of decomposition

The primary products of decomposition are often different for homolytic and heterolytic cleavages. For example cumene hydroperoxide decomposes largely into acetophenone and methyl alcohol in non-polar solvent by homolytic cleavage of the O-O bond, whereas the same substance decomposes quantitatively into phenol and acetone in certain very strongly acidic media where the initial cleavage is heterolytic$^{(3)}$.

(e) reaction products with the solvent

If the substance A:B is decomposed in an aromatic solvent, fragments of A:B are often found substituted on the aromatic ring. Where this substitution does not follow the directing influences of the groups already attached to the benzene nucleus, this is indicative of an initial homolytic cleavage A:B.

By use of these and other criteria it has been found that the cleavages of the peroxide linkage may be either homolytic or heterolytic. Some examples are given below, attention being focussed on the less familiar heterolytic decompositions.

HOMOLYTIC FISSION OF PEROXIDES

1. ALKYL HYDROPEROXIDES

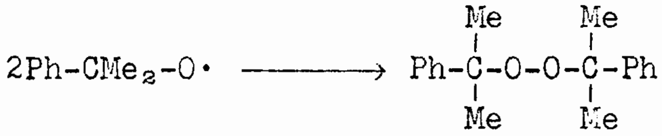
Two compounds whose decompositions have been intensively studied are t-butylhydroperoxide ($t\text{-}BuO_2H$)$^{(4)}$ and cumene hydroperoxide ($PhCMe_2O_2H$)$^{(5)}$. The most likely mechanism for the decomposition of the former involves a chain reaction producing t-butyl alcohol and oxygen:

$$(CH_3)_3COOH \longrightarrow (CH_3)_3CO\cdot + \cdot OH \qquad (3)$$

$$\left.\begin{array}{c}(CH_3)_3CO\cdot \\ \\ \cdot OH\end{array}\right] + (CH_3)_3COOH \longrightarrow \left.\begin{array}{c}(CH_3)_3COH \\ \\ HOH\end{array}\right] + (CH_3)_3COO\cdot \qquad (4)$$

$$2(CH_3)_3COO\cdot \longrightarrow 2(CH_3)_3CO\cdot + O_2 \qquad (5)$$

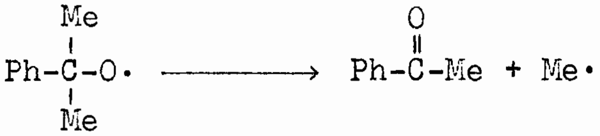
In the homolytic decomposition of cumene hydroperoxide the alkoxy radical Ph - CMe$_2$ - O· ,(I)is formed and then gives an appreciable amount of peroxide II by coupling:



$$2Ph\text{-}CMe_2\text{-}O\cdot \longrightarrow Ph\text{-}\overset{Me}{\underset{Me}{C}}\text{-}O\text{-}O\text{-}\overset{Me}{\underset{Me}{C}}\text{-}Ph \qquad (6)$$

I II

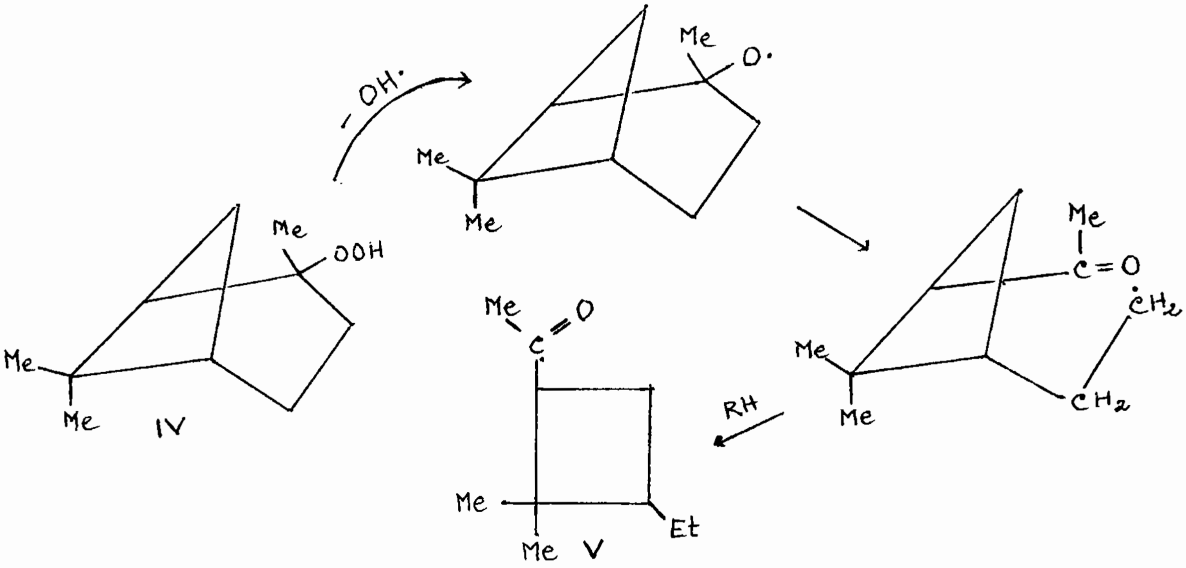
But at temperature higher than 100°, the radical decomposes to acetophenone and methyl radical:



$$Ph\text{-}\overset{Me}{\underset{Me}{C}}\text{-}O\cdot \longrightarrow Ph\text{-}\overset{O}{\overset{\|}{C}}\text{-}Me + Me\cdot \qquad (7)$$

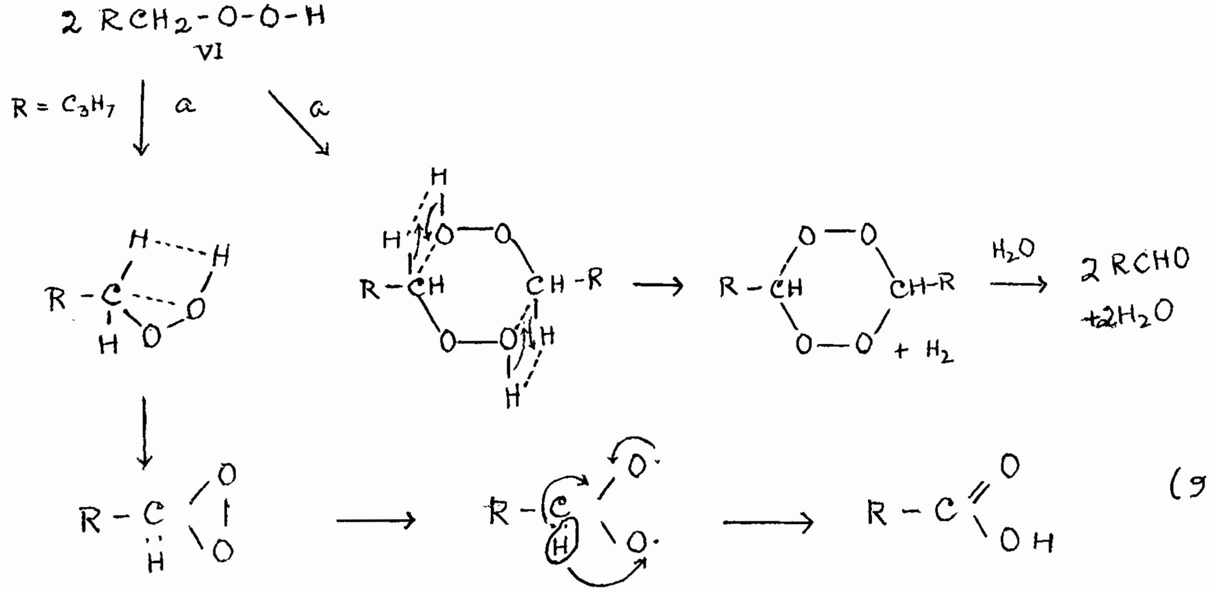
I III

The thermal decomposition of pinane hydroperoxide IV$^{(6)}$ gives 2,2-dimethyl-3-ethylacetylcyclobutane(V)by a similar mechanism:



(8)

n-Butyl hydroperoxide VI(7,8) on decomposition gives hydrogen, butyraldehyde, butyric acid, propane, n-butylalcohol and n-butylformate. Two courses (a) and (b) for the decomposition may be depicted:



(9a)

(9b)

$$\underset{VI}{R\text{-}CH_2\text{-}O\text{-}O\text{-}H} \xrightarrow{b} RCH_2\text{-}O\cdot + \cdot OH \longrightarrow \overset{RH}{\overset{\uparrow}{R\cdot}} + CH_2{=}O \qquad (10)$$

$$RCH_2O\cdot + CH_2{=}O \longrightarrow RCH_2O\text{-}CH_2\text{-}O\cdot \xrightarrow{\cdot OH} RCH_2O\text{-}CH{=}O + H_2O \qquad (11)$$

2. DIALKYL PEROXIDES

The decomposition of di-t-butyl peroxide(9-11) is a clear cut first order process and goes according to the scheme:

$$(CH_3)_3COOC(CH_3)_3 \longrightarrow 2(CH_3)_3CO\cdot \qquad (12)$$

$$(CH_3)_3CO\cdot \longrightarrow CH_3\cdot + CH_3COCH_3 \qquad (13)$$

Methyl radicals produced in the reaction (13) either dimerize:

$$2CH_3\cdot \longrightarrow C_2H_6 \qquad (14)$$

or react with acetone producing methane according to

$$CH_3COCH_3 + CH_3\cdot \longrightarrow \underset{VII}{CH_3COCH_2\cdot} + CH_4 \qquad (15)$$

It has been demonstrated that the $CH_3COCH_2\cdot$ radical (VII) produced in reaction (15) recombines with methyl radical to form methyl ethyl ketone:

$$CH_3COCH_2\cdot + CH_3\cdot \longrightarrow CH_3\text{-}CO\text{-}C_2H_5 \qquad (16)$$

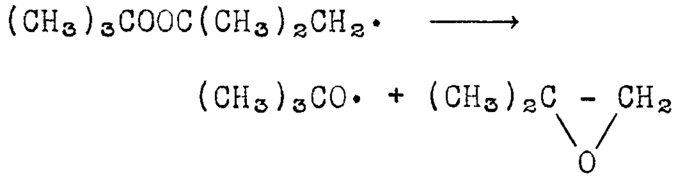
In a hydrocarbon solvent, instead of giving acetone and methyl radical, the $(CH_3)_3CO\cdot$ may simply extract a hydrogen atom and form t-butyl alcohol.

$$(CH_3)_3CO\cdot + HR \longrightarrow (CH_3)_3COH + R\cdot \qquad (17)$$

When pure di-t-butyl peroxide in the liquid phase undergoes decomposition, iso-butylene oxide VIII is a major product.

$$(CH_3)_3CO\cdot + (CH_3)_3COOC(CH_3)_3 \longrightarrow (CH_3)_3COH + (CH_3)_3COOC(CH_3)_2CH_2\cdot \qquad (18)$$

$$CH_3\cdot + (CH_3)_3COOC(CH_3)_3 \longrightarrow CH_4 + (CH_3)_3COOC(CH_3)_3CH_2\cdot \qquad (19)$$



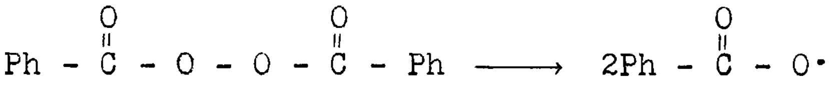
(20)

VIII

Other dialkyl peroxides undergo similar decompositions, but their reactions have been less studied.

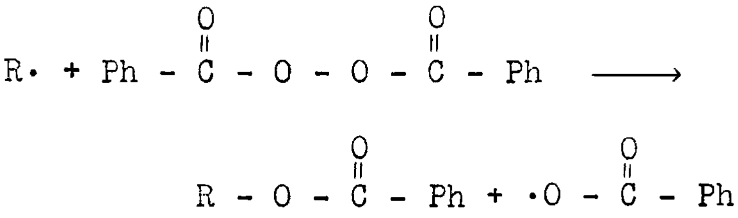
3. DIACYL PEROXIDES

The decomposition of dibenzoyl peroxide(12-15) proceeds in two paths in organic solvents. One of them is the spontaneous decomposition of the O-O bond, unimolecularly:



$$Ph - \overset{O}{\overset{\|}{C}} - O - O - \overset{O}{\overset{\|}{C}} - Ph \longrightarrow 2Ph - \overset{O}{\overset{\|}{C}} - O\cdot \qquad (21)$$

The other is the attack of one of the benzoyl-oxy radicals by a radical from the solvent:

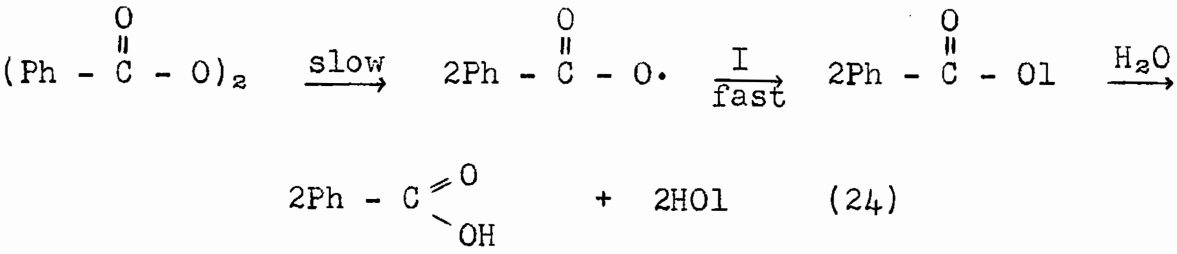


$$R\cdot + Ph - \overset{O}{\overset{\|}{C}} - O - O - \overset{O}{\overset{\|}{C}} - Ph \longrightarrow R - O - \overset{O}{\overset{\|}{C}} - Ph + \cdot O - \overset{O}{\overset{\|}{C}} - Ph \qquad (22)$$

When solvent is unreactive decarboxylation of the radical occurs:

$$Ph - \overset{O}{\overset{\|}{C}} - O\cdot \longrightarrow Ph\cdot + CO_2 \qquad (23)$$

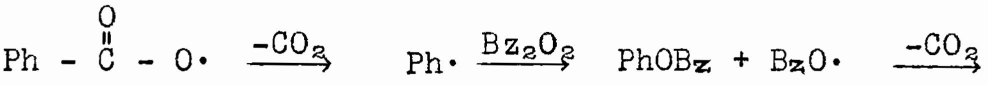
The phenyl radical thus formed may attack solvent, peroxide or dimerize. The decomposition of benzoyl peroxide has been studied in the presence of iodine in carbon tetrachloride solution. Iodine reacts with benzoyloxy radical giving benzoyl hypoiodite and decarboxylation is suppressed. On hydrolysis, hypoiodite gives benzoic acid quantitatively(14), proving spontaneous decomposition of benzoyl peroxide through benzoyloxy radical:



$$(Ph - \overset{O}{\overset{\|}{C}} - O)_2 \xrightarrow{slow} 2Ph - \overset{O}{\overset{\|}{C}} - O\cdot \xrightarrow[fast]{I} 2Ph - \overset{O}{\overset{\|}{C}} - OI \xrightarrow{H_2O}$$

$$2Ph - C\begin{matrix} \nearrow O \\ \searrow OH \end{matrix} \quad + \quad 2HOI \qquad (24)$$

In relatively inactive solvent such as carbon tetrachloride and aromatic hydrocarbons the induced decomposition proceeds by the following way:



$$Ph - \overset{O}{\overset{\|}{C}} - O\cdot \xrightarrow{-CO_2} Ph\cdot \xrightarrow{Bz_2O_2} PhOBz + BzO\cdot \xrightarrow{-CO_2} etc. \qquad (25)$$

The decomposition of benzoyl peroxide in acetic acid is faster than that in benzene; in aliphatic ethers and alcohols containing α-hydrogen atoms it is still faster. This has been taken to indicate that radicals from the solvents have come into play. Alcohol and ether give radicals of the type $R\dot{C}HOH$ and $R\dot{C}HOR'$. Benzoyloxy ethers have been isolated from the decomposition of benzoyl peroxide in aliphatic ethers(13).

The decomposition of diacetyl peroxide(16,17) is initiated by the O-O bond breaking reaction.

$$CH_3CO - O - O - CO - CH_3 \longrightarrow 2CH_3COO\cdot \qquad (26)$$

The main difference between the decomposition of benzoyl peroxide and acetyl peroxide is that the acetoxy radical(17) is extremely short lived. It does not react with highly active solvents or with iodine to give acetyl hypiodite but breaks down to methyl radical and carbon dioxide. This methyl radical is very reactive:

$$CH_3\cdot + PhCH_3 \longrightarrow CH_4 + PhCH_2\cdot \qquad (27)$$

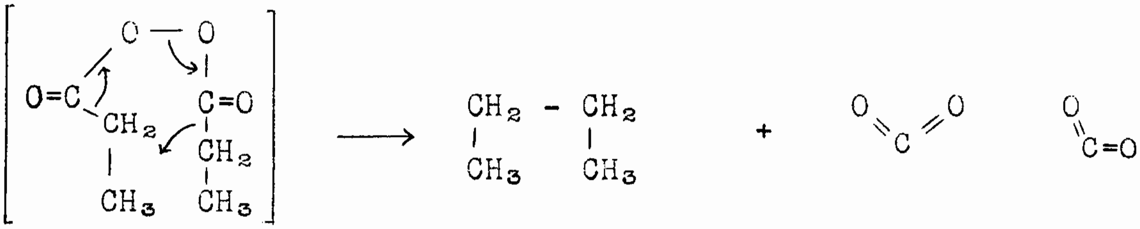
$$CH_3\cdot + CH_3COOMe \longrightarrow CH_4 + \cdot CH_2COOMe \qquad (28)$$

For the decomposition of propionyl and butyryl peroxide in a variety of solvents, it was shown that the primary reaction again involves the homolytic rupture of O-O bond and formation of R-COO· radicals which decarboxylate rapidly, yielding the corresponding hydrocarbon radicals. The formation of butane observed in the decomposition of propionyl peroxide may be attributed to a recombination process(18)

$$2C_2H_5 \longrightarrow C_4H_{10} \qquad (29)$$

However, evidence has been obtained that the reaction does not result from a bimolecular recombination process involving free radicals which lost their idenity, but from a cage combination involving two radicals formed from a single molecule of propionyl peroxide. The fraction of ethyl radicals that form butane has been found to be independent of the initial peroxide concentration. The reality of a cage effect is confirmed further. Small amounts of p-benzoquinone (an excellent scavanger for the free radical alkyls) added to a solution of propionyl peroxide in iso octane decreased considerably the formation of C_2 hydrocarbons (this is the result of the reaction C_2H_5 + p-quinone → nongaseous addition product). However, the ratio C_4H_{10}/CO_2 as well as the rate of decomposition were not affected by the presence of quinone.

Alternatively, this reaction may involve four-center type of mechanism:(19)



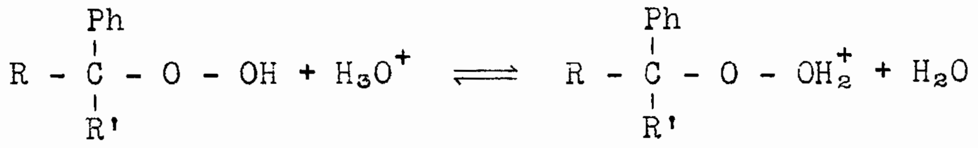
(30)

HETEROLYTIC FISSION OF PEROXIDE LINKAGE

1. ALKYL HYDROPEROXIDES

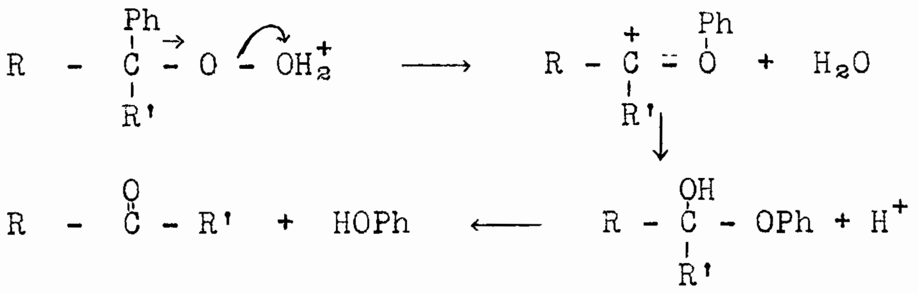
(a) acid-catalysed decompositions

Leffler(20) made some attempts to induce ionic decompositions of t-butyl hydroperoxide with acids. The only effect of acids was to reverse the addition of hydrogen peroxide to isobutylene by which t-butyl hydroperoxide is formed. Kharasch(21) and his co-workers in 1951, described the decomposition of ∝-phenyl ethyl hydroperoxide (IX; R=H; R'=CH_3) at 20-25°. The best result was



$$R - \underset{R'}{\overset{Ph}{C}} - O - OH + H_3O^+ \rightleftharpoons R - \underset{R'}{\overset{Ph}{C}} - O - OH_2^+ + H_2O \qquad (31)$$

(IX)



$$R - \underset{R'}{\overset{Ph}{C}} - O - OH_2^+ \longrightarrow R - \underset{R'}{\overset{+}{C}} = \overset{Ph}{O} + H_2O$$

$$R - \overset{O}{\overset{\|}{C}} - R' + HOPh \longleftarrow R - \underset{R'}{\overset{OH}{C}} - OPh + H^+ \qquad (32)$$

(X)

obtained by allowing a mixture of hydroperoxide, acetic acid and a trace of perchloric acid to stand at room temperature. The reaction product isolated were phenol (45%) and ∝-phenyl ethyl peracetate. The production of phenol indicated that in the acid catalysed decomposition of hydroperoxides containing an aromatic group and a hydrogen atom on the ∝-carbon atoms, migration of the aromatic group takes place in preference to the elimination of the hydrogen atom. No attempt was made to isolate the acetaldehyde (X; R=H, R'=CH_3) which must have been the other product of the rearrangement.

The mechanism of the decomposition of this and of similar peroxides catalysed by acid is best represented by (31) and (32).

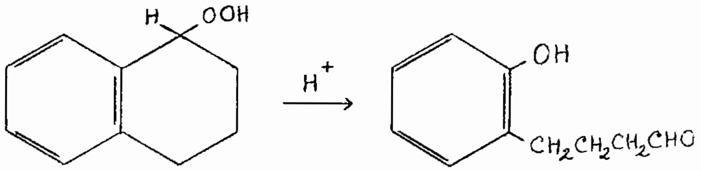
In this mechanism the exact timing of the electronic shifts is unspecified. However, it seems likely from analogy with the acid-catalysed decomposition of other peroxides (discussed below) that the shift of the phenyl group is concerted with the heterolytic fission of the peroxide linkage and that in fact this phenyl shift assists the fission of the peroxide linkage (cf. the non reactivity of t-butyl hydroperoxide). It will be noted that all the subsequent examples of acid-catalysed hydroperoxide decompositions involve an aryl and not an alkyl migration in keeping with the greater anchimeric effect of aryl groups(22).

The acid-catalysed decomposition of cumene hydroperoxide (IX, $R=R'=CH_3$) was first reported in 1944 by Hock and Lang(23) who used 10% aqueous sulfuric acid and obtained a 75% yield of phenol. Acetone (X, $R=R'=CH_3$) was shown by qualitative test to be formed. Kharasch(24) and his co-workers found the decomposition of this peroxide by strong acid to be highly exothermic and to proceed at an appreciable rate even at -80°. The decomposition was carried out in acetic acid (in which the hydroperoxide is stable at room temperature) in the presence of a trace of perchloric acid. Seubold and Vaughan(25) decomposed the peroxide in 50% aqueous acetic acid containing various amounts of p-toluenesulfonic acid and reported yields up to 92% of phenol and 81% of acetone. Although acetic acid increases the solubility of the cumene hydroperoxide, it was shown that the catalysis of the decomposition by molecular acetic acid is negligible. The rate of decomposition was shown to obey the following rate law very accurately:

$$\frac{-d(\mathrm{ROOH})}{dt} = k\left[\mathrm{H_3O^+}\right]\left[\mathrm{ROOH}\right],$$ where k is a constant, in agreement with the mechanism shown in equations (31) and (32).

Bartlett and Cotman(26) found that the addition of either sulfuric acid or perchloric acid (in the cold) to an ether solution of p-nitro-triphenylmethyl hydroperoxide (IX, R=Ph, $R'=O_2N-C_6H_4$) gave 94% of p-nitrobenzophenone and 81% of phenol (isolated as tribromophenol). The phenyl group migrates to the total exclusion of the p-nitrophenyl group, as expected for the mechanism given above. However, free radical decomposition of this peroxide is different. Simple heating of the hydroperoxide gives more p-nitrophenol than phenol, suggesting that under conditions of free radical fission of the O-O bond the p-nitrophenyl group has a greater migration tendency than the phenyl group. Further examples(27) of the acid-catalysed cleavage of hydroperoxides involving aryl migration are:

α - Tetrolyl hydroperoxide



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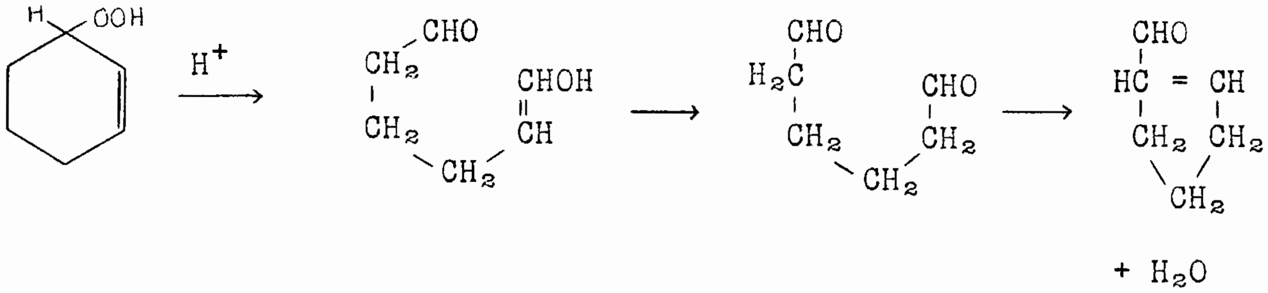
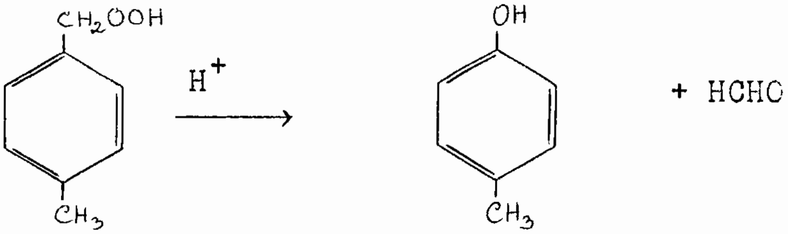
2-Cyclohexene-1-yl hydroperoxide



(34)

α-p-Xylyl hydroperoxide

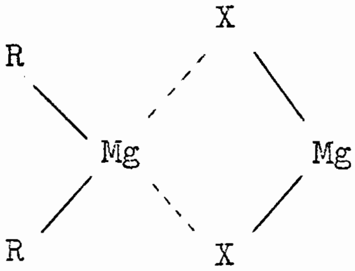


(35)

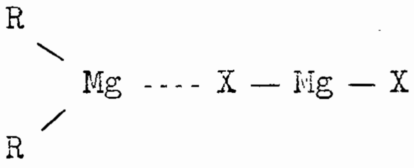
Many more examples are to be found in Leffler's review(28).

(b) <u>reactions with nucleophiles</u>

The peroxide linkage of alkyl hydroperoxides also reacts with strongly nucleophilic reagents without acid catalysis. Thus the reaction of the Grignard reagent with t-butyl hydroperoxide gives excellent yields of phenols or alcohol.(38) These reactions are also presumably heterolytic. In this connection something should be said about the structure of the Grignard reagent. New physical(29) evidence shows that the classical compound, RMgX does not exist; that it is, instead, a stable complex, $R_2Mg \cdot MgX_2$. This form may have the structures XI or XII

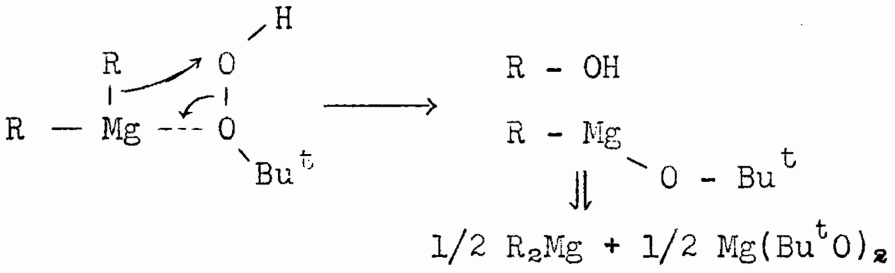


XI



XII (36)

So the mechanism of reaction of Grignard reagent and t-butyl hydroperoxide may be considered as



(37)

although obviously this formulation omits several features (e.g. the complexing of MgX_2 to R_2Mg and to the intermediates and products) of what must be a most complex reaction mechanism.

The reaction of hydroperoxides with trisubstituted phosphines was first reported by Horner and Jurgeleit(30). The reaction was found to be a simple one which proceeds

$$R'OOH + R_3P \longrightarrow R'OH + R_3PO \qquad (38)$$

to give the phosphine oxide and the alcohol derived from the hydroperoxide. However, they did not attempt to elaborate any detailed mechanism. More recently Walling and Rabinowitz(31) have found that trialkyl phosphites also react with hydroperoxides to give trialkyl phosphates and the alcohol derived from the hydroperoxide:

$$R' - OOH + (RO)_3P \longrightarrow R'OH + (RO)_3PO \qquad (39)$$

Although no studies of the mechanism were made, Walling and Rabinowitz(31a) suggested the following mechanism:

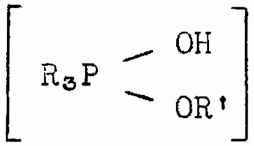
$$\left[\, R_3\overset{+}{P} - OR' + OH^- \,\right] \longrightarrow R_3PO + R'OH$$

XIII

$$R = R, - OR$$

One piece of evidence, which is pertinent to any discussion of mechanism, is the finding by Davies and Feld(31b). It showed that optically active α-phenyl ethyl hydroperoxide is reduced by triphenylphosphine with complete retention of configuration to α-phenyl ethyl alcohol, showing that the O-O rather than C-O undergoes fission. In a study of the mechanisms of these reactions Denney and his co-workers carried out a tracer study(32) using H_2O^{18}. Cumene hydroperoxide was allowed to react with triphenylphosphine in a mixture of ethanol - H_2O^{18}; similarly trans - 9 - decalyl hydroperoxide was reduced in ethanol - H_2O^{18} with tri-n-butyl-phosphine. In both cases the alcoholic product contained no excess oxygen - 18 , and in the case of cumene hydroperoxide reduction the triphenylphosphine oxide was also shown to contain no excess O^{18}. In a somewhat similar experiment cumene hydroperoxide was reduced with tri-n-butylphosphine in methanol. The product obtained was cumyl alcohol and no cumyl methyl ether could be detected. These results indicate that the two oxygens of the hydroperoxide ultimately find their way into the alcohol and phosphine oxide.

As the reductions by phosphines or phosphites appear to be essentially the same, it seems only reasonable to assume that they follow the same mechanism. So Walling and Rabinowitz's intermediate XIII could also arise in the phosphine reaction. But several pieces of evidence indicate that compound XIII cannot be an intermediate in the reaction. For example, if compound XIII is formed



XIV

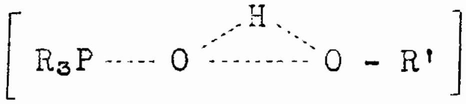
$$\left[R_3\overset{+}{P}\text{-OH} + OR^-\right]$$

XV

then it must decompose to products faster than the hydroxide ion equilibrates with the H_2O^{18}. This would have to be a remarkable process indeed. Furthermore in the phosphite reaction, XIII is composed of a tetralkoxyphosphonium ion and a hydroxide ion. In order to account for the fact that only one alcohol is obtained in the decomposition of XIII i.e. the one from the hydroperoxide, one must devise a mode of decomposition of XIII which will give only this alcohol. This is hard to rationalize since, in the absence of any other factors, one would predict a statistical mixture of alcohols and phosphates. All the available data indicate that XIII is not an intermediate in these reactions.

Another mechanistic possibility for these reactions involves the formation of a pentavalent compound XIV. A similar intermediate has been postulated to explain the decomposition of tetralkylphosphonium hydroxides to phosphine oxides and hydrocarbons(33). If XIV is to be an acceptable intermediate, it must decompose to products faster than it can ionize to XIII; otherwise one would find O^{18} in the products. Furthermore, XIV like XIII would be required to decompose to only one alcohol, a process which seems unreasonable.

A most reasonable mechanism for these reactions involves attack by the phosphine or phosphite on the hydroxyl oxygen of the hydroperoxide to give, in a smooth displacement reaction, the intermediate XV, which yields products by a simple proton transfer. Alternatively, one could suggest that the initial displacement reaction proceeds with simultaneous proton transfer via a transition state XVI. The only reason for considering such a transition state is the fact that phosphites reduce



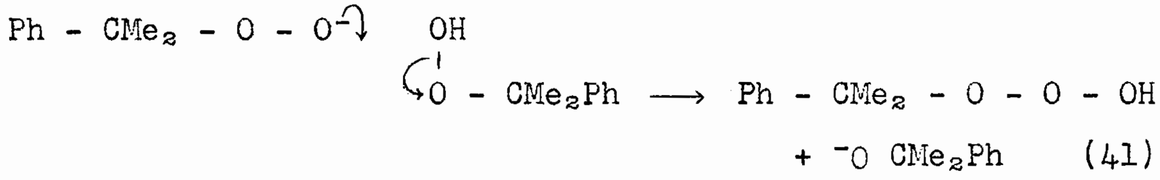
$$\left[R_3P\cdots O\overset{H}{\cdots\cdots}O-R'\right]$$

XVI

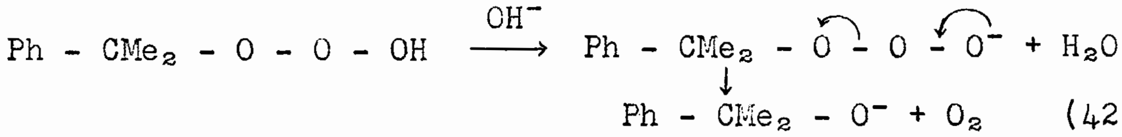
hydroperoxides essentially instantaneously in pentane at -40°.

The alkali-catalysed(34) decomposition of α-cumyl hydroperoxide to 2-phenyl propan-2-ol and oxygen may take place by nucleophilic attack of ionized peroxide on another molecule of peroxide as shown:

$$\mathrm{Ph - CMe_2 - O - OH \xrightarrow{OH^-} Ph - CMe_2 - O - O^-} \qquad (40)$$



$$\mathrm{Ph - CMe_2 - O - O^- \quad \overset{OH}{O} - CMe_2Ph \longrightarrow Ph - CMe_2 - O - O - OH + {}^-O\,CMe_2Ph} \qquad (41)$$

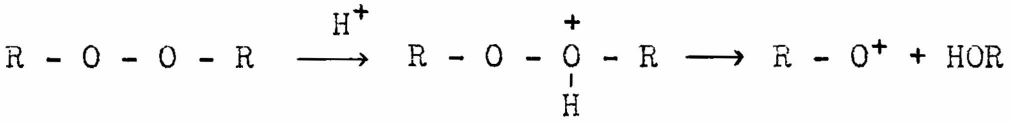


$$\mathrm{Ph - CMe_2 - O - O - OH \xrightarrow{OH^-} Ph - CMe_2 - O - O - O^- + H_2O}$$
$$\downarrow$$
$$\mathrm{Ph - CMe_2 - O^- + O_2} \qquad (42)$$

2. ALKYL PEROXIDES

(a) acid-catalysed reactions

The acid-catalysed decomposition of dialkyl peroxides would, like that of the alkyl hydroperoxides, be expected to proceed through an alkoxyl cation:



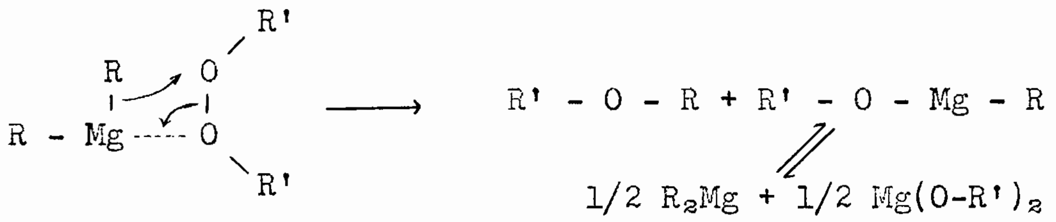
$$\mathrm{R - O - O - R \xrightarrow{H^+} R - O - \overset{+}{\underset{H}{O}} - R \longrightarrow R - O^+ + HOR} \qquad (43)$$

Baramki(35) obtained formaldehyde in 25% yield from the reaction of dimethyl peroxide in 95% sulfuric acid, presumably via such an alkoxyl cation:

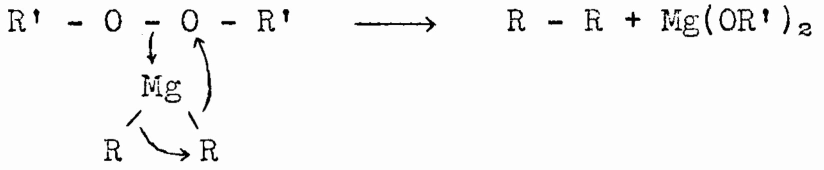
$$\mathrm{H - CH_2 - O^+ \longrightarrow H^+ + CH_2 = O} \qquad (44)$$

(b) reactions with nucleophiles

Gilman and Adams(36) found that triphenyl methyl peroxide was inert to phenylmagnesiumbromide but that diethyl peroxide with this reagent gave 34% phenetole and 30% of biphenyl.

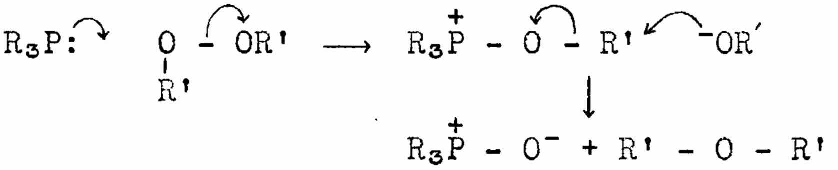


(45)



(46)

Edward and Baramki(35) reported that the reaction of dimethyl peroxide both with Grignard reagents and organolithium compounds gave good yields of methyl ethers. Campbell, Burney and Jacob(37) found that phenylmagnesiumbromide and t-alkyl Grignard reagents failed to react with di-t-butyl peroxide, but t-butyl ethers were obtained with primary and secondary aliphatic bromomagnesium compounds. With this peroxide, Lawesson and Yang(38) reported no reaction of phenylmagnesiumbromide even when the reaction was carried out at 80°. Decomposition of diethyl- and di-t-butyl peroxides with tertiary phosphines(30) afforded the corresponding ethers and phosphine oxides in good yields. The following mechanism may be suggested:

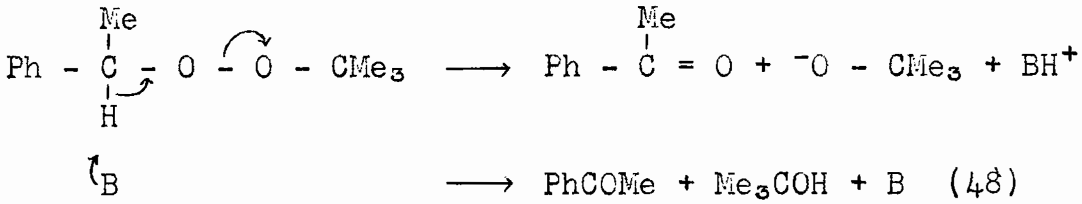


(47)

Horner and Knap(39) found that peroxides of the general formula $(R_1R_2N - CH_2 - O)_2$ where R_1 = alkyl and R_2 = phenyl, also react with triphenylphosphine in acetic acid or acetic anhydride to give an equivalent quantity of triphenylphosphine oxide.

(c) base-catalysed elimination reactions

Bases(40) such as potassium hydroxide, sodium ethoxide or piperidine cause 1-phenylethyl-t-butyl peroxide to undergo an elimination reaction rather than nucleophilic substitution:



$$Ph - \overset{Me}{\underset{H}{C}} - O - O - CMe_3 \quad B \longrightarrow Ph - \overset{Me}{C} = O + {}^{-}O - CMe_3 + BH^{+}$$

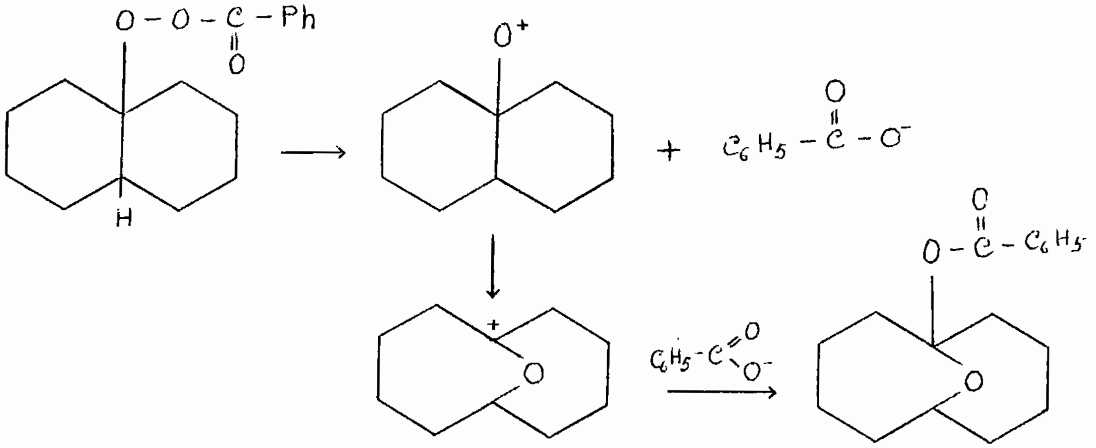
$$\longrightarrow PhCOMe + Me_3COH + B \qquad (48)$$

The reaction took place smoothly at room temperature. In contrast to this decomposition di-t-butyl peroxide is inert to bases such as potassium hydroxide or piperidine(41). This is to be expected, since according to the mechanism above only those dialkyl peroxides and alkyl hydroperoxides having a hydrogen on the carbon atom attached to the peroxide linkage will undergo a base catalysed decomposition.

3. HYDROPEROXIDE ESTERS

(a) decomposition in ionizing solvents

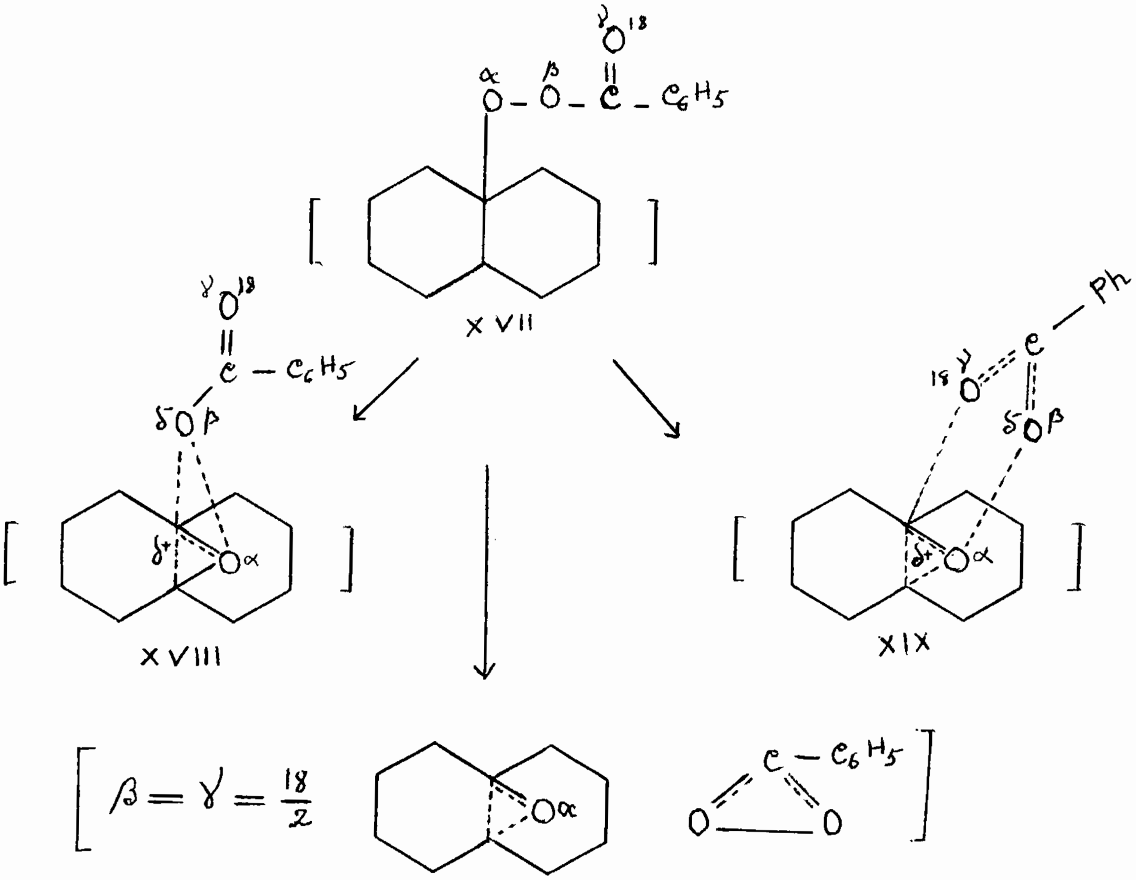
The benzoate of 9-decalyl hydroperoxide has the property of undergoing molecular rearrangement to 1-benzoyloxy-1,6-epoxycyclodecane rapidly in solvents of high ionizing power and slowly in poor ionizing solvents(42a). Criegee and Kaspar(42b) suggested that the rearrangement involves an ionic fission of the O-O linkage:

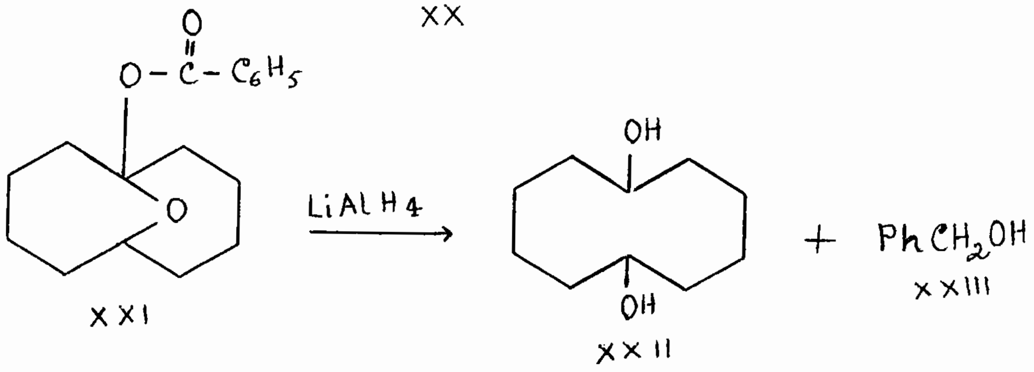


(49)

Bartlett and Kice(42a) carried out the rearrangement in the presence of labelled benzoate ion and concluded that not over 0.6% of the labelled benzoate ion entered into the product of rearrangement. It is obvious that the cation produced in the Criegee rearrangement exists only transiently in an ion pair or in a "solvent cage". Measurements were made of the rate of rearrangement of the 9-decalyl perbenzoate bearing nitro, bromo, methyl and methoxy substituents in the para position. With nitro group the rate was highest while with methoxy group it was lowest. This is in harmony with an ionic mechanism.

A brilliant investigation by Denney and Denney(43) showed that although this reaction may proceed by an ionic mechanism free ions are not involved. They studied the rearrangement using a benzoate labelled with O^{18} in the carbonyl oxygen in an attempt to distinguish between the three possible ion pairs intermediates.

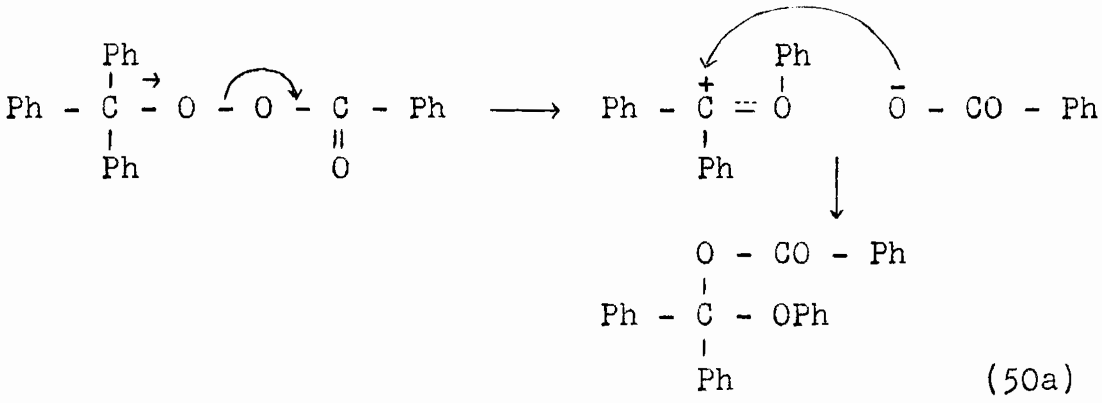




If the formation of XXI takes place through XVIII then all of the excess O^{18} in XXI would be in the carbonyl group. In intermediate XX, the two oxygen atoms in benzoyloxy group become equivalent and so in XXI, half of the excess O^{18} would be found in carbonyl group and other half in ether oxygen of carboxylate group. Formation of XXI via XIX would mean the presence of all excess O^{18} in the ether oxygen of carboxylate group.

The product XXI was reduced by lithium aluminium hydride to the alcohols XXII and XXIII. In the latter all of the excess O^{18} was found. This means that the rearrangement proceeds through XVIII in which the carbonyl oxygen is retained through the transformation.

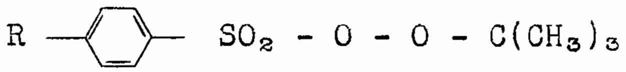
Maier and Wieland(44) could not isolate triphenylmethyl perbenzoate from the reaction of triphenylmethyl hydroperoxide with benzoyl chloride, diphenylphenoxycarbinol benzoate being isolated:



(50a)

It seems likely that the rearrangements of the benzoates of 9-decalyl hydroperoxide and of triphenylmethyl hydroperoxide owe their facility to anchimeric assistance by the migrating alkyl or aryl group. In the case of t-butyl perbenzoate, decomposition by a similar mechanism would involve anchimeric assistance from a migrating methyl group which is known to be much less effective than a phenyl or secondary alkyl group(22). Hence t-butyl perbenzoate is relatively stable. However, esters of t-butyl hydroperoxide having a more strongly electron attracting acyl group can undergo heterolytic fission. This was shown in an investigation by Bartlett and Hiatt(45) of the decomposition of a series of esters of the general formula $RCO\text{-}O\text{-}OCMe_3$, where R = trifluoromethyl, methyl, β-styryl, cinnamyl, 2-phenyl-2-propyl, 1,1-diphenylethyl and α-phenyl allyl. The thermal decomposition of these esters appears to involve the simultaneous rupture of an O-O bond and C-C bond with the formation of carbon dioxide in the primary step. Tert-butyl peracetate and perbenzoate are believed to undergo primary cleavage only at O-O bond while t-butyl trifluoroperacetate appears to undergo ionic rearrangement instead, showing an entirely different behaviour in both its kinetics and products. The rate showed an extreme degree of solvent dependence, and only 3% of the possible carbon dioxide was involved, the largest single product being trifluoroacetic acid. Later Bartlett and Simons(46) studied the decomposition of t-butyl trimethylperacetate, t-butyl trichloroperacetate and t-butyl phenylperacetate in the temperature range 58-88°. Kinetic study of all three peresters indicated a first order concerted cleavage to yield carbon dioxide, t-butoxy radical and t-butyl, trichloromethyl or benzyl radicals. However, there was also a prominent acid-catalysed ionic decomposition of t-butyl trichloroperacetate which could be suppressed by pyridine.

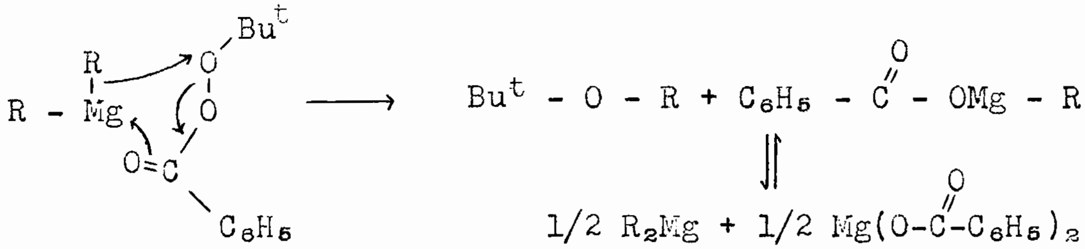
As even greater reactivity(47) is shown by the t-butyl arylpersulfonates,



where R = MeO, Me, H, Cl, Br. Only the two esters where R = MeO, Me are relatively stable. The products of decomposition of the perester in methanol at room temperature indicate the ionic mechanism in this solvent. Acetone was determined gravimetrically, in the form of the 2,4-dinitrophenylhydrazone in yields of up to 95-99%. The sulfonic acid was determined by titration and also by weighing the sodium salt; the yield was 100%.

(b) reaction with nucleophiles

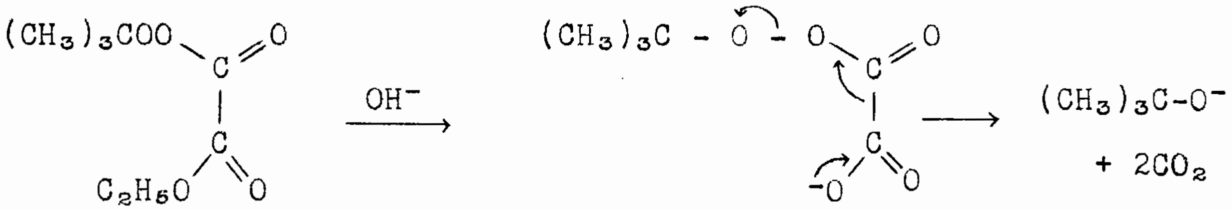
Tertiary butyl perbenzoate was found to react with a variety of Grignard reagents at 0° to give good yields of t-butyl ethers(38) and benzoic acid. The Grignard reagents employed were phenyl-, α-naphthyl-, p-tolyl-, p-anisyl-, ethyl-, cyclohexyl-, 2-propylmagnesium halides. The mechanism may be formulated as:



(50b)

Alternatively, t-butyl perbenzoate reacts with phenyl lithium at -60° to give phenyl t-butyl ether.

Bartlett and Pincock(48) reported ionic fission of an O-O bond by the attack of alkali upon ethyl t-butyl peroxyoxalate.



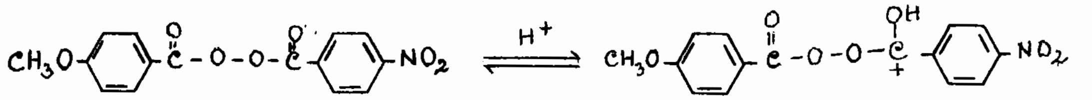
(51)

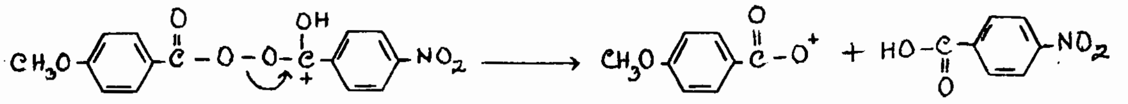
4. DIACYL PEROXIDES

(a) decomposition in ionizing solvents and in the presence of Brønstad acids

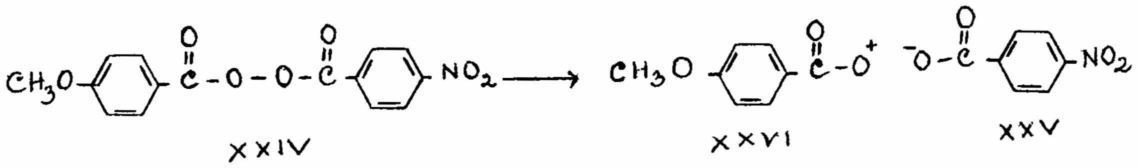
In an unsymmetrically substituted benzoyl peroxide it has been shown that a radical mechanism or an ionic mechanism can be made to predominate by a change of solvent as well as by the use of catalysts(49,50).

The decomposition of p-methoxy-p'-nitrobenzoyl peroxide(50) is very important in this connection. In benzene alone it is a radical reaction giving an almost equimolecular mixture of p-nitrobenzoic acid and p-methoxy-benzoic acids. But the unsymmetrical distribution of polar substituents makes the reaction take an ionic path under favorable circumstances. In strong contrast to the decomposition of benzoyl peroxide, the decomposition of p-methoxy-p'-nitrobenzoyl peroxide is markedly accelerated by acids such as acetic acid, and mono-, di-, and trichloroacetic acids. This appears to be a case of general acid catalysis and the cleavage proceeds through an ionic mechanism.

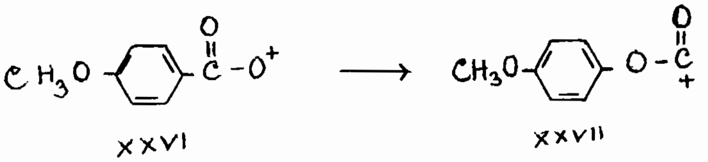

(52)


(53)

To confirm this point further, this peroxide was decomposed in a benzene solution of trichloroacetic acid. A theoretical yield of p-nitrobenzoic acid was obtained in contrast to the equal yields of p-nitrobenzoic acid and p-methoxybenzoic acid obtained in neutral benzene. Furthermore, while the decomposition of benzoyl peroxide is comparatively indifferent to solvent, the decomposition of p-methoxy-p'-nitrobenzoyl peroxide in nitrobenzene is ten times faster than that in benzene. Obviously, the peroxide is decomposing by a polar mechanism in a polar solvent. An ionic reaction would favor cleavage in the direction leading to p-nitrobenzoate anion and p-methoxybenzoyloxy cation which would lose carbon dioxide or rearrange. To avoid the complicated course of the reaction in nitrobenzene or in solvents having active hydrogen, the decomposition was tried in thicnyl chloride, a polar solvent. The main product of the reaction was the mixed anhydride XXVIII isolated in 38% yield.



(54)



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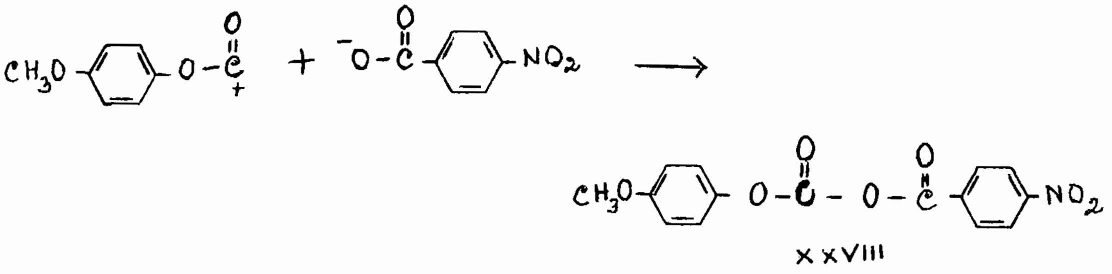
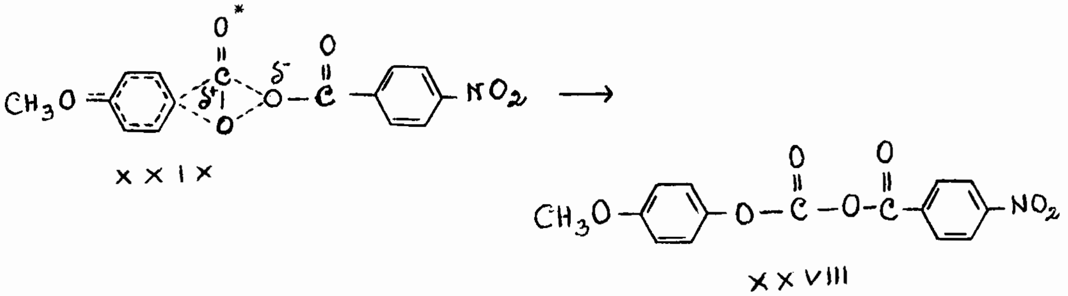


(56)

Denney⁽⁵¹⁾ has shown that during bond breaking of the O-O linkage the p-methoxyphenyl group migrates specifically to that oxygen which is developing the positive charge i.e. a concerted process is taking place, and the free oxygen cation XXVI is never formed as an intermediate in the reactions. This was done by using a compound labelled with O^{18} in the anisyl carbonyl group as shown:



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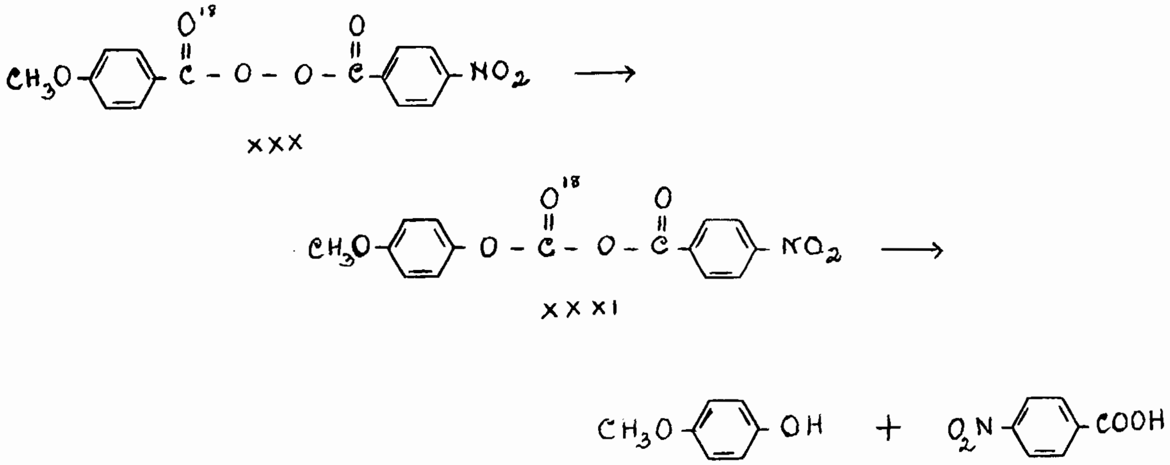

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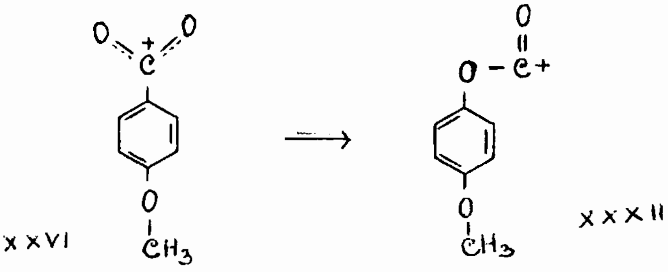
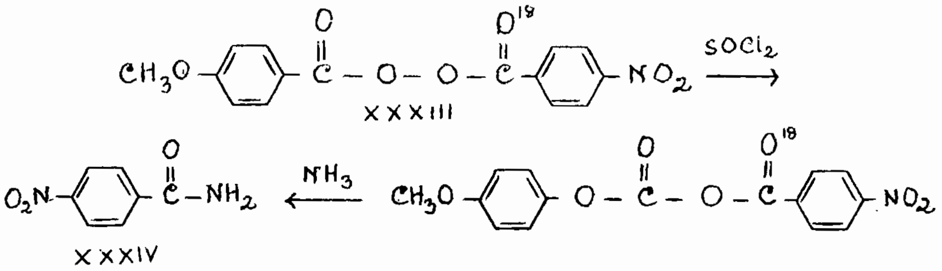


(59)

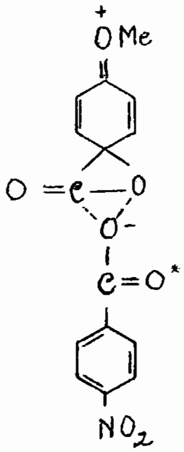
The labelled peroxide XXX was rearranged in thionyl chloride to the labelled carbonate XXXI. Basic hydrolysis of XXXI provided p-methoxy phenol which contained no excess oxygen-18. The only conclusion that can be drawn out of this result is that the excess oxygen-18 never entered into the p-methoxy phenols. Since both oxygens of the cation XXVI are equivalent, if it had existed one would expect 50% of the excess oxygen-18 to be in the p-methoxy phenol. An explanation which is consistent with these findings is that a concerted shift of the p-methoxy phenyl occurred as the O-O bond broke XXIX ⟶ XXVIII.

Secondly, Denney and Denney$^{(43)}$ have shown that the p-nitrobenzoate anion formed in the rearrangement is also never entirely free. They used a peroxide XXXIII labelled with O^{18} in the carbonyl of the p-nitrobenzoyl group. This peroxide after rearrangement and

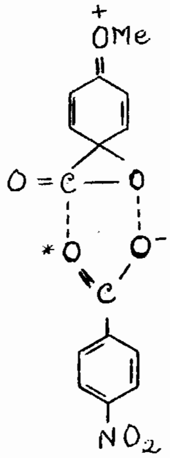


(60)

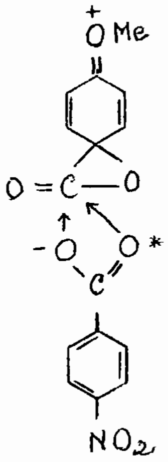
subsequent treatment with ammonia gave p-nitrobenzamide XXXIV. On analysis it was found that 66% of the excess oxygen-18 was retained as carbonyl oxygen. This result cannot be explained entirely by any one of the suggested mechanisms which involve the transition states shown:



XXXV



XXXVI

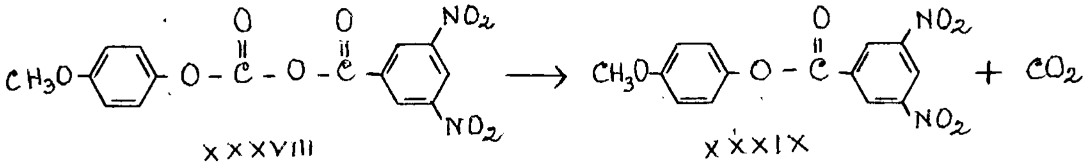


XXXVII

If the reaction went through XXXV, all ^{18}O should be retained by the carbonyl group. If it went through XXXVI, none of the labelled oxygen would be retained by the carbonyl group. The reaction cannot proceed through XXXVII alone; for in that case attachment by unlabelled oxygen would predominate. The specific and correct mechanism is still uncertain.

The 4-methoxy-3',5'-dinitro(52) substitution of benzoyl peroxide has even a greater effect, producing a 23 fold acceleration rate of decomposition in benzene at 51°. This is rather a large increase in rate for a radical reaction and suggests that this peroxide decomposes at least partly by a non-radical mechanism even in benzene.

In nitrobenzene the 4-methoxy-3',5'-dinitrobenzoyl peroxide decomposition at 51° is 94 times as fast as it is in benzene and about 2000 times as fast as the decomposition of benzoyl peroxide in benzene. Furthermore, 1,3,5-trinitrobenzene, a radical chain inhibitor, actually accelerates the reaction. But the yields of both anisic and dinitrobenzoic acids are lower. The carboxyl inversion product XXXVIII could not be purified but is undoubtedly present in the reaction mixtures from the polar solvents



(61)

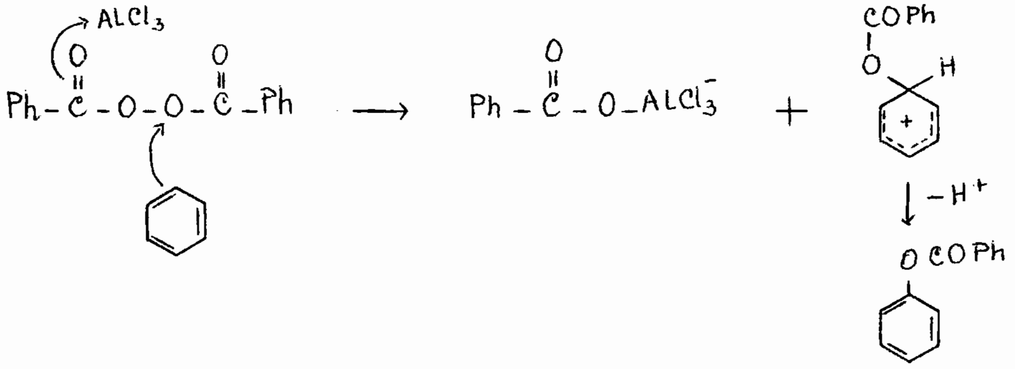
as is shown by the evolution of carbon dioxide and the formation of the ester XXXIX on recrystallization. The mechanism of this reaction will be discussed in Chapter II.

(b) decomposition in presence of Lewis Acids.

Reynhart(53,54) investigated the action of benzoyl peroxide on benzene when a powerful catalyst such as aluminium chloride or ferric chloride is used. At temperature lower than 0° and with aluminium chloride, benzoic acid and phenylbenzoate are formed, 1 mole of aluminium chloride being necessary for each mole of the peroxide transformed. The catalyst combines with phenyl benzoate to form a stable compound.

$$\mathrm{BzOOBz} + \mathrm{Ph{\cdot}H} \longrightarrow \mathrm{BzOPh} + \mathrm{BzOH} \qquad (62)$$

A possible mechanism for this reaction would be:



(63)

A similar mechanism has been postulated by Brown and co-workers in the Friedel-Crafts benzoylation of benzene(55) and acetylation of benzene and toluene(56).

Reynhart(53,54) reported that at higher temperatures less phenylbenzoate was formed; biphenyl and carbon dioxide made their appearance. With antimony pentachloride at ± 10°C and in pure petroleum ether as a solvent, the reaction proceeds according to the scheme(57):

$$\mathrm{Bz_2O_2} + \mathrm{SbCl_5} = \mathrm{BzOPh{\cdot}SbCl_5} + \mathrm{CO_2} \qquad (64)$$

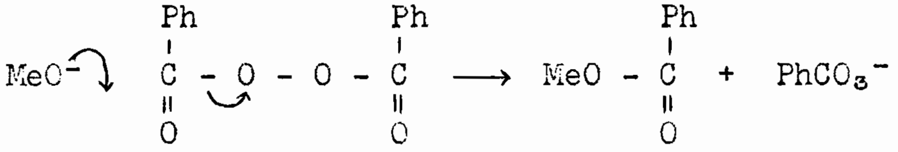
The mechanism of this reaction is discussed in Chapter II.

The decomposition of dibenzoylperoxide in the presence of other Lewis acids such as phosphorus pentachloride, zinc chloride and sulfurylchloride(57) has also been investigated. These acids do not markedly catalyse the decomposition in the way that $AlCl_3$ and $SbCl_5$ do; the mechanisms of the reactions are also discussed in Chapter. II.

(c) reactions with nucleophiles

(i) reactions with alkoxides

Dibenzoyl peroxide gives a yield of about 80% of perbenzoic acid by the action of sodium methoxide(58) or ethoxide(59) followed by acidification with dilute sulfuric acid. Evidently, the alkoxide ion preferentially attacks the carbonyl group rather than the peroxide linkage:



$$\mathrm{MeO^-}\;\underset{\underset{\displaystyle \mathrm{O}}{\|}}{\overset{\overset{\displaystyle \mathrm{Ph}}{|}}{\mathrm{C}}} - \mathrm{O} - \mathrm{O} - \underset{\underset{\displaystyle \mathrm{O}}{\|}}{\overset{\overset{\displaystyle \mathrm{Ph}}{|}}{\mathrm{C}}} \longrightarrow \mathrm{MeO} - \underset{\underset{\displaystyle \mathrm{O}}{\|}}{\overset{\overset{\displaystyle \mathrm{Ph}}{|}}{\mathrm{C}}} + \mathrm{PhCO_3^-} \qquad (65)$$

(ii) Grignard Reagents

Gilman and Adams(36) observed that the reaction of benzoyl peroxide with the Grignard reagent gave benzoate esters in about 30% yield. They put forward the following equation:

$$\mathrm{C_6H_5} - \overset{\overset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}} - \mathrm{O} - \mathrm{O} - \overset{\overset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}} - \mathrm{C_6H_5} + \mathrm{RMgX} \rightarrow \mathrm{C_6H_5} - \overset{\overset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}} - \mathrm{OR} + \mathrm{C_6H_5}\text{-}\overset{\overset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}\text{-}\mathrm{OMgX}$$

(66)

The yield of benzoic acid was abnormally high and partial hydrolysis of the unreacted benzoyl peroxide was suggested to account for the formation of the excess benzoic acid. Lawesson and Yang(38) re-investigated the reaction using purified benzoyl peroxide and phenylmagnesium bromide prepared from sublimed magnesium, and found that benzoyl peroxide was completely consumed at the end of the reaction. Thus, the abnormally high yield of benzoic acid cannot be derived from the unreacted peroxide. In addition to phenyl benzoate (35%) and benzoic acid (127%) based on equation (66) which were obtained in substantially the same yields as reported previously, a new product, bromobenzene (21%) was isolated. Since the Grignard reagent used was free of bromobenzene, bromobenzene must be a subsidiary product during the reaction. Although the reaction of ethylmagnesium bromide with benzoyl peroxide yielded no gaseous product, but ethylbenzoate (35%) and benzoic acid (145%), it is possible that ethylbromide was produced likewise, and owing to its similar volatility with respect to ether, it escaped isolation. The possibility was substantiated as the ether recovered was shown to give positive Beilstein test for halogen. Accordingly, a mechanism is postulated to account for the formation of these products which is in fair agreement with the observed stoichiometry.

$$RBr + Mg \longrightarrow R_2Mg \cdot MgBr_2 \quad ^{(29)}$$

$$MgBr_2 + (C_6H_5COO)_2 \longrightarrow (C_6H_5COO)_2Mg + Br_2 \qquad (67)$$

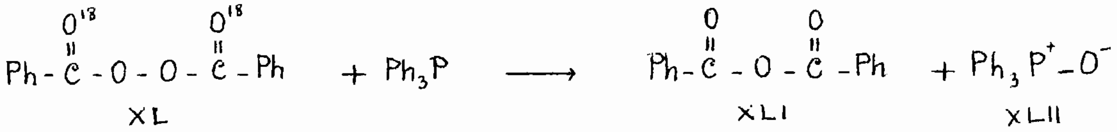
$$1/2\ R_2Mg + (C_6H_5COO)_2 \longrightarrow C_6H_5COOR + 1/2(C_6H_5COO)_2Mg \qquad (68)$$

$$1/2\ R_2Mg + Br_2 \longrightarrow RBr + 1/2\ MgBr_2 \qquad (69)$$

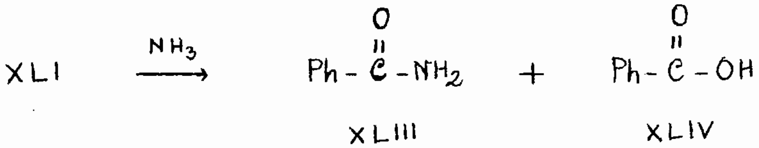
(iii) reaction with phosphines

Horner and Jurgeleit(30) reported that the reaction of acyl and aroyl peroxides with trisubstituted phosphines proceeds rapidly at room temperature in solvents such as pentane or ether to give anhydrides and phosphine oxides. Horner proposed that these reactions proceed by displacement on oxygen by the phosphine to give a phosphonium ion and an anion which can then react to give the products of equation 47.

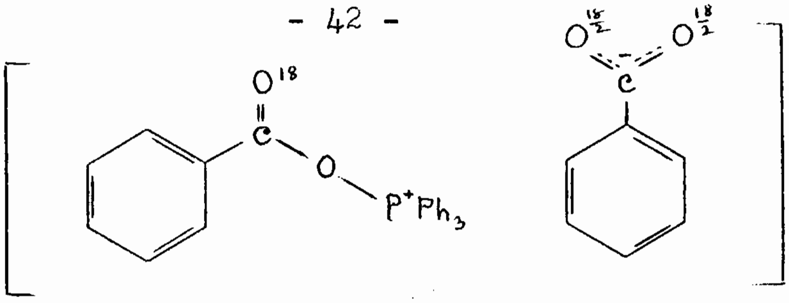
Later, Greenbaum, Denney and Hoffman(60) studied the mechanism of the conversion of benzoyl peroxide to benzoic anhydride by triphenylphosphine:



$$\underset{XL}{Ph-\overset{O^{18}}{\overset{\|}{C}}-O-O-\overset{O^{18}}{\overset{\|}{C}}-Ph} + Ph_3P \longrightarrow \underset{XLI}{Ph-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-Ph} + \underset{XLII}{Ph_3P^+-O^-} \qquad (70)$$



$$XLI \xrightarrow{NH_3} \underset{XLIII}{Ph-\overset{O}{\overset{\|}{C}}-NH_2} + \underset{XLIV}{Ph-\overset{O}{\overset{\|}{C}}-OH} \qquad (71)$$

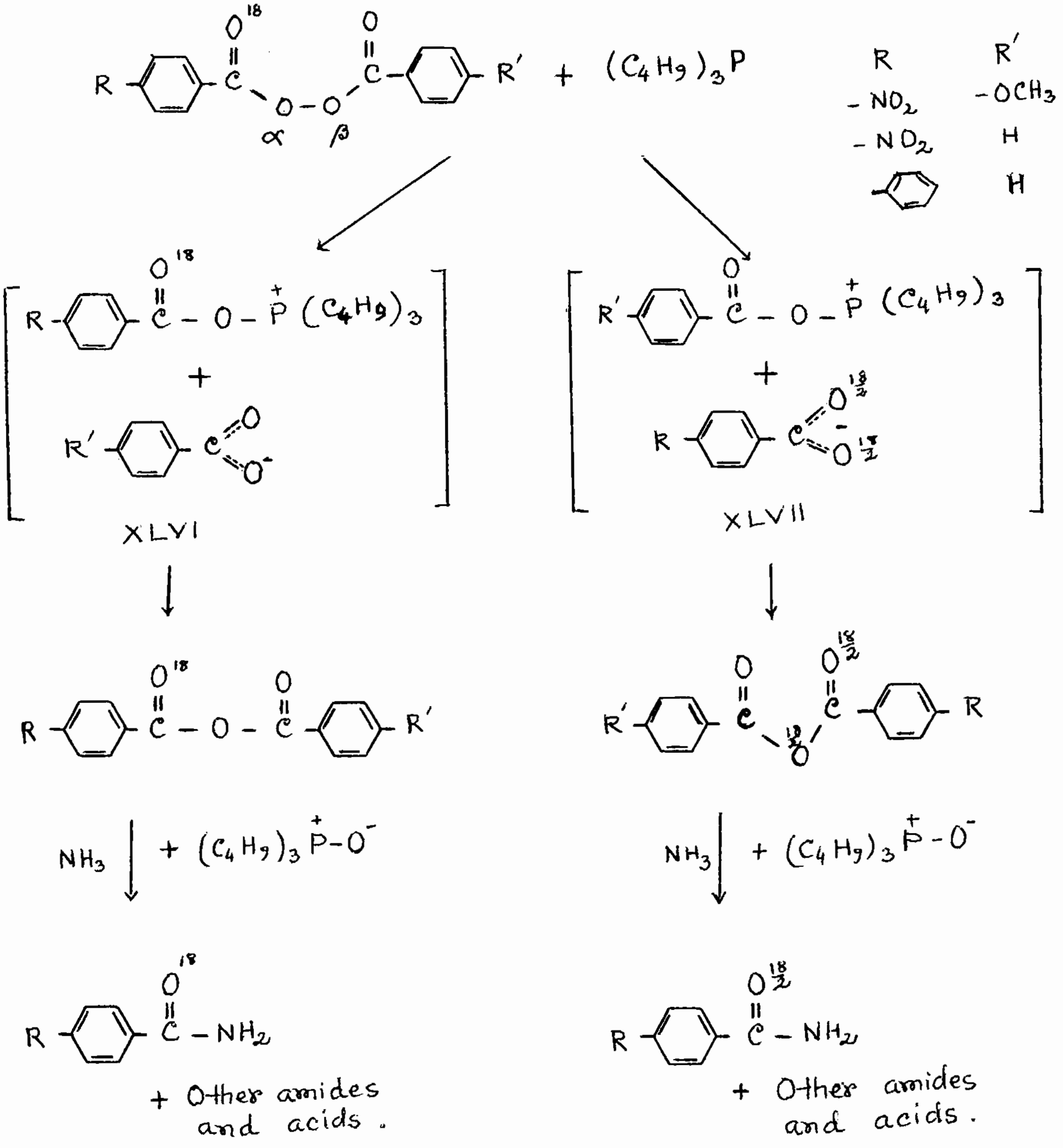


(72)

XLV

Benzoyl peroxide-carbonyl-O^{18} (XL) reacts with triphenylphosphine to give triphenylphosphine oxide (XLII) and benzoic anhydride (XLI). All of the excess oxygen-18 is found in the anhydride and none on the oxide. Treatment of (XLI) with ammonia affords benzamide (XLIII) and benzoic acid (XLIV). Analysis of (XLIII) and (XLIV) shows that in the anhydride one carbonyl was fully labelled and the other had half the original excess oxygen-18. These results are consistent with a mechanism in which triphenylphosphine displaces on a peroxidic oxygen to give a benzoate ion and a phosphonium acylate ion which exist most probably as an ion pair (XLV). Collapse of (XLV) gives the anhydride (XLI) and (XLII).

More recently, Denney and Greenbaum(61) studied the mechanism of the conversion of unsymmetrical aroyl peroxides to anhydrides by tertiary phosphines. The main point of interest was to acertain which oxygen atom of the peroxide linkage is attacked. Three unsymmetrical peroxides, p-nitrobenzoyl p-methoxybenzoyl peroxide-p-nitrobenzoyl carbonyl-O^{18}, p-nitrobenzoyl benzoyl peroxide-p-nitrobenzoyl carbonyl-O^{18}, and p-phenylbenzoyl benzoyl peroxide-p-phenylbenzoyl carbonyl-O^{18} were prepared and allowed to react with tri-n-butylphosphine. The reaction can proceed by attack on one or other of the peroxide oxygen atoms to give ion pairs (XLVI) or (XLVII).



It is shown in the flow sheet that attack at the α-oxygen which gives ion pair XLVI would ultimately afford an amide with the same oxygen-18 content in the carbonyl as was in the original anhydride. On the other hand, attack at the β-oxygen would lead to an amide which contained only one-half of the original excess oxygen-18. This isotopic study revealed that t-butylphosphine attacked the α-oxygen atom of p-nitro-p'-methoxybenzoyl peroxide and of p-nitrobenzoyl benzoyl peroxide to the extent of 100% and 95% respectively. With p-phenylbenzoyl benzoyl peroxide attack at the α-oxygen was 50%. Evidently, a p-nitro substituent markedly controls the position of attack by the phosphine. The mechanism of this control is undoubtedly due to the ability of the nitro group to lower the electron density at the α-oxygen both by resonance and induction(62). The creation of a partial positive charge favors the attack of phosphine at this point. The p-methoxy group increases electron density at β-position and is therefore unfavorable for attack. With p-phenylbenzoyl benzoyl peroxide, attack by tertiary phosphine is random because the p-phenyl group has little electronic effect here. This ability of the nitro group in p-nitro-p'-methoxy dibenzoyl peroxide to lower the electron density in the α-position leads to the heterolysis of the peroxide linkage with the p-methoxy benzoyloxy group separating with the pair of electrons. In contrast the intramolecular rearrangement of this peroxide to p-methoxyphenyl p-nitrobenzoyl carbonate involves the heterolysis(49,50) of the peroxide linkage with the p-nitrobenzoyloxy group separating with the pair of electrons.

When benzoyl peroxide (1 mole) is treated with phosphorus trichloride(63) alone, benzoyl chloride (2 mole) is the sole product of the reaction. The reaction probably involves the initial formation of phosphorus oxychloride and benzoic anhydride which then reacts with phosphorus trichloride to form benzoyl chloride;

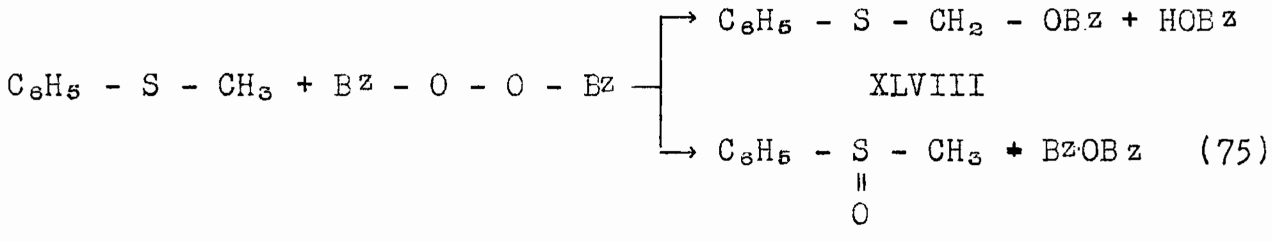
$$(PhO_2)_2 + PCl_3 \longrightarrow (PhCO)_2O + POCl_3 \qquad (73)$$

$$(PhCO)_2O + PCl_3 \longrightarrow 2PhCOCl + POCl \qquad (74)$$

Independent experiments have shown that benzoic anhydride reacts with phosphorus trichloride even in benzene solution forming benzoyl chloride.

(iv) <u>reactions with sulfides</u>

The decomposition of dibenzoylperoxide with thioanisol(64) is rather slow and takes two days to complete. The reaction products are benzoic acid, benzoyloxymethyl-phenylsulfide, methyl-phenylsulfoxide and benzoic anhydride. The last two reaction products resemble those from benzoyl peroxide and tert. phosphine(30,60,61).



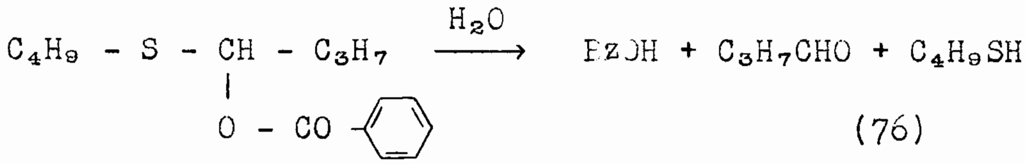
$$C_6H_5-S-CH_3+Bz-O-O-Bz \longrightarrow \begin{cases} C_6H_5-S-CH_2-OBz+HOBz \\ C_6H_5-\underset{\underset{O}{\|}}{S}-CH_3+Bz{\cdot}OBz \end{cases} \qquad (75)$$

XLVIII

XLIX

Similarly, 4,4'- dinitrobenzoyl-, 2,2'-dichlorobenzoyl- and diacetyl peroxides with thioanisal gave analogous reaction products. Dibenzylsulfide with dibenzoyl peroxide gave α-benzoyloxy-dibenzylsulfide and dibenzylsulfoxide in equivalent quantities, in addition to benzoic acid and benzoic anhydride.

The reaction of di-n-butyl sulfide is vigorous. The reaction products are benzoic acid, benzoic anhydride and di-n-butylsulfoxide. But the corresponding product (L) similar to structure XLVIII has not been isolated; however, its presence was indicated when hydrolysis afforded n-butylmercaptan, n-butyraldehyde and benzoic acid:



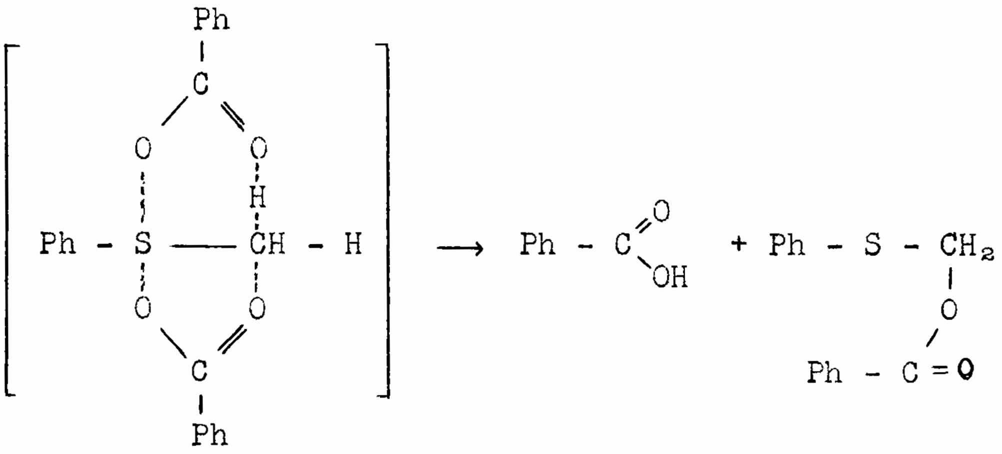
$$C_4H_9-S-\underset{\underset{O-CO-C_6H_5}{|}}{CH}-C_3H_7 \xrightarrow{H_2O} BzOH+C_3H_7CHO+C_4H_9SH \qquad (76)$$

L

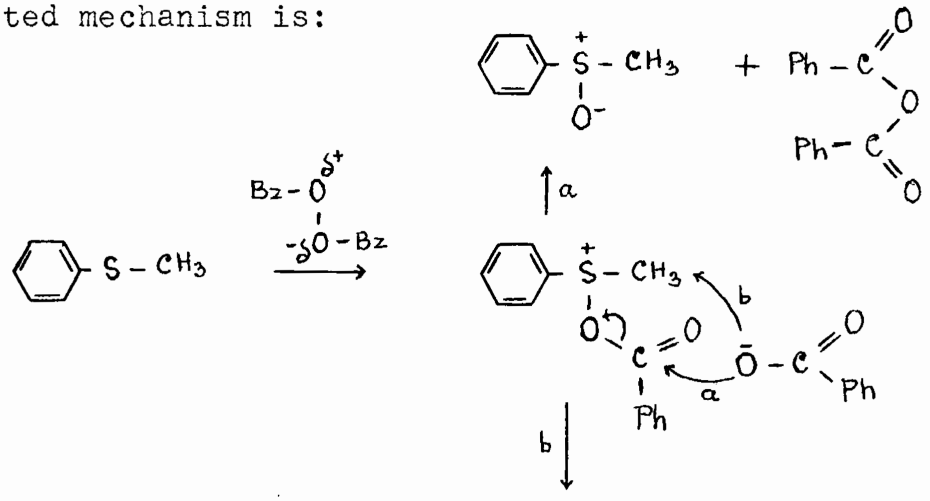
The reaction of diphenylsulfide is exceedingly slow. But out of the reaction mixture benzoic acid, benzoic anhydride and diphenylsulfoxide were isolated. Taking thioanisol and dibenzoyl peroxide as representative, Horner's(64) mechanism for the formation of benzoic acid and benzoyloxy methyl phenyl sulphide is:

$$\mathrm{Ph - CO - O - O - CO - Ph + Ph - S - CH_3} \longrightarrow$$

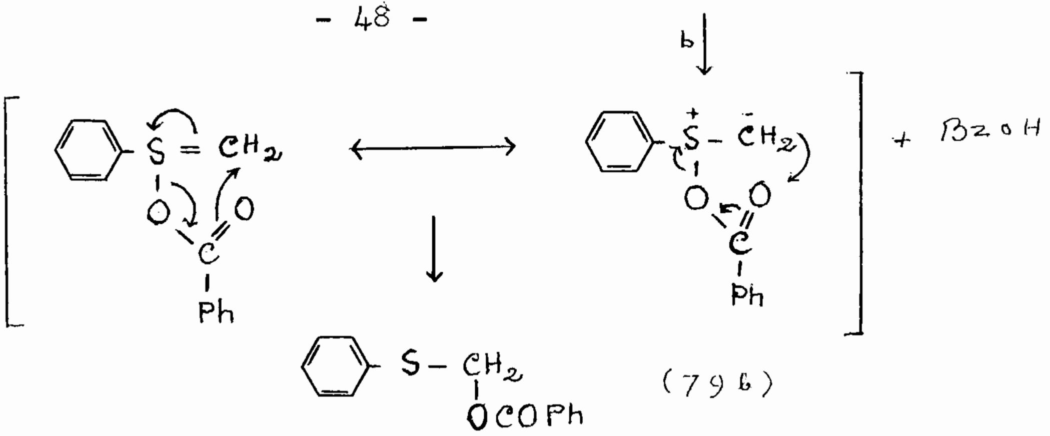
$$\left[\begin{array}{c}\mathrm{Ph - CO - O - O - CO - Ph} \\ \mathrm{Ph - S - CH_3}\end{array}\right] \longrightarrow$$


(77)

and a suggested mechanism is:


(79a)

(78)

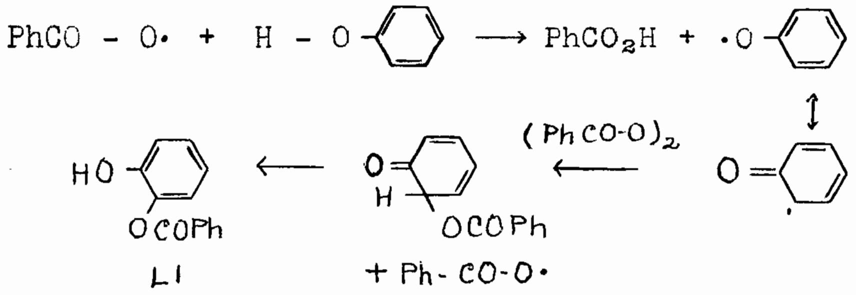


(79 b)

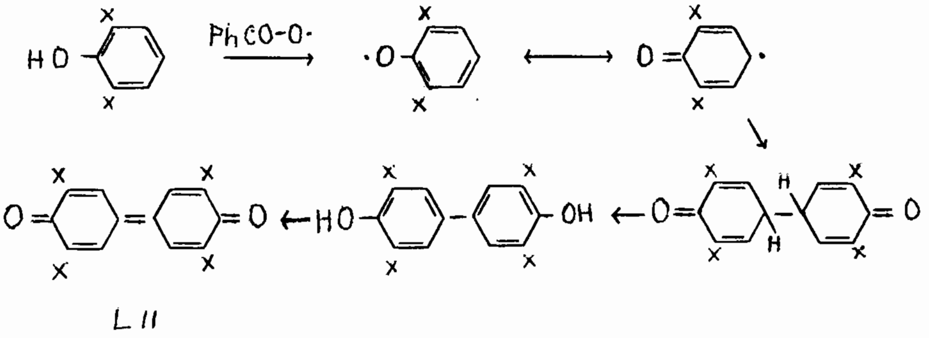
(v) phenols

Cosgrove and Waters(65a) made a thorough study of the decomposition of benzoyl peroxide with phenol, which is oxidized to catechol monobenzoate (LI). Substituted phenols having one free ortho position gave similar products; however, if both ortho positions are blocked, a diphenoquinone (LII) was formed.(65b) The oxidation of phenols with acetyl peroxide gives similar products(65c). Cosgrove and Waters advanced the following mechanism:

$$PhCO - O - O - COPh \longrightarrow 2PhCO - O\cdot \qquad (80)$$

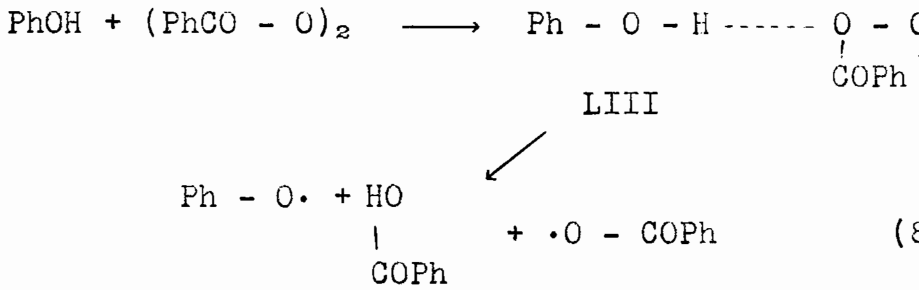


(81)



(82)

The possibility of such a radical chain reaction was disproved by Batten and Mulcahy(66), who showed that the rate of reaction was second-order. They considered the rate-determining step to be the formation of the hydrogen-bonded complex LIII, which then broke up into radicals.



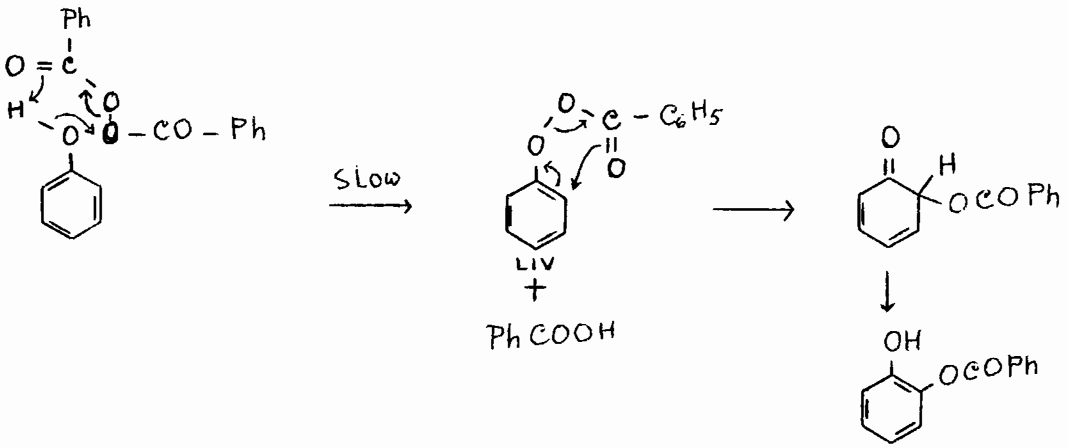
$$PhOH + (PhCO-O)_2 \longrightarrow \underset{\text{LIII}}{Ph-O-H\cdots\cdots\underset{COPh}{O}-OCOPh}$$

$$\swarrow$$

$$Ph-O\cdot + \underset{COPh}{HO} + \cdot O-COPh \qquad (83)$$

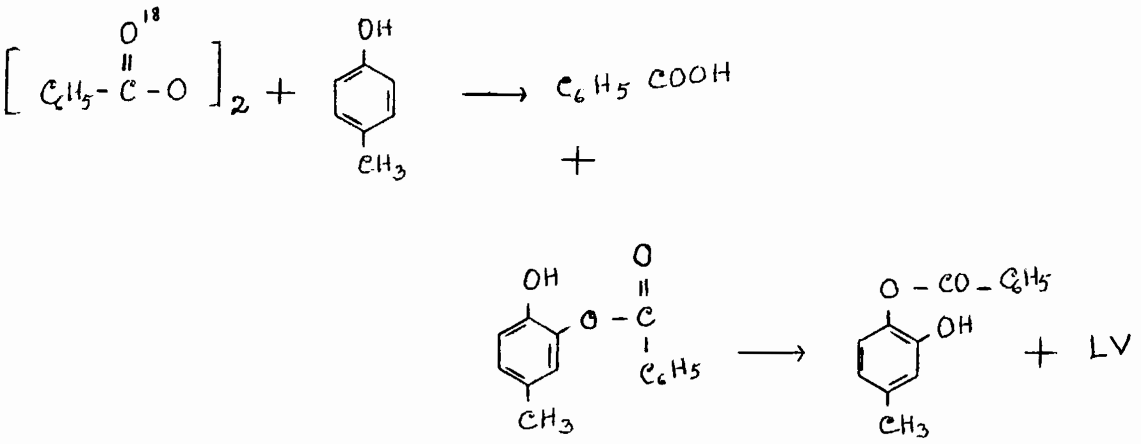
However, such a mechanism would be inapplicable to oxidations affected by acetyl peroxide, since the acetoxy radical decarboxylates almost instantaneously to form a methyl radical(17).

Walling and Hodgdon(67) also found that the reaction was cleanly bimolecular, first order in both phenol and peroxide. However, they also found that radical traps had no effect upon the rate or the products. They suggested that the reaction was almost certainly ionic:



(84)

Denney(68) and his co-worker studied the reaction of p-cresol with benzoyl peroxide, labelled with oxygen-18 in the carbonyl groups. The reaction proceeds to give initially LV which rapidly isomerizes to a mixture of LV and LVI and it was LVI which was isolated.

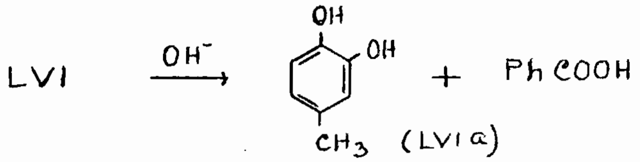


LV LVI

(85)

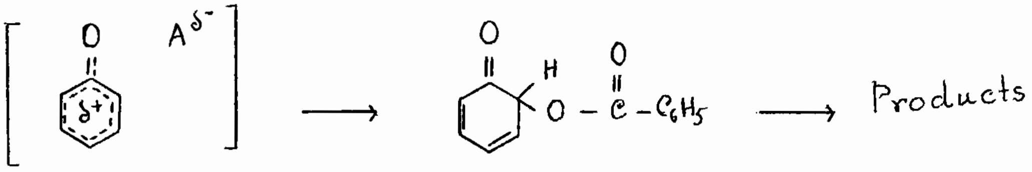
Oxygen-18 analysis of LVI showed that the carbonyl group contained essentially all of the excess O^{18} originally present in one carbonyl group of the benzoyl peroxide. From a mechanistic point of view this result completely eliminates the formation of a benzoyloxy radical during the reaction, since this would have led to LVI in which half of the O^{18} was in the ester carbonyl and the other half was in the phenolic hydroxyl group.

However, further tracer study by Denney(68) revealed that Walling and Hodgdon's mechanism required a modification



Hydrolysis of LVI to 2-hydroxy-4-methylphenol(LVIa)was effected by solution in aqueous potassium hydroxide at room temperature. Acidification afforded LVIa. Oxygen-18 analysis of it showed that it contained 13% of the excess oxygen-18 present in LVI. It is unthinkable that exchange of oxygen-18 took place under these conditions and therefore one can assign the following distribution of oxygen-18 to LVI: 87% of the excess oxygen-18 in the carbonyl group and 13% of the excess in the phenolic hydroxyl group.

So it is concluded from this tracer experiment that rearrangement of the per ester LIV leads to some equilibration but that the carbonyl oxygen retains 87% of the excess oxygen-18. These results can be explained in terms of an ion pair or ion pairs LVIb, which allow some equilibration.



LVIb

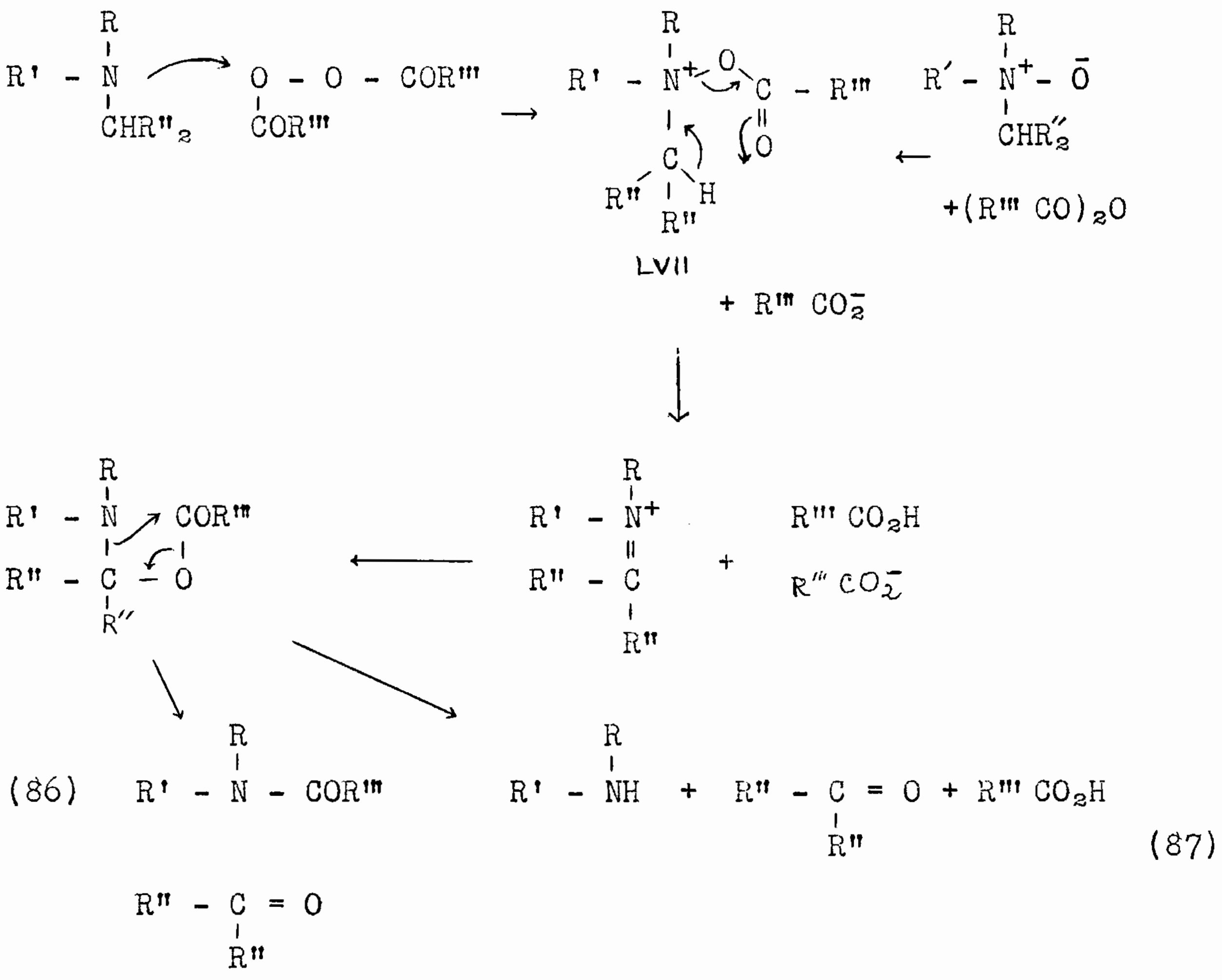
$A^{\delta-}$ = potential benzoate ion

(VI) reaction with amines

(α) tertiary aliphatic amines

Paolini(69) reported the formation of acetaldehyde and the benzoyl derivative of diethylamine from the reaction of benzoyl peroxide and triethylamine. This was reinvestigated by Horner and Kirmse(70) who found that the yield of aldehyde was not proportional to the amount of peroxide decomposed. They concluded that the aldehyde formed is used up during the course of peroxide decomposition. From the absorption of nitric oxide and oxygen the reaction was considered to proceed through radical formation.

It seems likely(71-73) that the reaction involves an acyloxy ammonium ion (LVII) as an intermediate. Such an acyloxyammonium ion was isolated by Geiger(72), who obtained N-acetoxytrimethylammonium (LVII, R = R' = Me, R" = H, R"' = Me) bromide from the reaction of trimethylamine with acetyl peroxide, followed by treatment with hydrogen bromide. A similar intermediate will be involved from the reaction of an amine oxide with an acid anhydride, since this reaction gives similar products to the reaction of the related tertiary amine with a diacyl peroxide(74). The subsequent decomposition of the acyloxyammonium ion may be interpreted as proceeding through a series of four-centre reactions as shown, rather than through radical intermediates.



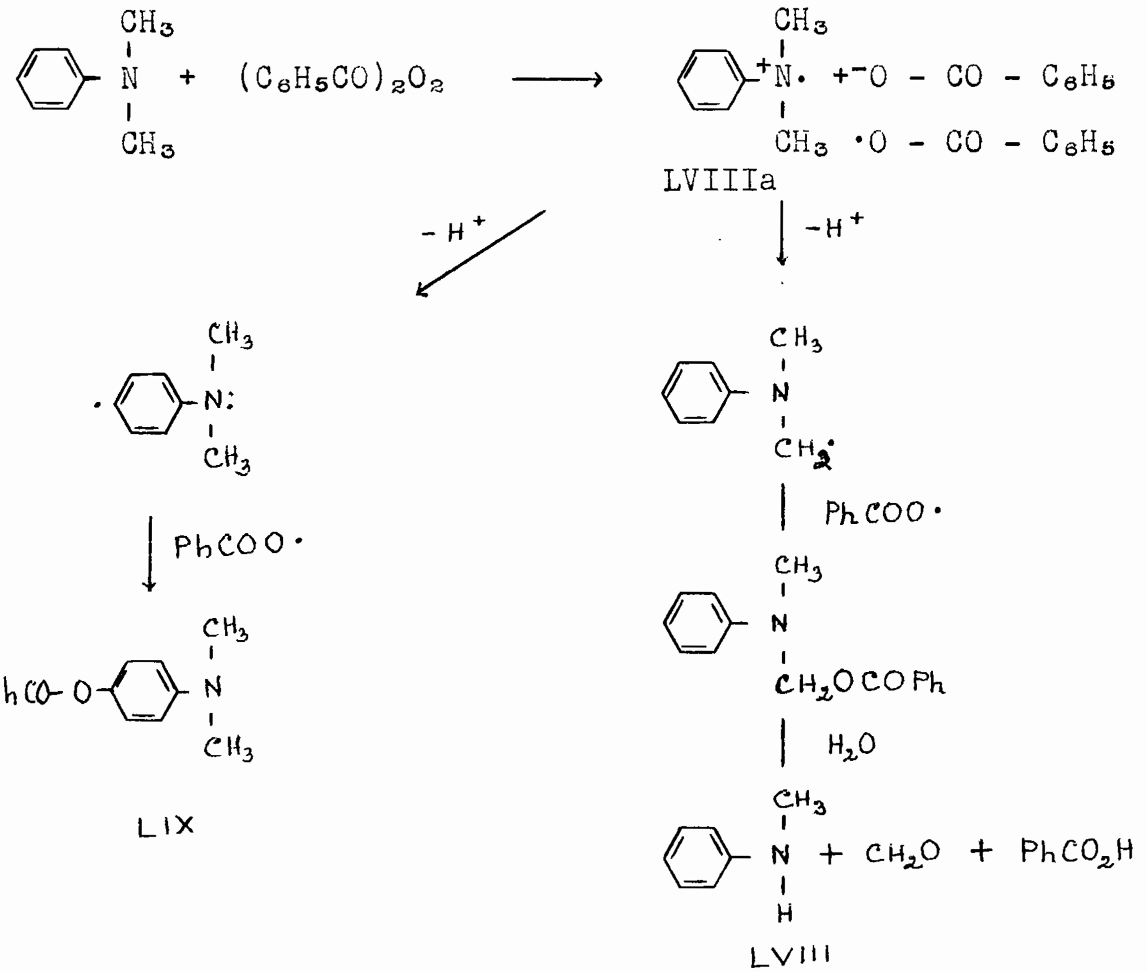
(86)

(87)

(β) <u>tertiary aromatic amines</u>

The reaction between benzoyl peroxide and tertiary aromatic amines has been found to be second-order(75-76). The products(75d) isolated from dimethylaniline (after aqueous treatment) are mainly benzoic acid, methyl aniline and formaldehyde plus smaller amounts of p-benzoyloxydimethylaniline and p,p'-di-(dimethylamino)-diphenylmethane. Thus with an excess of dimethylaniline Horner and Betzel(75d) obtained 38% of monomethylaniline

(LVIII) and 15% of p-benzoyloxydimethylaniline (LIX). They explained their results by radical formation:

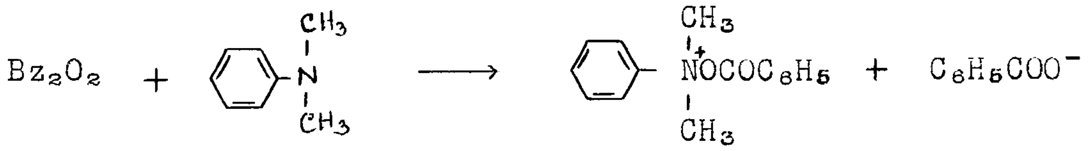


(88)

However, Imoto$^{(76)}$ and co-workers measured the radical efficiency of this reaction and reported from measurement of the initial velocity of polymerization of styrene that the process goes by radical formation only to the extent of 25%.

Walling and Indictor (77) determined the radical activity of the same system for the polymerization of styrene and methyl methacrylate at 0-80° and reported only 25-10% of radical formation. Although it seems clear that benzoyl peroxide and dimethylaniline undergo a bimolecular reaction giving rise to some free radicals, the exact nature of the process is certainly controversial. Thus Horner(75f) has proposed as the rate determining step the formation of a complex (eg. LVIIIa) which subsequently gives rise to the observed products, while Imoto(76) has suggested the reversible formation of a complex which subsequently decomposed into free radicals.

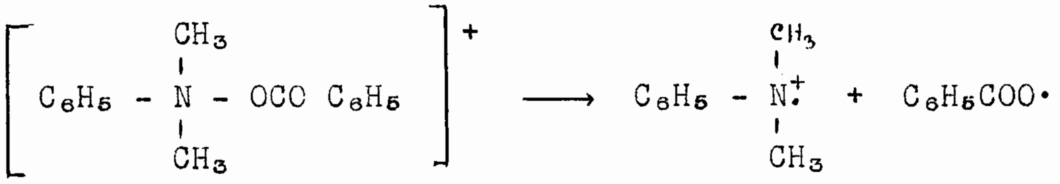
It seems more plausible(77) that the rate controlling step is a nucleophilic displacement on the peroxide by dimethylaniline to yield a quaternary hydroxylamine derivative



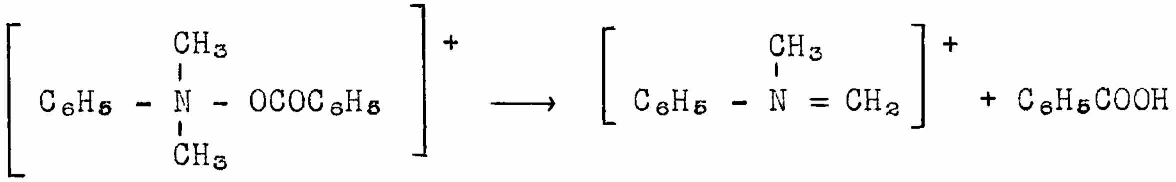
(89)

However, while a polar process such as (89) should show a solvent dependent rate, there is little correlation in the results reported by Walling and Indictor (77) with any such solvent properties as dielectric constant or solvating ability.

The product of reaction (89) has only transient existence and decomposes by at least two possible paths:

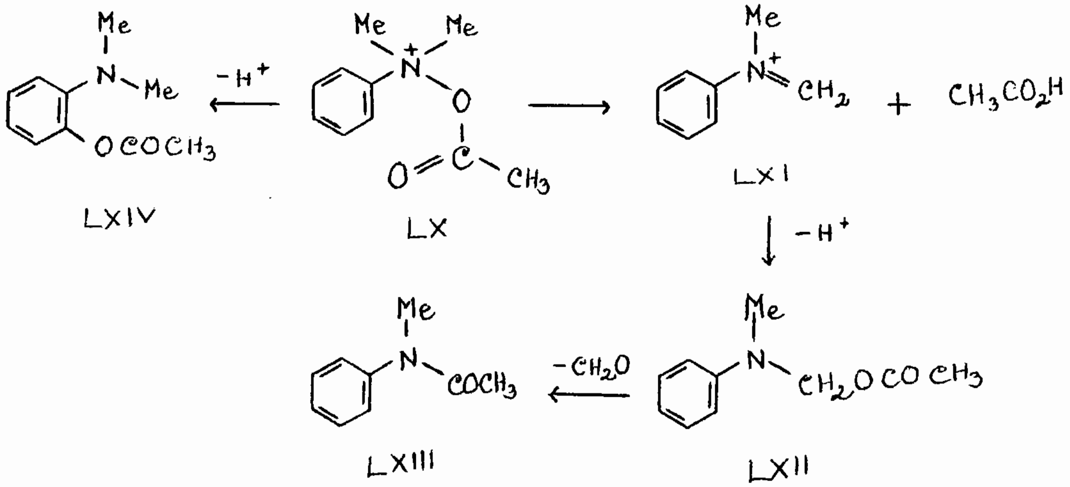


$$\left[C_6H_5 - \overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{N}} - OCO\ C_6H_5 \right]^+ \longrightarrow C_6H_5 - \overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{N^{\dot{+}}}} + C_6H_5COO\cdot \qquad (90)$$



$$\left[C_6H_5 - \overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{N}} - OCOC_6H_5 \right]^+ \longrightarrow \left[C_6H_5 - \overset{\displaystyle CH_3}{N} = CH_2 \right]^+ + C_6H_5COOH \qquad (91)$$

Reaction (90) represents a free radical path and would account for the initiation of polymerization. The polymerization studies indicate that this reaction takes place to only a minor extent. Since no significant amount of nitrogen is found in the resulting polymers the amine fragment may well disappear by reaction with further peroxide. Reaction (91) represents the non-radical mode of breakdown, which seems to be of major importance. This type of non-radical breakdown has also been advanced recently by Huisgen, Bayerlein and Heydkamp(78).

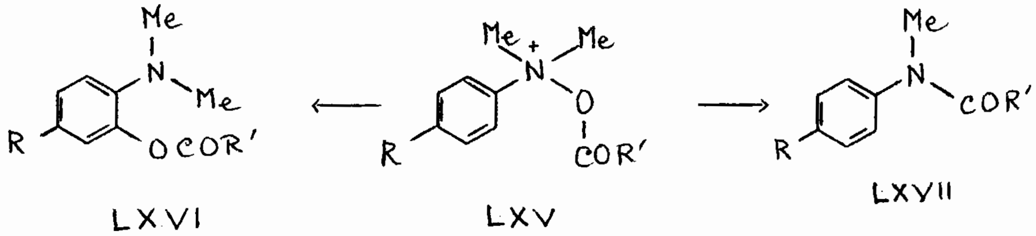


(92)

The analogous intermediate complex LX is formed both from dimethylaniline oxide with acetic anhydride and dimethylaniline with acetyl peroxide.

The system of N,N-dimethylaniline oxide and acetic anhydride showed little radical formation at 0° compared to dimethylaniline and diacetyl peroxide in which both radical and non-radical process are operative. Only in the former case have good yields of LXIII and LXIV been isolated. The reaction of dimethylaniline with acetyl peroxide does not give any (LXIV) at all.

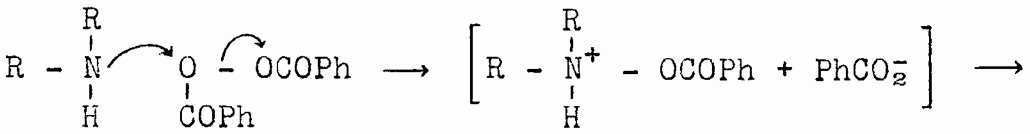
Horner and Betzel(75d) reported more than 70% of



LXVII(R = CH_3; R' = Ph) from the reaction of an excess of N,N-dimethyl-p-toluidine (LXV; R = CH_3) with dibenzoyl peroxide. Huisgen(78b) and co-workers repeated this reaction and got only 54% of the dealkylated product. At a ratio of 1:1 of dibenzoyl peroxide and dimethyl-p-toludine, the yield is as low as 16%, and no LXVI appeared to be formed. With N,N-dimethyl-p-chloroaniline (LXV; R = Cl) and diacetyl peroxide in the ratio of 1:1, however, 25% of LXVII (R = Cl, R' = CH_3) and 17% of LXVI (R = Cl, R' = CH_3) were reported, and nearly 65% of amine was undecomposed. But with N,N-dimethyl-p-chloroaniline oxide plus acetic anhydride LXVI (R = Cl, R' = CH_3) and LXVII (R = Cl, R' = CH_3) were isolated in 65% and 10% yields respectively(73).

(γ) secondary aliphatic amines

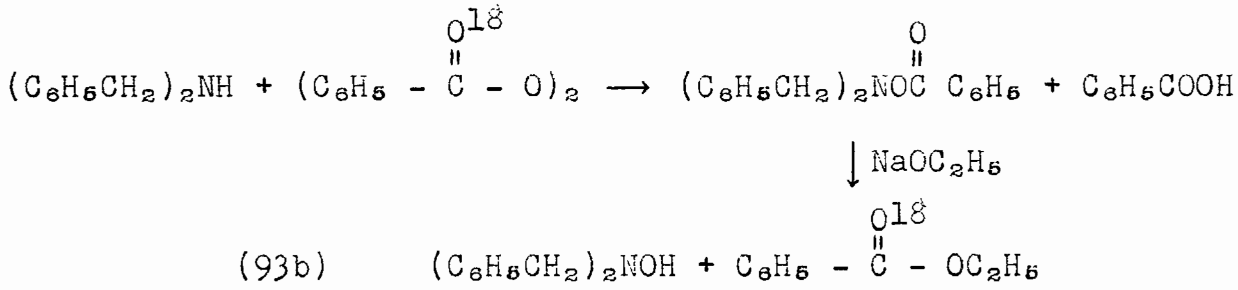
Secondary aliphatic amines react with benzoyl peroxide to give N,N-dialkyl-O-benzoyl hydroxylamine and benzoic acid(79). The most likely mechanism involves nucleophilic attack by the amine on the peroxide to give a pair of ions which undergo a proton transfer to give products:



$$\mathrm{R-\overset{R}{\underset{H}{N}}-\underset{COPh}{O}-OCOPh} \longrightarrow \left[\mathrm{R-\overset{R}{\underset{H}{N^{+}}}-OCOPh + PhCO_2^-}\right] \longrightarrow$$

$$\mathrm{R_2NOCOPh + PhCO_2H} \qquad (93a)$$

Effective proof of the correctness of this view has been obtained by allowing dibenzylamine to react with benzoyl peroxide, labelled with oxygen-18 in the carbonyl oxygens(68). The procedure was that of Gambarjan and Cialtician(80). The O-benzoylhydroxylamine obtained contained all of the excess oxygen-18

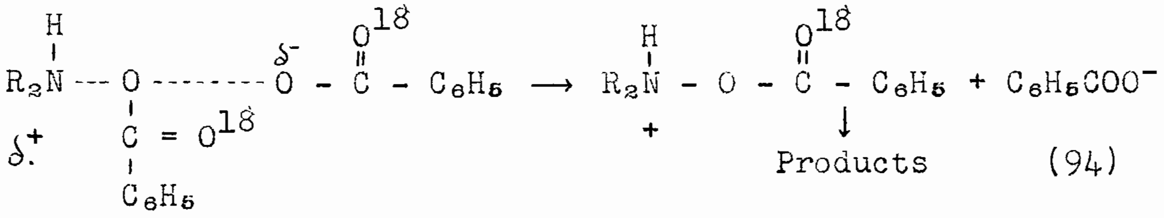


$$(C_6H_5CH_2)_2NH + (C_6H_5 - \overset{O^{18}}{\overset{\|}{C}} - O)_2 \longrightarrow (C_6H_5CH_2)_2NO\overset{O}{\overset{\|}{C}}\,C_6H_5 + C_6H_5COOH$$

$$\downarrow NaOC_2H_5$$

$$(93b) \qquad (C_6H_5CH_2)_2NOH + C_6H_5 - \overset{O^{18}}{\overset{\|}{C}} - OC_2H_5$$

originally incorporated in one of the carbonyl groups of benzoyl peroxide. Ethanolysis of the O-benzoylhydroxylamine afforded dibenzylhydroxylamine which contained no excess oxygen-18 and ethyl benzoate which contained all of the excess oxygen-18 present in the O-benzoylhydroxylamine. Thus the only reasonable mechanism for the reaction involves a transition state such as LXVIII



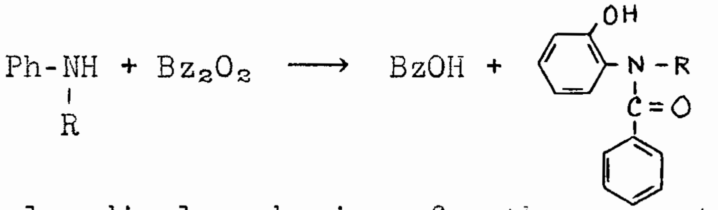
$$\underset{\delta^{+}}{R_2\overset{H}{\overset{|}{N}}} \cdots \underset{\substack{| \\ C\,=\,O^{18} \\ | \\ C_6H_5}}{O} \cdots\cdots \overset{\delta^{-}}{O} - \overset{O^{18}}{\overset{\|}{C}} - C_6H_5 \longrightarrow R_2\underset{+}{\overset{H}{\overset{|}{N}}} - O - \underset{\substack{\downarrow \\ \text{Products}}}{\overset{O^{18}}{\overset{\|}{C}}} - C_6H_5 + C_6H_5COO^{-} \qquad (94)$$

LXVIII

in which the amine displaces on one of the oxygens of the peroxide link to give a pair of ions which rapidly react to give products.

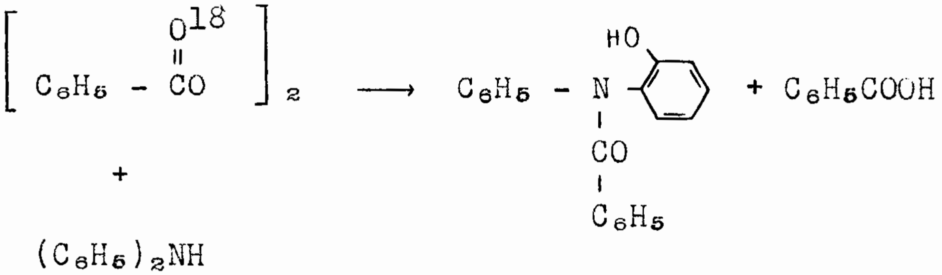
(δ) <u>secondary aromatic amines</u>

The reactions of secondary aryl or secondary aralkyl amines with benzoyl peroxide do not yield O-benzoylhydroxylamines but rather o-hydroxybenzanilides(81,82).



(95a)

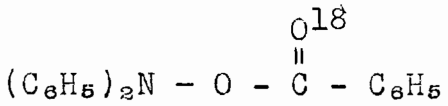
Several radical mechanisms for these reactions have been proposed(82-85) but no evidence for radical formation has been obtained; secondary amine-peroxide systems neither initiated polymerization nor absorbed oxygen(86). In a study of the mechanism of these reactions diphenyl amine was allowed to react with benzoyl peroxide labelled with oxygen-18 in the carbonyl positions(68). The hydroxybenzanilide obtained (LXIX) contained 95% of the excess oxygen-18 originally present in one of the carbonyl groups of the benzoyl peroxide. Evidently some loss of oxygen-18 occurred during the isolation and the purification of the amide. Basic hydrolysis of LXIX yielded o-hydroxydiphenylamine



(95b)

LXIX

which contained (45%) of the excess oxygen-18 present in LXIX. Since it has been demonstrated that monophenols do not undergo oxygen-18 exchange under basic conditions(87), one can then assign the following distribution of oxygen-18 to LXIX: carbonyl oxygen, (55%) of the excess; and the phenol oxygen, (45%) of the excess. The results show that practically complete equilibration of the label has occurred. These data, coupled with those obtained from the dibenzylamine reaction reported above, allow the formulation of a mechanism for these reactions. It seems only reasonable to assume that the initial reaction proceeds **to** give O-benzoyl-N,N-diphenyl hydroxylamine (LXX) in which oxygen-18 label



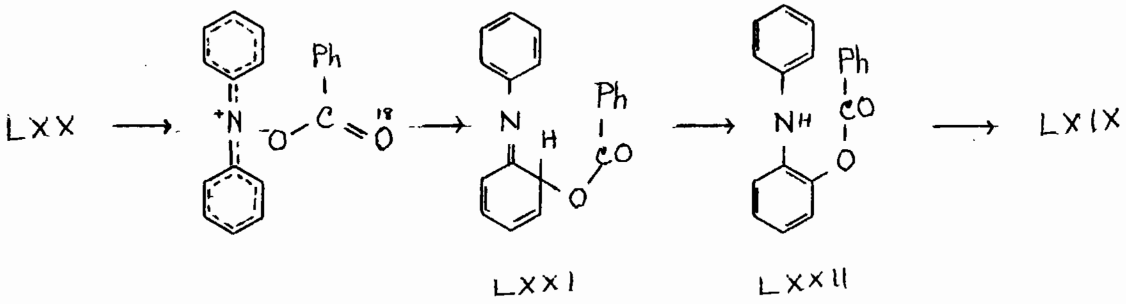
$$(C_6H_5)_2N - O - \overset{O^{18}}{\overset{\|}{C}} - C_6H_5 \qquad (96)$$

LXX

is localized in the carbonyl oxygen. This postulation follows naturally from the dialkylamine reaction. That LXX is an intermediate in this reaction and can isomerize to LXIX has been demonstrated by allowing diphenyl hydroxylamine to react with benzoyl chloride(68,88). When the reaction was carried out in ice-cold pyridine, the yield of LXIX was up to 78%; the benzoyloxy intermediate could not be isolated.

The rearrangement of LXX, which ultimately leads to LXIX, is probably an ionic process. Thus diphenylamine and acetyl peroxide react to form N-o-hydroxyphenylacetanilide, which is analogous to LXIX. The initial product of this reaction is undoubtedly O-acetyl-N,N-diphenylhydroxylamine. Rearrangement of this material by a homolytic process would involve the formation of acetoxy radicals which are known to decarboxylate spontaneously;(17) hence the acetanilide cannot be formed by this radical process.

Consequently, an ionic mechanism may be advanced:

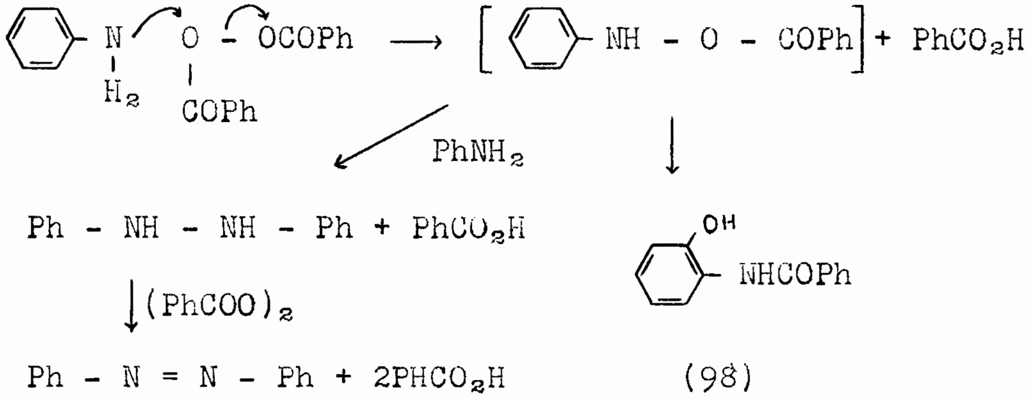


The partial equilibration of the label must occur during the conversion of LXX to LXXI, since isomerization of LXXII to LXIX is a simple intramolecular addition of the amine nitrogen of LXXII to the carbonyl carbon atom followed by ring opening and proton transfer. These transformations cannot account for oxygen-18 equilibration. The partial equilibration observed is reminiscent of several ion pair reaction studied by Denney(43).

(ε) primary aromatic amines

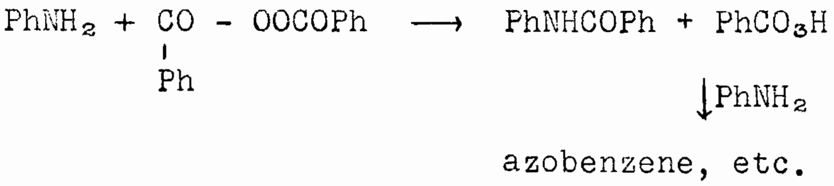
Primary aromatic amines and benzoyl peroxide give a complex mixture of products. The yields of o-benzamidophenols are very low(89). The neutral and the basic fractions from these reactions are mixtures from which the azo compound and N-arylbenzamide are obtained(89,75b). The following equations may be suggested to account for the products:

(a)



(98)

(b)



$$PhNH_2 + \underset{Ph}{CO} - OOCOPh \longrightarrow PhNHCOPh + PhCO_3H \xrightarrow{PhNH_2} \text{azobenzene, etc.}$$

(99)

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CHAPTER II

RESULTS AND DISCUSSION

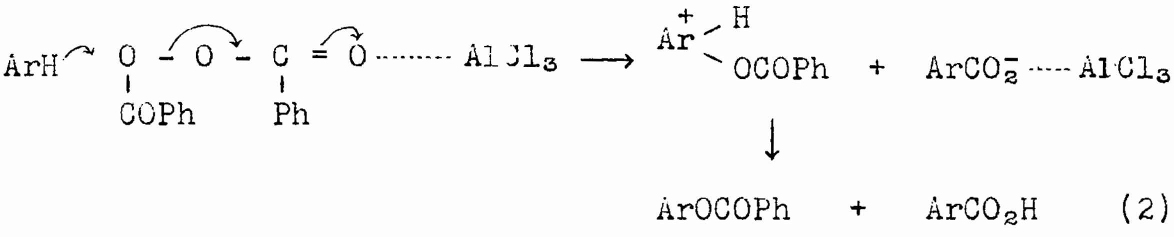
Decomposition of Dibenzoyl Peroxide by Aluminium Chloride.

A general method for introducing the benzoyloxy group directly into aromatic nuclei was suggested by the reported reaction of benzene with dibenzoyl peroxide in the presence of aluminium chloride (p. 37). Reynhart(1) claimed that this reaction at 0° afforded a yield of 90% of phenyl benzoate and 92% of benzoic acid, according to the equation:

$$\mathrm{PhH} + (\mathrm{PhCOO})_2 \longrightarrow \mathrm{PhCO_2Ph} + \mathrm{PhCO_2H} \qquad (1)$$

At higher temperatures the yield of phenyl benzoate was said to drop. However, in carrying out this reaction at 0-5° we obtained much lower yields of phenyl benzoate (Table I).

In view of recent studies on the mechanism of the Friedel-Crafts reaction(2), it was thought that the reaction represented in equation 1 probably had the mechanism:



$$\mathrm{ArH} \; \underset{\mathrm{COPh}}{\mathrm{O}} - \mathrm{O} - \underset{\mathrm{Ph}}{\mathrm{C}} = \mathrm{O} \cdots\cdots \mathrm{AlCl_3} \longrightarrow \overset{+}{\mathrm{Ar}}\!\begin{smallmatrix} \mathrm{H} \\ \mathrm{OCOPh} \end{smallmatrix} + \mathrm{ArCO_2^-} \cdots \mathrm{AlCl_3}$$
$$\downarrow$$
$$\mathrm{ArOCOPh} + \mathrm{ArCO_2H} \qquad (2)$$

With such a mechanism one should expect toluene to react more readily than benzene, and nitrobenzene to be unreactive and hence a suitable solvent for the reaction. However, the attempt to cause toluene to react with dibenzoyl peroxide in nitrobenzene again gave phenyl benzoate, and not o̲- and p̲- tolyl benzoates. Phenyl benzoate (49% yield) was also obtained by treating dibenzoyl peroxide with aluminium chloride in nitrobenzene alone.

These results indicated that phenyl benzoate was being formed from dibenzoyl peroxide alone, presumably by the reaction:

$$\mathrm{PhCO{\cdot}OO{\cdot}COPh} \longrightarrow \mathrm{PhOCOPh} + \mathrm{CO_2} \qquad (3)$$

In accordance with this equation it was found that the aluminium chloride - catalysed decomposition of dibenzoyl peroxide in benzene and in nitrobenzene gave 58% and 92% respectively of the amount of carbon dioxide expected from equation 3. This decomposition had already been observed by Reynhart(3) when dibenzoyl peroxide in petroleum ether at ± 10°C. was treated with antimony pentachloride (a Lewis acid, like aluminium chloride).

The course of the reaction in some other solvents is indicated in Table I. In methylene chloride phenyl benzoate was again obtained, while in a mixture of anisole and nitrobenzene p,p'-dianisyl (22-23% yield) was obtained. It seems that the dibenzoyl peroxide in this reaction is functioning as an oxidizing agent according to the equation:

$$2\ C_6H_5OMe + (C_6H_5COO)_2 \longrightarrow MeO \cdot C_6H_4 \cdot C_6H_4 \cdot OMe + 2\ C_6H_5CO_2H \quad (4)$$

(It is possible that dianisyls other than the p,p'-compound were also formed, but were not obtained crystalline). The high yield of benzoic acid in this reaction is in accord with equation 4. According to equation 3, the formation of phenyl benzoate does not involve the formation of benzoic acid also (as does equation 1), and indeed in reactions in which phenyl benzoate was formed in moderately high yield, the yield of benzoic acid was small (Table I). The reactions other than that typefied by equation 4 which may yield benzoic acid are discussed in the next section of this chapter.

In resorcinol dimethyl ether the reaction took yet another course, which is discussed later (p.87).

The use of Lewis acids other than aluminium chloride and antimony pentachloride has not yet been much investigated. Ferric chloride catalyses the decomposition of dibenzoyl peroxide in benzene, but forms a black complex with the phenyl benzoate initially produced(1). We found boron trifluoride-etherate in benzene at 0-5° without effect on the peroxide.

TABLE I

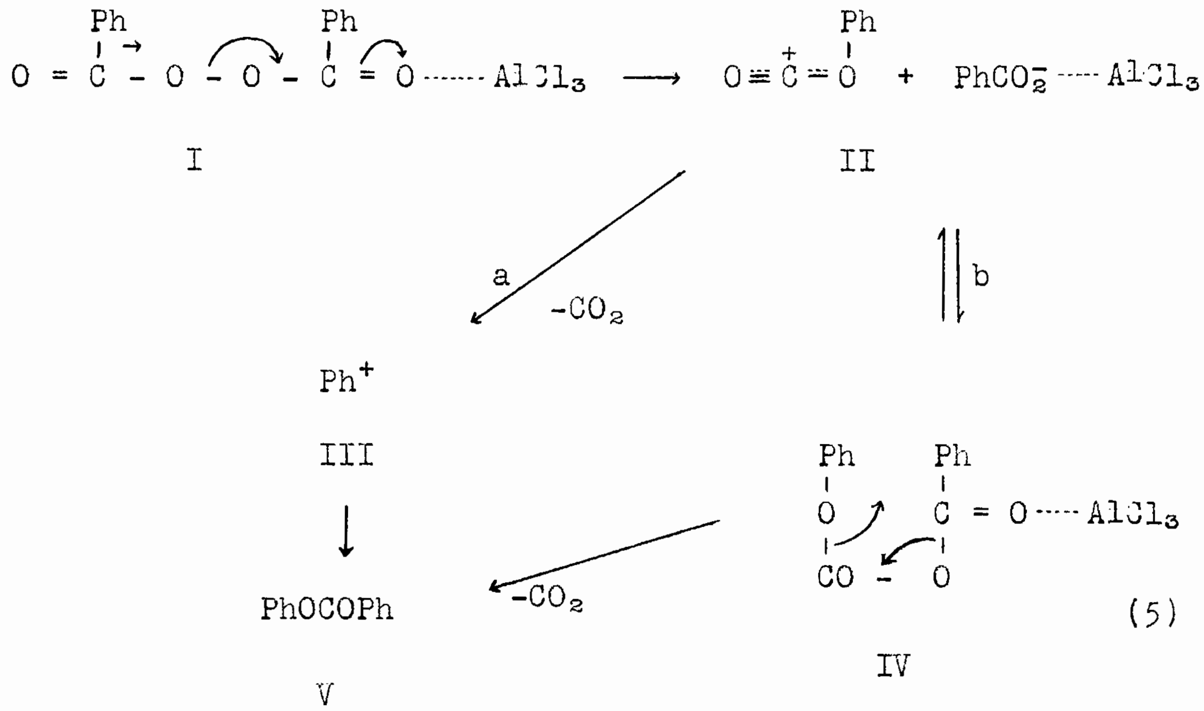
Yields (%) of products from the reaction of dibenzoyl peroxide-aluminium chloride in different solvents

Solvent	Phenyl benzoate	Benzoic acid[*]	Biaryl	Benzoyloxy Derivative
Methylene dichloride	26	27	-	-
Benzene	29	30	-	-
Nitrobenzene	49	16	-	-
Nitrobenzene-toluene	21	42	-	-
Nitrobenzene-anisole	-	76,79	23,22	-
Resorcinol dimethyl ether	-	66	-	3

[*] Based on : $Bz_2O_2 \longrightarrow 2\ BzOH$

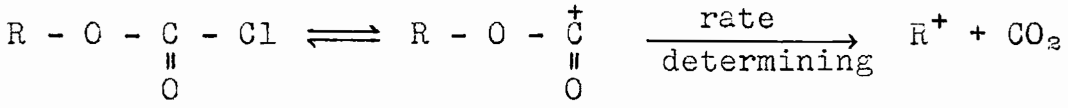
Mechanism of the Formation of Phenyl Benzoate from Dibenzoyl Peroxide - Aluminium Chloride.

The investigations of Leffler (p. 31) have shown that in the presence of Brønsted acid catalysts the ionic fission of the peroxide linkage in unsymmetrical diaroyl peroxides is favoured. It seems probable that in the presence of the much more powerful Lewis acid, aluminium chloride, dibenzoyl peroxide (I) undergoes such a heterolytic reaction with concomitant migration of the phenyl group of the incipient benzoyloxy cation to give a phenoxyformyl cation (II):



Phenyl benzoate (V) might then be formed by three routes:

(a) Loss of carbon dioxide from the phenoxyformyl cation to give a phenyl cation (III), which could then react with benzoate ion to give phenyl benzoate. The reaction II ⟶ III would be analogous to the loss of N_2 from the benzenediazonium ion to give the phenyl cation(4). It has been shown recently that cations such as RCO_2^+(5) (which is probably in the form $RO=\overset{+}{C}\equiv O$(6)) and $R{-}O{=}C^+$(7) readily lose CO_2 and CO to generate aliphatic carbonium ions, while the decomposition of alkyl chloroformates (VI) to alkyl chlorides may involve the reaction(8):



$$\underset{\text{VI}}{R - O - \underset{\underset{O}{\|}}{C} - Cl} \rightleftharpoons \underset{+Cl^-}{R - O - \underset{\underset{O}{\|}}{\overset{+}{C}}} \xrightarrow[\text{determining}]{\text{rate}} R^+ + CO_2 \qquad (6)$$

The loss of CO_2 from the aromatic ion (II) would be expected to occur less readily than from aliphatic $R - O = \overset{+}{C} \equiv O$ ions, for the same reason that aromatic diazonium ions decompose less readily than aliphatic diazonium ions, but should be possible.

As a test of this mechanism, attempts were made to isolate chlorobenzene from the reaction of dibenzoyl peroxide with aluminium chloride in nitrobenzene, by distillation of the reaction mixture through a Nester-Faust spinning-band column. No chlorobenzene could be isolated; however, from work with mixtures of chlorobenzene and nitrobenzene it appeared that chlorobenzene could not be isolated when present as less than about 1.2% of the mixture. Hence this experiment indicates only that chlorobenzene, if formed, is produced in less than about 25% yield. Obviously, this experiment must be repeated with more sensitive methods (e.g., gas chromatography) for detecting chlorobenzene in the mixture.

(b) Formation of benzoyl phenyl carbonate (IV), and its subsequent decomposition by ionization (IV → II), followed by a rate-determining loss of carbon dioxide from the phenoxyformyl cation (II). Such a mechanism would be similar to the possible mechanism for the decomposition of chloroformates (equation 6), and should like the first mechanism lead to the formation of some chlorobenzene.

(c) Formation of benzoyl phenyl carbonate (IV), followed by the intramolecular extrusion of carbon dioxide (IV → V), as shown. The general reaction:

$$\underset{\text{VII}}{\mathrm{RCO{\cdot}O{\cdot}CO{\cdot}OR'}} \longrightarrow \underset{\text{VIII}}{\mathrm{RCO{\cdot}OR'}} + \mathrm{CO_2} \qquad (7)$$

is well known, and generally requires elevated temperatures(9,10), but can occur at room temperature(10,11). The reaction is catalysed by Lewis acids: we have found that benzoyl ethyl carbonate (VII; R = Ph, R' = Et) in benzene at 0° in the presence of aluminium chloride gives a 48% yield of ethyl benzoate (VIII; R = Ph, R' = Et) (reaction 7) and a 14% yield of benzoic acid (presumably by reaction 8, discussed below), while recently the decomposition of this anhydride to ethyl benzoate has been reported to take place at room temperature in the presence of boron trifluoride etherate(10).

A possible mechanism for the reaction (IV → V), indicating the function of the Lewis acid, is shown above in equation 5.

Besides decomposing to esters and one mole of carbon dioxide, according to equation 7, mixed carboxylic-carbonic anhydrides (VII) can undergo intermolecular disproportionation(9,10) according to equation 8, with the liberation of half a mole of carbon dioxide:

$$\underset{\text{VII}}{2\ \mathrm{RCO{\cdot}O{\cdot}CO{\cdot}OR'}} \longrightarrow \underset{\text{IX}}{(\mathrm{RCO})_2\mathrm{O}} + \underset{\text{X}}{\mathrm{CO(OR')_2}} + \mathrm{CO_2} \qquad (8)$$

The decomposition of the mixed anhydride is said to take place more readily when R' is phenyl rather than alkyl, and reaction 8 then to be favoured over reaction 7(10); however, there is some evidence that Lewis-acid catalysis favours reaction 7(10). The 14% yield of benzoic acid obtained by us from the catalysed decomposition of benzoyl ethyl carbonate (VII; R = Ph, R' = Et) may have come from benzoic anhydride (IX; R = Ph) produced by reaction 8; the reaction mixture was not examined for ethyl carbonate (X; R' = Et). Similarly, the varying yields of phenyl benzoate, benzoic acid and carbon dioxide from the catalysed decomposition of dibenzoyl peroxide in different solvents may be due to the occurrence to differing extents of the competing reactions 7 and 8 (as well as others). Phenyl carbonate (X; R' = Ph), if formed by reaction 8, may in the presence of aluminium chloride react further with benzoic anhydride or benzoyl peroxide to form the gummy, involatile materials also produced in these reactions.

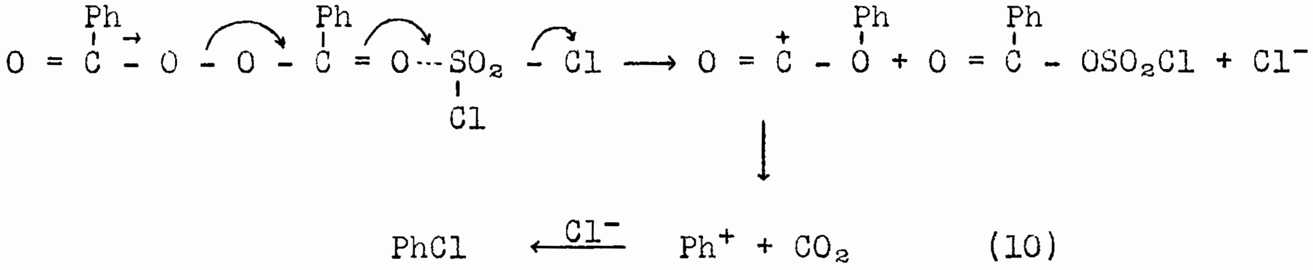
It is evident that final decision as to the mechanism of the formation of phenyl benzoate awaits further experimental work, but for the present mechanism (c) is favoured since it avoids the formation of the high-energy Ph^+ ion.

Decomposition of Dibenzoyl Peroxide in the Presence of Other Lewis Acids.

Sulphuryl chloride and phosphorus pentachloride are also Lewis acids, although less powerful than aluminium chloride(12). They do not accelerate the decomposition of dibenzoyl peroxide in the drastic manner of aluminium chloride(13), but it is possible that they also cause a heterolytic fission of the peroxide linkage. Pausacker and Karelsky(13) showed that the reaction of benzoyl peroxide with sulphuryl chloride in benzene solution at 78°C. went chiefly according to the equation:

$$(PhCOO)_2 + SO_2Cl_2 \longrightarrow PhCl + CO_2 + PhCO{\cdot}O{\cdot}SO_2Cl \qquad (9)$$

They advanced a free radical mechanism to account for the products. However, an ionic mechanism may equally well account for them:

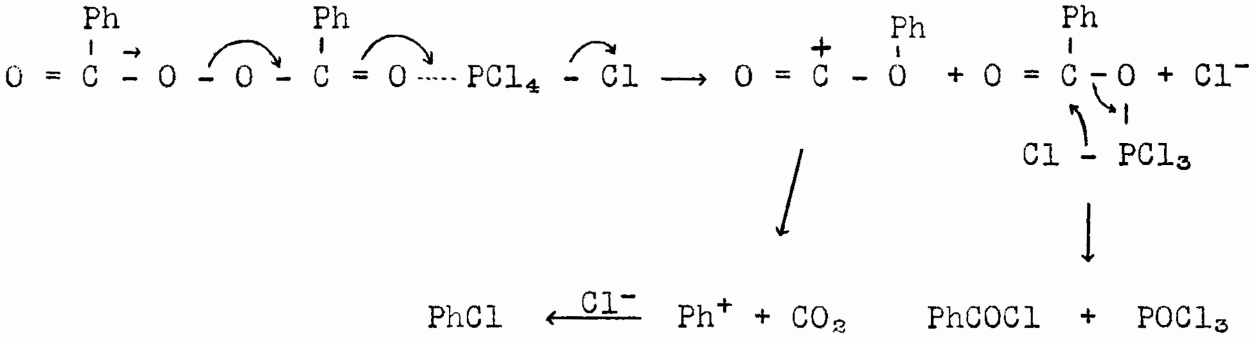


(10)

Reynhart(3) found that dibenzoyl peroxide heated alone with phosphorus pentachloride reacted chiefly according to the equation:

$$(PhCOO)_2 + PCl_5 \longrightarrow PhCl + CO_2 + PhCOCl + POCl_3 \qquad (11)$$

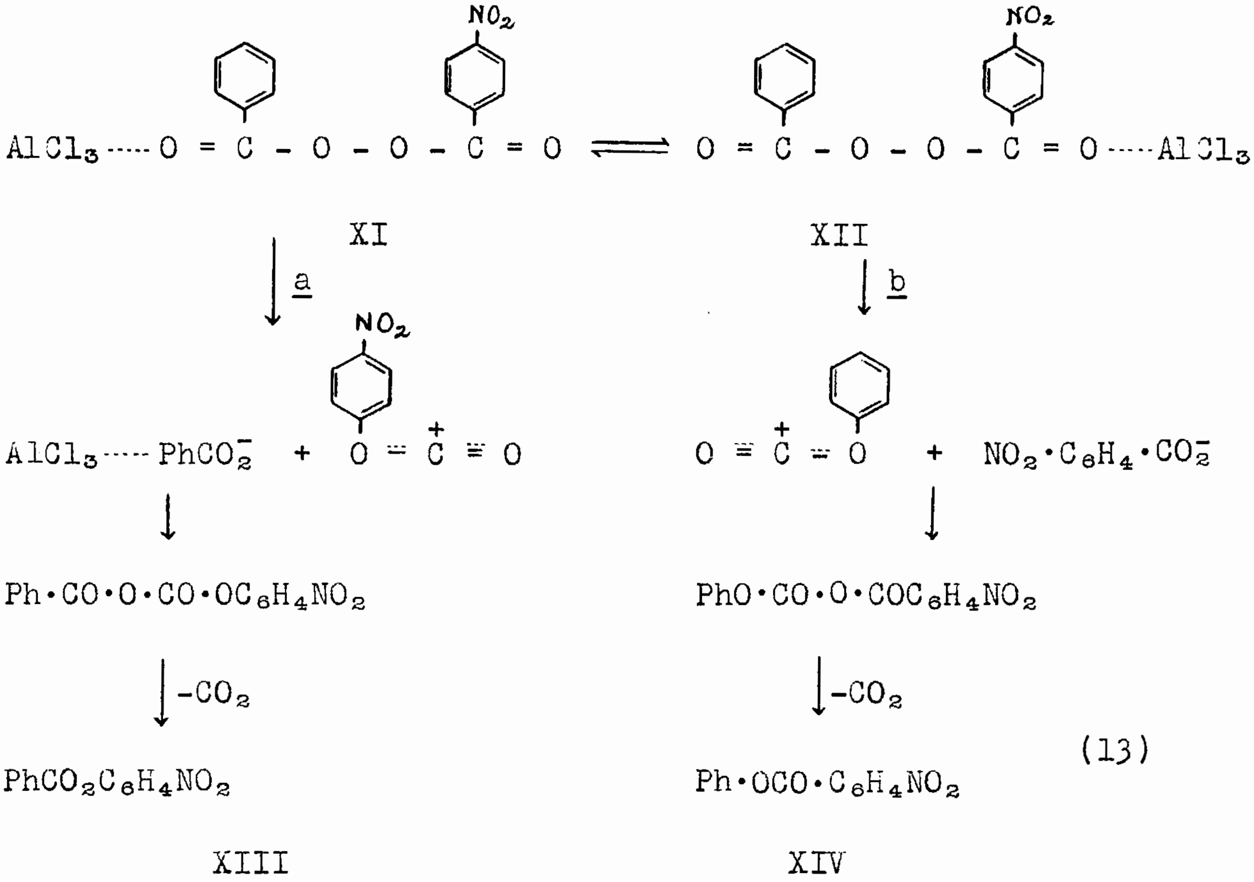
Again an ionic mechanism is possible:



(12)

Rearrangements of Unsymmetrical Peroxides.

The decomposition of the mixed peroxide, benzoyl p-nitrobenzoyl peroxide, in methylene chloride in the presence of aluminium chloride was next studied. This reaction is of interest because the nature of the product should be determined by two competing reactions, a and b:



(13)

Reaction a should be favoured by the greater basicity of the carbonyl group adjacent to phenyl, and hence by a greater concentration of the complex (XI) than of (XII); however, the heterolysis of the peroxide linkage of (XII) might be expected to take place more readily than that of (XI), because the anchimeric assistance of the phenyl group is superior to that of the nitrophenyl group (cf. p. 16). In the event, the rearrangement took mainly the course b, as evidenced by the isolation of a yield of 81% of phenyl p-nitrobenzoate (XIV) and of no p-nitrophenyl benzoate (XIII).

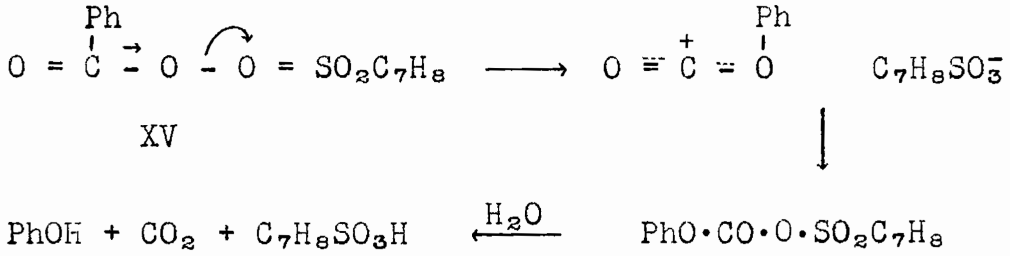
The small yield (12%) of p-nitrobenzoic acid probably arose *via* the anhydride, according to equation 8.

The decomposition of this peroxide in benzene and in nitrobenzene did not follow such a clear-cut path. The yield of p-nitrobenzoic acid was considerably larger and of neutral product considerably smaller. From the latter an impure material was obtained which appeared, from its infrared spectrum, to contain phenyl p-nitrobenzoate, but which could not be purified further. It is possible that the decomposition of the intermediate mixed anhydride according to equation 8 takes place more extensively in these solvents than in methylene chloride.

The decomposition of benzoyl p-toluenesulphonyl peroxide (XV), assumed to be formed by the reaction of sodium perbenzoate with p-toluenesulphonyl chloride:

$$C_6H_5CO\cdot OONa + C_7H_8SO_2Cl \longrightarrow \underset{\text{XV}}{C_6H_5CO\cdot OO\cdot SO_2C_7H_8} + NaCl \quad (14)$$

was next investigated. Dibenzoyl peroxide and a small quantity of phenol (identified as the tribromo derivative) were isolated from the reaction. The isolation of phenol indicates that the unsymmetrical peroxide rearranges under the conditions of the reaction:



$$\begin{tikzcd} O=\overset{Ph}{C}-O-O=SO_2C_7H_8 \arrow[r] & O\equiv\overset{+}{C}=\overset{Ph}{O}\quad C_7H_8SO_3^- \arrow[d] \\ PhOH + CO_2 + C_7H_8SO_3H & PhO\cdot CO\cdot O\cdot SO_2C_7H_8 \arrow[l, "H_2O"'] \end{tikzcd} \qquad (15)$$

XV

The small yield of phenol is to be expected, in view of its susceptibility to oxidation in the reaction medium. The dibenzoyl peroxide probably arises from the benzoylation of sodium perbenzoate by benzoyl p-toluenesulphonyl anhydride (XVI), formed as shown:

$$\begin{tikzcd} Ph\cdot CO\cdot OO^- Na^+ \arrow[r] & Ph\cdot CO\cdot O^- Na^+ \;+\; 1/2\ O_2 \arrow[d, "C_7H_8SO_2Cl"] \\ & PhCO\cdot O\cdot SO_2C_7H_8 \;+\; NaCl \quad \text{XVI} \arrow[d, "Ph\cdot CO\cdot OONa"] \\ & PhCO\cdot OO\cdot COPh \;+\; C_7H_8SO_3Na \end{tikzcd} \qquad (16)$$

This instability (under the conditions of its formation) of benzoyl p-toluenesulphonyl peroxide (XV) contrasts with the stability of acetyl cyclohexanesulphonyl peroxide, which can be isolated as a crystalline compound$^{(14)}$, and is probably due to two reasons:

1. The latter peroxide is prepared by irradiation of a mixture of acetic anhydride, cyclohexane, sulphur dioxide and oxygen, i.e. in a relatively non-polar medium; while the preparation of the former was attempted in water, a medium which should favour the heterolytic fission of the peroxide.

2. This heterolysis should also receive more anchimeric assistance from a migrating phenyl group than from a migrating methyl group (cf. p. 29).

Rearrangement and Friedel-Crafts Reaction of Bis(p-nitrobenzoyl)peroxide.

The p-nitrophenyl group, because of the electron-withdrawing properties of the nitro group, should provide much less anchimeric assistance than the phenyl group to the heterolysis of the peroxide linkage. This accords with its lesser migratory aptitude compared to the phenyl group (p. 16), and suggests that bis(p-nitrobenzoyl)peroxide might rearrange less readily in the presence of aluminium chloride than dibenzoyl peroxide, the greater tendency of the p-nitrobenzoyloxy group to break away as a benzoate ion being more than counterbalanced by the lesser tendency of the rearranging p-nitrobenzoyloxy cation to be formed. Under such circumstances it seemed possible that Friedel-Crafts attack of sufficiently nucleophilic aromatic compounds on the peroxide linkage might take place, according to equation 2 ($O_2N \cdot C_6H_4$ in place of Ph) (p.70). This anticipation was realized, as shown in Table II. However, it is obvious from the high yields of p-nitrobenzoic acid that a competing

TABLE II

Products of the reaction of bis(p-nitrobenzoyl)peroxide aluminium chloride in different aromatic solvents

Solvent	p-Nitrobenzoate Identity	p-Nitrobenzoate Yield(%)	Yield* of p-nitrobenzoic acid
m-xylene	2,4-dimethylphenyl	5	72
mesitylene	mesityl	34	68
anisole	2-methoxyphenyl	7	57
	4-methoxyphenyl	21	
phenetole	2-ethoxyphenyl	10	
	4-ethoxyphenyl	12	54
veratrole	(trace)		77
resorcinol dimethyl ether	2,4-dimethoxyphenyl	20	59

---

* based on $(O_2N \cdot C_6H_4 \cdot COO)_2 \longrightarrow 2\ O_2N \cdot C_6H_4 \cdot CO_2H$

oxidation reaction is taking place, although in no case were the expected biaryls isolated. (The yield of p-nitrobenzoic acid is based on the equation:

$$(O_2N{\cdot}C_6H_4{\cdot}COO)_2 \longrightarrow 2\ O_2N{\cdot}C_6H_4{\cdot}CO_2H$$

Evidently the maximum yield obtainable from the Friedel-Crafts type reaction is 50%).

The identities of the p-nitrobenzoates obtained from anisole, phenetole, and m-xylene (Table II) were established by comparison with authentic specimens prepared by the reaction of p-nitrobenzoyl chloride with the appropriate phenols. The p-nitrobenzoate obtained from resorcinol dimethyl ether was shown to be 2,4-dimethoxyphenyl p-nitrobenzoate by being different from the other two possible isomers, 2,6-dimethoxyphenyl and 3,5-dimethoxyphenyl p-nitrobenzoates, both of which were synthesized from the phenols. The structure of the p-nitrobenzoate obtained from mesitylene was not proved, but seems overwhelmingly probable. All the p-nitrobenzoates, except those obtained from anisole, are new compounds. The orientation of substitution revealed by these different products is in accord with an electrophilic attack on the aromatic nucleus, as required by the mechanism in equation 2.

Without fairly strongly electron-releasing substituents, the benzene ring is insufficiently reactive to undergo this type of Friedel-Crafts substitution, as shown by the low yield of substitution product obtained from m-xylene. A suspension of bis(p-nitrobenzoyl)peroxide in benzene in the presence of aluminium chloride at room temperature was attacked only very slowly, 21% of p-nitrobenzoic acid being obtained, and 70% of the peroxide being recovered after 48 hours. The neutral residue after removal of benzene showed strong absorption at 1748 cm^{-1} indicative of an ester carbonyl group, which might be due to a product of rearrangement or to Friedel-Crafts substitution, but no crystalline product could be isolated. On the other hand, in methylene dichloride a 65% yield of the rearrangement product, p-nitrophenyl p-nitrobenzoate was obtained. The occurrence of rearrangement so much more readily in methylene dichloride than in benzene may be due to the greater solubility of the peroxide and of aluminium chloride in the former solvent.

Attempts to effect Friedel-Crafts substitution of naphthalene by using nitrobenzene and nitromethane as solvents gave only gummy and intractable neutral products. Even the reaction of resorcinol dimethyl ether with the peroxide gave an intractable product when carried out in methylene chloride solution. It is to be expected that the bimolecular reaction of peroxide with an aromatic compound will be disfavoured by dilution with an inert solvent, as compared with the unimolecular decomposition of the peroxide.

However, it was not possible to isolate p-nitrophenyl p-nitrobenzoate from this reaction. The failure to carry out a Friedel-Crafts reaction of bis(p-nitrobenzoyl)peroxide in a solvent represents a very severe limitation of its usefulness.

The fact that bis(p-nitrobenzoyl)peroxide could take part in either a rearrangement or a Friedel-Crafts reaction, depending on the solvent, suggested that with dibenzoyl peroxide the Friedel-Crafts reaction might compete successfully with the rearrangement reaction in a sufficiently reactive solvent. Such was found to be the case in resorcinol dimethyl ether, a very small yield of 2,4-dimethoxyphenyl benzoate (Table I) being obtained. When the reaction was carried out in mesitylene a high-boiling liquid mixture was obtained which showed strong absorption at 1740 cm^{-1} indicative of an ester carbonyl group, but no crystalline product could be isolated.

Reaction of Dibenzoyl Peroxide with Grignard Reagents and Organolithium Compounds.

The limitations of the Friedel-Crafts reaction suggested that possibly the benzoyloxy group might with advantage be introduced into aromatic nuclei *via* their magnesium or lithium derivatives:

$$RMgX + (PhCOO)_2 \longrightarrow PhCOOR + PhCO_2MgX \qquad (17)$$

$$RLi + (PhCOO)_2 \longrightarrow PhCOOR + PhCO_2Li \qquad (18)$$

(The Grignard reagent is shown for convenience in the conventional formula, now known to be incorrect(15).) Gilman and Adams(16) reported a 30% yield of phenyl benzoate from the reaction of phenylmagnesium bromide with dibenzoyl peroxide. We have obtained 15-44% yields of benzoate esters from four different Grignard reagents. The yield of phenyl benzoate was decreased when the reaction of phenylmagnesium bromide with peroxide was run in the presence of additional magnesium bromide. This finding, and the high yields of

TABLE III

Yields from reactions of dibenzoyl peroxide with Grignard Reagents RMgBr

R	Yield of ester (%)*	Yield of benzoic acid(%)+
n-butyl	20	80
cyclohexyl	44	71
phenyl	23	72
p-biphenylyl	15	51

* Based on equation 17.

\+ Based on: $Bz_2O_2 \rightarrow 2\ BzOH$.

benzoic acid, have since received an explanation from the work of Lawesson and Yang(17), published since our investigation was completed. Lawesson and Yang found that the Grignard reagent, shown by Dessy(15) to have the formula $R_2Mg \cdot MgBr_2$, may react in two different ways:

1. to give benzoate ester and benzoic acid:

$$R_2Mg + 2(PhCOO)_2 \longrightarrow 2\ PhCOOR + (PhCOO)_2Mg \qquad (19)$$

From this reaction the maximum yield of benzoic acid (based on $(PhCOO)_2 \longrightarrow 2\ PhCO_2H$) can only be 50%.

2. to give alkyl or aryl bromide and benzoic acid (maximum yield, 100%):

$$2\ MgBr_2 + 2(PhCOO)_2 \longrightarrow 2\ Mg(OCOPh)_2 + 2\ Br_2 \qquad (20)$$

$$2\ Br_2 + R_2Mg \longrightarrow 2\ RBr + MgBr_2 \qquad (21)$$

$$MgBr_2 + R_2Mg + 2(PhCOO)_2 \longrightarrow 2\ Mg(OCOPh)_2 + 2\ RBr \qquad (22)$$

Thus the results with cyclohexylmagnesium bromide (Table III) indicate that in this case reaction 19 and reaction 22 are of almost equal importance, while those with n-butylmagnesium bromide indicate that with this reagent reaction 22 becomes more important than reaction 19.

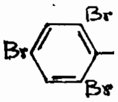
From the reaction of p-biphenylylmagnesium bromide was obtained a 9% yield of quaterphenyl; however, part or all of this may have been formed from p-bromobiphenyl by a coupling reaction during the formation of the Grignard reagent.

Because organolithium compounds are frequently easier to prepare than organomagnesium compounds, a few experiments were carried out with them, but they appeared to be markedly inferior for the present purposes. Phenylithium reacted with dibenzoyl peroxide to give a 71% yield of triphenylcarbinol and 10% of tribromophenol. The latter may be formed by the sequence of reactions:

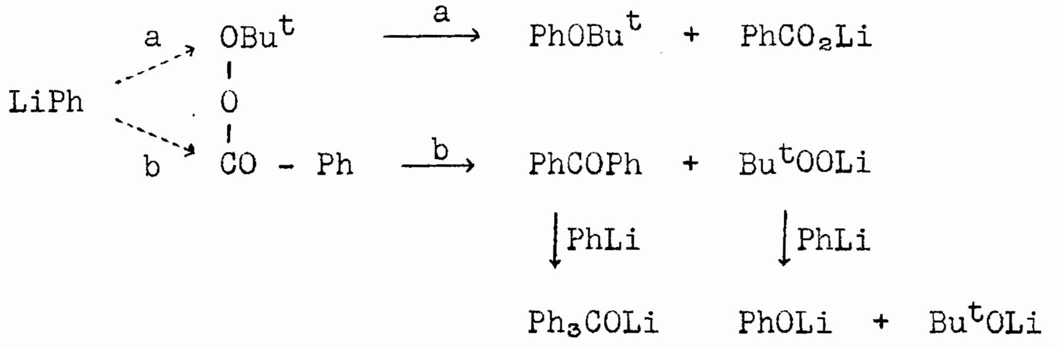
$$\mathrm{PhLi} + (\mathrm{PhCOO})_2 \longrightarrow \mathrm{PhCOPh} + \mathrm{Ph{\cdot}CO{\cdot}OOLi} \qquad (23)$$

$$\mathrm{PhCOOOLi} + \mathrm{PhLi} \longrightarrow \mathrm{PhCO_2Li} + \mathrm{PhOLi} \qquad (24)$$

$$6\ \mathrm{LiBr} + 3(\mathrm{PhCOO})_2 \longrightarrow 6\ \mathrm{PhCOOLi} + 3\ \mathrm{Br_2} \qquad (25)$$

$\mathrm{PhOLi} + 3\ \mathrm{Br_2} \longrightarrow$  OH + LiBr + 2 HBr (26)

although various alternative reaction sequences may be envisaged. The reaction of phenylithium with t-butyl perbenzoate at 0-5°C afforded 41% of phenyl t-butyl ether, 41% of t-butyl alcohol, 28% of phenol, 28% of benzoic acid, and 12% of triphenylcarbinol. Lawesson and Yang(17) obtained 59% of phenyl t-butyl ether from this reaction run at -60°. It is evident that nucleophilic attack of phenyllithium may take place about equally readily either on the peroxide oxygen (reaction a) or on the carbonyl carbon (reaction b):



$$\begin{array}{llll} & \overset{a}{\dashrightarrow}\ \mathrm{OBu^t} & \xrightarrow{a} & \mathrm{PhOBu^t} + \mathrm{PhCO_2Li} \\ \mathrm{LiPh} & \qquad \mathrm{O} & & \\ & \overset{b}{\dashrightarrow}\ \mathrm{CO-Ph} & \xrightarrow{b} & \mathrm{PhCOPh} + \mathrm{Bu^tOOLi} \\ & & & \ \ \downarrow \mathrm{PhLi} \qquad\quad \downarrow \mathrm{PhLi} \\ & & & \mathrm{Ph_3COLi} \quad \mathrm{PhOLi} + \mathrm{Bu^tOLi} \end{array} \qquad (27)$$

In the reaction of phenylmagnesium bromide route a is more favoured, yields of 67% of phenyl t-butyl ether and 85% of benzoic acid being obtained. (Lawesson and Yang(17) reported yields of 65% and 80-90% respectively).

It is evident that the introduction of the benzoyloxy group *via* the bromomagnesium form of the Grignard reagent goes in poor yields. However, the discovery by Lawesson and Yang of the important competing reaction (equations 20-22) raises the possibility of improving yields: e.g., by using chloromagnesium Grignard reagents. This possibility is being currently explored in this laboratory.

Reaction of Bis(p-nitrobenzoyl)peroxide with Phenols.

The availability of bis(p-nitrobenzoyl)peroxide, prepared for the Friedel-Crafts experiments described above, led us to investigate its usefulness for the oxidation of phenols according to the procedure of Cosgrove and Waters(18) (cf. p. 48). It was anticipated that the reaction might take place more readily, and that the products formed might crystallize more easily than those from dibenzoyl peroxide. In fact, the reactivities of the two peroxides appear not to be notably different, although no detailed comparison was made. Thus, the oxidation of p-nitrophenol by bis(p-nitrobenzoyl)peroxide was excessively slow, the peroxide being 98% recovered after seven hours reaction in refluxing chloroform. This would appear to indicate that the phenolic oxygen attacks the peroxide linkage as a nucleophile, and that the p-nitro group of the phenol reduces its nucleophilicity.

TABLE IV

Yields of products from the reactions of phenols with bis(p-nitrobenzoyl)peroxide

Phenol	Yield of ester (%)	Yield of p-nitrobenzoic acid (%)*
p-Cresol	44	61
p-Bromophenol	16	80
α-Naphthol	40	62
β-Naphthol	80	59

* Based on: $(ArCOO)_2 \longrightarrow 2\ ArCO_2H$

On the other hand, reaction of bis(p-nitrobenzoyl)peroxide with phenol and with p-methoxyphenol took place readily, but led to the formation of large amounts of p-nitrobenzoic acid (90% and 91% respectively) and to no isolable quantity of ortho-substituted phenol. Some phenols which did react with bis(p-nitrobenzoyl)peroxide to yield useful quantities of ortho-substituted derivatives are listed in Table IV.

It may be noted that high yields of p-nitrobenzoic acid are associated with low yields of ortho-substituted phenols, and *vice versa*. This relationship is to be expected. The reaction giving the substituted phenol, can give a

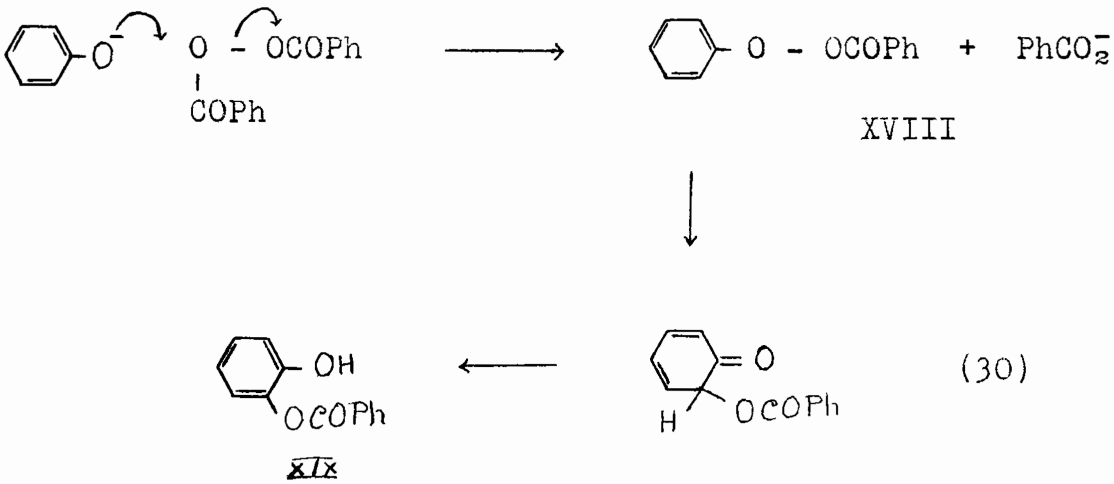
$$C_6H_5OH + (ArCOO)_2 \longrightarrow \underline{o} - ArCOO\cdot C_6H_4\cdot OH + ArCO_2H \qquad (28)$$

maximum yield of only 50% of p-nitrobenzoic acid, $ArCO_2H$ (based on $(ArCOO)_2 \longrightarrow 2\ ArCO_2H$), while the oxidative coupling reaction as well as subsequent oxidation of XVII to

$$2\ C_6H_5OH + (ArCOO)_2 \longrightarrow \underset{XVII}{HO\cdot C_6H_4\cdot C_6H_4\cdot OH} + 2\ ArCO_2H \qquad (29)$$

quinones(19), etc. can give a maximum yield of 100% of p-nitrobenzoic acid. Consequently, the yields of the acid may be expected to vary between 50% and 100%, according to whether reaction 28 or 29 is favoured.

Lithium phenoxide is a far more powerful nucleophile than phenol, and hence the reaction of lithium phenoxide with dibenzoyl peroxide was expected to give a good yield of catechol monobenzoate (XIX), via Walling and Hogdon's(20) intermediate (XVIII):



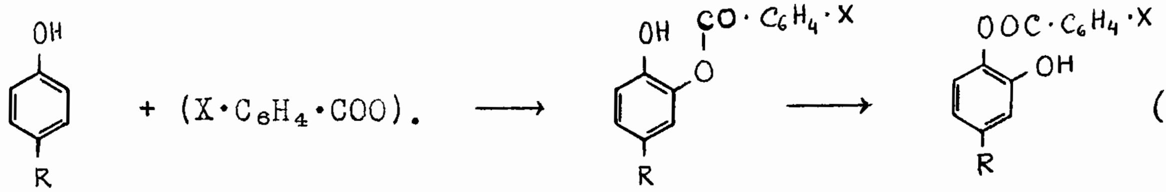
XVIII

XIX

(30)

Reaction took place under relatively mild conditions, but no catechol monobenzoate could be separated from the phenolic fraction in the reaction mixture.

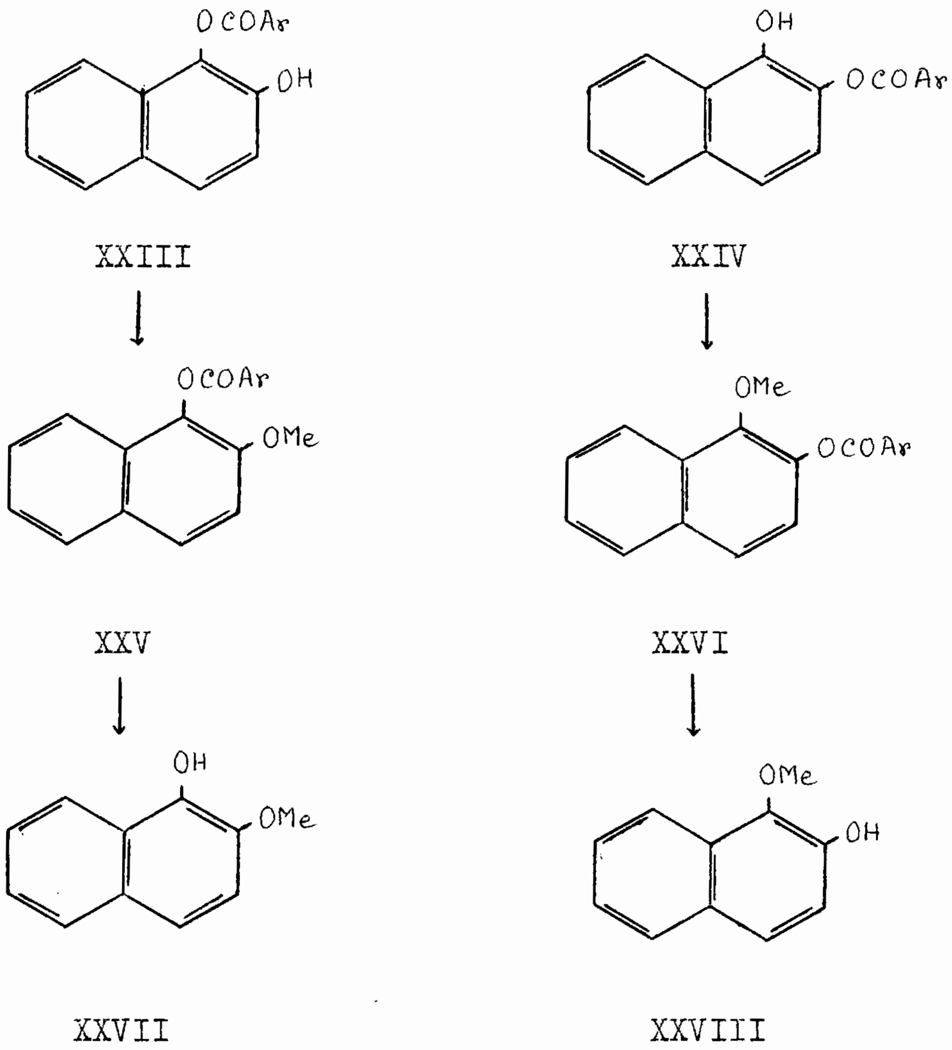
The nitro-ester obtained from p-cresol (XX; R = Me) in slightly better yield (44%) than the corresponding ester (XXII; R = Me, X = H) obtained by Cosgrove and Waters(18) using dibenzoyl peroxide (35%), probably also has the m-cresol formula (XXII; R = Me, X = NO_2), because it slowly gives a



XX XXI XXII (31)

greenish colour on treatment with p-aminodimethyl aniline and sodium hypochlorite, very similar to the colour given by (XXII; R = Me, X = H). This colour reaction is considered to be diagnostic of a free <u>para</u> position of a phenol$^{(18)}$. On the other hand, no colour was given by the product obtained from <u>p</u>-bromophenol (XX; R = Br), which may indicate that it has the structure (XXI; R = Br, X = NO_2). However, the results of such colour reactions can be considered only very tentative indications.

Dibenzoyl peroxide oxidized β-naphthol to give a 63% yield of benzoic acid, but no crystalline phenolic product could be obtained. On the other hand, bis(<u>p</u>-nitrobenzoyl)peroxide reacted with both α- and β-naphthol to give good yields of a single <u>p</u>-nitrobenzoyloxy derivative, which must consequently have the formula (XXIII; Ar = $C_6H_4{\cdot}NO_2$) or (XXIV; Ar = $C_6H_4{\cdot}NO_2$), the original compound



in one reaction undergoing an acyl migration. An attempt was made to establish the structure by methylating the naphthol with diazomethane, under conditions so mild that further aycl migration is most unlikely, to give the methyl ether (XXV or XXVI); this was then hydrolysed to a methoxy naphthol melting at 90°. This is most probably α-methoxy-β-naphthol (XXVIII), for which a melting point of 90.5° is reported(21); however, the alternative β-methoxy - α-naphthol (XXVII) is not reported, and might conceivably also have a melting point of 90°. Consequently, the methoxynaphthol was benzoylated, in the hope that its melting point would be sufficiently different from that reported for β-methoxy- α-naphthyl benzoate (XXV; Ar = Ph) (110°)(22) to establish the structure XXVI (Ar = Ph)(a compound not yet reported). In fact, the methoxynaphthyl benzoate melted at 107°. The structure (XXIV; Ar = $C_6H_4 \cdot NO_2$) for the oxidation product thus cannot be considered as more than tentative at the moment, but could be confirmed by a comparison of the methoxynaphthyl benzoate, m.p. 107°, with authentic β-methoxy- α-napthyl benzoate.

Reaction of Benzoyl p-Nitrobenzoyl Peroxide with Phenols.

The reaction of tri-n-butylphosphine with benzoyl p-nitrobenzoyl peroxide takes place by nucleophilic attack on the more positive peroxide oxygen adjacent to the p-nitrobenzoyl group(23). Consequently, it was expected that if the attack of a phenol on this peroxide also took place by nucleophilic attack on oxygen, the p-nitrobenzoyloxy rather than benzoyloxy derivative of the phenol, and benzoic rather than p-nitrobenzoic acid would be formed. The oxidation of p-cresol with the unsymmetrical peroxide gave a mixture of benzoic acid and p-nitrobenzoic acids, in the proportion of about 3:17 (respectively), and a gummy phenolic fraction from which a 13% yield of the p-nitrobenzoyloxy derivative (XXII; R = Me, X = NO_2) could be obtained. The remaining product could not be purified by distillation at 270°/0.1 mm. or by chromatograph on alumina or paper.

The results of the oxidation of β-naphthol with the mixed peroxide were similar, a mixture of benzoic and p-nitrobenzoic acids, in the proportion of 7:13 and an 11% yield of 2-p-nitrobenzoyloxy-1-naphthol being isolated. However, considerably larger quantities of tarry material were obtained, which could not be separated into pure compounds by chromatography on alumina or by distillation at reduced pressure up to 275°/0.1 mm.

It can thus be seen that in each case the p-nitrobenzoyloxy rather than benzoyloxy derivative of the phenol was formed, as expected. However, the reactions were much less clean-cut than that of the phosphine, and mixtures of benzoic and p-nitrobenzoic acids were formed, probably by concurrent processes involving coupling of phenols, etc.

Oxidation of Secondary Aromatic Amines with Diaroyl Peroxides.

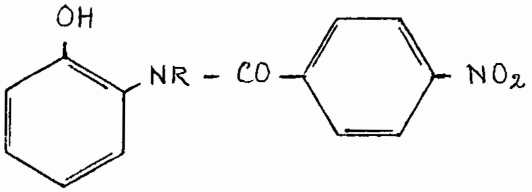
The oxidation of several aromatic secondary amines with bis(p-nitrobenzoyl)peroxide was next investigated

(Table V). Yields of phenolic products were slightly higher than those obtained using dibenzoyl peroxide(24). These phenols are assumed all to have the structure

TABLE V

Yields of products from the reaction of amines with bis(p-nitrobenzoyl)peroxide

Amine	Yield of phenol(%)	Yield of p-nitrobenzoic acid
N-Methylaniline	38	55
N-Ethylaniline	45	59
N-Butylaniline	42	65
Diphenylamine	52	55



XXIX

XXIX. The phenol (XXIX; R = Et) derived from N-ethylaniline showed a marked tendency to crystallize from benzene, toluene or bromobenzene with a certain amount of firmly-held solvent, probably entrapped by clathrate formation, which is known to be particularly easy with crystals of phenolic materials(25).

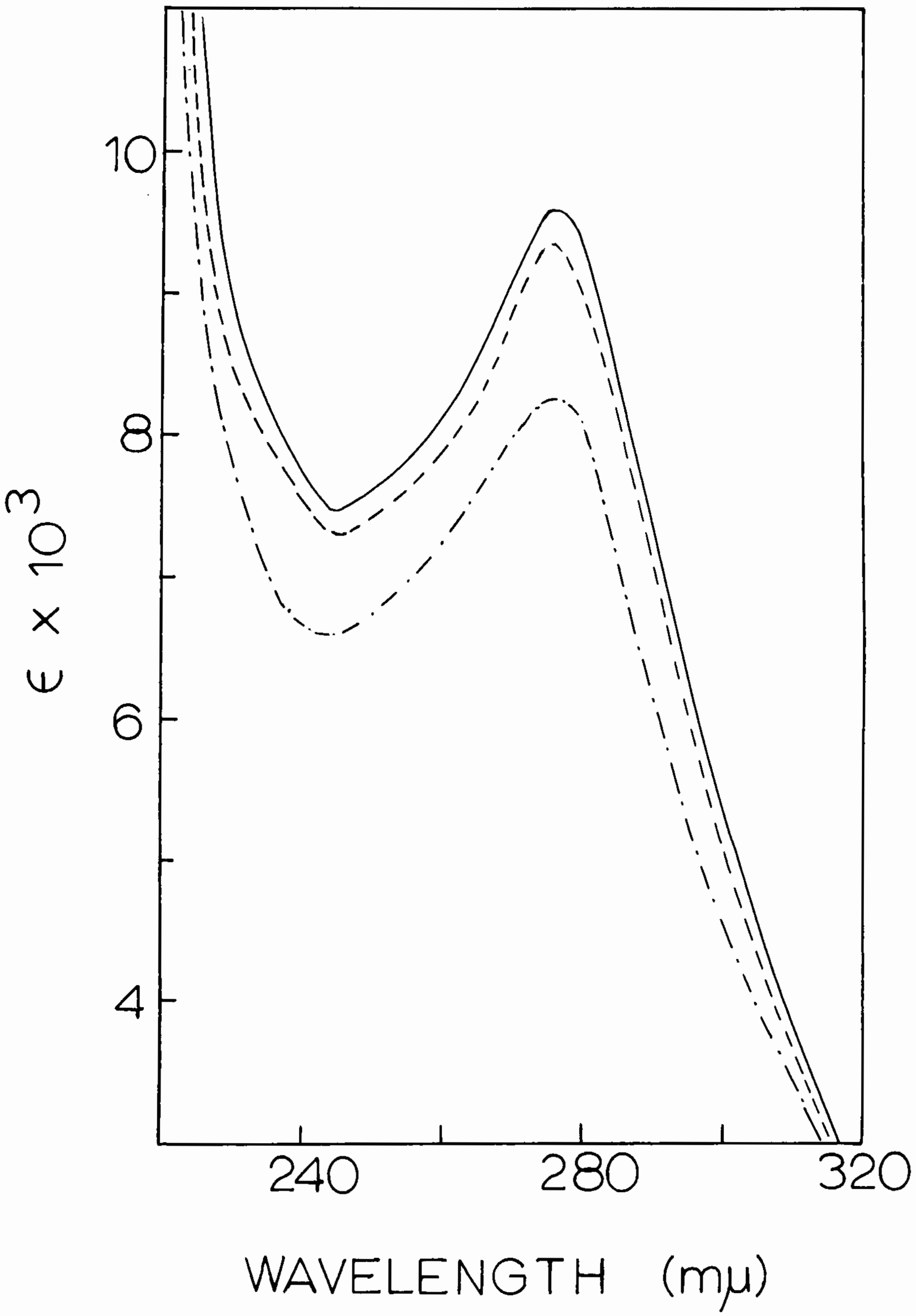
The ultraviolet absorption spectra of o-(N-ethyl-p'-nitrobenzamido)phenol (XXIX; R = Et), o-(N-methyl-p'-nitrobenzamido)phenol (XXIX; R = Me), and o-(N-butyl-p'-nitrobenzamido)phenol (XXIX; R = Bu), all crystallized from benzene and dried at 20°/1 mm., are shown in Fig. 1. On the assumption that the molar extinction coefficient of the N-ethyl compound should be the mean of those of the N-methyl and N-butyl compound, the lower absorption of the N-ethyl compound may be explained by the inclusion of 3.2 molecules of the weakly-absorbing benzene(26) for each six molecules of phenol. When the N-ethyl compound (XXIX; R = Et) was dried at 80°/1 mm., the amount of benzene (estimated by elemental analysis) dropped to one molecule for six molecules of phenol. No solvent was trapped when this phenol was crystallized from alcohol.

The reaction of diphenylamine with benzoyl p-nitrobenzoyl peroxide might be expected to give o-(N-phenyl-p-nitrobenzamido)phenol (XXIX; R = Ph) and benzoic acid (cf. p.97). Instead, it gave a mixture of phenolic compounds, from which (XXIX; R = Ph) was isolated in 17% yield, and a mixture of benzoic and p-nitrobenzoic acids in the ratio of about 1:2. Analysis indicated that the phenolic material was not a simple mixture of (XXIX; R = Ph) and of o-N-phenylbenzamidophenol; the nature of the other phenolic compounds is at present obscure.

Figure 1

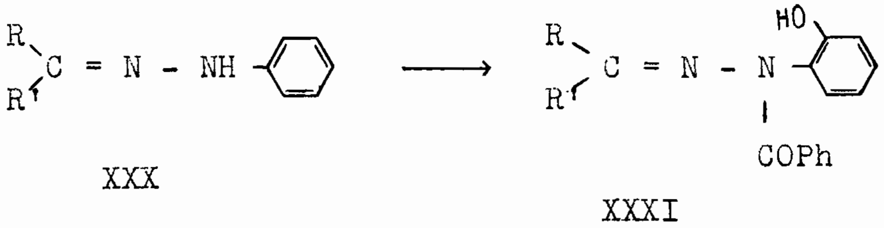
Ultraviolet absorption spectra in absolute ethanol of the following phenols:

o-(N-Butyl-p'-nitrobenzamido)phenol	(———)
o-(N-Methyl-p'-nitrobenzamido)phenol	(-----)
o-(N-Ethyl-p'-nitrobenzamido)phenol	(-.-.-.)


10
8
6
4
ϵ × 10^3
240
280
320
WAVELENGTH (mμ)

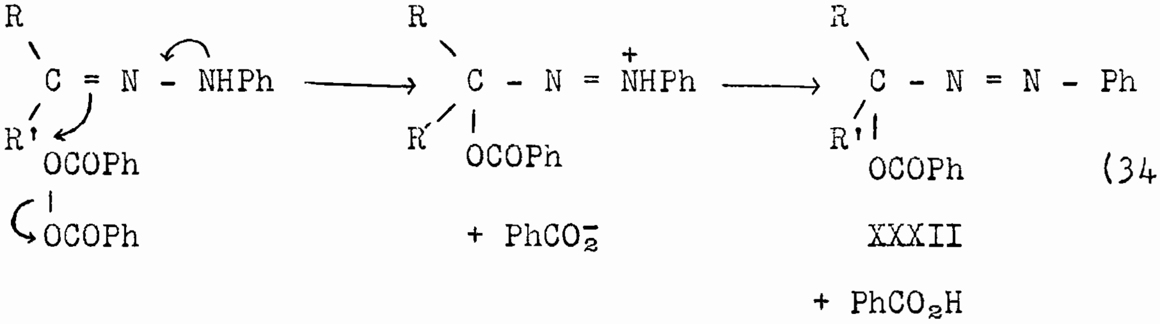
Oxidation of Phenylhydrazones with Dibenzoyl Peroxide.

The oxidation of phenylhydrazones (XXX) with dibenzoyl peroxide was investigated with the expectation of obtaining o-hydrazinophenolic derivatives (XXXI):



(33)

However, phenolic products were not obtained. The product of the oxidation of benzophenone phenylhydrazone (XXX; R = R' = Ph) was a neutral yellow solid, $C_{26}H_{20}O_2N_2$, having absorption maxima at 271 $m\mu$ and 400 $m\mu$ (ϵ_{max} 8030 and 222 respectively) (Fig. 2). This spectrum indicates a phenylazo chromophor, phenylazomethane having λ_{max} 261, 404 $m\mu$, ϵ_{max} 8000, 90(27), and hence the structure (XXXII; R = R' = Ph) formed by the reaction sequence:



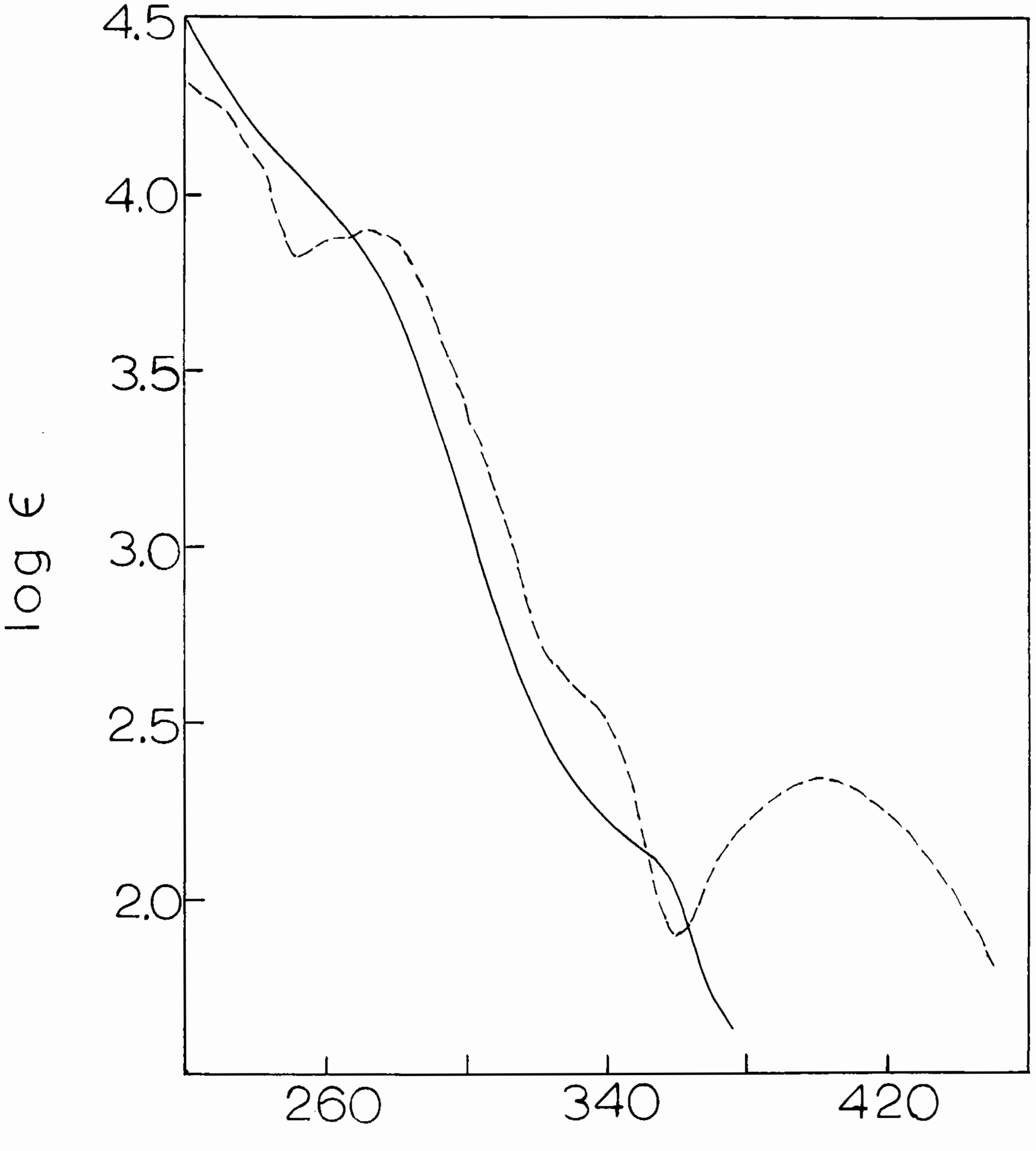
(34)

Figure 2

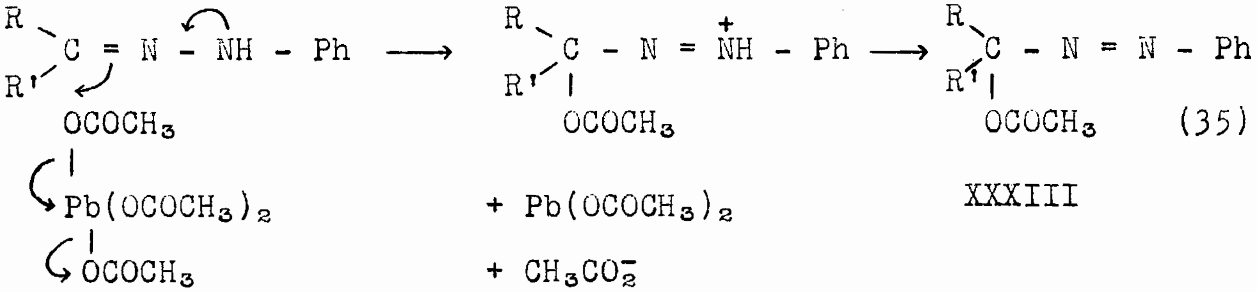
Ultraviolet absorption spectra of ethanolic solutions of:

α,β -Dibenzoyl- α -phenylhydrazine (————)

and Phenylazodiphenylcarbinol Benzoate (-------)

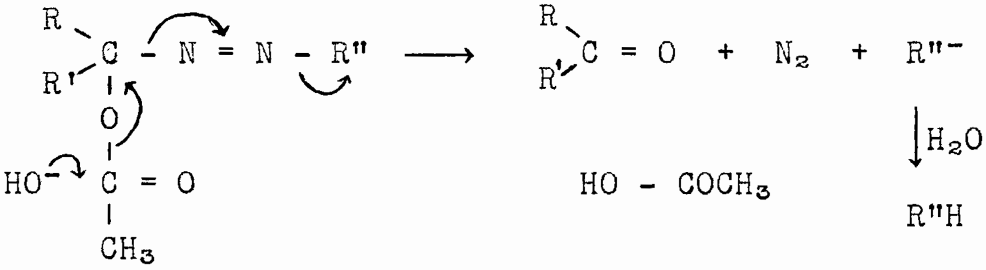

4.5
4.0
3.5
3.0
2.5
2.0
log ∊
260
340
420
WAVELENGTH (mμ)

Recently a series of closely-similar phenylazo acetates (XXXIII) have been reported from the oxidation of phenylhydrazones with lead tetraacetate(28), a compound known to be very similar to diaroyl peroxides in its oxidizing action(29):


(35)

XXXIII

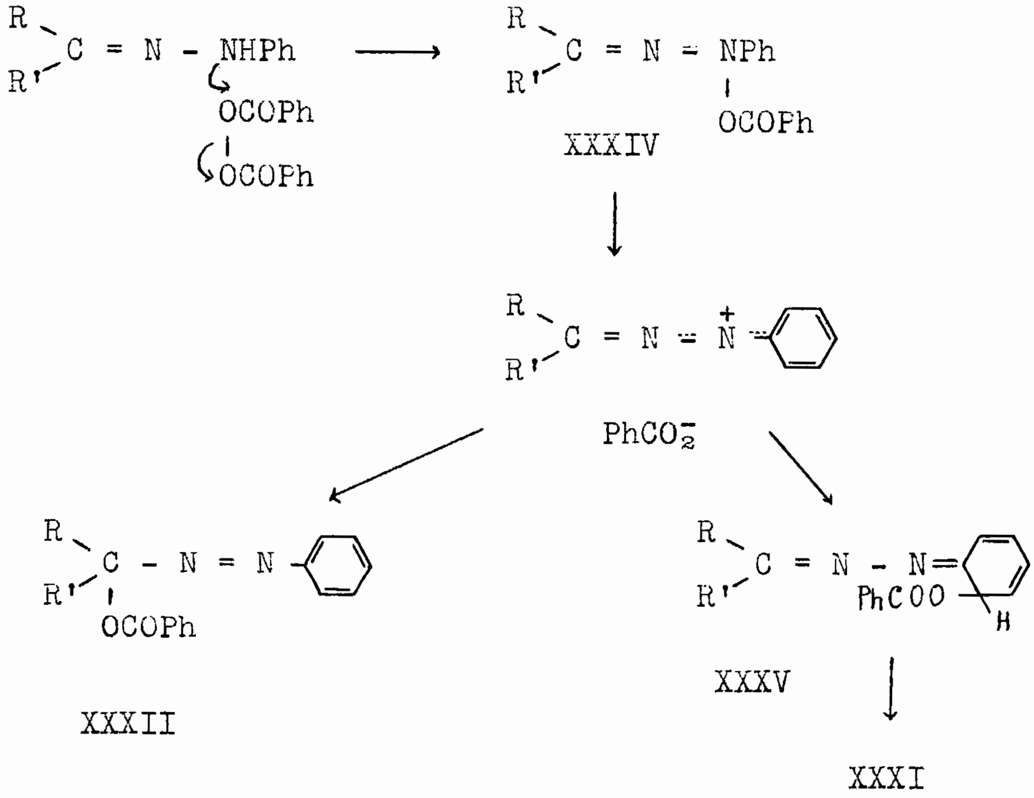
These compounds are reported as having λ_{max} 266-279 $m\mu$, ϵ_{max} 10,000-40,000. They are hydrolysed in alkaline solution to acetic acid, the parent carbonyl compound, and the hydrocarbon corresponding to the original hydrazone(28):


(36)

We have found that our compound $C_{26}H_{20}O_2N_2$ is hydrolysed by alkali to benzoic acid (85%) and benzophenone (54%;

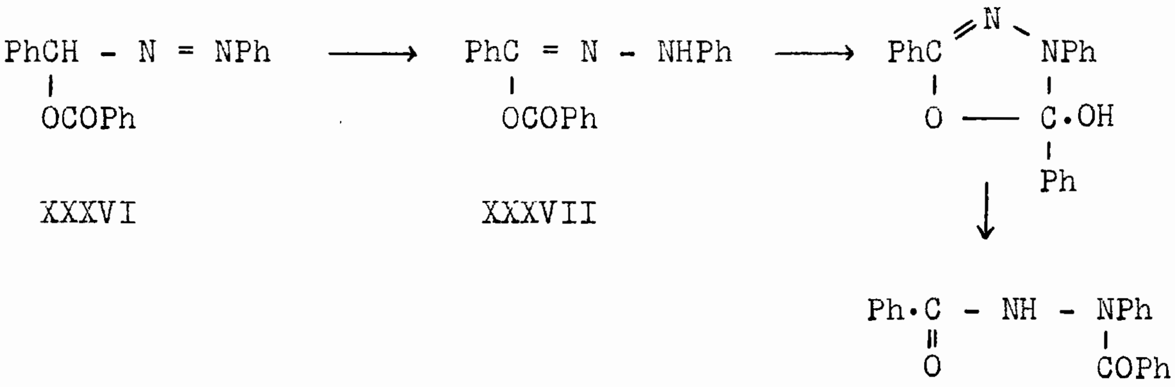
isolated as 2,4-dinitrophenylhydrazone) in harmony with the structure (XXXII; R = R' = Ph).

While reaction 34 presents a possible mechanism for the formation of the azo compound (XXXII; R = R' = Ph), another possible mechanism would involve the hydroxylamine derivative (XXXIV), ionizing in a fashion similar to that proposed by Denney and Denney(30) in the oxidation of diphenylamine:



The route from this intermediate to the product (XXXII; R = R' = Ph) would be more favourable than that to the phenol (XXXI; R = R' = Ph), because the formation of the latter involves the high-energy quinonoid intermediate (XXXV; R = R' = Ph) in which much of the resonance energy of a benzene ring is lost.

The oxidation of benzaldehyde phenylhydrazone (XXX; R = Ph, R' = H) also gave a non-phenolic compound, which had the formula $C_{20}H_{16}O_2N_2$. However, this compound lacked the ultraviolet absorption peaks characteristic of the phenylazo group (Fig. 2), and showed several infrared absorption peaks (at 3420 (m), 1670 (s), 1585 (w) cm^{-1}) which could be attributed to an amide grouping(31). It was identified as α,β-dibenzoylphenylhydrazine (XXXVIII), probably formed from the initially-produced phenylazo compound (XXXVI):

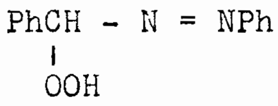


XXXVI

XXXVII

XXXVIII

The prototropic tautomerization of azo compounds to the more stable hydrazones (e.g. XXXVI ⟶ XXXVII) is well-known(32); however, it is interesting to speculate on why it should take place with the product (XXXVI) of the oxidation of benzaldehyde phenylhydrazone with dibenzoyl peroxide, and not with the hydroperoxide (XXXIX) formed by the autoxidation of this hydrazone(33). It is possible that the formation of benzoic acid in the former reaction



$$\underset{\mathrm{OOH}}{\mathrm{PhCH}} - \mathrm{N} = \mathrm{NPh}$$

XXXIX

may furnish a catalyst acid enough to catalyze the tautomerization, and that by conducting the reaction with dibenzoyl peroxide in a buffered medium the azo compound (XXXVI) might be isolated.

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CHAPTER III

EXPERIMENTAL

Materials.

Dibenzoyl peroxide was crystallised by addition of methanol to its concentrated solution in chloroform and dried at room temperature under vacuum. Bis(p-nitrobenzoyl)peroxide was prepared from p-nitrobenzoyl chloride and sodium peroxide by the method of Price and Krebs(1). t-Butyl perbenzoate was commercially available. Benzoyl p-nitrobenzoyl peroxide was prepared by the method of Wieland(2). The almost colorless peroxide crystallized from ethanol and melted at 113° with decomposition.

Infrared Absorption Spectra Determinations.

A Perkin-Elmer Model 21 double beam recording infrared spectrophotometer equipped with a sodium chloride prism was used for the determination of infrared spectra. All spectra of liquid compounds were studied by preparing thin contact films of the liquids between two sodium chloride plates. This technique was also used with syrups. Solids were studied by preparing 2% solutions of them in "spectro grade" carbon tetrachloride or chloroform or by making a pallet with anhydrous potassium bromide.

In reporting the band intensities in infrared at the various frequencies, the following symbols are used: strong (s), medium (m), weak (w), shoulder (sh) and broad (bd).

Reactions of Diaroyl Peroxides in the Presence of Aluminium Chloride: General Procedure.

The reactions were carried out under a nitrogen atmosphere with constant stirring. Benzoyl peroxide additions were usually made in solution, at 0-5°. Bis(*p*-nitrobenzoyl)peroxide was added to aluminium chloride suspension in the solid form slowly at room temperature and the reaction mixture was kept overnight at 0°.

In each case, the reaction mixture was acidified with dilute hydrochloric acid and filtered; a solid residue was left. The aqueous layer was separated from the organic solution. Carboxylic acids were removed by extraction with aqueous sodium bicarbonate both from the solid residue and from the organic solvent. The organic solution was then washed with water, dried, and the organic solvent was removed by distillation under reduced pressure. The residue was purified by crystallization, adsorption chromotography or vacuum distillation.

Reactions of Dibenzoyl Peroxide in Different Organic Solvents:

(a) Methylene chloride

At 8-10°C, to a suspension of aluminium chloride (2.7 gms.; 0.02 mole) in methylene chloride (50 ml.), 4.82 g. (0.02 mole) of peroxide in 25 ml. of the same solvent was added. The mixture was left overnight at 0°C. Benzoic acid (1.3 g.; 27%) and a gummy neutral product were recovered. The latter on distillation at reduced pressure afforded a fraction, b.p. 124-128°/0.5 mm., which solidified to a solid, m.p. 69°, identified by m.p. and mixed m.p. as phenyl benzoate (1.05 g.; 26%). A considerable amount (1.5 g.) of resinous solid was left which did not distil below 230°/0.5 mm.

(b) Benzene

To 6.75 g. (0.05 mole) of aluminium chloride suspended in 50 ml. of benzene was added 12.1 g. (0.05 mole) of dibenzoyl peroxide dissolved in 60 ml. of benzene. The nitrogen passing slowly over the reaction mixture was led through a known volume of standard alkali, which was subsequently titrated for carbon dioxide(3): found, 0.029 mole (58%). After 8 hours the reaction mixture was worked up to give 3.65 g. (30%) of benzoic acid and 2.8 g. (29%) of phenyl benzoate, b.p. 184°/26 mm., m.p. and mixed m.p. 69°.

(c) Nitrobenzene

To 13.5 (0.1 mole) of aluminium chloride in 100 ml. of nitrobenzene, 23.4g (0.099 mole) of peroxide dissolved in the same volume solvent was added and the reaction was allowed to take place for 4 hours at 0-4°. The carbon dioxide (0.089 mole; 92%) that evolved was absorbed by a known volume of standard sodium hydroxide solution, and estimated by titration of the solution(3). The reaction mixture gave 3.9 g. (16%) of benzoic acid and 9.5 g. (49%) of phenyl benzoate, b.p. 122-128°/0.5 mm., m.p. 69°, alone or mixed with an authentic specimen.

(d) Nitrobenzene-toluene

To 13.5 g. (0.1 mole) of aluminium chloride, dissolved in 125 ml. of nitrobenzene, 24.2 g. (0.1 mole) of benzoyl peroxide dissolved in 125 ml. of toluene was added. After 7 hours of reaction, from the mixture 10.05 g. (42%) of benzoic acid and 4.1 g. (21.5%) of phenyl benzoate m.p. and mixed m.p. 69°, were obtained.

(e) Nitrobenzene-anisole

To 13.5 g. (0.1 mole) of aluminium chloride in 125 ml. of nitrobenzene, 24.2 g. (0.1 mole) of benzoyl peroxide in 125 ml. of anisole was added and kept for 7 hours. The yield of benzoic acid was 18.65 g. (76%).

Anisole and nitrobenzene were removed by steam distillation from the organic solution. The residue was taken in ether and distilled; at b.p. 154°/0.5 mm., *p*,*p*'-bianisyl (5.0 g.; 23%) was obtained. Crystallized from ethanol, it had m.p. 169°, alone or mixed with an authentic specimen. No phenyl benzoate was isolated. When repeated 4.75 g. (22%) of bianisyl and 19.1 g. (79%) of benzoic acid were obtained.

(f) Resorcinol Dimethyl Ether

To 4.05 g. (0.03 mole) of aluminium chloride suspended in 40 ml. of resorcinol dimethyl ether, 7.26 g. (0.03 mole) of benzoyl peroxide was added at 5-8° and left overnight at 0°. Benzoic acid (4.8 g.; 66%) was obtained. The neutral organic liquid after being washed and dried, was distilled at 195°/1 mm. to give 2.1 g. of a gum having a strong absorption peak at 1743 cm^{-1}. The gum was chromatographed on alumina using petroleum ether and benzene as eluents. The fractions were combined as long as pure petroleum ether was used. These on evaporation left a semisolid mass which crystallized from petroleum ether in colorless rods m.p. 89° (reported melting point for 2,4-dimethoxyphenyl benzoate is 90°)(4). Infrared spectrum $\nu_{max}^{CCl_4}$ in cm^{-1}: 3030 (m), 2960 (m), 2840 (m), 1740 (s), 1600(s), 1470(s), 1443 (s), 1318 (s), 1270-1245 (s,bd), 1180 (s), 1162 (s), 1125 (s), 1080 (s), 1062 (s), 1030 (s), 925 (m). Calc. for $C_{15}H_{14}O_4$: C, 69.76; H, 5.42%. Found: C, 69.95; H, 5.50%. Yield, 0.24 g. (3%).

(g) Mesitylene

To a suspension of aluminium chloride (2.7 g.; 0.02 mole) in 15 ml. of mesitylene was added 4.82 g. (0.02 mole) of benzoyl peroxide in 30 ml. of the same solvent at 5-8°C. The mixture was left overnight at 0°. The yield of benzoic acid was 1.38 g. (29%). The neutral organic solvent after being washed and dried was distilled at 150-160°/1 mm. to give 2.5 g. of a liquid having a strong absorption peak at 1740 cm^{-1}.

Reactions of Bis(*p*-nitrobenzoyl)peroxide in Different Organic Solvents.

(a) Methylene Dichloride

From 1.35 g. (0.01 mole) of aluminium chloride and 3.32 g. (0.01 mole) of peroxide in 50 ml. of methylene chloride left overnight at 0°, 1.07 g. (32%) of *p*-nitrobenzoic acid was obtained. The methylene chloride solution was then washed, dried and concentrated under reduced pressure. The residue crystallized from ethanol as colorless needles, m.p. 159°, identified as *p*-

nitrophenyl-p-nitrobenzoate(5) by mixed m.p. Yield, 1.88 g. (65%).

(b) Benzene

To a suspension of 1.35 g. (0.01 mole) of aluminium chloride in benzene (75 ml.), 3.32 g. (0.01 mole) of peroxide in the solid state was added at 22°. The mixture was allowed to react for 48 hours. After addition of ice-cold water and acidification, 0.69 g. (21%) of p-nitrobenzoic acid was obtained from insoluble material in the reaction mixture and from the benzene solution by sodium bicarbonate extraction. The residue of insoluble material was unreacted peroxide; further crops were obtained from the benzene mother liquor on concentration, giving a total of 2.30 g. (70%) of recovered peroxide. Complete evaporation of benzene left a tar (0.57 g.), which was chromotographed on alumina using light petroleum (b.p. 66-75°) and benzene as eluants. No crystalline product was isolated and the fractions in infrared spectroscopy gave only a weak peak at 1748 cm^{-1}.

(c) Anisole

To 1.35 g. (0.01 mole) of aluminium chloride in anisole (35 ml.) was added 3.32 g. (0.01 mole) of peroxide at 22°C. The mixture was allowed to react for seven hours. It gave 1.9 g. (57%) of p-nitrobenzoic acid. From the mother liquor anisole was removed by distillation under reduced pressure using a water pump. The gummy residue (0.87 g.) was chromotographed on alumina using three solvents, petroleum ether (b.p. 66-75°), benzene, and ether as eluants. The first few fractions gave 0.19 g. (7%) of pale yellowish needles of o-methoxyphenyl p′-nitrobenzoate, m.p. 102°, alone or when mixed with an authentic specimen (recorded m.p. 102°)$^{(6)}$. Later fractions gave 0.57 g. (21%) of almost colorless needles of p-methoxyphenyl p-nitrobenzoate, m.p. 112°, alone or mixed with an authentic specimen (recorded m.p. 113-115°)$^{(6)}$.

(d) Phenetole

This reaction was carried out under the same conditions as the reaction above, phenetole (35 ml.) being used in place of anisole, and gave 1.81 g. (54%) of p-nitrobenzoic acid. The organic solution after removal of acid was distilled at 44°/1 mm. and left a residue of 1.15 g. This was chromotographed on aluminium oxide. The first few fractions melted sharply at 114°, after crystallizing from ethanol as yellowish plates (0.31 g.; 10%) and were identified as o-ethoxyphenyl p'-nitrobenzoate by comparison (m.p. and mixed m.p.) with the authentic compounds prepared from the reaction of o-ethoxyphenol (Eastman Kodak) and p-nitrobenzoyl chloride in pyridine. Calc. for $C_{15}H_{13}O_5N$: C, 62.72; H, 4.53; N, 4.88%. Found: C, 62.90; H, 4.66; N, 4.82%.

Infra-red spectrum: $\nu_{max}^{CCl_4}$ in cm^{-1}: 3040 (w), 2980 (m), 2925 (m), 2872 (w), 1740 (s), 1700 (w), 1600 (s), 1490 (s), 1470 (s), 1450 (m), 1405 (m), 1340 (s), 1275-1225 (s), 1175 (s), 1110 (m), 1060 (s), 1035 (m), 920 (w), 835 (m).

The next few fractions (0.31 g.) had unsharp melting points (92-99°). However, later fractions on crystallization from ethanol gave plates (0.37 g.; 12%) having a sharp melting point at 118°. This compound was identified as p-ethoxyphenyl p'-nitrobenzoate by comparison (m.p. and mixed m.p.) with the authentic compound prepared from p-ethoxyphenol and p-nitrobenzoyl chloride in pyridine. Found: C, 62.63; H, 4.56; N, 4.98%. Infra-red spectrum: $\nu_{max}^{CCl_4}$ in cm^{-1}: 3055 (w), 2985 (m), 2940 (w), 1740 (s), 1478 (m), 1345 (s), 1275-1225 (s), 1185 (m), 1105 (w), 1070 (m), 1042 (m).

(e) Resorcinol Dimethyl Ether

To 1.35 g. (0.01 mole) of aluminium chloride in 35 ml. of resorcinol dimethyl ether, was gradually added 3.32 g. (0.01 mole) of peroxide. p-Nitrobenzoic acid (1.98 g.; 59%) was obtained. After removal of acid, the organic solution was washed, dried and distilled. 2,4-Dimethoxyphenyl p-nitrobenzoate, b.p. 225°C/1 mm., was obtained as a solid distillate; it crystallized from ethanol as colourless rods, m.p. 128° (0.61 g.; 20%). Calc. for $C_{15}H_{13}O_6N$: C, 59.41; H, 4.29; N, 4.62%. Found: C, 59.65; H, 4.39; N, 4.65%. It showed a depression of melting point when admixed with 2,6-dimethoxyphenyl p-nitrobenzoate and 3,5-dimethoxyphenyl p-nitrobenzoate (see below). Infrared spectrum: $\nu_{max}^{CHCl_3}$ in cm^{-1}: 3030 (w), 2940 (m), 2840 (m), 1740 (s), 1609 (s), 1495 (w), 1460 (m), 1350 (s), 1320 (m), 1157 (m), 1120 (m), 1070 (s), 1015 (w), 865 (w).

2,6-Dimethoxyphenyl p-nitrobenzoate, prepared from 2,6-dimethoxyphenol and p-nitrobenzoyl chloride, crystallized from ethanol as pale yellowish needles, m.p. 164°. Found: C, 59.57; H, 4.33; N, 4.55%. 3,5-Dimethoxyphenyl p-nitrobenzoate, crystallized from ethanol as pale yellowish needles, m.p. 141°. Found: C, 59.51; H, 4.26; N, 4.59%.

(f) Veratrole

To 1.335 g. (0.01 mole) of aluminium chloride in 35 ml. of veratrole, 3.32 g. of (0.01 mole) of peroxide was added. The yield of p-nitrobenzoic acid was 77% (2.55 g.). The washed, dried and neutral mother liquor of the reaction mixture was distilled. At b.p. 150°/1 mm., a trace of product distilled, which crystallized in ethanol in colourless rods, m.p. 135°. Infrared spectrum: $\nu_{max}^{CCl_4}$ in cm^{-1}: 3030 (w), 2960 (m), 2840 (m), 1742 (s); 1605 (m), 1495 (s), 1475 (m), 1347 (s), 1275-1225 (s), 1165 (m), 1090 (s), 1100 (w), 870 (m), 690 (w).

(g) m-Xylene

To a suspension of aluminium chloride (1.33 g.; 0.01 mole) in 45 ml. of m-xylene, was added 3.32 g. (0.01 mole) of peroxide gradually. p-Nitrobenzoic acid (2.4g; 72%) was obtained, and then 1.01 g. of a gummy neutral material, left after removal of xylene by distillation under reduced pressure. The gum was chromotographed on alumina using petroleum ether (b.p. 66-75°) and benzene as eluents. A few semisolid fractions were obtained, which were triturated with ethanol and which then crystallized from ethanol (charcoal) as colourless needles, m.p. 112°, undepressed by admixture with authentic 2,4-dimethylphenyl p-nitrobenzoate (m.p. 112°). Yield, 0.132 g. (5%). Calc. for $C_{15}H_{13}NO_4$: C, 66.42; H, 4.79; N, 5.16. Found: C, 66.21; H, 4.92; N, 5.11%.

(h) Mesitylene

To 1.33 g. (0.01 mole) of aluminium chloride in 50 ml. of mesitylene, 3.32 g. (0.01 mole) of p,p'-dinitrobenzoyl peroxide was added. The yield of p-nitrobenzoic acid was 2.29 g. (68 %). The mesitylene solution was then washed and dried, with magnesium sulfate and most of the mesitylene was removed by distillation under reduced pressure. The residue was chromotographed on alumina using petroleum ether (b.p. 66-75°) and benzene as eluents, giving a few solid fractions. This solid crystallized from ethanol in the form of slightly brownish plates, m.p. 122°, of mesityl p-nitrobenzoate (0.96 g.; 34%). Calc. for $C_{16}H_{15}O_4N$: C, 67.37; H, 5.26; N, 4.91%. Found: C, 67.30; H, 5.33; N, 5.00%. Infrared spectrum: $\nu_{max}^{CCl_4}$ in cm^{-1}: 3030 (m,sh), 2940 (s), 2870 (m), 1743 (s), 1610 (s), 1525 (m), 1487 (s), 1350 (s), 1322 (m), 1275-1240 (s), 1195 (m), 1140 (s), 1080 (s), 1010 (w), 870 (m), 695 (w,sh).

(i) Resorcinol Dimethyl Ether-Methylene Chloride

From 1.35 g. (0.01 mole) of aluminium chloride, 3.32 g. (0.01 mole) of peroxide, and 4 ml. (0.03 mole) of resorcinol dimethyl ether in 50 ml. of methylene chloride, mixed at 20° and left overnight at 0°, 1.04 g. (31%) of p-nitrobenzoic acid was obtained. The methylene chloride solution was then washed and dried. On slow concentration a product separated that crystallized from benzene in colourless flakes and was identified as p-nitrobenzoic anhydride (0.5 g.; 16%) m.p. and mixed m.p. 191°. (Recorded melting point, 189°C.)$^{(7)}$. The mother liquor on further concentration afforded a semisolid gummy mass which did not distil at temperatures up to 270°/1 mm., and which on alumina column chromotography did not afford any crystalline product.

Reaction of Benzoyl p-Nitrobenzoyl Peroxide in Different Organic Solvents:

(a) Methylene chloride

To a stirred suspension of aluminium chloride (1.35 g.; 0.01 mole) in 50 ml. of methylene chloride, was added 2.87 g. (0.01 mole) of peroxide at 8-10°. The mixture was then left for 2 hours with stirring, and then kept overnight at 0°. The acid removed by sodium bicarbonate extraction was p-nitrobenzoic (0.35 g.; 12%), m.p. 236-237°. The mother liquor was washed, dried and evaporated at room temperature. The residue on crystallization from petroleum ether (b.p. 55-75°) gave 1.97 g. (81%) of colorless flakes of phenyl p-nitrobenzoate (m.p. and mixed m.p. 129-130°).

(b) Benzene

To 1.35 g. (0.01 mole) of aluminium chloride, suspended in 60 ml. of dry benzene was added 2.87 g. (0.01 mole) of peroxide at room temperature. The mixture was left overnight at 0°. Extraction with bicarbonate removed a mixture (0.83 g.; m.p. 227-232°) of p-nitrobenzoic and benzoic acids. The neutral mother liquor, after washing and drying, was concentrated to a small volume and chromatographed on alumina. The fractions eluted by petroleum ether (b.p. 65-75°C.) and benzene gave a solid (0.41 g.) that crystallized in colourless flakes from ethanol. This product melted over the range of 100-115°, and the range did not diminish on further recrystallization. Its infrared spectrum showed $\nu_{\max}^{CCl_4}$ in cm^{-1}: 3060 (w), 1953 (w), 1751 (s), 1709 (w), 1612 (m), 1530 (w), 1492 (s), 1454 (w), 1416 (w), 1353 (s), 1322 (m), 1260 (s), 1198 (s), 1166 (s), 1072 (s), 1015 (w), 915 (w), 873 (m), 845 (m), 685 (m).

(c) Nitrobenzene

In an experiment run under similar conditions with the same quantities of reagents in 50 ml. of nitrobenzene, 0.82 g. of a mixture m.p. 230-234°, of p-nitrobenzoic and benzoic acid was obtained, and 0.36 g. of neutral product melting at 100-120°. The latter had an infrared spectrum identical with that of the neutral product of the previous experiment.

Decomposition of Benzoyl Ethyl Carbonate by Aluminium Chloride in Benzene.

To 4.05 g. (0.03 mole) of aluminium chloride, suspended in dry benzene under a nitrogen atmosphere 5.82 g. (0.03 mole) of benzoyl ethyl carbonate, prepared according to Tarbell and Leister(8a) was added with constant stirring at room temperature. The reaction mixture was left overnight, and then worked up in the usual way to yield benzoic acid (0.51 g.; 14%). The neutral solution was washed, dried, and distilled. A liquid, b.p. 78-80°/1 mm., was collected and identified as ethylbenzoate by its refractive index$^{(8b)}$ ($\underline{N}_D^{23}$ 1.5046, compared with $\underline{N}_D^{17}$ 1.5068 for an authentic specimen) and its infrared spectrum: ν_{max}^{film} in cm^{-1}: 3045 (m), 2960 (m), 2920 (m), 2880 (m,sh), 1725 (s), 1608 (m), 1500 (m), 1458 (s), 1372 (s), 1318 (s), 1275 (s), 1180 (s), 1110 (s), 1068 (s), 1030 (s), 937 (w), 875 (w), (850 (w), 700 (w), 685 (m). An authentic specimen of ethylbenzoate showed an identical infrared spectrum. The yield was 2.26 g. (48%).

Reaction of Sodium Perbenzoate and p-Toluene Sulfonyl Chloride.

Sodium perbenzoate was prepared according to Braun$^{(9)}$. To a cold aqueous solution (300 ml.; 0.08 mole) of sodium perbenzoate was slowly added with stirring 30.48 g. (0.16 mole) of p-toluene sulfonyl chloride in 100 ml. benzene. The mixture was stirred a further 6 hours at room temperature and then left overnight, by which time the aqueous layer was strongly acidic. The benzene layer was thoroughly washed with water and extracted with sodium bicarbonate solution, which on acidification gave 1.84 g. (19%) of benzoic acid. The benzene layer was then extraced with potassium hydroxide solution (3%). The alkali solution was acidified and extraced with ether; the ether on evaporation left a gum which on bromination gave 0.15 g. (1%) of tribromophenol, m.p. and mixed m.p. 94°. The benzene mother liquor was kept in contact with a little excess of sodium bicarbonate solution for seven days with occassional stirring. The benzene layer was then washed, dried and concentrated giving benzoyl peroxide (5.75 g.; 76%), m.p. and mixed m.p. 104°.

Reactions of Grignard Reagents with Dibenzoyl Peroxide.

General Procedure.

The Grignard reagents were prepared according to Kharasch and Reinmuth(10) by the addition of alkyl or arylbromide to a suspension of magnesium in ether under nitrogen, and estimated by titration of the base formed on adding an aliquot of the solution to water. The solution of organometallic compound was then added under nitrogen with stirring to a suspension of peroxide in dry ether, cooled to 0-4°. After addition, the reaction mixture was stirred an additional 30-60 minutes, followed by the addition of cold water and acidification by dilute hydrochloric acid. The ether layer was separated from the aqueous layer and extracted with sodium bicarbonate solution which on acidification gave benzoic acid. The ether layer was then extracted with 3-5% caustic potash solution to remove any phenol. After removal of acid and phenol, the ether layer was washed with water and dried by anhydrous sodium sulfate. The ether was removed by distillation and the residue was purified by crystallization, adsorption chromotography or vacuum distillation.

(a) n-Butylmagnesium Bromide

From 24.2 g. (0.1 mole) of benzoyl peroxide and 0.1 mole of n-butylmagnesium bromide were obtained benzoic acid (19.4 g.; 80%) and butyl benzoate (3.6 g.; 20%), b.p. 119-120°/11 mm., N_D^{27} 1.4942 (reported N_D^{20} 1.4972(11); found for authentic butyl benzoate, N_D^{27} 1.4950), ν_{max}^{film} in cm^{-1}: 3050 (w), 2990 (m), 2900 (m), 1725 (s), 1610 (w), 1458 (m), 1320 (m), 1280 (s), 1180 (w), 1115 (m), 1075 (m), 1030 (m), 940 (w), 840 (w), 710 (s), 690 (w). The infrared spectrum of an authentic specimen of butyl benzoate was identical.

(b) Cyclohexylmagnesium Bromide

From 12.1 g. (0.05 mole) of benzoyl peroxide and (0.05 mole) of cyclohexylmagnesium bromide was obtained benzoic acid (8.55 g.; 71%) and cyclohexyl benzoate

(4.49 g.; 44%), b.p. 164°/24 mm., N_D^{27} 1.5182, ν_{max}^{film} in cm^{-1} : 3040 (w), 2940 (s), 2870 (s), 1717 (s), 1690 (sh), 1605 (w), 1450 (s), 1435 (s), 1375 (w), 1318 (s), 1280 (s), 1180 (s), 1160 (m), 1110 (s), 1025 (m), 905 (m), 860 (m), 810 (w), 710 (s), 695 (m). An authentic specimen of cyclohexyl benzoate, b.p. 192-193°/61 mm., N_D^{27} 1.5173, showed an identical infrared spectrum.

(c) Phenylmagnesium Bromide

From 24.2 g. (0.1 mole) of benzoyl peroxide and 0.1 mole of phenylmagnesium bromide were obtained 17.5 g. (72%) of benzoic acid and 4.6 g. (23%) of phenyl benzoate, which crystallized from the ether solution on concentration. Recrystallized from ligroin, phenyl benzoate had m.p. and mixed m.p. 68-69°.

(d) p-Biphenylylmagnesium Bromide

From 0.07 mole of *p*-biphenylylmagnesium bromide and 17.8 g. (0.07 mole) of peroxide were obtained 0.9 g. (9%) of quaterphenyl, m.p. and mixed m.p. 309° (reported m.p. 315°$^{(12)}$), as an ether insoluble solid; 8.6 g. (51%) of benzoic acid; and 2.87 g. (15%) of colourless needles of *p*-biphenylyl benzoate, m.p. and mixed m.p. 149° (reported m.p. 150°$^{(13)}$). Calc. for $C_{19}H_{14}O_2$: C, 83.21; H, 5.11%. Found: C, 83.25; H, 5.19%.

Reaction of Dibenzoyl Peroxide with Phenyllithium.

To 12.1 g. (0.05 mole) of benzoyl peroxide in ether, 0.05 mole of phenyllithium was added. A yield of 8.47 g. (70%) of benzoic acid was obtained. A caustic potash (5%) extract of the ether solution gave on acidification a product which crystallized from ethanol and was identified as tribromophenol (0.42 g.; 10%) m.p. 93° alone or when mixed with an authentic specimen. The residue left after the evaporation of ether crystallized from ligroin (b.p. 60-70°) as needles of triphenylcarbinol (3.2 g.; 71%), m.p. and mixed m.p. 160°.

Reaction of Tertiarybutyl Perbenzoate with Phenylmagnesium Bromide.

From the reaction of 19.4 g. (0.1 mole) of *t*-butyl perbenzoate and 0.1 mole of phenylmagnesium bromide were obtained 10.8 g. (88%) of benzoic acid and 10.1 g. (67%) of phenyl *t*-butyl ether, b.p. 80°/20 mm. (reported b.p. 80°/20 mm.$^{(14)}$), N_D^{20} 1.4866 (reported N_D^{20} 1.4869$^{(14)}$), ν_{max}^{film} in cm^{-1} : 3044 (s), 2961 (s), 2890 (s), 1595 (s), 1500-1495 (s), 1250-1150 (s), 1069 (s), 1021 (s), 925-875 (s), 810 (s), 775 (s), 690 (s).

Reaction of Tertiarybutyl Perbenzoate with Phenyllithium.

From 8.9 g. (0.046 mole) of perbenzoate and 0.092 mole of phenyllithium were obtained 1.6 g. (28%) of benzoic acid and 1.2 g. (28%) of phenol (characterized as tribromophenol). The ether solution of neutral products was distilled through a Nester-Faust spinning-band distillation column, and gave 1.4 g. (41%) of t-butanol, b.p. 83°, N_D^{20} 1.3872 (reported N_D^{20} 1.3878(15)) and 2.85g (51%) of t-butyl phenyl ether b.p. 80°/20 mm., N_D^{22} 1.4868. The residue from distillation was triphenylcarbinol (1.5 g.; 12%), m.p. and mixed m.p. 160°.

Oxidation of Phenols by Diaroyl Peroxides; General Procedure.

Chloroform solutions of equimolar quantities of the phenol and peroxide were refluxed 4-6 hours, moisture being excluded. Carboxylic acids were removed by extraction with aqueous sodium bicarbonate solution, and the chloroform solution was then dried (sodium sulphate) and evaporated. The residue dissolved in the minimum quantity of hot benzene slowly deposited crystals of phenolic materials on cooling.

Oxidations by Bis(p-nitrobenzoyl)peroxide.

(a) p-Cresol

Oxidation of 1.08 g. (0.01 mole) of p-cresol in 50 ml. chloroform resulted in the formation of 2.08g (61%) of p-nitrobenzoic acid, m.p. 240°, and 1.19 g. (44%) of pale yellow plates of 4-p-nitrobenzoyloxy-m-cresol, m.p. 164°. Calc. for

$C_{14}H_{11}O_5N$: C, 61.54; H, 4.03; N, 5.13%. Found: C, 61.73; H, 4.12; N, 5.20%. Infra-red spectrum: $\nu_{max}^{CHCl_3}$ in cm^{-1}: 3620 (s), 3400-3260 (m,bd), 3030 (w), 2940 (m), 2870 (m), 1737 (s), 1610 (s), 1350 (s), 1110 (s), 1015 (s), 925-890 (m).

(b) <u>p-Bromophenol</u>

Oxidation of 1.73 g. (0.01 mole) of <u>p</u>-bromophenol in 50 ml. of chloroform gave 2.65 g. (80%) of <u>p</u>-nitrobenzoic acid and 0.57 g. (16%) of 2-<u>p</u>-nitrobenzoyloxyphenyl-5-bromophenol, crystallizing from benzene in colourless needles, m.p. 187-188°. Calc. for $C_{13}H_8O_5NBr$: C, 46.15; H, 2.36; N, 4.14%. Found: C, 46.19; H, 2.30; N, 4.15%. Infrared spectrum: $\nu_{max}^{CHCl_3}$ in cm^{-1}: 3590 (m), 3250-3150 (s,bd), 1735 (s), 1597 (s), 1475 (s), 1340 (s), 1310 (s), 1100 (s), 1055 (s), 1005 (s), 880 (s), 860 (s).

(c) <u>α-Naphthol</u>

Oxidation of 1.44 g(0.01 mole) of α-naphthol gave 2.05 g. (62%) of <u>p</u>-nitrobenzoic acid and 1.21 g. (40%) of 2-<u>p</u>-nitrobenzoyloxy-α-naphthol, yellow needles from benzene, m.p. 182°. Calc. for $C_{17}H_{11}O_5N$: C, 66.02; H, 3.56; N, 4.53%. Found: C, 66.14; H, 3.57; N, 4.59%. Infrared spectrum: $\nu_{max}^{CHCl_3}$ in cm^{-1}: 3608 (s), 3400-3260 (m,), 3030 (w), 1745 (s), 1605 (s), 1470 (w), 1395 (w), 1355 (s), 1090 (s), 1017 (m), 965 (w).

(d) β-Naphthol

Oxidation of 1.44 g. (0.01 mole) of β-naphthol gave 1.95 g. (59%) of p-nitrobenzoic acid and 2.54 g. (83%) of 2-p-nitrobenzoyloxy-α-naphthol, m.p. 182°.

2-p-Nitrobenzoyloxy-1-methoxy naphthalene.

A solution of diazomethane in dry ether was added to an ethereal solution of 2-p-nitrobenzoyloxy-α-napthol (3.11 g., 0.01 mole) until a yellow colour persisted. After 20 minutes, the excess diazomethane was destroyed with dilute hydrochloric acid. The ether solution was extracted with 4% aqueous potassium hydroxides to remove unreacted phenol, washed, dried, and concentrated. The residue crystallized from ethanol in yellow needles, m.p. 140°, of 2-p-nitrobenzoyloxy-1-methoxy naphthalene (1.65 g., 51%). Calcd. for $C_{18}H_{13}O_5N$: OMe, 9.59%. Found: 9.49%. Infrared spectrum: $\nu_{max}^{CHCl_3}$ in cm^{-1}: 3060 (w), 2940 (m), 2850 (w), 1745 (s), 1475 (m), 1385 (s), 1350 (s), 1320 (m), 1235 (s), 1120 (m), 1075 (s), 1000-970 (m), 870 (m), 850 (m).

α-Methoxy-β-naphthol.

A solution containing 2-p-nitrobenzoyloxy-1-methoxy naphthalene (1 g.) and potassium hydroxide (5 g.) in 100 ml. of methanol-water (9:1 v/v) was refluxed for 3 hours. After removal of most of the methanol at reduced pressure, the solution was acidified. The resultant precipitate was washed with aqueous sodium bicarbonate. The residue (0.32 g.) crystallized from ligroin as colourless plates, m.p. 90° (reported m.p. 90.5°(16)). Calc. for $C_{11}H_{10}O_2$: C, 75.86; H, 5.75%. Found: C, 75.51; H, 5.52 %.

α-Methoxy-β-naphthyl Benzoate[*]

α-Methoxy-β-naphthol (0.1 g.) was benzoylated with benzoyl chloride (0.3 ml.) in anhydrous pyridine (2 ml.). The reaction mixture was diluted with 5% sodium carbonate solution (10 ml.), and the precipitated solid was removed by filtration, washed with water, and then crystallized from methanol as colourless rods (0.053 g.), m.p. 107°, $\nu_{max}^{CCl_4}$ in cm^{-1}: 3050 (m), 2980 (m), 2875 (w), 1750 (s), 1610 (m), 1490 (m), 1470 (m), 1410 (s), 1280 (s), 1210 (s), 1190 (s), 1090 (s), 1070 (s), 1030 (s), 1000 (m), 950 (w), 850 (m), 705 (s). Calc. for $C_{18}H_{14}O_3$: C, 77.40; H, 5.04%. Found: C, 77.59; H, 5.17%.

Oxidations by Benzoyl p-Nitrobenzoyl Peroxide.

(a) p-Cresol

The reaction of 2.87 g. (0.01 mole) of peroxide with 1.08 g. (0.01 mole) of *p*-cresol in 50 ml. chloroform gave 1.72 g. of a mixture of benzoic and *p*-nitrobenzoic acids m.p. 198-210° (the melting point corresponds to a

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[*] The author is indebted to Mr. H.S. Chang for this preparation.

mixture of 75% of p-nitrobenzoic and 25% of benzoic acids), 0.35 g. (13%) of p-nitrobenzoyloxy-m-cresol (m.p. and mixed m.p. 164°) and a gum (1.63 g). The gum was chromotographed on alumina using petroleum ether (b.p. 60-70°) and benzene as eluents. The chromotographic fractions were non crystallizable; showed strong absorption bands for hydroxyl group at 3350 cm^{-1} and ester carbonyl group at 1745 cm^{-1}.

Attempts to develop a paper chromatographic method to separate 4-benzoyloxy-m-cresol and 4-p-nitrobenzoyloxy-m-cresol, which might be applied to the gum, were unsuccessful. Solvents like n-butanol-pyridine-petroleum ether (b.p. 65-75°) 1:1:2 (v/v), n-butanol saturated with water, n-butanol-pyridine- sat. aq. NaCl 1:1:2 (v/v), benzene-acetic acid-petroleum ether 2:2:1 (v/v), and n-butanol-acetic acid-petroleum ether 4:1:5 (v/v) were tried, but gave the same R_f values for the two phenols.

(b) β-Naphthol

The reaction of 5.74 g. (0.02 mole) of peroxide in 90 ml. of chloroform with 2.88 g. (0.02 mole) of β-naphthol gave (1) a mixture (2.78 g.), m.p. 188-199° of p-nitrobenzoic and benzoic acids (the melting point corresponds to a mixture of 65% of p-nitrobenzoic and 35% of benzoic acids); (2) 0.67 g. (11%) of 2-p-nitrobenzoyloxy-α-naphthol (m.p. and mixed m.p. 182°) and (3) a gum (3.95 g.). The infrared spectrum of the gum gave sharp peaks of 3600 cm^{-1} and 1730 cm^{-1} showing that it contained compounds with hydroxyl and carbonyl groups. However, chromotography on alumina using petroleum ether and benzene failed to give any crystalline product.

Reaction of Lithium Phenoxide with Dibenzoyl Peroxide.

To a 200 ml. of an ether solution of lithium phenoxide prepared from 9.4 g. (0.1 mole) of phenol and 0.7 g. (0.1 gram atom) of lithium, 19.36 g. (0.08 mole) of peroxide was added slowly at 0-4°. The reaction mixture was acidified with dilute hydrochloric acid after one hour. The ether layer gave benzoic acid (12.7 g.; 65%) by sodium bicarbonate extraction. The ether mother liquor was then extracted with 5% caustic potash solution which on acidification and subsequent extraction by ether gave 4.5 g. of crude phenol. No crystals separated when a solution of this phenolic material in petroleum ether was chilled. On concentration, the ether solution left a semisolid mass. This was dissolved in petroleum ether (b.p. 65-75°). The solution on cooling gave 3.57 g. of unreacted benzoyl peroxide, and finally on concentration an uncrystallizable gum (3.1 g.).

Oxidation of Secondary Aromatic Amines by Diaroyl Peroxides: General Procedure.

The peroxide as a solid, bis(p-nitrobenzoyl)peroxide or in solution (dibenzoyl peroxide) was added gradually with stirring, under nitrogen atmosphere, to a solution of the amine at temperatures of 0-5°C. (dibenzoyl peroxide) or 20-25°C. bis(p-nitrobenzoyl)peroxide . After standing overnight, the reaction mixture was extracted with aqueous sodium bicarbonate to remove benzoic or p-nitrobenzoic acid and then with 5% aqueous potassium hydroxide to remove phenolic products which frequently had partially crystallized from the reaction mixture. The acids and phenols were recovered by acidification of the aqueous solutions.

Oxidation by Dibenzoyl Peroxide of Diphenylamine.

The oxidation of 6.1 g. of diphenylamine by 8.8 g. of dibenzoyl peroxide in 75 ml. of benzene afforded 5.98 g. (68%) of benzoic acid and 2.1 g. (25%) of o-N-phenylbenzamidophenol, m.p. 216° (reported m.p. 214°(17). When the reaction was carried out in chloroform solution, the yield of phenol was 30%. Gambarjan(17) reported a 48% yield for the reaction in chloroform.

Oxidations by Bis(p-nitrobenzoyl)peroxide.

(a) N-Methylaniline

From the reaction of 1.07 g. (0.01 mole) of N-methylaniline and 3.32 g. (0.01 mole) of peroxide in 50 ml. of benzene were obtained p-nitrobenzoic acid, m.p. 238° (1.82 g., 55%) and o-(N-methyl-p'-nitrobenzamido)phenol, colourless plates (1.02 g., 38%), m.p. 197-198°, from ethanol (charcoal). Calc. for $C_{14}H_{12}O_4N_2$: C, 61.76; H, 4.41; N, 10.29%. Found: C, 61.92; H, 4.26; N, 10.14%. Infrared spectrum: ν_{max}^{KBr} in cm^{-1}: 3300-3100 (s), 2950 (m), 2860 (m), 1625 (s), 1525-1500 (s), 1425 (m), 1340 (s), 1197 (m), 1090 (m), 1055 (w), 1010 (w), 882 (w), 857 (s), 850 (s), 820 (w), 765 (s), 732 (s), 680 (m).

(b) N-Ethylaniline

The oxidation of 1.21 g. (0.01 mole) of N-ethylaniline by 3.32 g. (0.01 mole) of peroxide in 40 ml. benzoic acid gave 1.98 g. (60%) of p-nitrobenzoic acid, m.p. 240°, and 1.3 g. (45%) of o-(N-ethyl-p'-nitrobenzamido) phenol, crystallizing from 50% aqueous ethanol as colourless plates m.p. 152°. Calc. for $C_{15}H_{14}O_4N_2$: C, 62.93; H, 4.89; N, 9.78%. Found: C, 62.83; H, 4.93; N, 9.63%. The phenol crystallized from benzene in plates, which after being dried at 80°/3 mm. for 24 hours melted at 90-92°, resolidified, and then melted at 118°. Calc. for $6\ C_{15}H_{14}O_4N_2 + C_6H_6$:

C, 64.21; H, 5.01%. Found: C, 63.82; H, 4.97%. Crystallized from toluene, the phenol formed prisms, m.p. 120°. Calc. for 12 $C_{15}H_{14}O_4N_2$ + C_7H_8: C, 63.68; H, 4.99; N, 9.53%. Found: 63.26; H, 5.18; N, 9.60%. Crystallized from bromobenzene, the phenol formed prisms, m.p. 130°. Calc. for 3 $C_{15}H_{14}O_4N_2$ + C_6H_5Br: C, 60.29; H, 4.63; N, 8.28%. Found: C, 60.18; H, 4.92; N, 8.18%.

(c) N-Butylaniline

N-butylaniline (1.50 g., 0.01 mole) and peroxide (3.32 g., 0.01 mole) in benzene (50 ml.) afforded p-nitrobenzoic acid (2.15 g., 65%) and o-(N-butyl-p'-nitrobenzamido)phenol. The latter after crystallization from ethanol (charcoal) and then benzene separated as colourless plates (1.31 g., 42%), m.p. 167°. Calc. for $C_{17}H_{18}O_4N_2$: C, 64.97; H, 5.73; N, 8.91%. Found: C, 64.86; H, 5.55; N, 8.69%. Infrared spectrum: ν_{max}^{KBr} in cm^{-1}: 3240 (s), 2940 (m), 2860 (w), 1620 (s), 1580 (s), 1520 (s), 1425 (m), 1347 (s), 1225 (w), 1157 (m), 1105 (w), 860 (s), 850 (s), 820 (m), 762 (s), 730 (m).

(d) Diphenylamine

The oxidation of 1.69 g. (0.01 mole) of diphenylamine in 50 ml. of benzene by 3.32 g. (0.01 mole) of peroxide gave 1.82 g. (55%) of p-nitrobenzoic acid m.p. 242° and 1.74 g. (52%) of o-(N-phenyl-p'-nitrobenzamido) phenol which crystallized from ethanol (charcoal) in yellow plates, m.p. 240°. Calc. for $C_{19}H_{14}O_4N_2$: C, 68.26; H, 4.19; N, 8.38%. Found: C, 68.08; H, 4.16; N, 8.56%. Infrared spectrum: ν_{max}^{KBr} cm^{-1}: 3250-3150 (s), 1665 (m), 1630 (s), 1590 (s), 1525 (m), 1490 (m), 1460 (s), 1410 (m), 1347 (m), 1300 (m), 1100 (w), 962 (w), 875 (w), 860 (w), 835 (s), 770 (m), 760 (m), 747 (s), 665 (w).

Oxidation of Diphenylamine by Benzoyl p-Nitrobenzoyl Peroxide.

Diphenylamine (3.32 g.; 0.02 mole) in benzene (70 ml.), oxidized in the usual way by p-nitrobenzoyl benzoyl peroxide (5.74 g.; 0.02 mole), gave a mixture (3.1 g.) of benzoic and p-nitrobenzoic acids, m.p. 193-200°. This acid mixture was dissolved in alkali, filtered and acidified. The precipitated acids were removed by filtration, dried and analysed for nitrogen. Calc. for 37% $C_7H_6O_2$ + 63% $C_7H_5O_4N$: 5.31%. Found, 5.31%. A phenolic material (0.75 g.), m.p. 206-208° (decomp.) had separated from the benzene solution; a further 0.8 g. of phenolic material, m.p. 202-206° (dec.) was extracted from benzene solution by alkali. The first phenolic fraction was analysed. Calc. for $C_{19}H_{15}O_2N$: (N-phenyl-o-benzamidophenol)C, 78.86; H, 5.23; N, 4.85%;for $C_{19}H_{14}O_4N_2$: o-(N-phenyl-p'-nitrobenzamide)phenol C, 68.26;

H, 4.19; N, 8.38%. Found: C, 65.72; H, 4.41; N, 6.80%. The mixture of phenols was only very sparingly soluble in common organic solvents, such as petroleum ether, benzene, acetone, ether, carbon tetrachloride or carbon disulfide. It was moderately soluble in ethanol, but no pure product crystallized from this solvent. However, on crystallization from acetic acid 1.05 g. (17%) of o-(N-phenyl-p'-nitrobenzamido)phenol, m.p. and mixed m.p. 239°, was recovered.

Reaction of Benzoyl Peroxide with Benzaldehyde Phenylhydrazone.

To 10 g. (0.051 mole) of benzaldehyde phenylhydrazone dissolved in 125 ml. of benzene was added 12.34 g. (0.051 mole) of benzoyl peroxide. The mixture was left overnight. Extraction with bicarbonate removed 6.3 g. (51%) of benzoic acid. The residual benzene solution was washed, dried and allowed to evaporate slowly, when some crystalline product (4.45 g.; 27%) separated. The tarry mass (8.5 g.) left after complete evaporation of benzene was chromotographed on alumina using benzene and ether as eluents and gave a further yield of crystalline product (4.15 g.; 25%). This product crystallized from ethanol in colourless needles, m.p. 181°, undepressed by admixture with authentic α, β -dibenzoyl-α-phenylhydrazine (reported m.p. 180°(18)).

The infrared spectrum of the compound was also identical with that of α, β-dibenzoyl- α-phenylhydrazine: $\nu^{CHCl_3}_{max}$ in cm^{-1}: 3420 (m), 1672 (s), 1600 (m), 1585 (m), 1470 (m), 1420 (m), 1345 (s), 1306 (m), 1078 (w), 1075 (w), 1027 (w), 925-890 (w), 732 (w).

Reaction of Benzoyl Peroxide with Benzophenone Phenylhydrazone.

To 6 g. (0.022 mole) of benzophenone phenylhydrazone (m.p. 137°) in 50 ml. benzene was added 5.32 g. (0.022 mole) of benzoyl peroxide. The mixture was stirred 3 hours and left overnight. After removal of benzoic acid (2.37 g., 45%) the benzene solution was washed with water, dried, and evaporated. The gummy residue crystallized from ethanol in yellow needles, m.p. 147°, of phenylazodiphenylcarbinol benzoate (5.43 g., 63%). Calc. for $C_{26}H_{20}N_2O_2$: C, 79.59; H, 5.10; N, 7.14%. Found: C, 79.57; H, 5.15; N. 7.31%. Infrared spectrum: $\nu^{CCl_4}_{max}$ in cm^{-1}: 3090 (m), 1743 (s), 1498 (m), 1457 (s), 1318 (m), 1270 (s), 1177 (s), 1090 (s), 1067 (m), 914 (w), 687 (s).

Hydrolysis of Phenylazodiphenylcarbinol Benzoate.

To 2.1 g. of the benzoate dissolved in 150 ml. of methanol, 5 g. of caustic potash in 15 ml. of water was added and the mixture was refluxed for 4 hours. Most of the methanol was removed by distillation at ordinary pressure. The residue was treated with 80 ml. of water when some oily material separated; it was taken up in ether. The ether extract was washed, dried, evaporated and on treatment with 2,4-dinitrophenylhydrazine gave benzophenone 2,4-dinitrophenylhydrazone (1.04 g; 54%), m.p. and mixed m.p. 236° (reported m.p. 238°(19)). The alkaline aqueous solution on acidification with dilute hydrochloric acid gave 0.55 g. (85%) of benzoic acid.

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SUMMARY AND CLAIMS TO ORIGINAL RESEARCH

1. The decomposition of dibenzoyl peroxide by aluminium chloride in the presence of various solvents was studied. In methylene chloride, benzene, nitrobenzene and a mixture of nitrobenzene with toluene, this peroxide underwent intramolecular rearrangement to give phenyl benzoate and carbon dioxide.
2. Boron trifluoride-etherate in benzene at 0-5° had no effect on dibenzoyl peroxide.
3. Dibenzoyl peroxide added to a suspension of aluminium chloride in anisole-nitrobenzene solution afforded 23% of _p_,_p_'-bianisyl.
4. Resorcinol dimethyl ether was substituted to give 2,4-dimethoxyphenyl benzoate by aluminium chloride and dibenzoyl peroxide.
5. Bis(_p_-nitrobenzoyl)peroxide and benzoyl _p_-nitrobenzoyl peroxide when decomposed by aluminium chloride in methylene chloride gave excellent yields of _p_-nitrophenyl _p_-nitrobenzoate and phenyl _p_-nitrobenzoate respectively.
6. In presence of aluminium chloride, nucleophilic solvents like _m_-xylene, mesitylene, anisole, phenetole, veratrole and resorcinol dimethyl ether underwent substitution by bis(_p_-nitrobenzoyl)peroxide to give the corresponding p-nitrobenzoates.

7. Bis(*p*-nitrobenzoyl)peroxide effected substitution of *p*-cresol, *p*-bromophenol, α-naphthol, and β-naphthol, giving a *p*-nitrobenzoyloxy-substituted phenol or napthol. The two naphthols gave the same product.
8. With *p*-nitrophenol, bis(*p*-nitrobenzoyl)peroxide was inert; phenol and *p*-methoxyphenol, on the other hand reacted with this peroxide to give high yields of acid but no isolable quantity of ortho-substituted phenol.
9. The reaction of *p*-cresol or β-naphthol with benzoyl *p*-nitrobenzoyl peroxide gave low yields of *p*-nitrobenzoyloxy derivatives. Mixtures of benzoic and *p*-nitrobenzoic acids were obtained.
10. Secondary aromatic amines were oxidized by bis(*p*-nitrobenzoyl)peroxide to phenols, assumed to be *o*-(N-alkyl or aryl-*p*'-nitrobenzamido)phenols. Benzoyl *p*-nitrobenzoyl peroxide with diphenylamine gave a low yield of *o*-(N-phenyl-p'-nitrobenzamido)phenol.
11. Oxidation of benzophenone phenylhydrazone by dibenzoyl peroxide gave phenylazodiphenylcarbinol benzoate.
12. Oxidation of benzaldehyde phenylhydrazone by dibenzoyl peroxide gave *α*,*β*-dibenzoyl-α-phenylhydrazine.
13. The following compounds were prepared for the first time:
    (a) *o*-Ethoxyphenyl *p*'-nitrobenzoate.
    (b) *p*-Ethoxyphenyl *p*'-nitrobenzoate.
    (c) 2,4-Dimethoxyphenyl *p*-nitrobenzoate.

(d) 2,4-Dimethylphenyl p-nitrobenzoate.

(e) Mesityl p-nitrobenzoate.

(f) 4-(p'-Nitrobenzoyloxy-m-cresol).

(g) 2-p-Nitrobenzoyloxyphenyl-5-bromophenol.

(h) 2-p-Nitrobenzoyloxy-α-naphthol.

(i) α-Methoxy-β-naphthyl benzoate.

(j) o-(N-Methyl-p'-nitrobenzamido)phenol.

(k) o-(N-Ethyl-p'-nitrobenzamido)phenol.

(l) o-(N-Butyl-p'-nitrobenzamido)phenol.

(m) o-(N-Phenyl-p'-nitrobenzamido)phenol.

(n) Phenylazodiphenylcarbinol benzoate.