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THE SYNTHESIS OF PEROXYESTERS

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fulfilment of the requirements
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ABBREVIATIONS

PBA = peroxybenzoic acid

MCPBA = meta-chloroperoxybenzoic acid

NMR = nuclear magnetic resonance

IR = infrared

UV = ultraviolet

R and R' = aliphatic / aralkyl group

Ar = aromatic group

Ph = C₆H₅-

temp = temperature

r.t. = room temperature

h = Planck's constant (Js)

c = speed of light (ms⁻¹)

λ = wavelength (m)

ν = frequency (s⁻¹)

ppm = parts per million

bp = boiling point

mp = melting point

RMM = relative molecular mass

R_f value (tlc) = $\frac{\text{distance travelled by sample}}{\text{distance travelled by solvent front}}$

tlc = thin layer chromatography

ABSTRACT

The aim of the work described herein was to establish an alternative route to peroxyester formation, using milder conditions and following a more simplified laboratory procedure to those of methods presently known. The positive results obtained were via carbocation intermediates, and disproved the claim by Magelli and Sheppard *et al.*¹ that peroxyesters could not be synthesised by the alkylation of peroxyacids or their salts. The new procedure tended to be more successful in forming tertiary peroxyesters, and stable primary allylic and benzyl peroxyesters were also seen. Tertiary-butyl 3-chloroperoxybenzoate, a new compound, was formed and its spectroscopic data recorded. Two previously unknown peroxyesters were also formed, namely prop-2-enyl- and benzyl-3-chloroperoxybenzoate, and their ¹H NMR spectra were recorded. The method did not yield simple primary peroxyesters.

As well as the peroxyesters formed, other organic peroxides too were prepared or purified and analysed. This thesis also provides IR, and ¹H and ¹³C NMR spectra of high resolution previously unseen, together with details of a new route to peroxyester synthesis and new compounds.

CONTENTS

	Page
ACKNOWLEDGEMENTS	2
ABBREVIATIONS	3
ABSTRACT	4
CONTENTS	5
1.1 <i>Introduction</i>	6
1.2 <i>Preparation of Organic Peroxides and Esters</i>	8
1.2.1 <i>Preparation of Peroxyesters</i>	8
1.2.2 <i>Preparation of Esters</i>	13
1.2.3 <i>Preparation of Peroxyacids</i>	17
1.2.4 <i>Preparation of Acyl Peroxides</i>	24
1.2.5 <i>Preparation of Hydroperoxides</i>	26
1.3 <i>Carbocation and Organic Radical Intermediates</i>	37
1.3.1 <i>Carbocations</i>	37
1.3.1.1 <i>Structure and Stability of Carbocations</i>	37
1.3.1.2 <i>Carbocation Formation</i>	41
1.3.1.3 <i>Reactions of Carbocations</i>	44
1.3.2 <i>Organic Radicals</i>	47
1.3.2.1 <i>The Production of Radicals</i>	48
1.3.2.2 <i>Radical Reactions</i>	54
1.4 <i>Principal Reactions of Peroxyesters, Hydroperoxides, Peroxyacids and Acyl Peroxides</i>	63
1.4.1 <i>O-O Heterolysis</i>	64
1.4.1.1 <i>Intermolecular Nucleophilic Substitution at Oxygen</i>	64
1.4.1.2 <i>Intramolecular Nucleophilic Rearrangement</i>	77
1.4.1.3 <i>Other Redox Reactions</i>	85
1.4.2 <i>Acid-Catalysed Decomposition</i>	91
1.4.3 <i>Base-Catalysed Decomposition</i>	92
1.4.4 <i>Thermally Induced O-O Homolysis</i>	94
1.4.5 <i>Hydrolysis of Peroxyesters</i>	100
1.4.6 <i>Postulated Peroxide and Peroxonium Ion Intermediates</i>	101
1.5 <i>Physical Properties of Organic Peroxides</i>	107
1.5.1 <i>Structure</i>	107
1.5.2 <i>Stability</i>	110
1.5.3 <i>Spectroscopic Data</i>	112
CHAPTER 2 – RESULTS AND DISCUSSION	122
CHAPTER 3 – EXPERIMENTAL	157
REFERENCES	174
APPENDIX	181
SPECTRA	182

CHAPTER 1 – INTRODUCTION

1.1 Introduction'

Although organic peroxides have been known for as long as 135 years, since Brodie² synthesised the first organic peroxide, benzoyl peroxide in 1858, the hazards associated with handling and preparing them on a relatively large scale discouraged early investigators. During the early 1900's, many of the important classes of organic peroxides were first prepared and studied, and industrial interest began when it was found that benzoyl peroxide was an effective bleaching agent for edible oils – and later, an excellent bleaching agent for flour. Since the 1930's and especially during and after the Second World War, great progress has been seen which shows no sign of abating. The war demanded synthetic rubber and plastics, and so the use of organic peroxides as initiators of polymerisation began to develop. The continued growth of radical polymerisation after the war stimulated the development of many organic peroxide products to meet the consumer market.

Some 1.5×10^6 tons of hydrogen peroxide and its derivatives are industrially produced worldwide each year³. This shows the commercial importance of the chemistry of organic peroxides today, used especially in the manufacture of the major polymers, as:

- (a) initiators for free radical polymerisation and/or copolymerisation of vinyl and diene monomers to obtain polyethylene, polyvinyl chloride, polypropylene, polystyrene and polyacrylates. (Using for example, benzoyl peroxide, tertiary-butyl peroxide, tertiary-butyl hydroperoxide and tertiary-butyl peroxyneodecanoate.)
- (b) curing agents for thermoset resins to prepare for example, thermoset polyesters and silicone rubbers. (Using for example, tertiary-butyl peroxybenzoate, methyl ethyl ketone peroxides, tertiary-butyl hydroperoxide and benzoyl peroxide.)
- (c) crosslinking agents for polyethylene and elastomers such as ethylene-propylene and styrene-butadiene rubbers. (Organic peroxides used include OO-tertiary-butyl O-isopropylmonoperoxy carbonate [$(\text{CH}_3)_2\text{CHOCO}_3\text{C}(\text{CH}_3)_3$].)

Organic peroxides are also used as disinfectants; bleaching agents for gums, flour, waxes, fats and oils for example, and include peroxyethanoic acid and benzoyl peroxide; and as epoxidising agents using MCPBA and peroxyethanoic acid for example.

Although they are used in small amounts in polymerisation, the organic peroxides are not true catalysts as they take part in the reaction, the radical fragment becoming an end group of the polymer chain. The temperature at which the peroxide can be made to decompose into useful free radicals largely determines the application area. Other important factors include cost, solubility and safety aspects.

As well as finding their way into almost every field of commercial interest involving organic chemicals, organic peroxides can also be

unwanted reaction intermediates as in the oxidative deterioration of petrol, lubricating oils and rubber, the ageing of skin and the rancidification of fats. The positive involvement of organic peroxides in polymerisation, bleaching and epoxidising reactions, also extends to the drying of paints and many combustion processes.

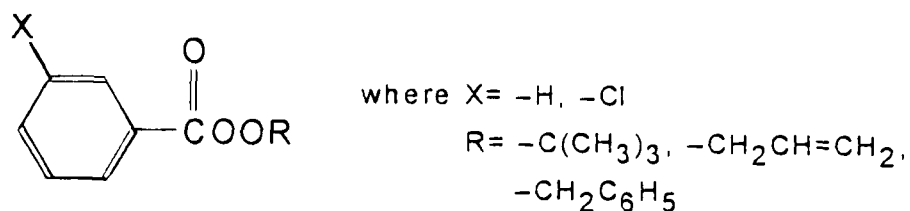
Although much knowledge has been acquired on radical reaction mechanisms, especially from polymerisation processes, not all reactions involving oxygen can be explained successfully by radical pathways. These oxygen reactions may possibly be explained by positive oxygen species. As described towards the end of this thesis, these species have been generated – the bulk of work having been carried out in the last ten years – and may also be formed from peroxyesters, the subject of the author's research. Thus, as there is relatively little known about positive oxygen, the work described herein was undertaken with its potential to forming these species which may then be studied and ultimately increase the knowledge of positive oxygen chemistry.

The present work described here involves peroxyesters and also peroxyacids, acyl peroxides and hydroperoxides. A summary of their well known preparations and physical properties will be discussed, followed by their principal chemical reactions together with the preparation of carboxylic esters.

1.2 Preparation of Organic Peroxides and Esters^{4,5}

1.2.1 Preparation of Peroxyesters^{4,5}

As the experimental work described here involves a new synthetic route to peroxyester formation, specifically alkyl/aralkyl peroxy-carboxylates,



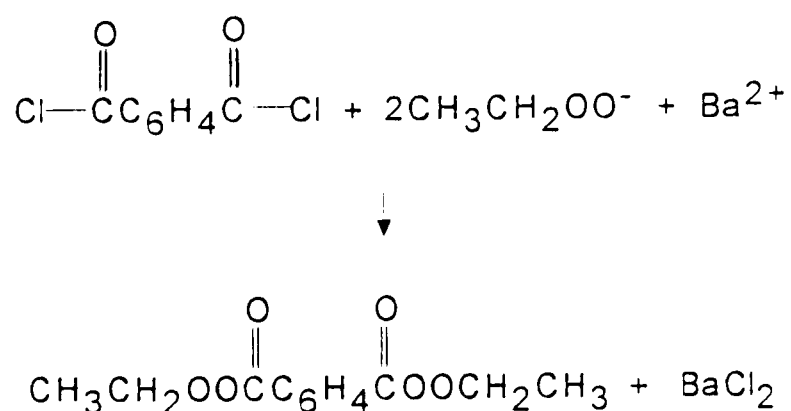
some of the most commonly known methods to the various forms of peroxyesters will be discussed to present a comprehensible outline on the general synthetic approach to peroxyesters.

The preparation followed is dependent upon whether the resultant peroxyester is primary, secondary or tertiary. For example, primary and secondary peroxyesters are base-sensitive as they have readily extractable protons, whereas tertiary peroxyesters can be prepared in mildly alkaline solutions.

Some of the most utilised preparative methods are as follows:

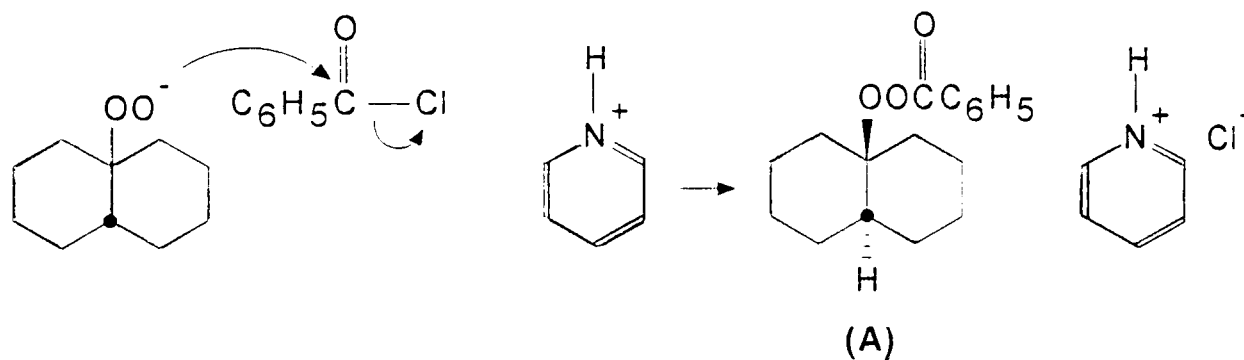
1. Baeyer-Villiger procedure,
2. Schotten-Baumann procedures,
 - (i) Criegee method,
 - (ii) Milas and Surgenor method,
3. Other acylation procedures,
4. Imidazolid procedure.

1. Baeyer and Villiger⁶ prepared the first peroxyester, diethyl diperoxyterephthalate, by treating a barium salt of a hydroperoxide (barium ethyl peroxide) with an acid chloride (terephthaloyl chloride) under neutral conditions. The lone pair of the anion attacks the carbonyl carbon which then breaks its bond with the chlorine.



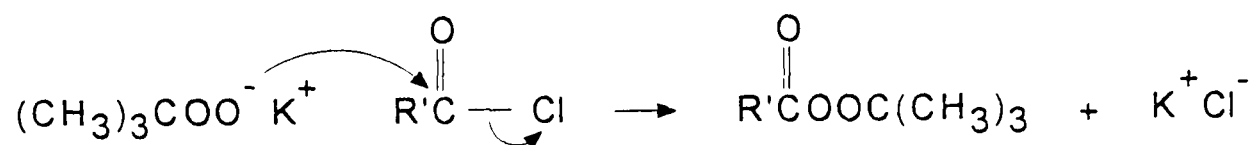
This method can be useful when the peroxyester is base sensitive, and was used as the only method of peroxyester formation until 1944, up to when only five peroxyesters⁷ were definitely known: ethyl peracetate, dimethyl, diethyl and di-isopropyl perterephthalates and sec.-methyl perester tert.-methyl camphorate.

2.(i) The Schotten-Baumann procedure first utilised by Criegee⁸, is suitable for tertiary peroxyesters as it employs either aqueous alkali or pyridine as the base, usually at ice temperature or lower. Criegee prepared trans-9-decalyl peroxybenzoate (A) from the corresponding hydroperoxide and benzoyl chloride in pyridine by this new method. Pyridine forms the counter ion of the hydroperoxide anion by abstracting the proton, and then neutralises any hydrogen chloride formed.



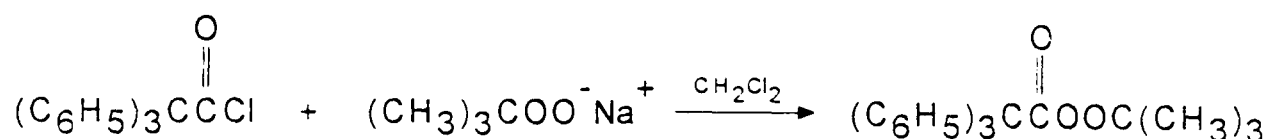
This method of preparation via the salt⁹ is convenient for alkyl hydroperoxides which are sensitive to acid or are difficult to acylate according to the common methods shown below.

(ii) Shortly after, Milas and Surgenor⁷ demonstrated the availability of the previously unknown tertiary-butyl peroxyesters, by simultaneously adding an acid chloride and aqueous alkali (30% potassium hydroxide) to cold (10°-20°C) tertiary-butyl hydroperoxide.

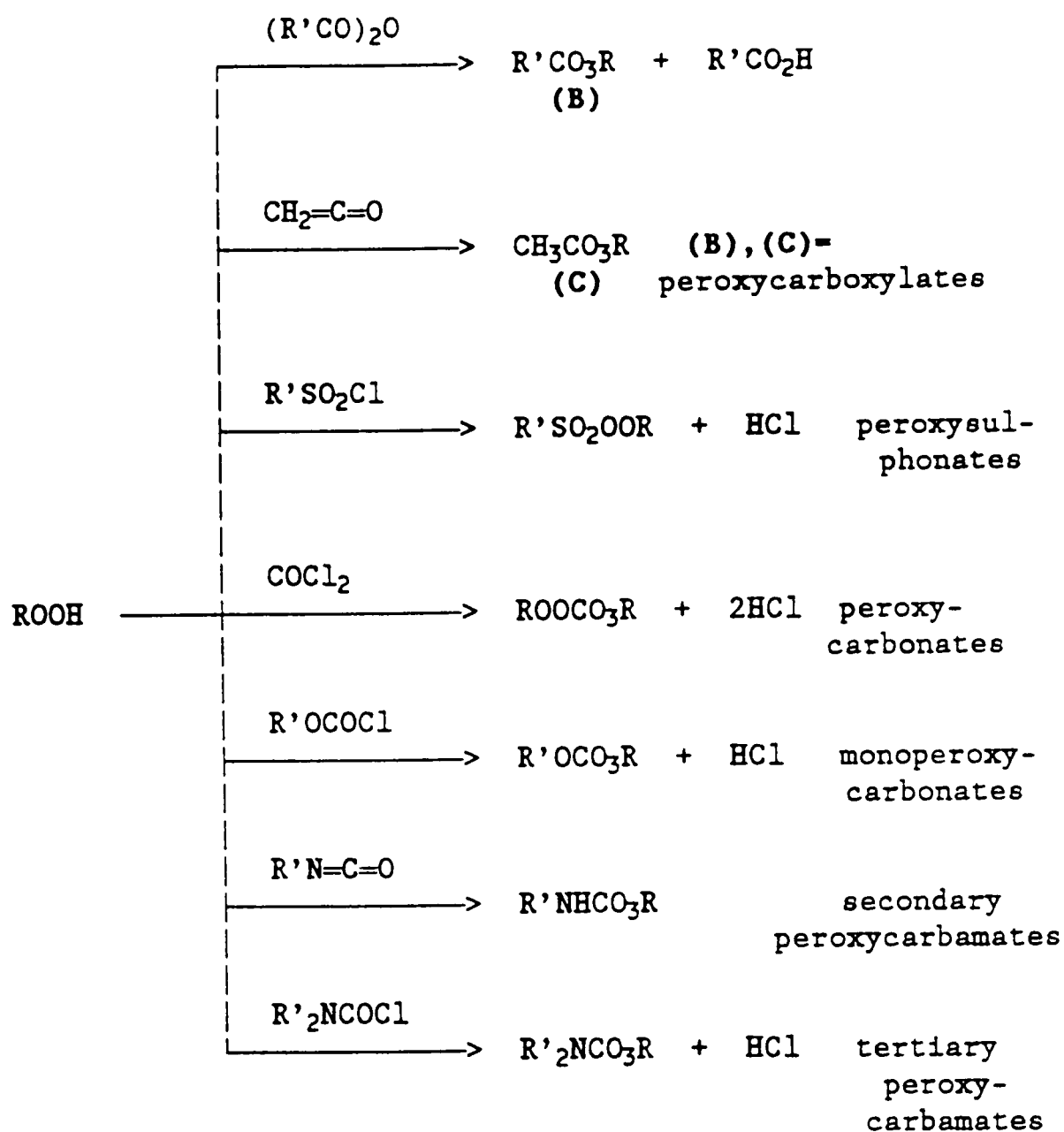


Later, Milas *et al.*¹⁰ modified this procedure by omitting the alkaline conditions and rapidly removing the hydrogen chloride formed by creating a vacuum (60-70mmHg) rather than using a base. This method was originally used to show that tertiary-alkyl and tertiary-aralkyl chlorides undergo solvolysis with tertiary-alkyl hydroperoxides, to form substantial yields of di-tertiary-alkyl or mixed tertiary-alkyl aralkyl peroxides when the hydrogen chloride is quickly removed¹¹. With no need of basic conditions, relatively high yields of peroxyesters could be made as well as, in some cases, the formation of new types of peroxyester not usually formed in the presence of base¹⁰.

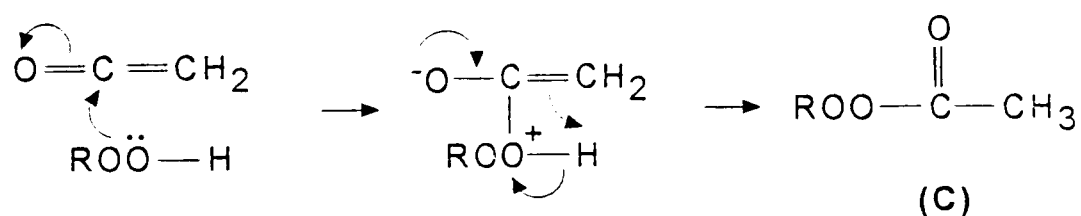
Lorand and Bartlett¹² found that yields of peroxyesters could also be improved by using the sodium salt of tertiary-butyl hydroperoxide (from tertiary-butyl hydroperoxide and sodium hydride). For example, tertiary-butyl triphenylperoxyacetate which is not available from the acid chloride, tertiary-butyl hydroperoxide and pyridine, was obtained in 55% yield by this variation.



3. The acylation methods discussed so far have involved the acylation of the salts of hydroperoxides. The procedures shown below involve acylation of the hydroperoxide itself, where the carbonyl carbons are electrophilic enough to be attacked by the peroxy oxygen of the hydroperoxide (as they have electron withdrawing groups attached to the carbonyl carbon or sulphonyl sulphur). These include the use of acid anhydrides, ketenes, sulphonyl chlorides, phosgene, chloroformates, isocyanates and carbamoyl chlorides:

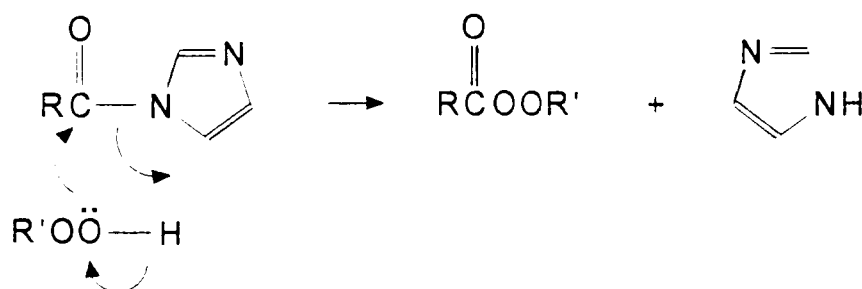
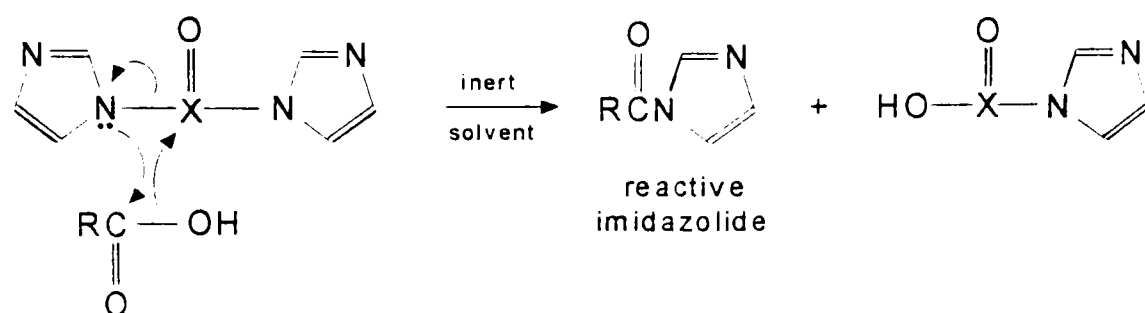
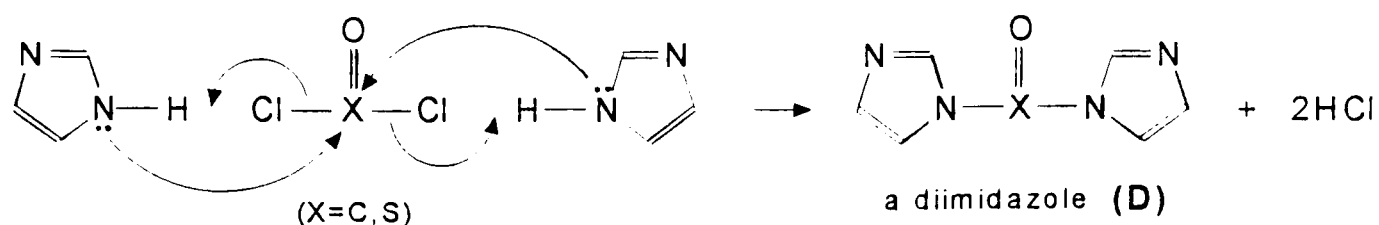


The type of mechanism is outlined below in the reaction of the hydroperoxide with ketene:

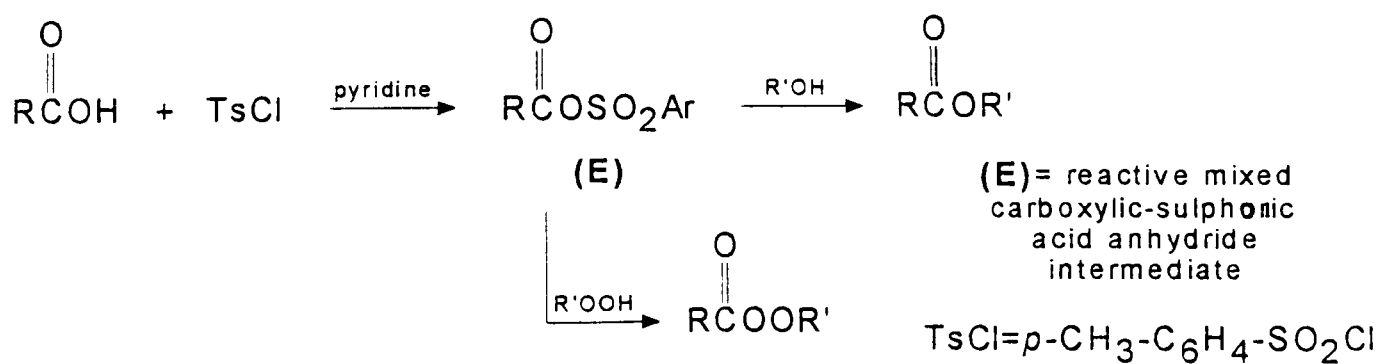


The other acylations proceed via similar mechanisms.

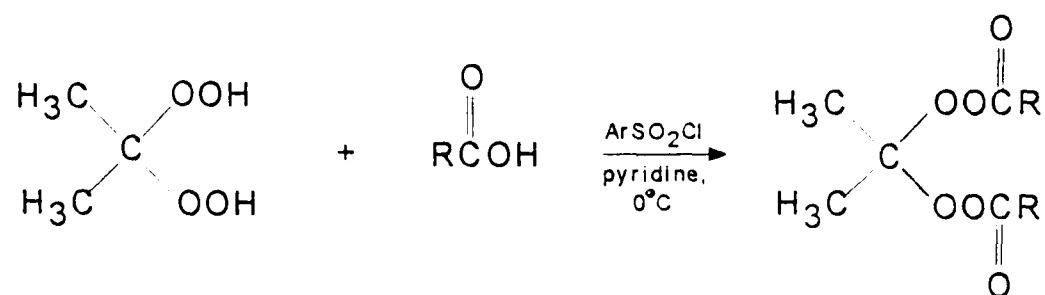
4. Another successful approach to peroxyesters utilises imidazolides as intermediates in the acylation of hydroperoxides. Rüchardt and Hecht¹³ prepared these reactive amides by reacting a carboxylic acid with either N,N-carbonyl- or N,N-thionyl- diimidazole (D). The imidazole is produced by reacting either thionyl chloride or phosgene with the appropriate secondary amine which is generated.



This synthesis is similar to the Brewster-Ciotti esterification procedure¹⁴, where esters are prepared directly from carboxylic acids by treating the latter with *p*-toluenesulphonyl chloride (TsCl) and pyridine in the presence of alcohols. This method was used by Milas and Golubović^{15,16} for peroxyester preparation by substituting hydroperoxides for alcohols.



For example, in the preparation of alkylidene peroxyesters, the acid and hydroperoxide are treated with arylsulphonyl chloride at 0°C^{15,16}.



All the above methods to organic peroxyesters have involved acylating hydroperoxides or their salts. The literature^{4,17} classes them as derivatives of organic acids and hydroperoxides rather than of peroxyacids and alcohols (which yield hydroperoxides when in acidic conditions¹⁸), as attempts to esterify peroxyacids have not yet met with success (unlike the successful reactions of carboxylic acids with alcohols to yield esters – the OR of the alcohol displacing the OH of the acid). The experimental work described later will be an attempt to disprove this approach, and involves the peroxy oxygen of a peroxyacid being nucleophilic enough to attack a carbocation.

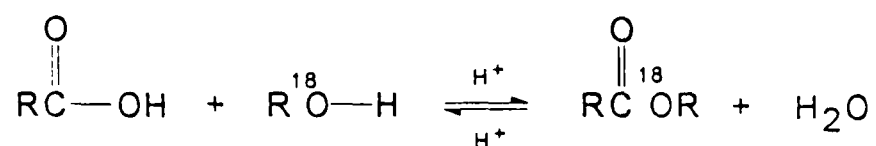
1.2.2 Preparation of Esters¹⁹

As a new route to peroxyester formation is the basis of the experimental work described here, a discussion on the preparation of esters for comparison and contrast would be relevant.

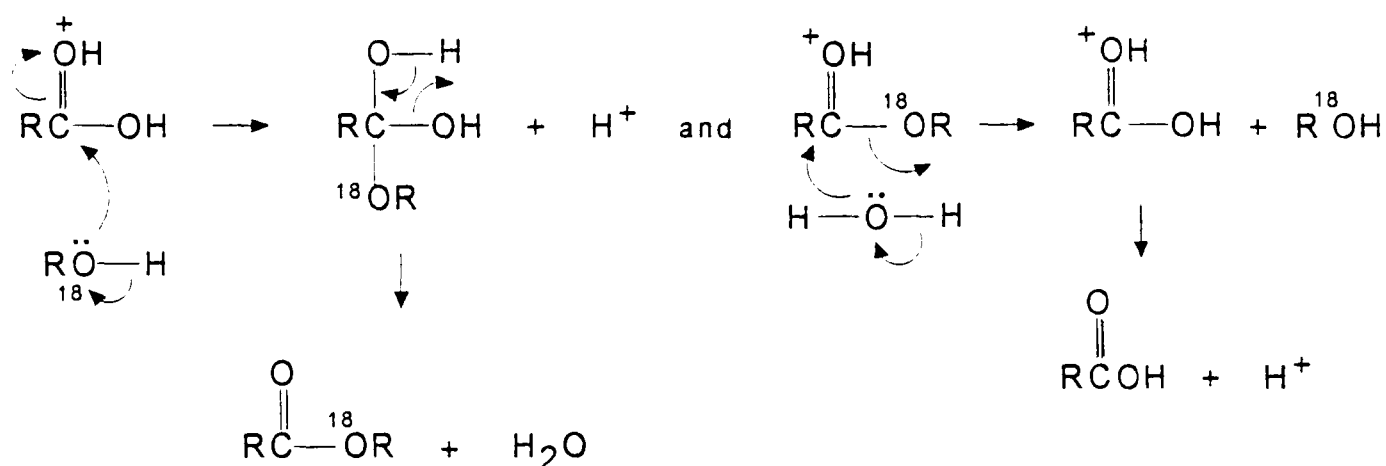
Unlike peroxyesters, esters can be prepared by the direct esterification of carboxylic acids as well as their derivatives, and is the most utilised method of ester formation. Five methods will be discussed and are as follows:

1. Direct esterification of carboxylic acids,
 - (i) Heating with an alcohol,
 - (iii) Brewster-Ciotti method,
2. Intramolecular esterification,
3. Schotten-Baumann procedure,
4. Baeyer-Villiger rearrangement,
5. Use of the silver salt of a carboxylic acid.

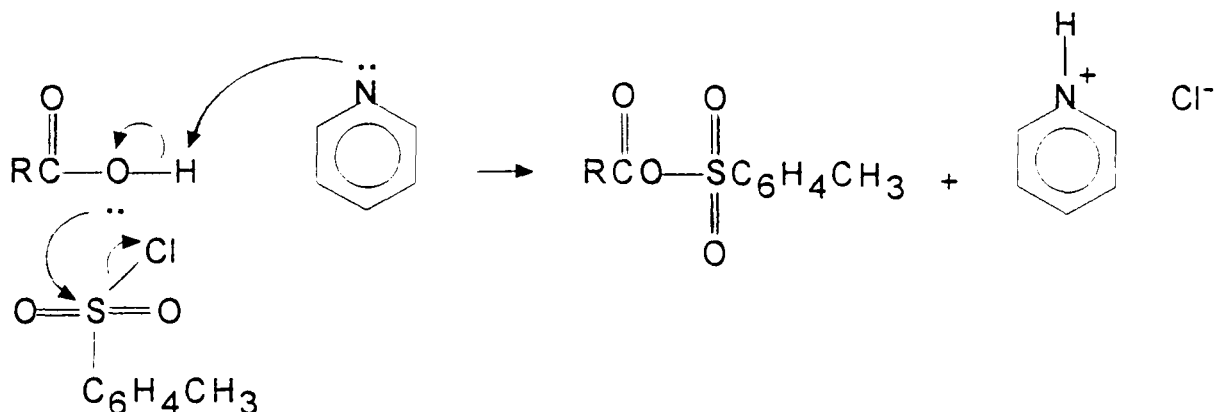
1.(i) A carboxylic acid is converted directly into an ester when heated with an alcohol in the presence of an acid catalyst, usually concentrated H_2SO_4 or dry HCl . The reaction is slower than with acid anhydrides or acid chlorides. Equilibrium is generally reached when there are appreciable quantities of both reactants and products present but, if either the acid or alcohol is cheap and readily available, it can be used in excess as a way to shift the equilibrium. Studies employing both hydrolysis and esterification show that bond cleavage occurs between oxygen and the acyl group.

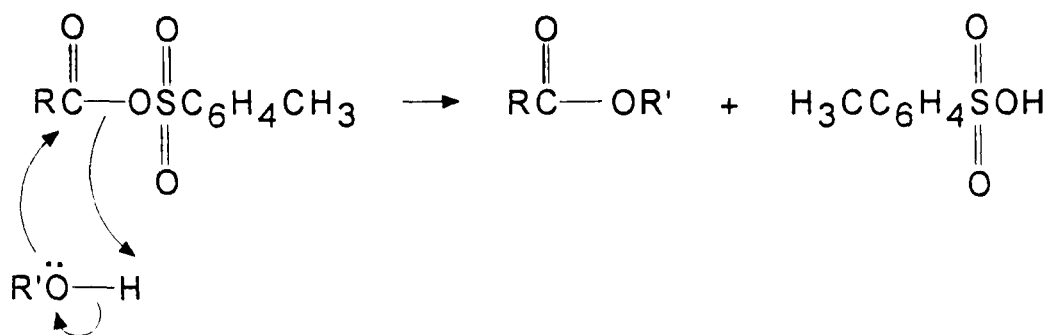


The simplified mechanisms for the acid-catalysed preparation of esters and hydrolysis are outlined below.

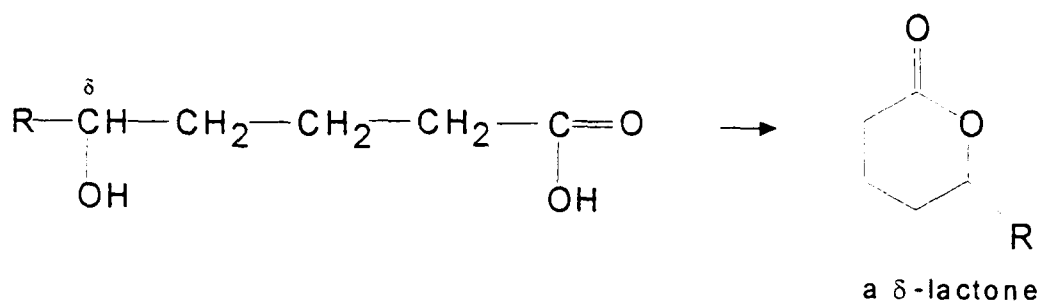
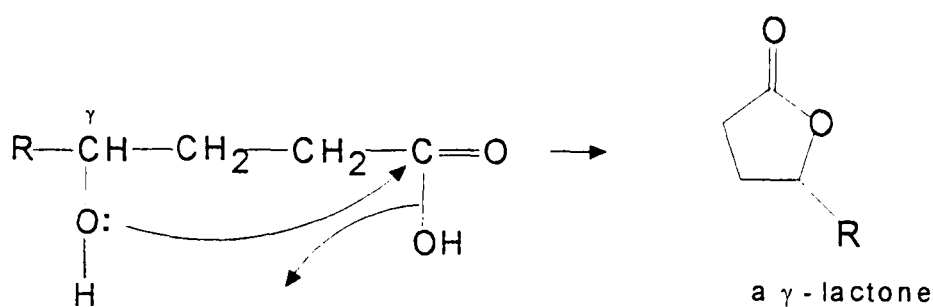


(ii) The Brewster-Ciotti esterification¹⁴ is another direct method to esters. A "one pot reaction" occurs when a carboxylic acid is treated with an arylsulphonyl chloride and pyridine in the presence of an alcohol.

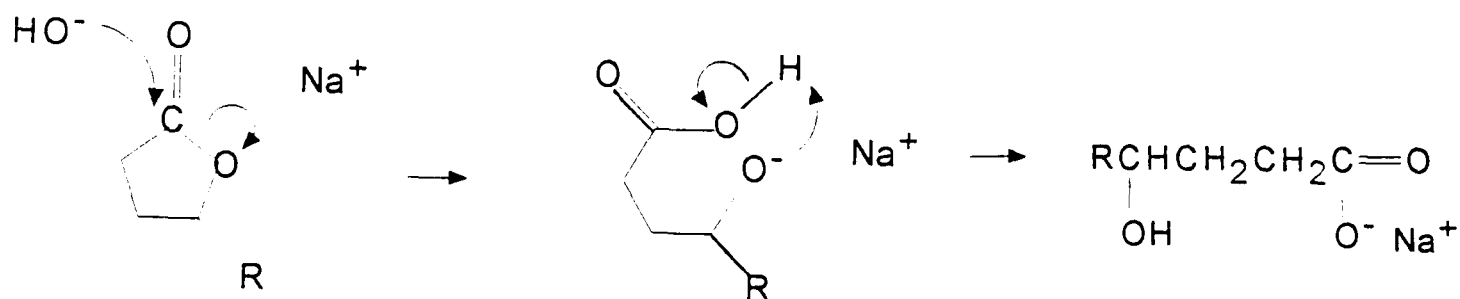




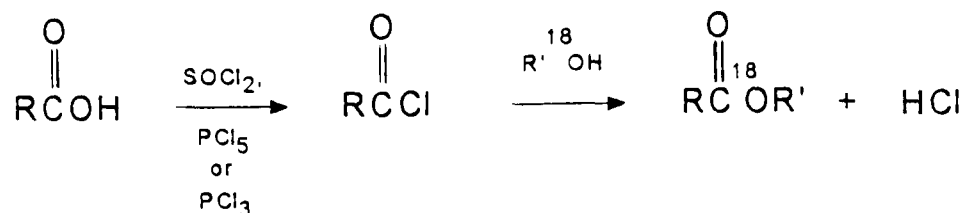
2. Intramolecular esterification occurs with γ - and δ - hydroxyacids. As they are both alcohol and acid they can lose water simultaneously to yield cyclic esters.



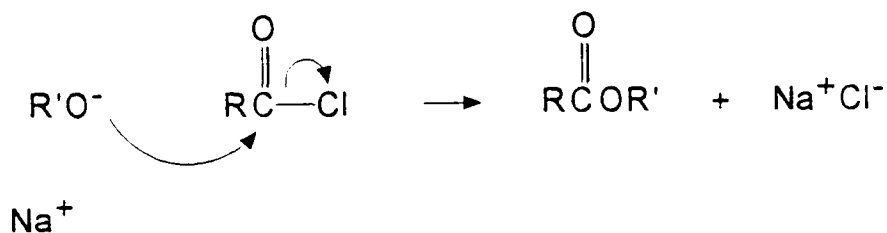
Hydrolysis with base rapidly opens the lactone ring to give the open-chain salt.



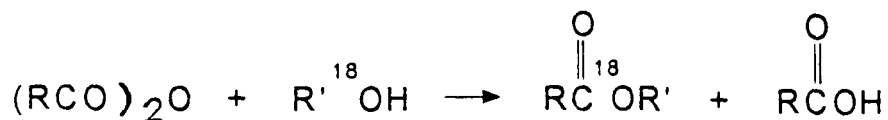
3. As well as esterifying carboxylic acids directly, acids are frequently converted into their esters via acid chlorides as they are more reactive and the reaction goes to completion.



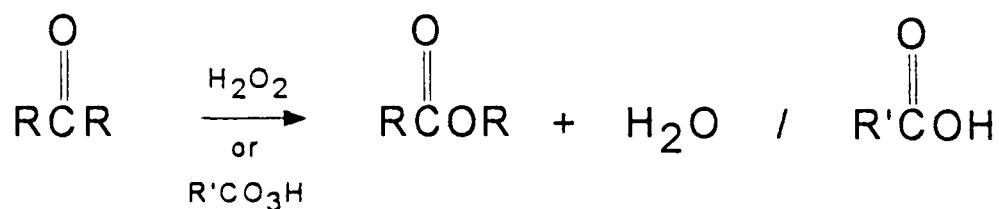
Aromatic acid chlorides however, are considerably less reactive than their aliphatic counterparts (carbonyl carbon charge lost by resonance into the aromatic ring). To compensate, the Schotten-Baumann procedure can be used, and as in the related reaction to peroxyesters, the acid chloride is added in portions (followed by vigorous shaking) to a mixture of the hydroxy compound and a base – usually aqueous sodium hydroxide or pyridine. Again, the base catalyses the reaction by removal of the proton of the hydroxy group, as well as neutralising the hydrogen chloride formed, for example, by using aqueous sodium hydroxide.



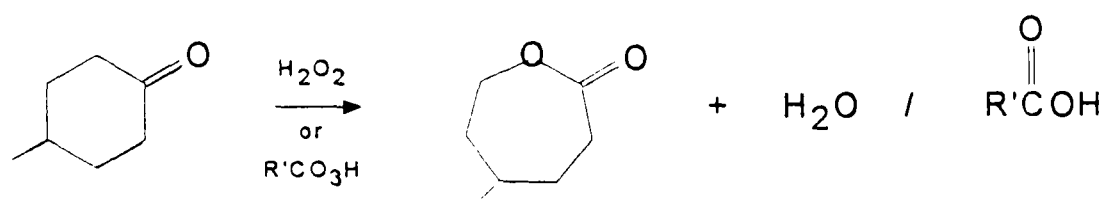
Acid anhydrides undergo the same reactions as acid chlorides but a little more slowly, and yield a molecule of carboxylic acid rather than hydrogen chloride.



4. The Baeyer-Villiger rearrangement also affords esters and involves the oxidation of ketones by the addition of a peroxide to the carbonyl group, followed by rearrangement (see below). The reaction is accomplished by the acid-catalysed reaction with hydrogen peroxide or a peroxyacid.

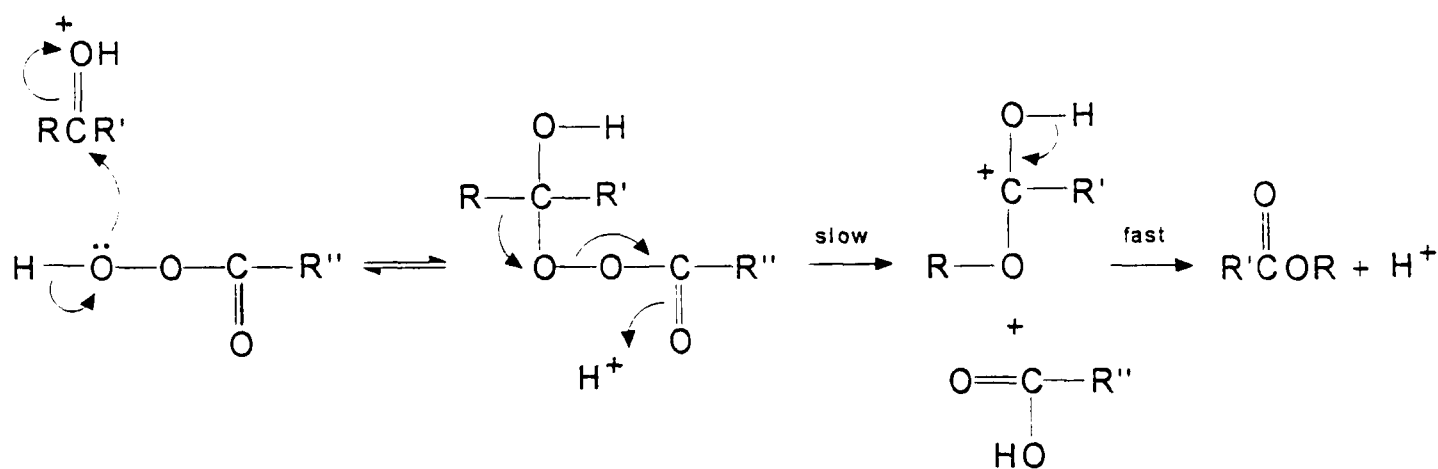


Cyclic ketones are converted into lactones.

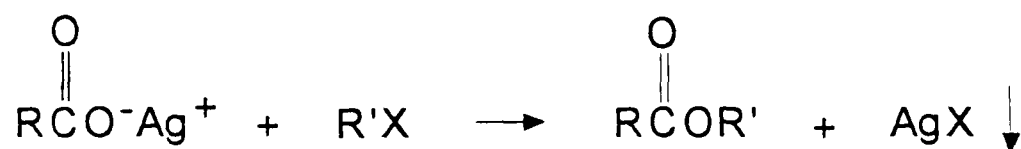


The reaction is catalysed by acid, and the rate of oxidation accelerated by electron-donating groups in the ketone and by electron-withdrawing groups in the peroxyacid^{19b}. Trifluoroperoxyacetic acid is one of the more reactive peroxyacids in this reaction.

The reaction is believed to proceed as follows, where R has a greater migratory aptitude than R'.



5. A more expensive method of ester formation involves the silver salt of the carboxylic acid. The nucleophilic carboxylate ion readily attacks an alkyl halide (R'X) to yield an ester and silver halide precipitate.



1.2.3 Preparation of Peroxyacids^{5,20,21}

Peroxyacids play a vital role in the new synthetic route to peroxyesters, and thus their most commonly known preparations will be discussed. They are very important in industry, with the reactive peroxy

oxygen utilised in epoxidations²² and bleaching²³ reactions especially. However, up until now^{4,17}, they have been unrecognised as being sufficiently reactive to be alkylated.

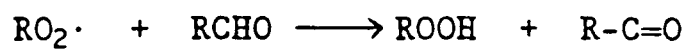
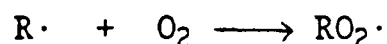
The four main methods to peroxyacid formation have been summarised below.

1. By the oxidation of aldehydes,
2. From (i) carboxylic acids or (ii) acid anhydrides, with hydrogen peroxide,
3. From acid chlorides and sodium peroxide or hydrogen peroxide,
4. From (i) acyl peroxides and alcoholates, and (ii) hydrogen peroxide and boric carboxylic anhydrides.

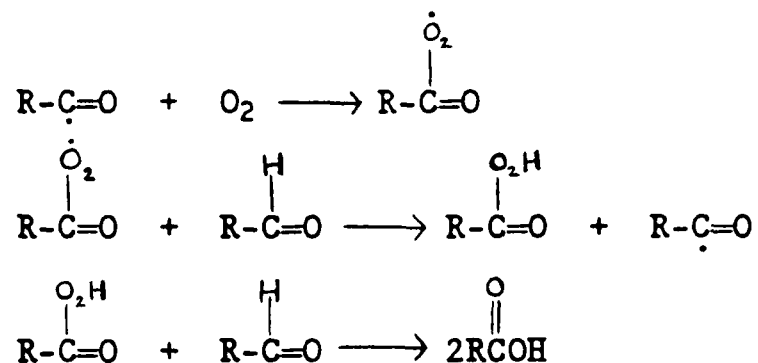
1. Since 1900, it has been known that a peroxyacid is the intermediate in the oxidation of an aldehyde²⁴. (Bäckström²⁵ was the first to formulate the chain reaction mechanism involved.)

The initiation step involves homolytic decomposition of the aldehyde to R· and ·CHO induced by UV radiation, traces of metallic salts or small quantities of ozone, and subsequent formation of RCO as shown below. The resultant radical then reacts with oxygen (also an odd electron species) in the propagation step, to form the acylperoxy radical, RCO₂· which then abstracts a hydrogen atom from an additional aldehyde. The peroxyacid is thus formed and can react with excess aldehyde to form two moles of carboxylic acid²⁶. Also, the radical R-C=O is regenerated and continues the chain reaction.

Initiation

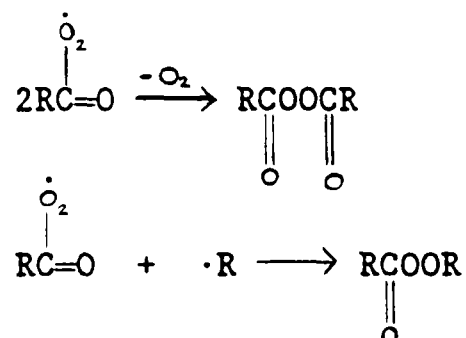
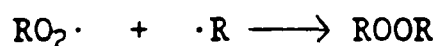


Propagation

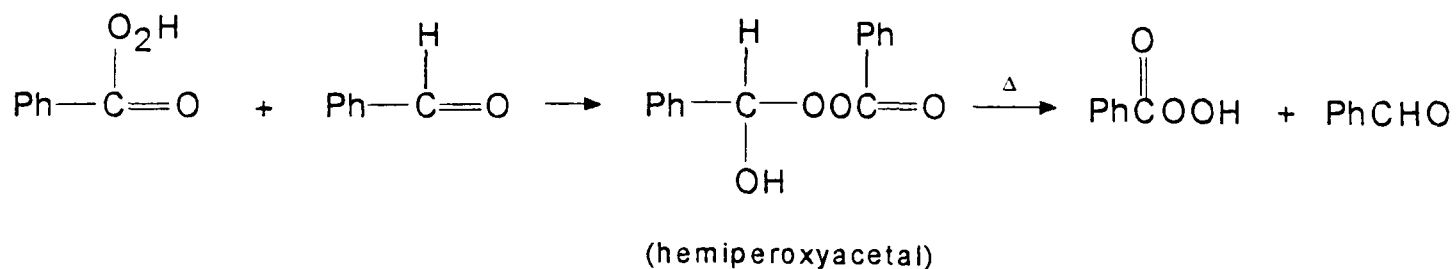


Termination

For example:



Under appropriate low temperature conditions, a hemiperoxyacetal can form. When formed from acetaldehyde and peroxyacetic acid, the resultant hemiperoxyacetal is extremely explosive and must be carefully decomposed (thermally)²⁷ and the products separated. In the preparation of peroxybenzoic acid from benzaldehyde, the explosion hazard is apparently a minor one²⁸.



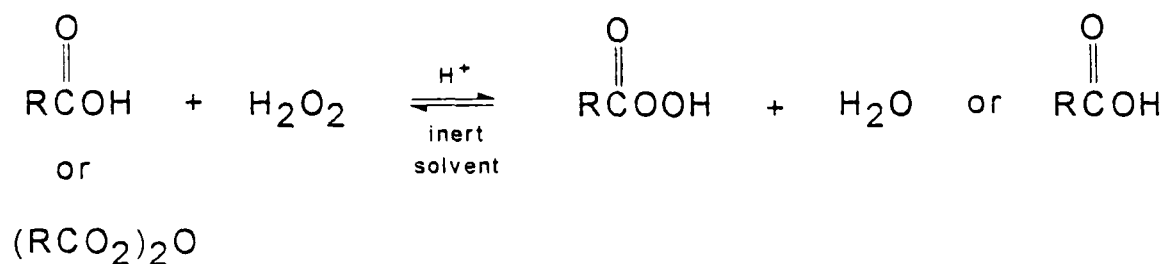
Unless there are controlled conditions and removal of the peroxyacid as it is prepared, especially in the case of aliphatic aldehydes (as they are more reactive towards the aldehyde than their aromatic counterparts), then the peroxyacid will only be an intermediate as shown above.

Dick and Hanna²⁹ showed that yields of peroxybenzoic and substituted peroxybenzoic acids from the corresponding aldehydes are

solvent-dependent (high in polar ones and low in non-polar ones). For example, in methyl or ethyl acetate solution, peroxybenzoic acid can be prepared in 90% yields at 98+% benzaldehyde consumption by action of oxygen and catalytic quantities of ozone. Similarly 4-methyl-, 2-chloro-, 4-chloro-, 3-nitro-, and 4-nitro- peroxybenzoic acids were prepared in 60-83% yields.

2. Another, more practical method to peroxyacids, involves allowing carboxylic acids or anhydrides, or mixtures of the two, to react with concentrated solutions (30-90%) of hydrogen peroxide in the absence or presence of catalysts. These could be mineral acids, for example H_2SO_4 , phosphoric and boric acid. However, attainment of equilibrium is impractically slow in the absence of a strong acid catalyst. This method to peroxyacids is utilised in the standard route for the in situ epoxidation of alkenes, where the alkene is treated with glacial acetic acid and 90% hydrogen peroxide, without performing the peroxyacid.

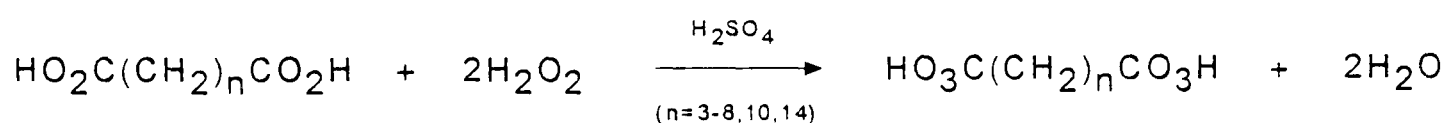
A serious problem is the use of such high percentage solutions of hydrogen peroxide, which as previously mentioned, are potentially explosive in the presence of organic compounds. The equilibrium reaction is however the most utilised method for the preparation of aliphatic peroxyacids³⁰.



(1) Reaction with carboxylic acids

Along with the aliphatic acid and hydrogen peroxide, an inert solvent (for example n-propyl acetate) and acidic catalyst are used. As the reaction is reversible, yields of peroxyacid are highest by the use of excess aliphatic acid and/or more concentrated hydrogen peroxide. Under vacuum, the inert solvent acts as an azeotroping agent for the continuous removal of water from the reaction mixture. This also provides a way of driving the reaction to completion³¹ (not applicable to the preparation of peroxymethanoic acid owing to its instability).

The reaction was originally developed and extensively studied by D'Ans and co-workers for the preparation of short chain water-soluble peroxyacids³⁰. With water-insoluble aliphatic carboxylic acids up to C₁₆, concentrated H₂SO₄ (95%) is an excellent mutual solvent and reaction medium³². The C₁₈ and longer chain aliphatic acids are too insoluble in H₂SO₄ for their conversion to peroxyacids by this method, but methanesulphonic acid (CH₃SO₃H) may be used instead³³. If the acids are insoluble in CH₃SO₃H, they can be replaced by their more soluble methyl esters, as seen for the preparation of diperterephthalic and peroxy palmitic acid³⁴. Also, this method may be used for certain aliphatic acids containing functional groups sensitive to H₂SO₄, as well as for the preparation of α-aliphatic diperoxyacids³⁵.



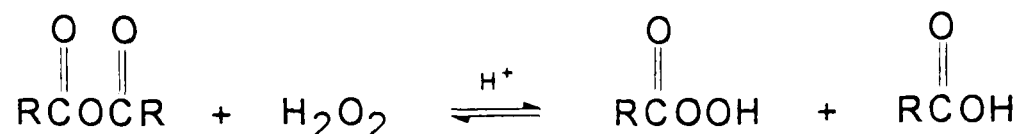
Until 1962, there was no satisfactory procedure for the direct preparation of aromatic peroxyacids from the corresponding carboxylic acid and H₂O₂. The major problems were the insolubility of the aromatic carboxylic acids in H₂O₂, and if H₂SO₄ is used as solvent and reaction medium, excess and sometimes violent oxidation of the aromatic nucleus occurs. Its low solvation capacity for most of the aromatic acids, as for the longer chain aliphatic acids is another problem too. CH₃SO₃H was shown to be a satisfactory non-oxidizing solvent and catalyst system for preparing aromatic peroxyacids³⁴. The procedure has been successfully applied to the preparation of peroxybenzoic acid, *p*-tertiary-butyl-, *p*-nitro-, *o*-nitro-, *p*-cyano- peroxybenzoic and diperoxyterephthalic acids, and others. However, attempts to prepare the corresponding peroxyacids from *p*- and *m*- methoxybenzoic acids by this method were unsuccessful³⁴ because of ring attack.

This procedure is equally applicable to the preparation of aliphatic peroxyacids. Labile functional groups present in the acids such as cyano, hydroxyl and halogen, are unattacked by this system³⁴.

(ii) Reaction with anhydrides

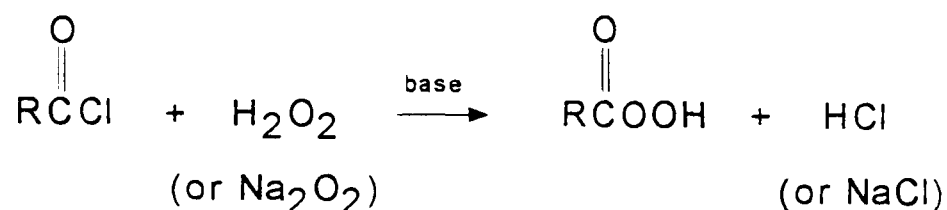
The reaction of acid anhydrides with 30-98.5% H₂O₂ was one of the first methods used to prepare anhydrous solutions of peroxyacids^{30a}. In

the aliphatic series, only the short chain anhydrides (ethanoic, propanoic and butanoic) are usually readily available, limiting the method's generality.



The main drawbacks to this reaction are that the aliphatic anhydride or carboxylic acid may react with the peroxyacid to form the corresponding acyl peroxide. Compare the latter reaction with 1.2.4 "Preparation of Acyl Peroxides". This lowers the conversion of H₂O₂ to peroxyacid. Also, only half of the anhydride is directly convertible to peroxyacid, thus limiting yields to 50% based on anhydride.

3. The reaction of acyl halides with sodium peroxide or H₂O₂ and base (to neutralise any hydrogen chloride formed), has also been used to obtain peroxyacids.



In the aliphatic series it is now rarely used, because acyl peroxides are frequently major byproducts and methods are now available for preparing peroxyacids directly from acids and aldehydes as shown above. In fact, this reaction is better suited to the preparation of aliphatic acyl peroxides than of peroxyacids. (See this Chapter, 1.2.4 "Preparation of Acyl Peroxides".)

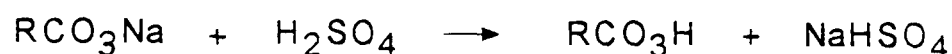
In the aromatic series on the other hand, this method has been and continues to be a method of widespread use, since acyl halides are readily obtained³⁶ and yields of peroxyacids have been raised considerably by procedural improvements, for example with peroxybenzoic acid³⁷.

The method of Silbert³⁴ et al. proves unsatisfactory when the aromatic ring also contains electron-donating groups which favour ring attack. With such systems, the acyl halide is preferable.

There is a number of further reactions for the preparation of organic peroxyacids which Swern²¹ has summarised. The reactions tend to be towards specific products or give low yields. For example, D'Ans^{30a} describes how the reaction of ketene and H₂O₂ yields peroxyacetic acid, though the reaction is better suited for the preparation of acetyl peroxide.

4. The reaction of acyl peroxides and alcoholates has little utility for the preparation of aliphatic peroxyacids, which are more conveniently obtained directly from the corresponding carboxylic acids (see above).

(i) Aroyl peroxides are in general easily available solids which are relatively stable and easy to purify. Thus, the reaction has had its most widespread use in the preparation of aromatic peroxyacids, and most particularly peroxybenzoic acid itself^{38a,39,40} (the method being used by the present author), because of the commercial availability of benzoyl peroxide. Unfortunately, only 50% of the aroyl groups are convertible to peroxyacid by basic hydrolysis followed by acidification. Excess acid can destroy the peroxyacid⁷¹.



(ii) In 1912^{30a} and 1950⁴¹, D'Ans also showed how anhydrous peroxyacids could be prepared by reaction of boric carboxylic anhydrides with H₂O₂.

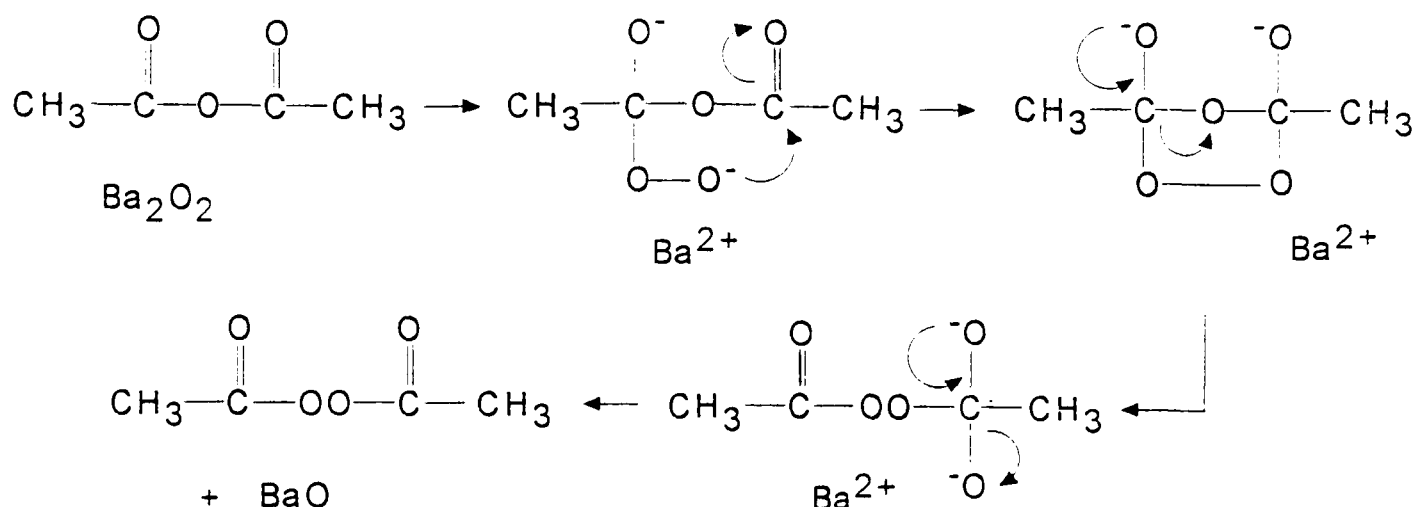


1.2.4 Preparation of Acyl Peroxides¹⁷

The preparations of acyl peroxides have also been considered as benzoyl peroxide was involved in peroxybenzoic acid formation, itself to be esterified to the corresponding tertiary-butyl peroxyester. Many of the peroxides of this class, particularly (but not exclusively) the lower members, are explosive and sensitive to shock and friction, and are thus usually prepared as solutions or in situ at low temperatures and many require cold storage. The route to formation depends upon whether symmetrical or unsymmetrical peroxides are to be prepared.

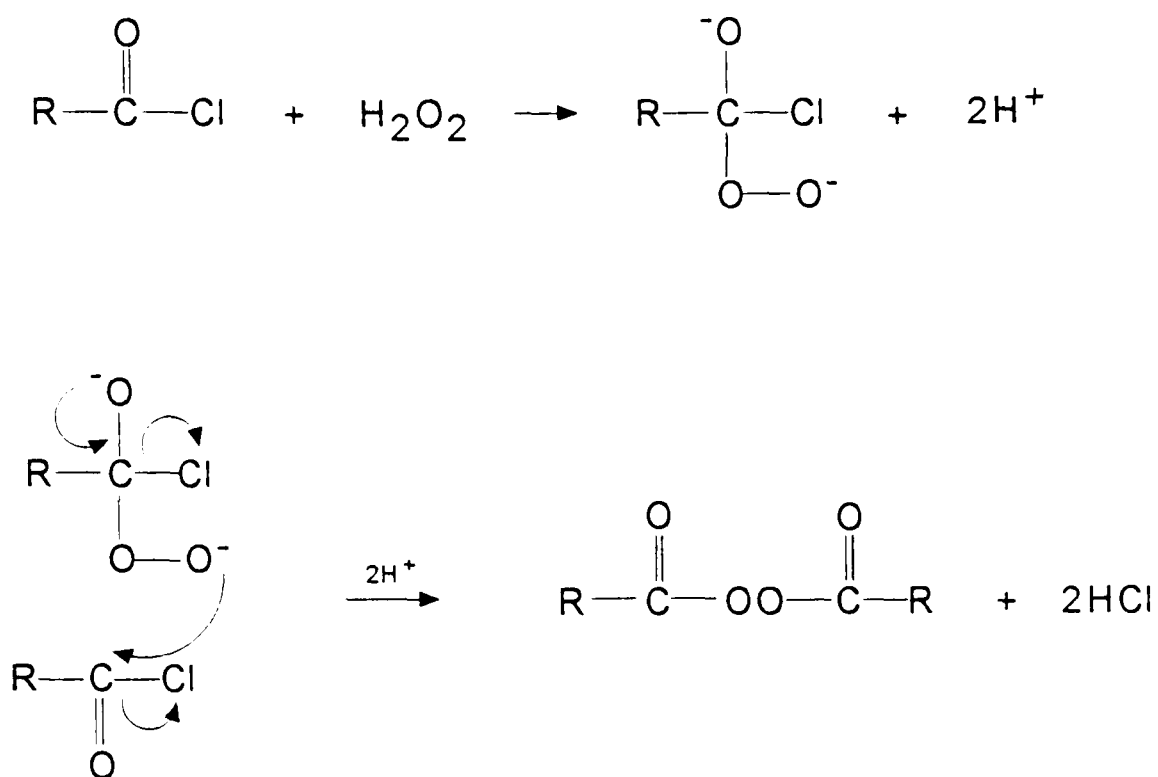
1. Symmetrical acyl peroxides: by reacting an acid chloride or anhydride with sodium peroxide or hydrogen peroxide in the presence of base.
2. Unsymmetrical acyl peroxides: by reacting an acid chloride or anhydride and the sodium salt of a peroxyacid, or the peroxyacid itself.

1. Brodie² prepared the first acyl peroxide (acetyl peroxide) by treatment of barium peroxide with acetic anhydride.



The more common method (to prepare aliphatic acyl peroxides especially) has been adapted from that by Brodie, and involves a base like pyridine, sodium hydroxide, sodium bicarbonate or sodium acetate, to

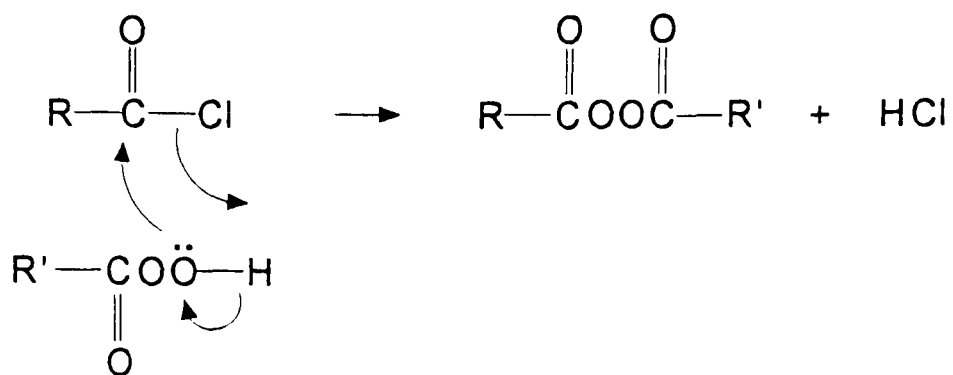
remove the hydrogen chloride formed if an acid chloride and hydrogen peroxide are used in the preparation.



(Compare this with peroxyacid preparations which use the same reagents.)

Benzoyl peroxide can be obtained in about 70% yield by treating benzoyl chloride with aqueous H_2O_2 ³⁸, or with sodium peroxide in aqueous acetone. If the acyl peroxide is readily hydrolysed, a mild base such as sodium bicarbonate should be used, or the preparation carried out under anhydrous conditions using for example, a hydrogen peroxide-urea $[\text{CO}(\text{NH}_2)_2]$ complex. Higher acid chlorides (C_8 - C_{18}) form stable aqueous emulsions and are better treated with 50-65% hydrogen peroxide in the presence of pyridine rather than caustic soda.

2. Similarly, for unsymmetrical acyl peroxide production, a base, for example pyridine, is used to neutralise the hydrogen chloride formed if an acid chloride and peroxyacid are reacted.



1.2.5 Preparation of Hydroperoxides^{1,42}

The most utilised routes to peroxyester synthesis proceed via the nucleophilic attack by the peroxy oxygen of hydroperoxides, either as a salt of the hydroperoxide or as the hydroperoxide itself. Milas and Surgenor⁷ also found that peroxyesters are hydrolysed more readily than their corresponding esters - the former requiring a temperature of 5°C and the latter heating - to give a hydroperoxide (see this Chapter, 1.4.5 "Hydrolysis of Peroxyesters") and a carboxylic acid.

Alkyl hydroperoxides are structurally the simplest derivatives of the powerful nucleophile hydrogen peroxide. They may be primary, secondary or tertiary.

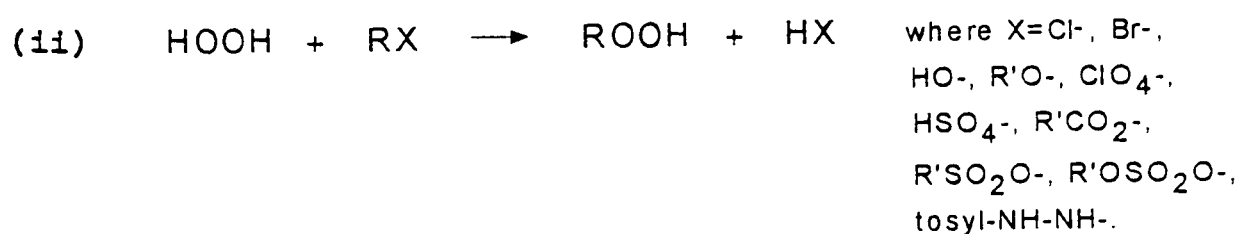
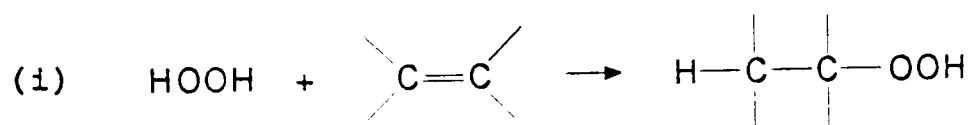
Hydroperoxides may be prepared from organic compounds by the action of:

1. Hydrogen peroxide,
2. Molecular oxygen (autoxidation),
3. Hydrolysis,
4. Miscellaneous reactions.

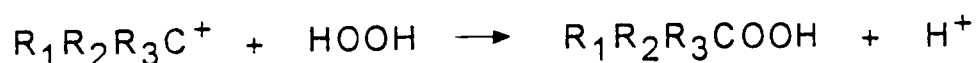
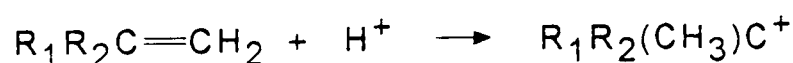
The use of ozone is also known, but its reactions are limited to producing α -alkoxy hydroperoxides ($\text{R}_2\text{C}(\text{OR}')\text{CR}_2\text{OOH}$, where R=alkyl, aralkyl or hydrogen), and so this reaction will not be discussed further here.

1. Use of hydrogen peroxide is the most commonly used procedure, but yields are low if the compound is not tertiary, and the solutions can be hazardous with potential detonation when hydrogen peroxide is present in more than 30% by weight⁴³.

As hydrogen peroxide (or sodium peroxide) has the O-O linkage already present, it is frequently used in hydroperoxide synthesis. The hydrogen peroxide molecule and its anion are highly reactive nucleophiles and react with (i) many alkenes by addition and (ii) suitable alkyl compounds RX by displacement, where X is an electronegative leaving group or where R can stabilise a positive charge at the carbon attached to X.



The reactions with alkenes and alcohols in the presence of strong mineral acid proceed through a carbocation intermediate^{20a}.



N-Alkyl-N'-tosylhydrazines can be easily oxidised in THF at room temperature with high yields (90-95%) into hydroperoxides, by the action of hydrogen peroxide or sodium peroxide^{20b}. The hydrazines themselves are obtained by the reduction of the corresponding tosylhydrazones (R₂C=N-NHTs) or tosylhydrazides (RCONHNHTs).

The mechanism of hydroperoxide formation is believed to be as follows:

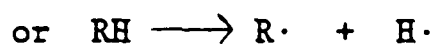
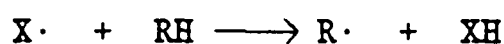
2. The formation of hydroperoxides from molecular oxygen offers the greatest scope but is the most complex method and involves autoxidation^{1,17,42} (that is, the reaction with molecular oxygen generally below 120°C and in the absence of a flame) and its corresponding free radical chain reactions.

A wide variety of organic compounds will undergo autoxidation to yield hydroperoxides, with the rate of formation being highly dependent on the compound's structure. Organic and organometallic compounds can include alkanes bearing tertiary hydrogens, aralkanes, alkenes, ethers, alcohols and ketones, with their mechanisms of autoxidation well understood at temperatures of less than 200°C.

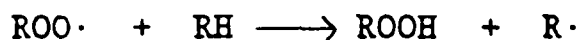
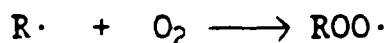
Organic Compounds

(a) Initiation

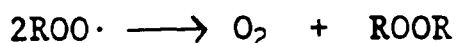
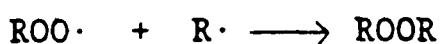
$X_2 \longrightarrow X\cdot$ (where $X\cdot$ is any radical, for example from benzoyl peroxide)



(b) Propagation



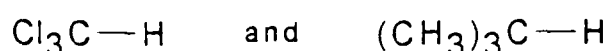
(c) Termination



(a) The initiation reaction can be brought about by the action of light, in the absence or presence of a photosensitizer, or for example by radicals generated from peroxides or azo ($-N=N-$) compounds.

(b) In the propagation reactions, the cleavage of the RH bond is about 10^6 to 10^8 times slower than the reaction of $R\cdot$ with oxygen, thus being

an important step. Steric and electronic factors that weaken or strengthen the RH bond will therefore have a significant effect on the rate of autoxidation. For example,



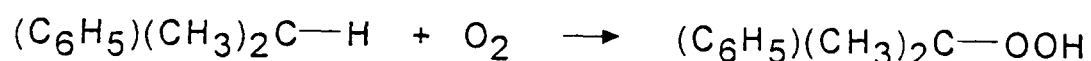
Generally, auto-oxidative attack occurs in a molecule RH where the most stable radical R· is formed upon cleavage of a C-H bond. A tertiary carbon atom will be more susceptible to attack than a primary one, whereas a carbon attached to chlorine atoms, for example Cl₃C-H, would form an even less stable radical. Steric and polar effects need also to be considered.

(c) The route of termination reaction taken will also depend on the structure of RH, and as well as oxygen pressure and foreign molecules, especially of the antioxidant type.

Autoxidation can be carried out in a homogeneous solution (in the autoxidisable compound itself, or in a nonoxidisable solvent) or an aqueous emulsion. The hydroperoxide is then usually isolated by extraction with aqueous alkali to form a salt, and regenerated by careful acidification.

(i) Autoxidation at saturated sites

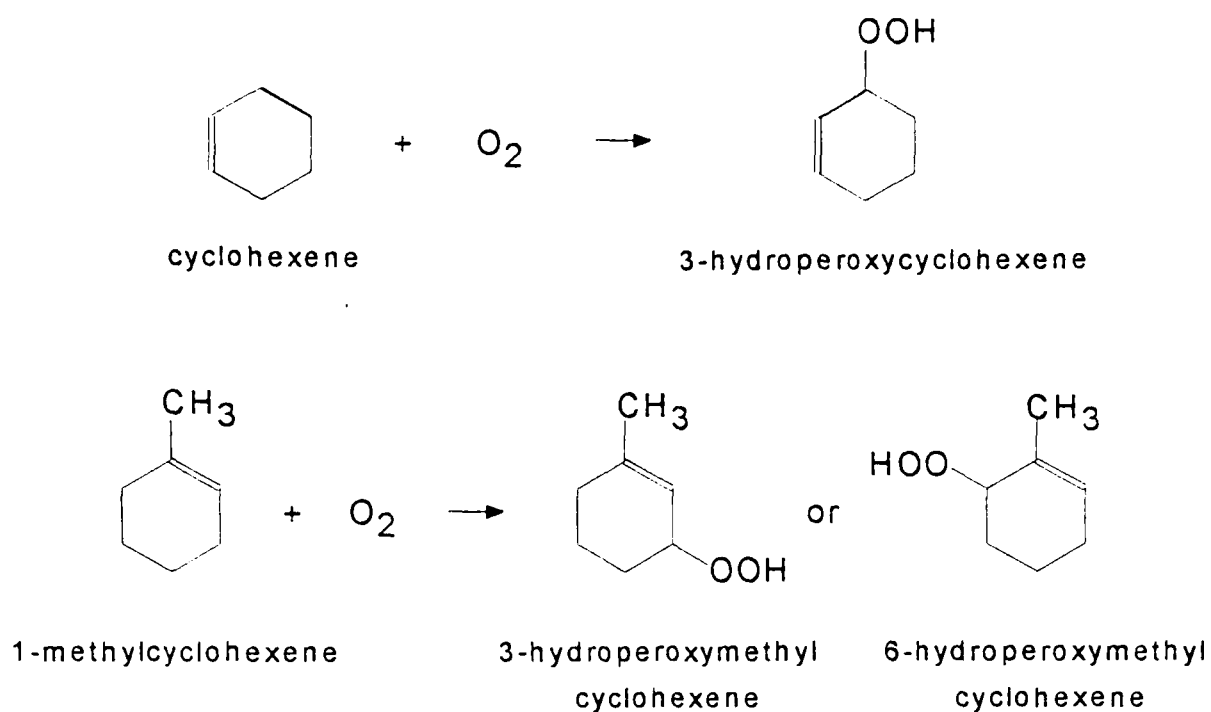
Cumene hydroperoxide is a product of the autoxidation of cumene and is prepared commercially on a large scale. The hydroperoxide formed is decomposed with catalytic amounts of strong mineral acid to give phenol and acetone, both in very high yield. (See this Chapter, 1.4.1.2 "Intramolecular Nucleophilic Rearrangement".)



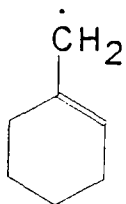
(ii) Autoxidation at unsaturated sites

The site of autoxidation is dependent on whether or not a photosensitizer is used.

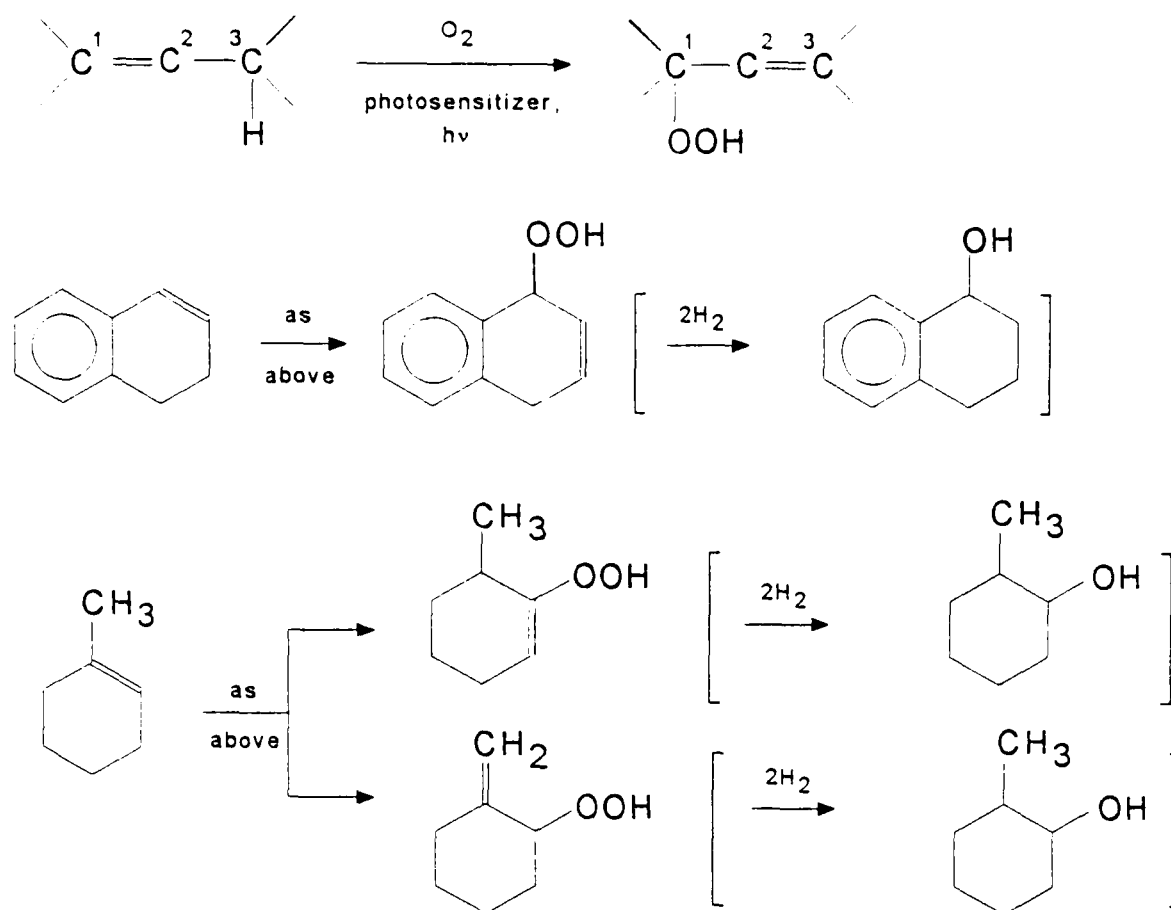
(a) If not, the double bond seems to activate the allylic carbon atom, so that the -OOH group is found attached to the allylic carbon, with the double bond remaining intact⁴⁵.



In the latter case, no hydroperoxycyclohexene is formed at the methyl group, presumably because the intermediate allylic radical would be a less stable primary one:

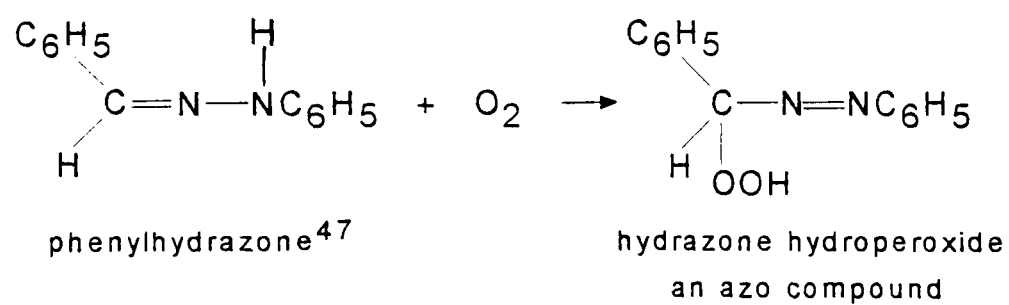


(b) When autoxidation is photosensitized (for example with chlorophyll), an sp² hybridised carbon is attacked instead, accompanied by an allylic rearrangement⁴⁶.

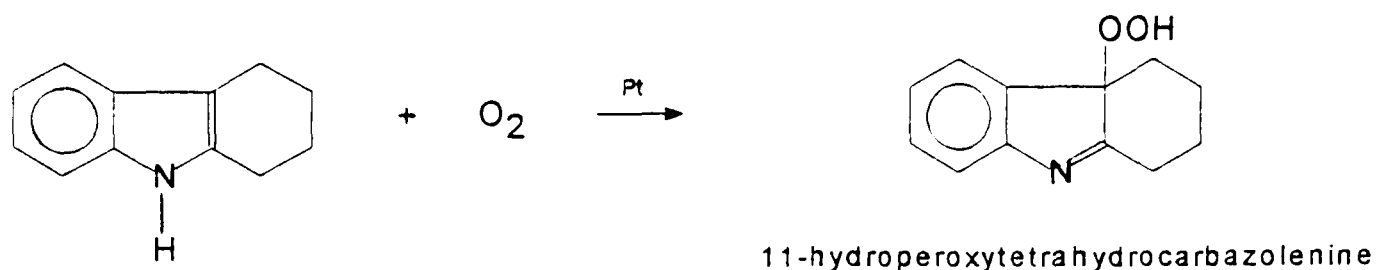


(c) Similar rearrangements occur in the autoxidation of many nitrogen-containing compounds. Compounds containing $-\text{C}=\text{X}-\text{NH}-$, where X is C or N autoxidise easily, frequently at room temperature without added catalysts, giving hydroperoxides $-\text{C}(\text{OOH})-\text{X}=\text{N}-$.

X=N For example,



X-C For example,

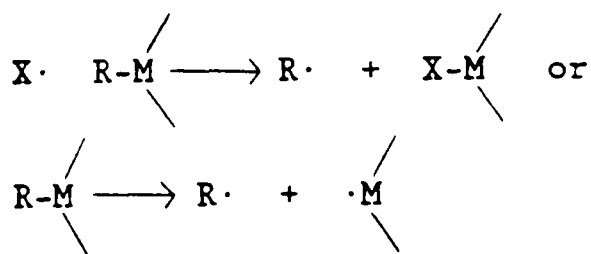


1,2,3,4-tetrahydrocarbazole⁴⁸

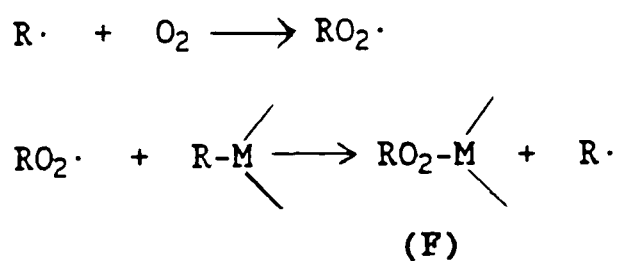
(iii) Autoxidation of organometallic compounds

These compounds autoxidise readily by a free radical mechanism and sometimes inflammably.

Initiation

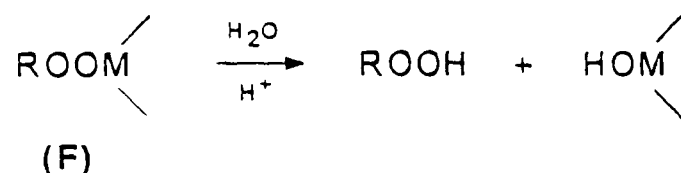


Propagation

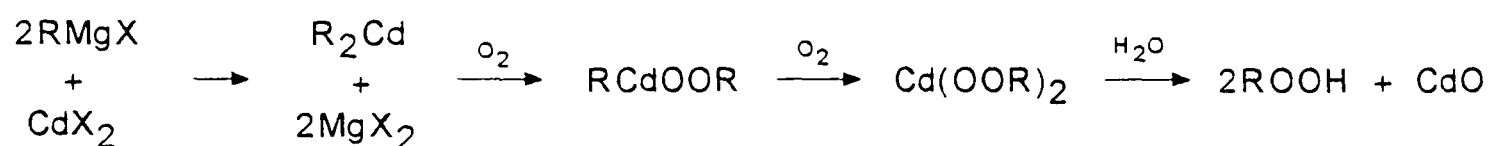
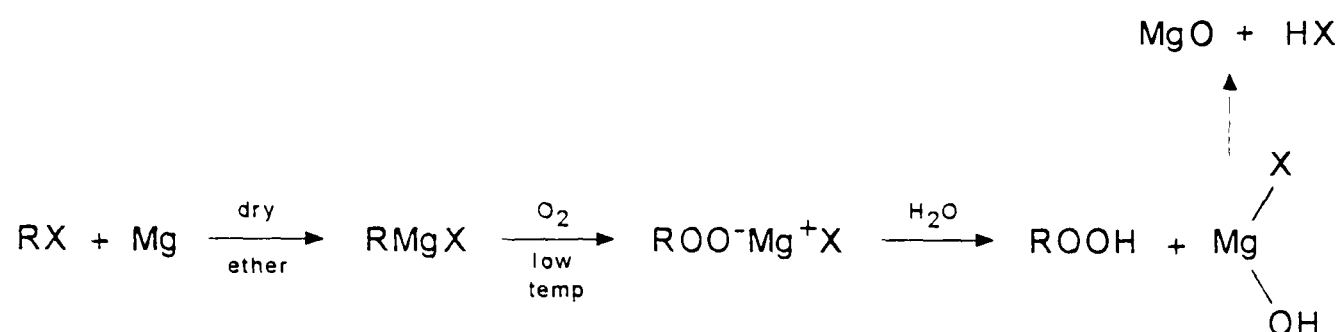


The autoxidation of alkyl derivatives of magnesium (Grignard reagents), lithium, boron, zinc and cadmium, yields the corresponding alkylperoxy derivatives (F), which readily hydrolyse to the hydroperoxide

in reasonable yield. (See this Chapter, 1.4.5 "Hydrolysis of Peroxyesters".)



For example,



The mild conditions of low temperature autoxidation and subsequent hydrolysis of Grignard reagents, is a useful procedure for preparing simple primary and secondary hydroperoxides, often difficult to obtain by other methods⁴⁹. (This can be compared with the potentially mild hydrolysis of primary and secondary peroxyesters as described by Milas and Surgenor⁷ for the tertiary peroxyester, tertiary-butyl peroxybenzoate – see this Chapter, 1.4.5 "Hydrolysis of Peroxyesters".) The reaction was first developed by Walling and Buckler⁵⁰, giving 90% yields from tertiary Grignards and 57-66% yields from primary and secondary ones.

For higher homologues, Wilke and Heimbach⁵¹ found that autoxidation of alkyl boranes gave better results, yielding diperoxyboranes which were

further oxidised with peroxyacid, then hydrolysed to 30-50% yields of hydroperoxide.

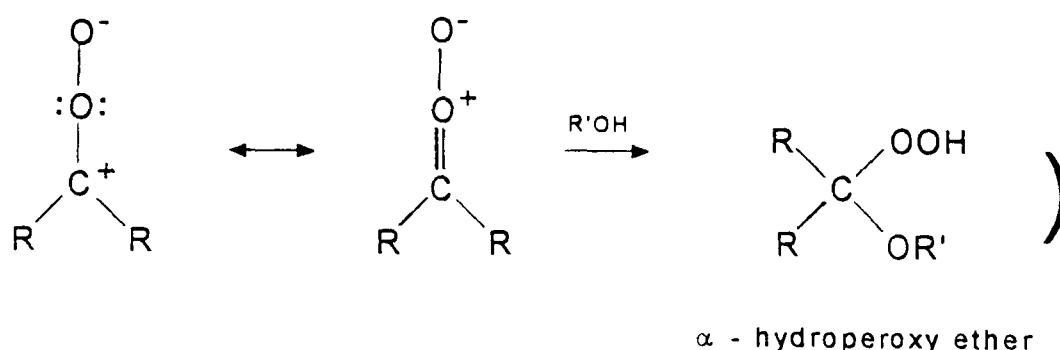
3. Hydrolysis of various organic peroxides can also yield hydroperoxides.

(a) On careful acidification of alkali metal and alkaline earth metal salts of hydroperoxides, the corresponding hydroperoxide is formed as discussed previously (the source of alkylperoxy salt derivatives (F) is shown in 2.(b)(iii) above).

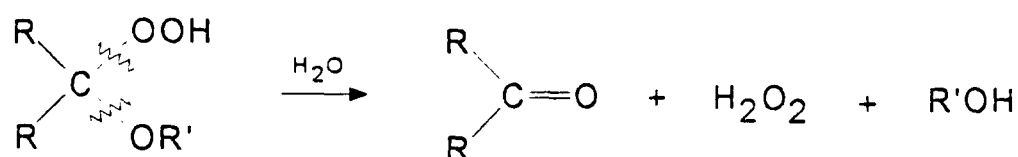
The alkylperoxy derivatives of zinc, cadmium, aluminium, silicon, germanium, tin, lead, phosphorus, arsenic and antimony have also been hydrolysed to the hydroperoxide⁵², as has those of boron⁵³.



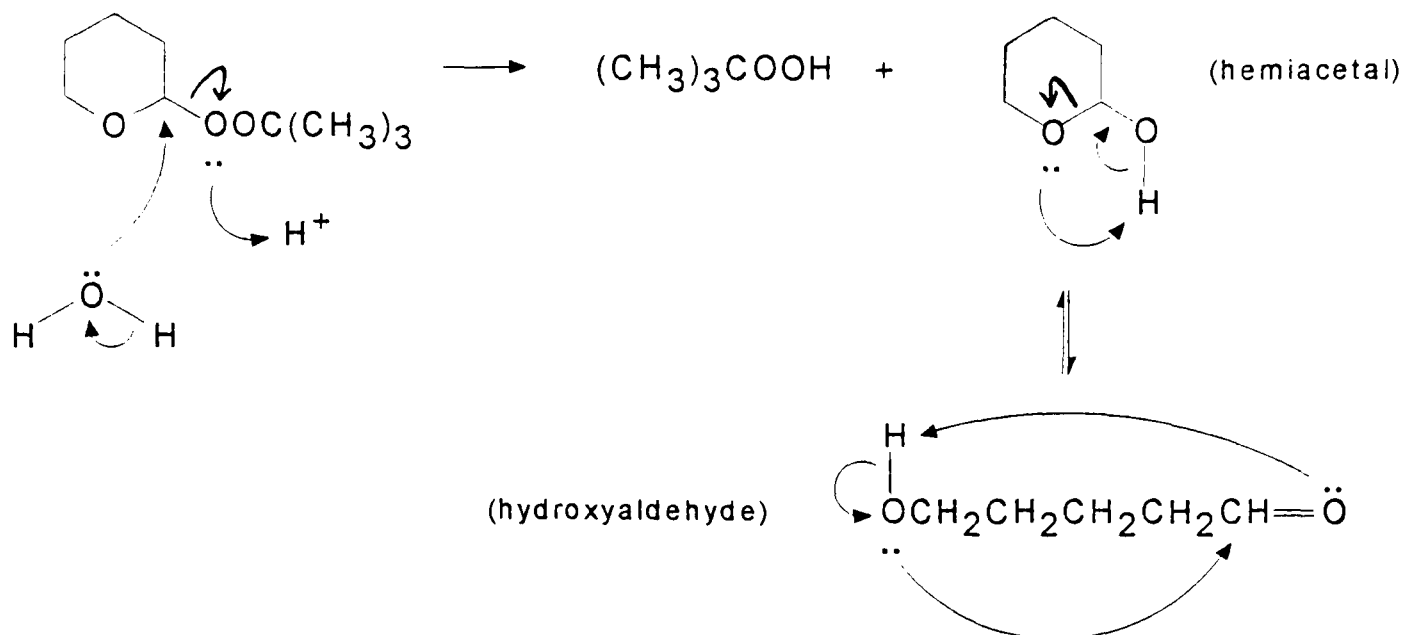
(b) Ether-substituted hydroperoxides (prepared from ozonolysis of alkenes (see this Chapter, 1.4.6 "Postulated Peroxide Intermediates") in the presence of alcohols⁵⁴:



are readily hydrolysed to hydrogen peroxide, alcohol and aldehyde or ketone depending on R¹⁰³.

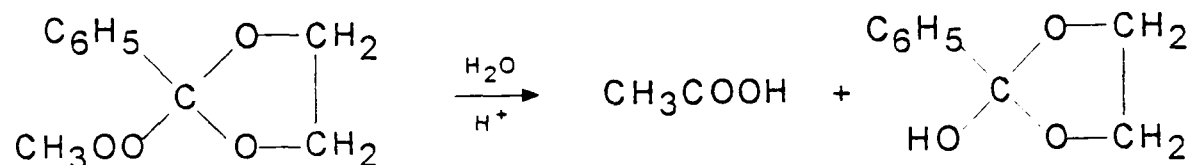


Ether-substituted peroxides are readily hydrolysed to the unsubstituted hydroperoxides⁵⁵. For example:



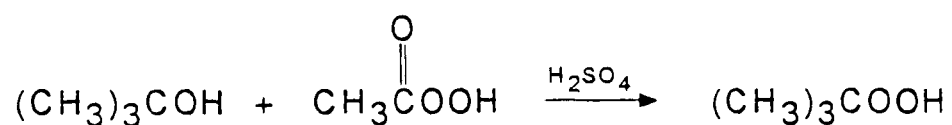
The mechanism being similar to that for the hydrolysis of acetals^{54b}.

(c) Acid hydrolysis of peroxides of acetals also gives hydroperoxides⁵⁶.



(d) The saponification of peroxyesters to yield hydroperoxides and carboxylic acids⁷ is discussed in 1.4.5 "Hydrolysis of Peroxyesters".

4.(a) Another reaction to be considered that yields hydroperoxides, is that of alcohols and peroxy-carboxylic acids under acidic conditions¹⁸. For example,



(b) The reaction of dry hydrogen chloride and alkylperoxy derivatives of silicon, germanium, tin, lead, arsenic and antimony, also leads to hydroperoxides⁵².



1.3 *Carbocation and Organic Radical Intermediates*

1.3.1 Carbocations¹⁹

A brief discussion will be given on the subject of carbocations, as their formation was critical to the success of the new synthetic route to peroxyesters described within this thesis, where the formation of tertiary and primary (n-alkyl, allylic and benzylic) carbocations was attempted. Their structure, stability, formation and reactions will be reviewed as outlined below:

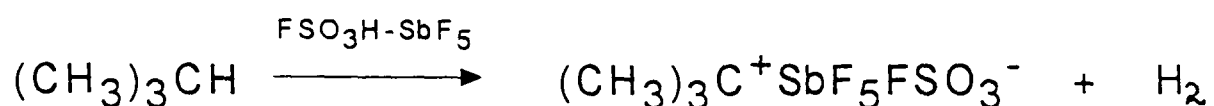
- 1.3.1.1 Structure and Stability of Carbocations,
- 1.3.1.2 Carbocation Formation:
 - (i) heterolytic fission of neutral species,
 - (ii) cation addition to neutral species,
 - (iii) formation from other cations,
- 1.3.1.3 Reactions of Carbocations:
 - (i) combination with a nucleophile,
 - (ii) elimination of a proton,
 - (iii) rearrangement.

1.3.1.1 *Structure and Stability of Carbocations*

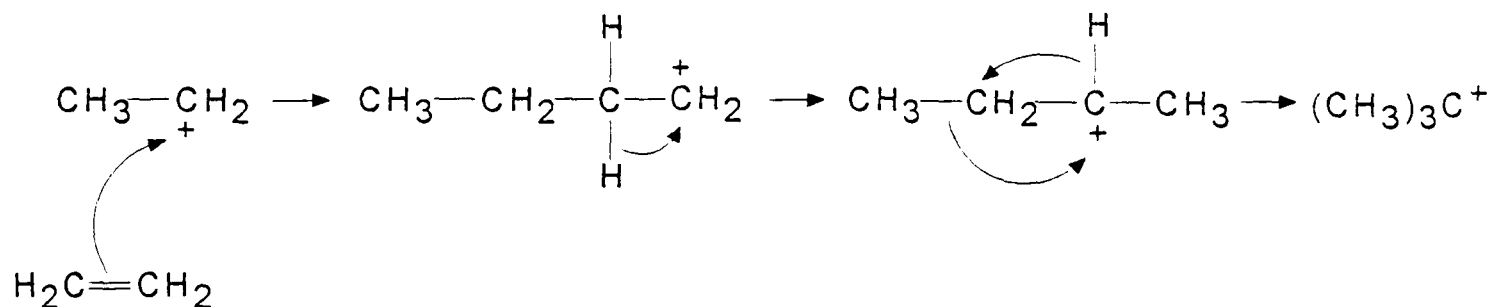
The more stable of the carbocations have been prepared in solution and in a few cases even as solid salts. In solution they may be free (more likely in polar solvents, where solvation occurs), or exist as an ion pair, that is, closely associated with a negative ion (counter ion) (more likely in nonpolar solvents). Evidence for their existence can be obtained for example, by NMR⁵⁷ and analysis of the products of chemical reactions.

Among simple alkyl carbocations⁵⁸, the order of stability is tertiary, $[(\text{CH}_3)_3\text{C}^+] >$ secondary, $[(\text{CH}_3)_2\text{CH}^+] >$ primary, $[\text{CH}_3\text{CH}_2^+] > [\text{CH}_3^+]$. Often primary and secondary carbocations rearrange to tertiary ones (see 1.3.1.3(iii) in this section). Simple alkyl carbocations are not stable in ordinary strong acid solutions, for example in H_2SO_4 or HBF_4 . However, Olah et al.'s⁵⁹ work with "super acids" discovered that many of them could be stabilised for long periods of time in solutions of mixtures of fluorosulphonic acid (HSO_3F) and antimony pentafluoride (SbF_5). These

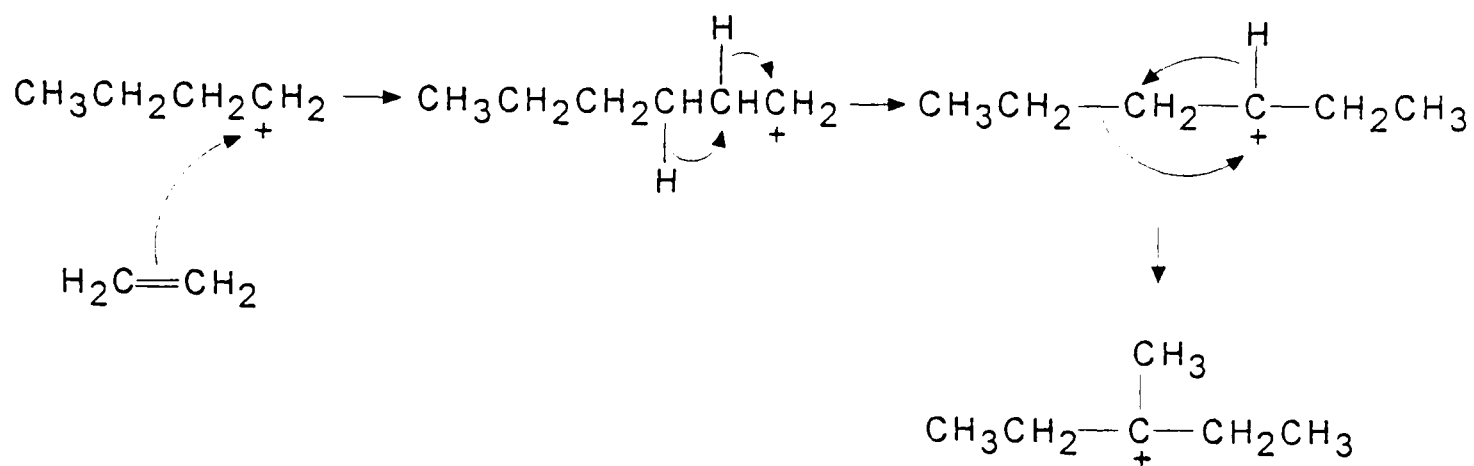
mixtures, usually dissolved in SO_2 or SO_2ClF , are among the strongest acidic solutions known. $(\text{CH}_3)_3\text{C}^+$ for example, remains unchanged after heating at 170°C in $\text{SbF}_5/\text{FSO}_3\text{H}$ for four weeks. Olah *et al.*'s⁵⁹ original experiments involved the addition of alkyl fluorides to SbF_5 : $\text{RF} + \text{SbF}_5 \rightarrow \text{R}^+\text{SbF}_6^-$, but then it was found that the same carbocations could be generated from alcohols by dissolving them in "super acid" in SO_2 at -60°C ⁶⁰, and from alkenes by dissolving them in "super acid" or HF-SbF_5 in SO_2 or SO_2ClF at low temperatures⁶¹, where a proton is added to the double bond. Alkanes can also give rise to carbocations by loss of H^- in "super acid". For example, isobutane gives the tertiary butyl carbocation:



No primary carbocation has yet survived long enough for detection. When treated with SbF_5 , neither methyl or ethyl fluoride has given the corresponding carbocation. At low temperatures, methyl fluoride gave only an $\text{SbF}_5\text{-FCH}_3$ complex⁶² and ethyl fluoride rapidly formed tertiary-butyl and tertiary-hexyl carbocations by addition of the initially formed ethyl carbocation and n-butyl carbocation respectively, to ethylene molecules also formed, followed by rearrangement⁵⁸.



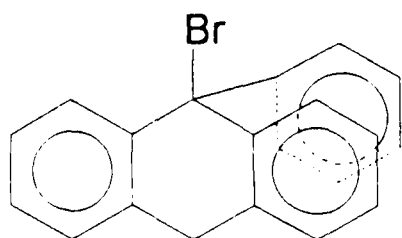
and,



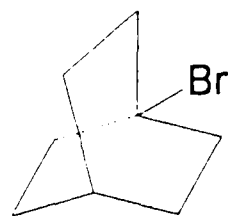
At room temperature, methyl fluoride also gave tertiary-butyl carbocations^{62a}. This information and the fact that n- and iso- propyl fluorides gave isopropyl cation, all four butyl fluorides (n-, iso-, secondary and tertiary) gave tertiary-butyl cation, and all seven of the pentyl fluorides gave tertiary-pentyl cation, gives evidence for the stability order of simple alkyl carbocations. The most stable of all is the tertiary-butyl cation - even the relatively stable tertiary-pentyl and tertiary-hexyl cations fragment at higher temperatures to produce tertiary-butyl cations, as do all other alkyl cations with four or more carbons⁵⁸. Even n-butane, in "super acid" gave only tertiary-butyl cation as a result of rearrangement of the initially formed n-butyl cation. Also at high temperatures when treated with "super acid", methane, ethane and propane yield tertiary-butyl cations as the main products⁶³. As a result of the order of stability, hydride ion is abstracted from alkanes by "super acid" most readily from tertiary and least readily from primary positions.

Structure

In a carbocation, the electron-deficient carbon is bonded to three other atoms using sp^2 hybrid orbitals which give a trigonal planar distribution. If a system cannot become planar, there is the consequent difficulty in carbocation formation. For example, the rigidity of the structures of 1-bromo-triptycene and 1-bromo-bicyclo[2.2.2]octane explain the non-ionisation of the tertiary halides.



and

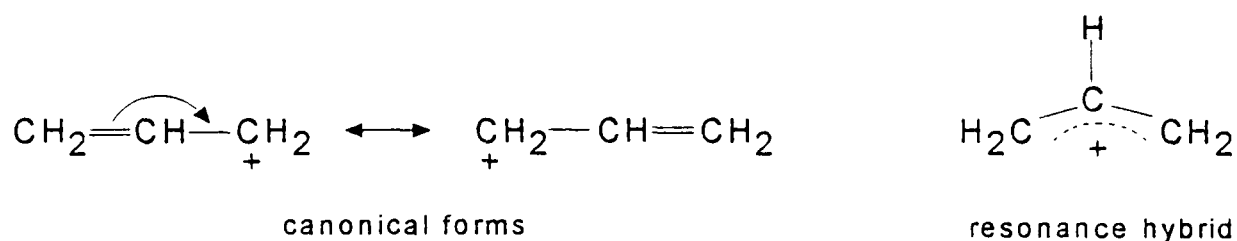


(a) stability by induction

The relative stability of a carbocation is determined by how well it can accommodate the charge - with dispersal of the charge its stability is increased. The inductive effect depends on the tendency of the substituents attached to the electron-deficient carbon, to release or withdraw electrons. Releasing electrons disperses the charge and hence stabilises the cation. Alkyl groups are electron releasing, and thus the greater the number the more stable the carbocation (which explains the stability order $3^\circ > 2^\circ > 1^\circ > \text{CH}_3$).

(b) stability by resonance (delocalisation of electrons)

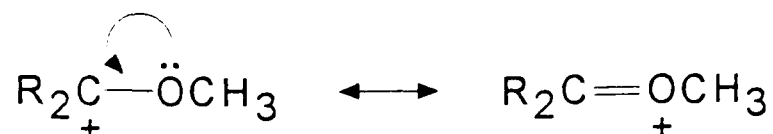
More stable carbocations are formed when the dispersal of the positive charge occurs by delocalisation of electrons through overlapping p orbitals to give the resonance effect. For example, the allylic and benzylic carbocations have π orbitals in conjugation with the positive charge, over which delocalisation can effectively occur.



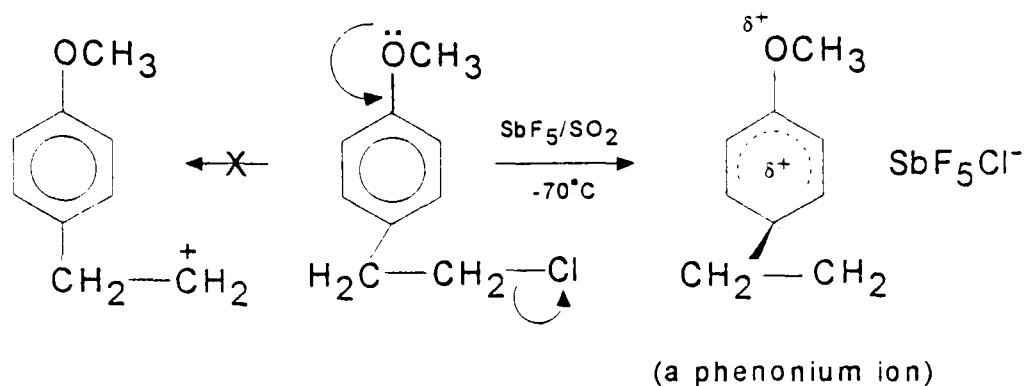
Where resonance stability is lacking, as in the phenyl or vinyl carbocations, the ion is usually very short lived. Neither simple vinyl nor phenyl carbocations⁶⁴ have been prepared as a stable species in solution, though solutions of aryl-substituted vinyl cations have been reported to be stable for a short time at low temperature, and NMR spectra obtained⁶⁵.

Conjugation of the electron-deficient carbon with a hetero atom bearing unshared pairs of electrons (for example, nitrogen, sulphur and oxygen) also leads to resonance. This is seen for example with oxonium

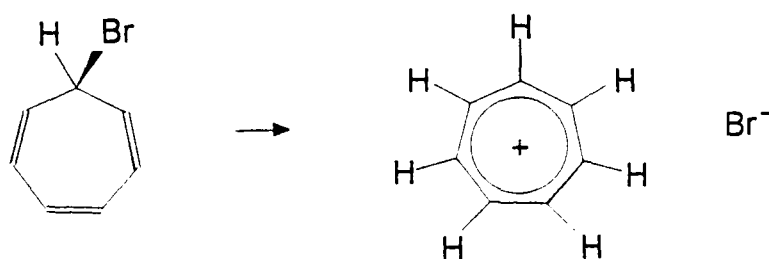
ion formation, where the empty p orbital of carbon overlaps with a filled p orbital of oxygen:



Also, the delocalisation can occur through a "neighbouring group effect", as a result of the formation of a "bridged" carbocation.



Stabilisation through delocalisation can also occur through aromatisation to give non-benzenoid aromatic carbocations, for example the tropylium cation.



The 6π electrons can be accommodated in the three bonding molecular orbitals spread over the seven carbon atoms. It is thus a Hückel $4n+2$ system ($n=1$) like benzene ($n=1$).

1.3.1.2 Carbocation Formation

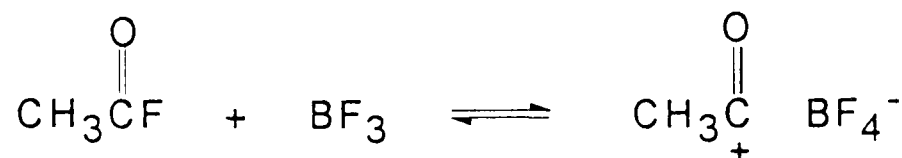
(1) Heterolytic fission of neutral species

Ionisation of a covalent molecule RY happens where a group attached to a carbon atom leaves with the bonding electrons to form an ion pair, R^+Y^- . Usually, a highly polar, powerfully ion-solvating medium is necessary, otherwise the use of a silver salt for example, can promote the formation of R^+ . This is often practised for halides that do not readily undergo $\text{S}_{\text{N}}1$ attack (or to shift from an $\text{S}_{\text{N}}2$ to an $\text{S}_{\text{N}}1$ mode). Adding the silver salt forms the carbocation and precipitates the silver

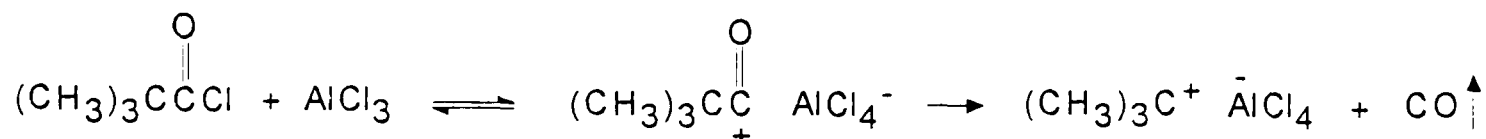
halide.



Ionisation may also be induced by Lewis acids, for example boron trifluoride.



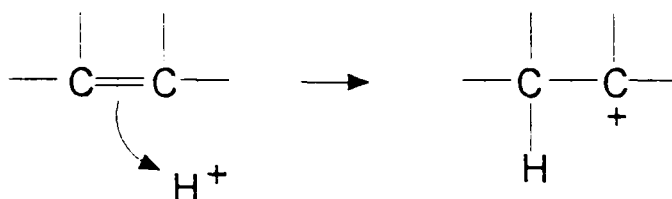
In the case above, the acyl cation has as its counterion the very stable tetrafluoroborate anion. Aluminium trichloride may also be used.



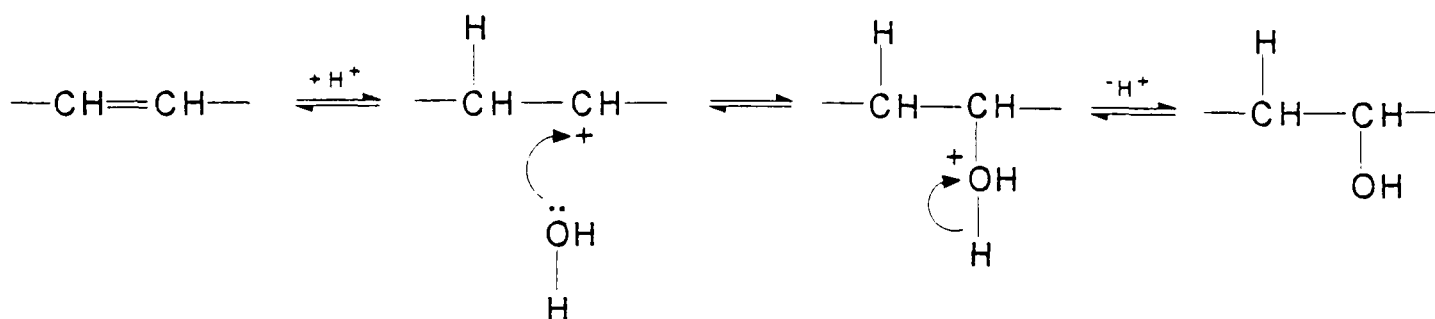
The relatively unstable acyl cation decomposes to yield the very stable $(\text{CH}_3)_3\text{C}^+$.

(ii) Cation addition to neutral species

The most common cation is H^+ , adding to a carbon atom of an unsaturated linkage, that is, protonation. The adjacent carbon atom is then left with a positive charge.

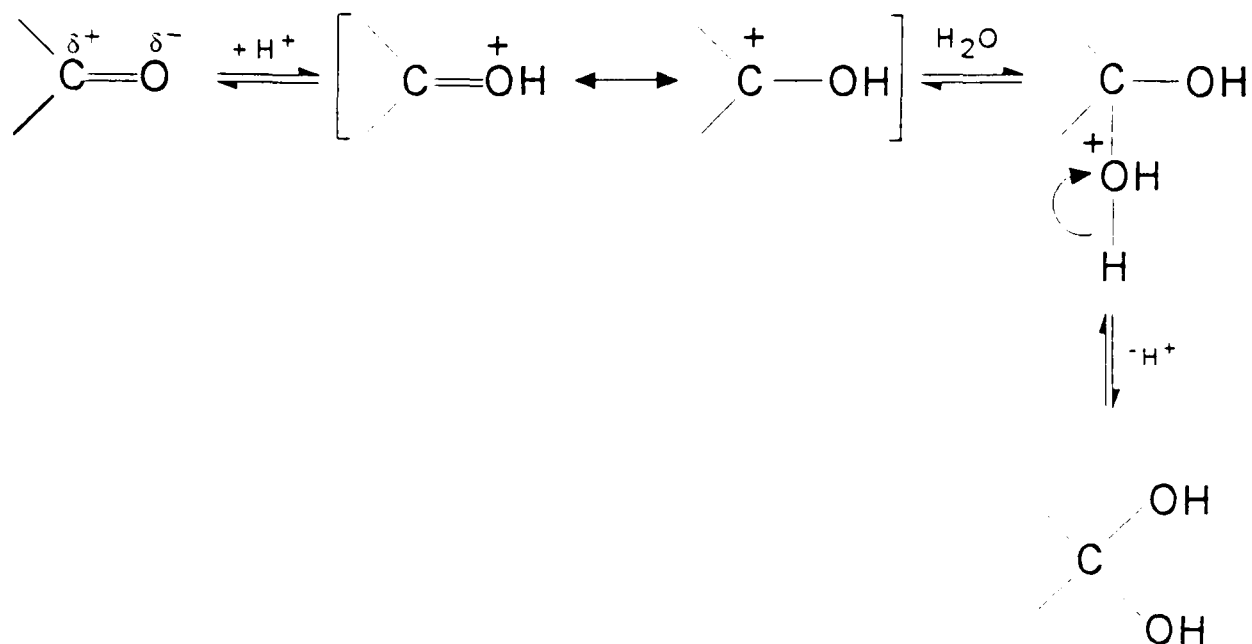


This occurs for example, in the acid-catalysed hydration of alkenes.

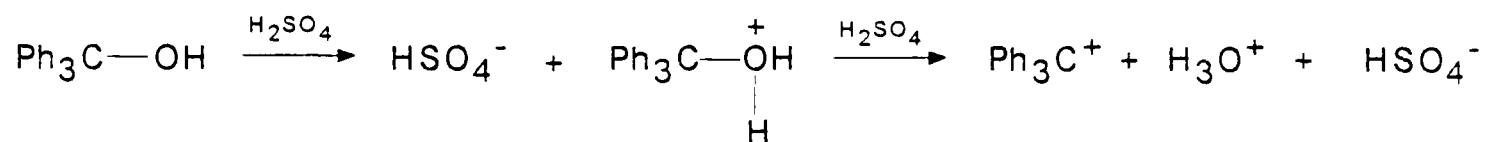


The reverse reaction is possible and is the acid-catalysed dehydration of alcohols.

The acid-catalysed hydration of carbonyl compounds also proceeds via a carbocation intermediate as the oxygen is protonated.

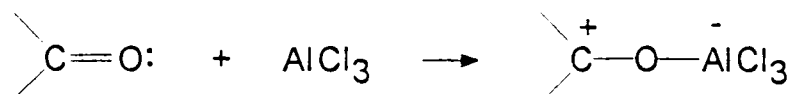


Protonating an atom with a lone pair such that it becomes a better leaving group, can also generate carbocations. For example,

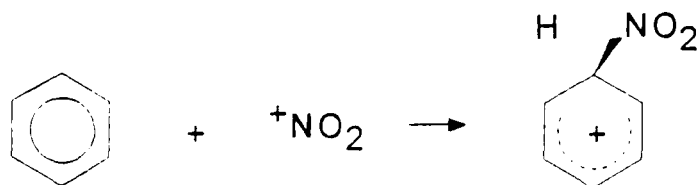


In this instance, compared to the protonation of OH in the acid-catalysed dehydration of alcohols, a water molecule "lost" does not promote elimination of a proton from an adjacent carbon atom because there is not one to lose, although generally dehydration is the observed outcome.

Lewis acids may also be used to generate carbocations by adding on to a lone pair.

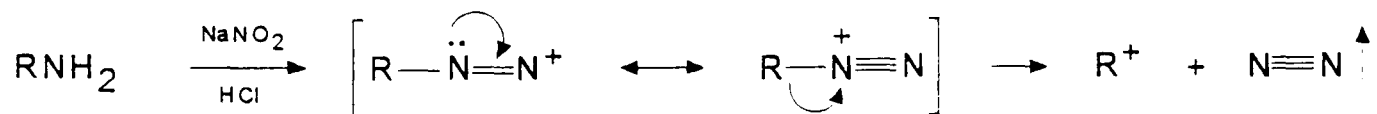


Other cations, for example ${}^+\text{NO}_2$ in the nitration of benzene, can add on to a neutral species.

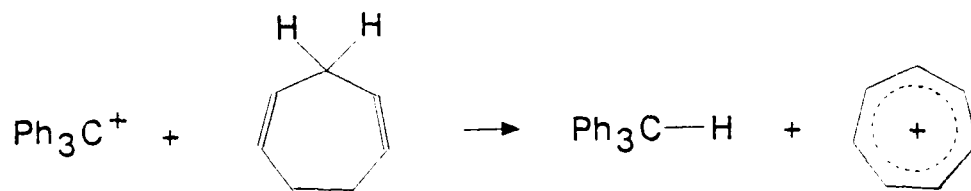


(iii) Formation from other cations

Decomposition of carbocations can yield other carbocations, as seen for example by the action of NaNO_2/HCl on RNH_2 to give the diazonium ion shown below, which then readily decomposes.



Readily available carbocations can be used to generate not so accessible ones, for example the formation of the tropylium carbocation.



Rearrangements are discussed as a type of carbocation reaction (see below).

1.3.1.3 Reactions of Carbocations

Formed by any of the processes described above, carbocations are most often short-lived and react further without being isolated. Carbocations are found to undergo the basic types of reactions as discussed below.

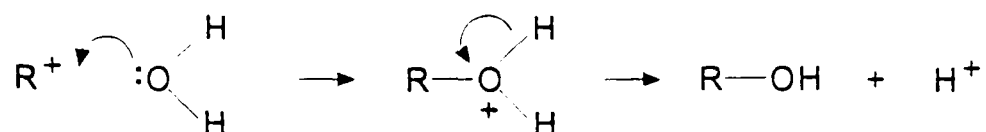
Combination with a nucleophile and elimination of a proton often lead to the formation of stable end-products, whereas rearrangement leads to different carbocations which themselves must react further to give stable products, ultimately via the other two reactions. The combination and elimination reactions are in fact the reverse of methods of carbocation formation.

(i) Combination with a nucleophile

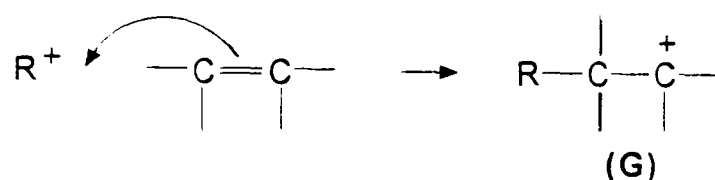
The carbocation may combine with a species possessing an electron pair (Lewis acid-base reaction),



with the species Y^- , as H^- , OH^- , halide ion, or another anion. It may also be a neutral species with a pair of electrons to donate, where the intermediate bears a positive charge. For example,



Or, a carbocation may add to an unsaturated bond, generating a positive charge at a new atom for example,

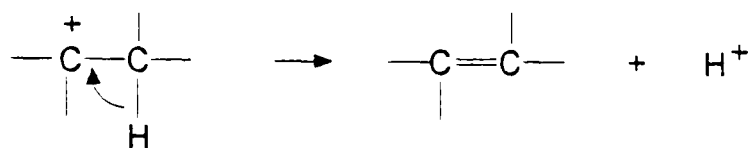


If the new carbocation reacts at another unsaturated site, and so on, cationic polymerisation will occur. As discussed later in Chapter 2, this reaction following elimination of a proton, may have contributed to the low mass of peroxyesters formed in the present author's experiments, as well as in the unsuccessful ones.

As cationic polymerisation is initiated by acids including H_2SO_4 , $AlCl_3$ and BF_3 , plus a trace of water, in the present author's experiments it seems possible that the generated BF_4^- may have been competing with the peroxyacid and alkene for reaction with the carbocation, also contributing to less peroxyester formation.

(ii) Elimination of a proton

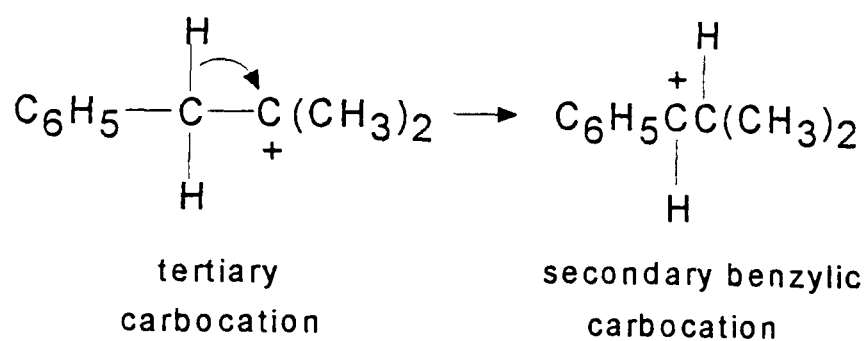
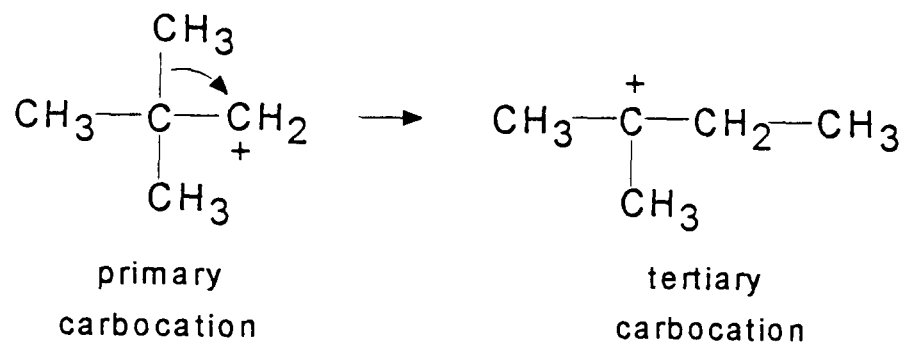
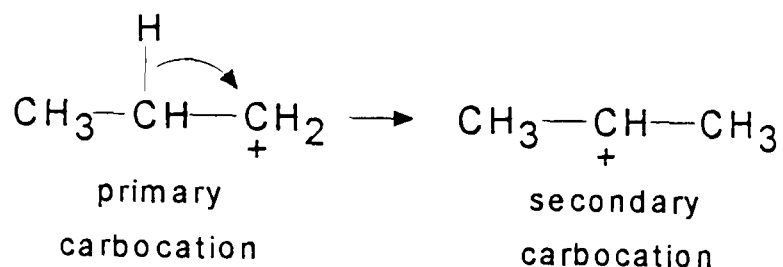
The carbocation may lose a proton (or much less often, another positive ion) from the adjacent atom to form an alkene.



As mentioned above, this reaction may be of relevance to the present author's work.

(iii) Rearrangement

Rearrangement also gives a positive charge at a new carbon centre. An alkyl or aryl group, or a hydrogen atom (sometimes another group) migrates with its electron pair to the positive centre leaving another positive charge behind, often a more stable one. For example,



In the last example, the secondary carbocation is more stable than the tertiary because the positive charge can now be delocalised more readily into the π orbital system of the benzene ring.

As mentioned above, whether the carbocation reacts further to yield another carbocation by addition to a multiple bond or by rearrangement, the new carbocation normally reacts further in an effort to stabilise itself, usually by combination with an anion or elimination of a proton. However, (G) may add to another alkene, and this product may then add to another alkene, and so on. This is one of the mechanisms for vinyl polymerisation. The termination product ultimately has of course, a saturated or unsaturated terminus (via combination with an anion or elimination of a proton, respectively).

1.3.2 Organic Radicals^{66,67}

The majority of knowledge regarding the peroxide bond is the result of its relative ease of homolytic cleavage with an average bond enthalpy of 146kJmol^{-1} at 25°C ⁶⁸. Indeed as previously explained, this concept is greatly utilised in some of the most important commercial industrial processes. For example, in polymerisation as in the rubber and plastics industries, the thermal cracking of petroleum and in the preparation of synthetic organic chemicals such as acetone and phenol. Other industrial uses include as bleaching agents and ignition accelerators for diesel fuels. Organic radicals are also vital to many life processes including respiration and photosynthesis. In other processes, radicals are not useful but undesirable. For example in the rancidification of fats, the ageing of skin, and the oxidative deterioration of petrol, lubricating oils and rubber. Because of their importance in many processes, whether desirable or not, it seems logical to include a section on the formation of radicals and their subsequent reaction mechanisms.

A radical can be defined as an atom or a group of atoms with an unpaired electron, for example, $\text{CH}_3\cdot$. A diradical is a species with two unpaired electrons, for example, triplet $\text{CH}_2:$ (carbene) or $\cdot\text{CH}_2\text{CH}_2\text{CH}_2\cdot$.

It was in 1937 that detailed radical mechanisms were published to explain reactions which until then had been difficult to explain. Included was the anti-Markovnikov addition of hydrogen bromide to alkenes and the homolytic aromatic substitution reaction. In the same year it was suggested that addition polymerisation might proceed via a radical mechanism.

The formation of radicals will be discussed, as will their principal reactions:

1.3.2.1 The Production of Radicals:

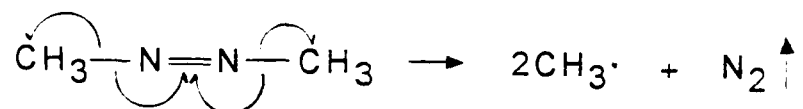
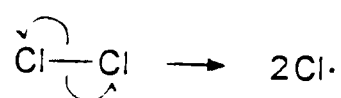
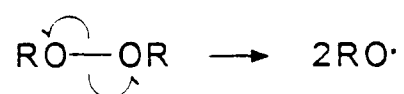
- (i) by irradiation: photochemistry,
- (ii) by thermal homolysis,
- (iii) from radical-forming redox (oxidation-reduction) reactions.

1.3.2.2 Radical Reactions:

- (i) termination reactions,
- (ii) propagation reactions.

1.3.2.1 *The Production of Radicals*

Radical centres are formed in pairs by the homolytic cleavage of two-electron bonds. Examples include peroxide dissociations, the photolysis of halogens, and the decomposition of azo compounds – the first being particularly appropriate to the work within this thesis.



Radicals can be formed essentially by three types of processes: irradiation, thermal homolysis and oxidation-reduction reactions.

(i) By irradiation: photochemistry⁶⁷

Photochemistry results from the absorption of light. Light can be transmitted, refracted, scattered or absorbed by a system. Only when it is absorbed can a chemical or physical change occur, where each quantum of light absorbed activates a single molecule. The absorbed energy is then lost by physical or chemical processes – physical processes include fluorescence and chemical processes are either radical or non-radical reactions. Sometimes, the processes occur in competition. For example, as the concentration of anthracene in benzene is increased, the intensity of fluorescence decreases while the amount of dimer product increases.

As mentioned above, the average bond enthalpy of a peroxide bond is

relatively low compared with for example a C-C single bond of 348kJmol^{-1} at 25°C^{68} . At room temperature, the Boltzmann distribution law shows how a negligible fraction of the species is excited. The law states that the relative number of particles n_1 and n_2 , in two (equally degenerate) levels 1 and 2 separated by an energy gap ΔE , is given by the expression,

$$n_2 / n_1 = e^{-\Delta E/RT} \quad \text{where } R = \text{gas constant} = 8.3143\text{JK}^{-1}\text{mol}^{-1}.$$

Taking for example the energy difference of 146kJmol^{-1} between n_1 and n_2 (the value for the average bond enthalpy of the O-O bond at 25°C), to achieve a concentration of only 1% of the excited species would require a temperature of around 3540°C :

$$\begin{aligned} n_2 / n_1 &= 1/100 = e^{-146,000/8.3143 \times T} \\ \text{Therefore, } -146,000 / 8.3143 \times T &= \log_e 1/100 \\ \text{and } -146,000 / 8.3143 \times T &= -4.61 \\ \text{so } T &= 3809\text{K} = 3536^\circ\text{C} \end{aligned}$$

(Similarly, an energy difference of 348kJmol^{-1} [C-C bond enthalpy at 25°C] would require a temperature of around 8816°C .)

However, if under the same conditions the molecules were to absorb radiation at a wavelength of 500nm (from visible light, ca. 400 to 700nm) as a result of outer electronic transition, then electronic excitation would occur.

$$\begin{aligned} E = hc/\lambda &= 6.6 \times 10^{-34} (\text{Js}) \times 3.0 \times 10^8 (\text{ms}^{-1}) / 5.0 \times 10^{-7} (\text{m}) \\ &= 4.0 \times 10^{-19} \text{J} \end{aligned}$$

That is, each quantum of energy from a light source of 500nm supplies $4.0 \times 10^{-19}\text{J}$ of energy.

A mole of species containing the O-O bond requires 146kJ of energy for its rupture. That is,

$$\begin{aligned} 146,000/N \text{ J per molecule} &= 2.5 \times 10^{-19} \text{J}, \text{ where } N = \text{Avogadro's constant} \\ &= 6 \times 10^{23} \text{mol}^{-1}. \end{aligned}$$

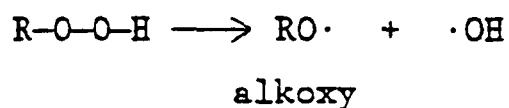
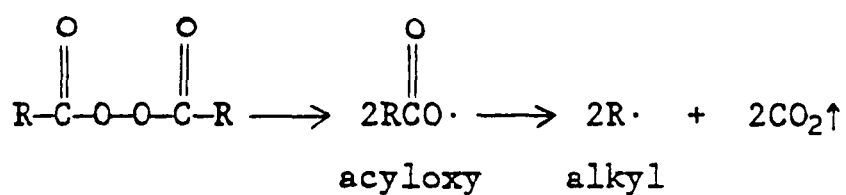
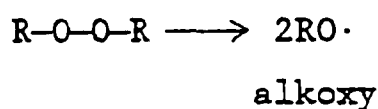
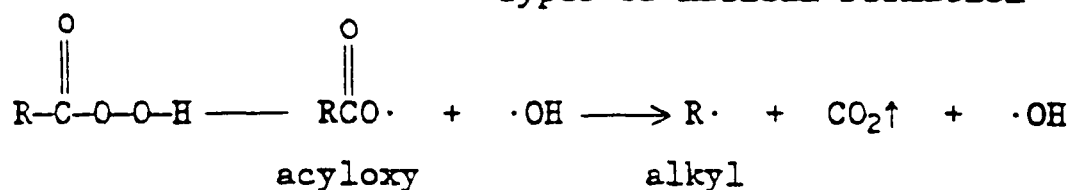
Thus, a quantum of energy from a light source of 500nm provides more energy than required to rupture one molecule containing an O-O bond.

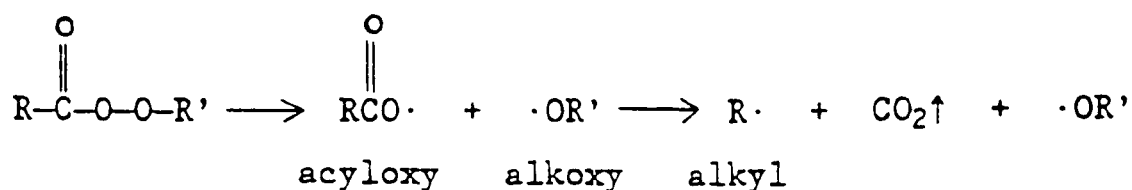
For C-C bond cleavage however, ca. $5.8 \times 10^{-19}\text{J}$ per molecule is required, and thus irradiation by light of 500nm would not be sufficient.

(ii) By thermal homolysis

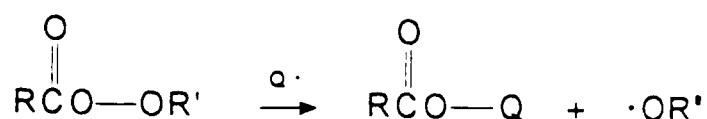
As the normal C-C bond energy is about 348kJmol^{-1} at 25°C , thermal excitation of molecules becomes sufficient to break these bonds at temperatures of $350^\circ\text{-}550^\circ\text{C}$ (utilised in the thermal cracking of petroleum). Some compounds have exceptionally weak bonds, and decompose to form radicals at lower temperatures. These compounds can also be used to initiate radical processes at temperatures of $50^\circ\text{-}150^\circ\text{C}$, and so molecules with bond energies of about 105 to 146kJmol^{-1} become viable radical initiators at these temperatures. Although there are several types of compounds with bond strengths in this range, by far the most commonly used are those containing the peroxide O-O bond. Under these conditions, organic peroxides can undergo thermally induced O-O homolysis at appreciable rates giving alkoxy ($\text{RO}\cdot$) and/or acyloxy ($\text{RCO}_2\cdot$) radicals. However, when the peroxide carries electronically dissimilar groups (for example, in peroxyesters of strong acids), or when the nucleophilic migratory aptitude of alkyl groups in the α -position is high), the heterolytic mechanism of decomposition may compete (for example, the Criegee rearrangement in tertiary peroxyesters). Also, if there is simultaneous scission of both the O-O and C-C bonds, an alkyl radical may form together with a molecule of carbon dioxide.

Types of Radical Formation





If R possesses appreciable stability as a free radical, then simultaneous scission of the O-O and C-C bonds occurs. In addition, induced decomposition can occur, where radicals attack the peroxide and cause its decomposition. The attacking radicals can be produced from the peroxide itself ($\text{RCO}_3\text{R}' \longrightarrow \text{R}\cdot + \text{CO}_2 + \cdot\text{OR}'$).

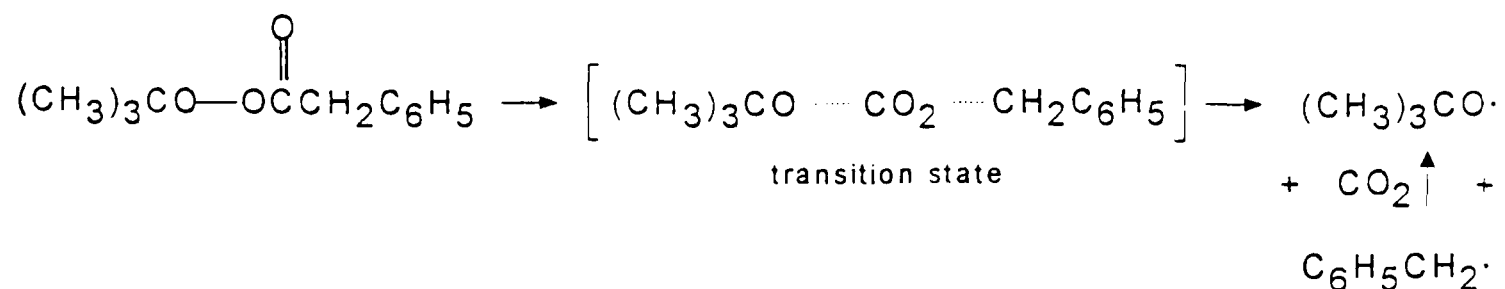


As shown in table (A) below, peroxyesters are seen to decompose at a faster rate as the R group is varied so as to form the more stable radical. Thus, tertiary-butyl peroxyethanoate is the most stable peroxyester, forming the least stable radical R.

Table (A)

Peroxyester [$\text{RCO}_3\text{C}(\text{CH}_3)_3$] half-lives at 60°C	
R	minutes
CH_3-	5.0×10^5
C_6H_5-	3.0×10^5
$\text{C}_6\text{H}_5\text{CH}_2-$	1.7×10^3
$(\text{C}_6\text{H}_5)_2\text{CH}-$	26.0

These data suggest how the stability of the R group as a free radical affects the rate of the O-O bond scission. It can be said that peroxyesters that do not have specially stabilised R groups undergo normal O-O scission, whereas relatively stable radicals give rise to a synchronous scission of the two bonds to split out a carbon dioxide molecule as described above, with the odd electron density being localised on the R group at the transition state. Tertiary-butyl peroxyacetate and peroxybenzoate are shown to decompose at a very similar rate. In these compounds neither the methyl or phenyl radicals are particularly stable, and the peroxyesters therefore decompose with simple O-O bond scission. Tertiary-butyl peroxyphenylacetate on the other hand, decomposes 10^2 times faster than the corresponding peroxyacetate and peroxybenzoate, giving the benzyl free radical. The localisation of some of the odd electron density on the benzyl carbon at the transition state, leads to the pronounced rate enhancement of the radical formation involving carbon dioxide formation:



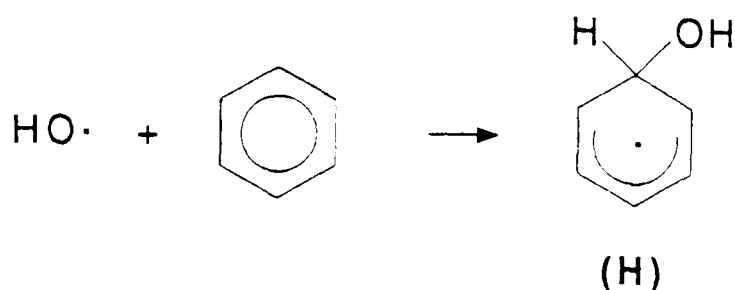
(iii) From radical-forming redox (oxidation-reduction) reactions

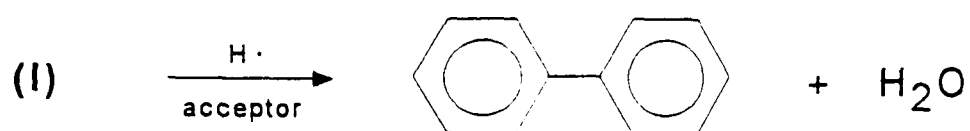
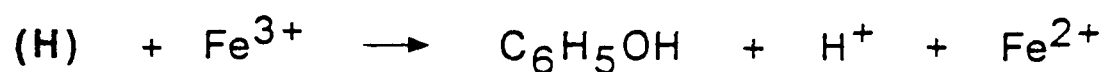
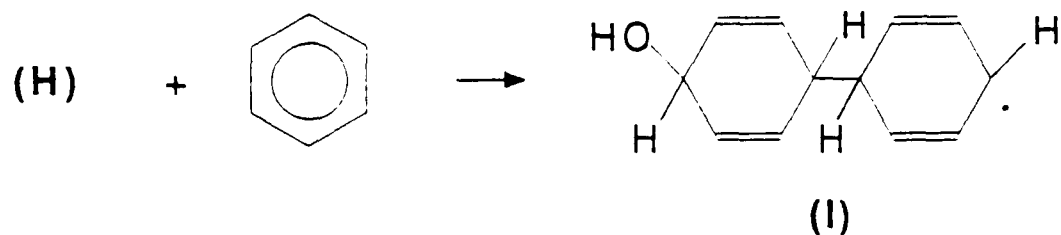
The final method involved in radical formation is that of redox reactions.

To produce radicals by one-electron oxidation-reduction reactions provides a source at lower temperatures than by the use of unstable initiators (though usually requiring greater than room temperature) such as peroxides. Radicals can be produced either by oxidation or reduction. The most important radical-forming redox reactions are those involving a metal ion that can undergo a one-electron transfer. One of the oldest reactions of this type, is that of Fenton (1894), with the mechanism being drawn up in 1932 by Haber and Weiss. It involved the catalytic decomposition of hydrogen peroxide by ferrous ions. Reactions include:

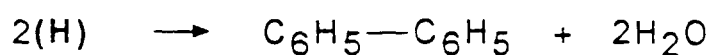
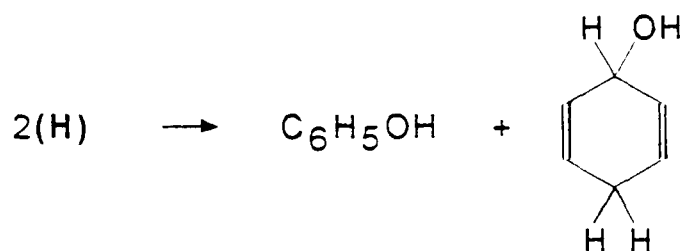


Fenton's reagent (H_2O_2 and Fe^{2+}) can also be used to oxidise organic materials. Sometimes the oxidised products are dimers, and sometimes they are the result of substitution reactions by hydroxyl radicals. For example, benzene is converted to a mixture of biphenyl and phenol, with higher ratios of phenol to biphenyl if the concentration of ferric ions is kept high⁶⁹.

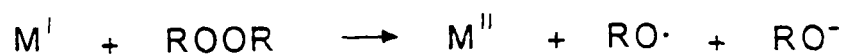




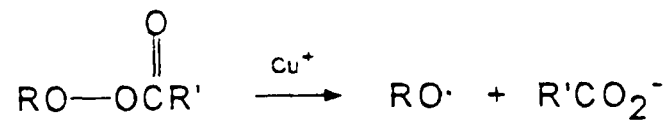
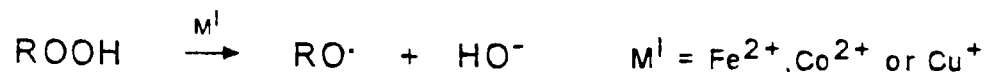
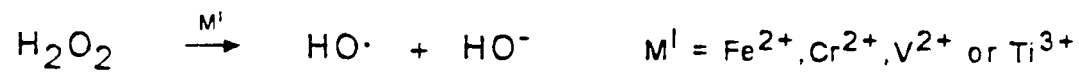
Products can also be formed from the dimerisation and disproportionation of (H).



A similar reaction type to that in Fenton's reagent also occurs with ions of other metals, and with hydroperoxides, peroxides and peroxyesters, as well as with hydrogen peroxide. The reaction can be written generally as:



The above reaction however, is often not the exclusive one. M^{I} is a transition metal in one valence state, and M^{II} is the next higher oxidation valence state. Examples are given below.



Consideration of the peroxyester reaction shows how readily, in the presence of water or acid, the corresponding normal carboxylic acid could result.

As mentioned above, redox initiators are of importance because they can be used at much lower temperatures than peroxides. Their rates of radical formation can be controlled by varying the concentrations of both the oxidant (the peroxide) and the metal-ion catalyst, as well as by changing the temperature.

1.3.2.2 Radical Reactions

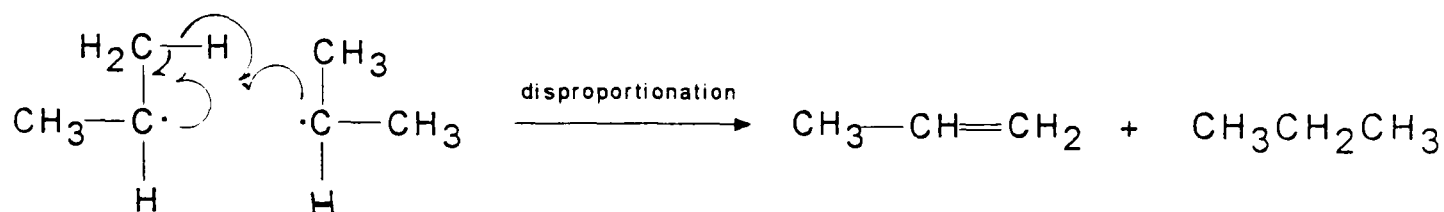
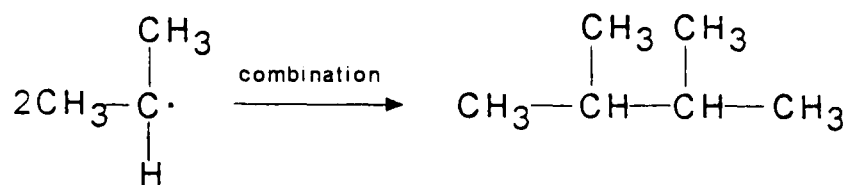
Reactions of radicals either give stable products (via termination reactions) or lead to other radicals, which themselves react further (via propagation steps).

(i) Termination reactions

(a) The most common termination reactions are simple combinations of similar or different radicals. For example,



(b) However, higher alkyl radicals terminate by two competitive processes that occur simultaneously, namely combination and disproportionation. In disproportionation a hydrogen atom is transferred from one radical to the other, thus the isopropyl radical terminates as shown below.

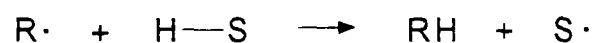


(c) Another type of termination reaction is inhibition. The controlled use of inhibitors is of great practical utility. For example, polymerisation monomers are sold with an added inhibitor to reduce the amount of polymer formed during storage; this inhibitor is removed before using the monomer. Iron wire is kept in bottles of ether for example, as ethers readily autoxidise at room temperature to form hydroperoxides. These are dangerously explosive, but their amounts can be reduced and their concentration controlled in the presence of iron.

(ii) Propagation reactions

There are five principal propagation reactions.

(a) Hydrogen abstraction is the most common reaction that radicals undergo. It can be generalised as shown below, where SH is any hydrogen donor.

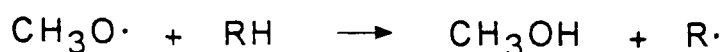
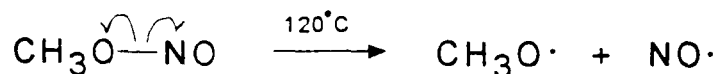
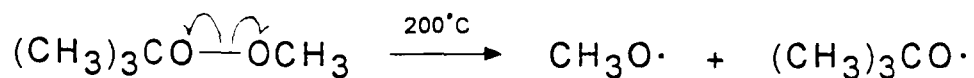


Hydrogen transfer occurs either as a principal reaction or as an unavoidable side reaction in almost every radical system. The energy required to break a C-H bond is so large that the reaction cannot occur unassisted, and some bond-making occurs in the transition state.

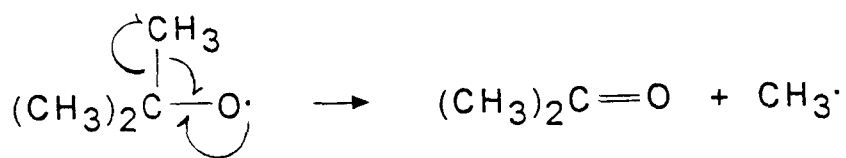
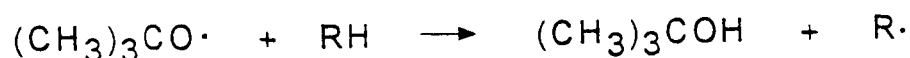


In the above bimolecular process, a radical abstracts a hydrogen atom from another molecule SH, and the energy necessary for bond breaking is

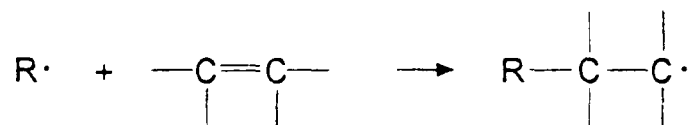
partially supplied by making the new bond. For example, simple alkoxy radicals react largely by hydrogen abstraction, as is the case for tertiary-butyl methyl peroxide and methyl nitrite, which both yield methoxy radicals which abstract hydrogen from various hydrogen donors.



When RH is an active donor such as cyclohexane, almost quantitative yields of methanol are formed. More complex alkoxy radicals usually react in more than one way. The tertiary butoxy radical for example, can either abstract a hydrogen atom from a hydrogen donor RH or undergo β -scission to form acetone.



(b) Addition to a multiple bond is the other most common radical propagating reaction.

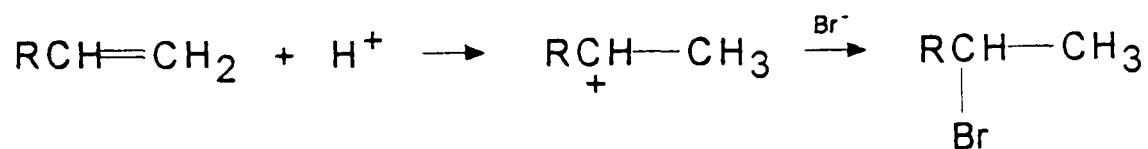


In 1937, Kharasch in America and Hey and Waters in England independently proposed a radical chain mechanism for the anti-Markovnikov addition of hydrogen bromide to alkenes in the presence of peroxidic materials.

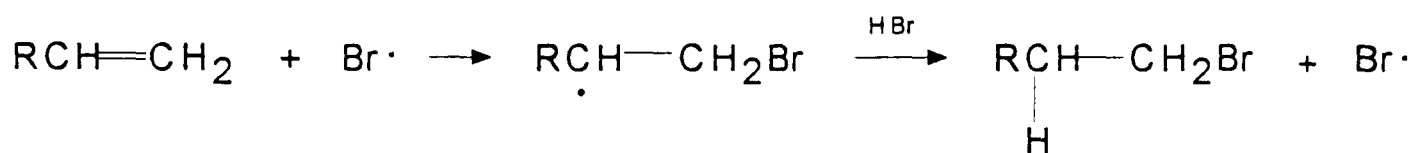
The stabilities of radicals and carbocations increase in the same order, namely, primary < secondary < tertiary. In the ionic addition of

hydrogen bromide to an alkene, the proton adds first and forms the more stable carbocation; in the radical case, a bromine atom adds first to produce the more stable radical.

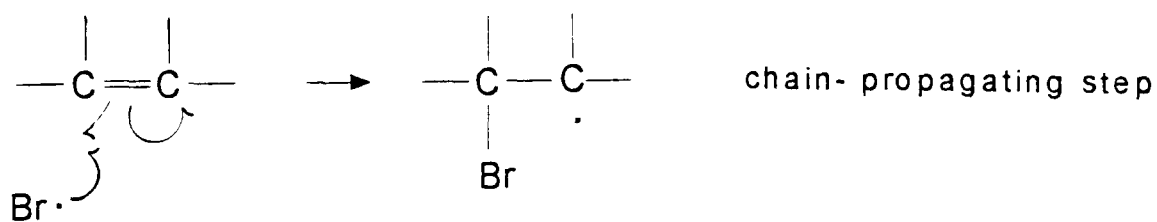
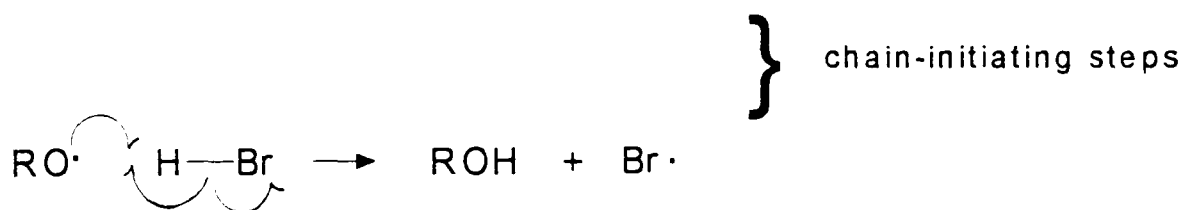
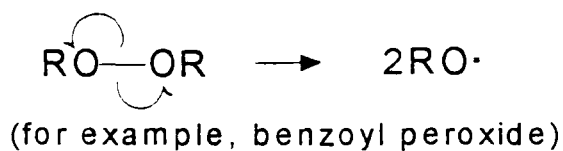
Ionic addition

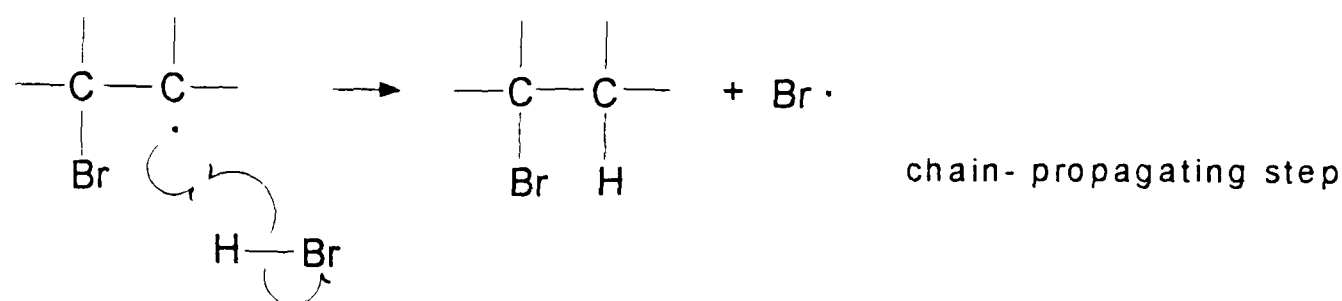


Radical addition



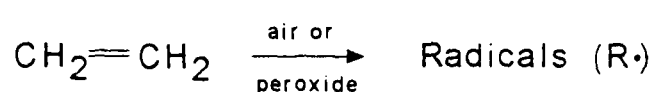
It is the presence of peroxide that generates the bromine atoms which then add to the double bond homolytically rather than heterolytically as in the ionic case:



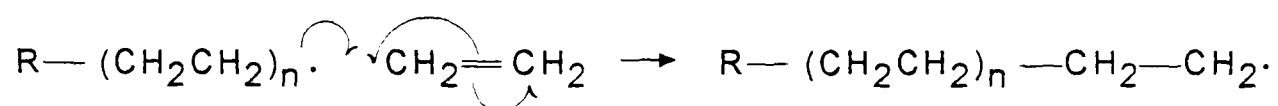


The radical formed initially may add to another double bond. This is one of the main mechanisms for free radical polymerisations in which the repeating unit in the chain is identical with the monomer.

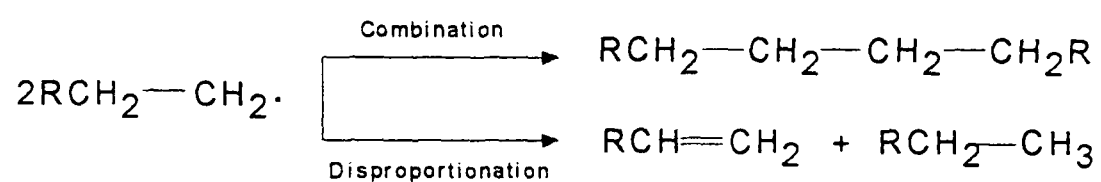
Initiation



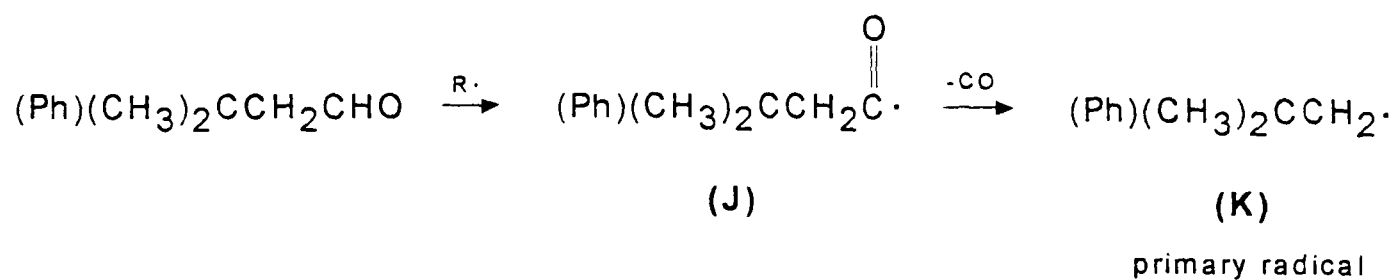
Propagation

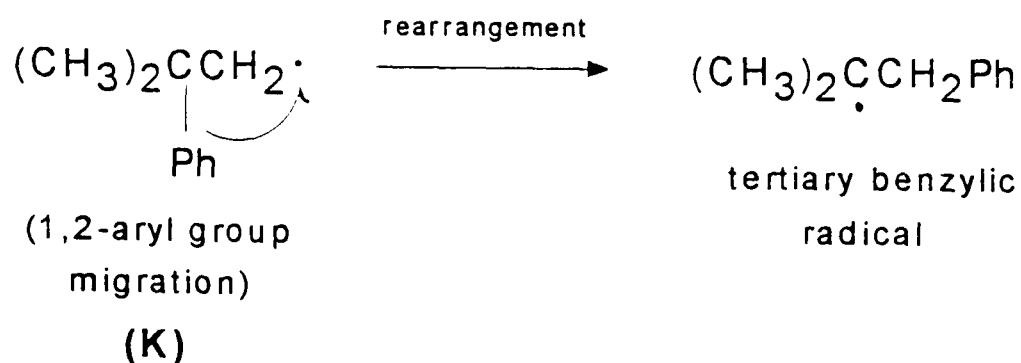


Termination

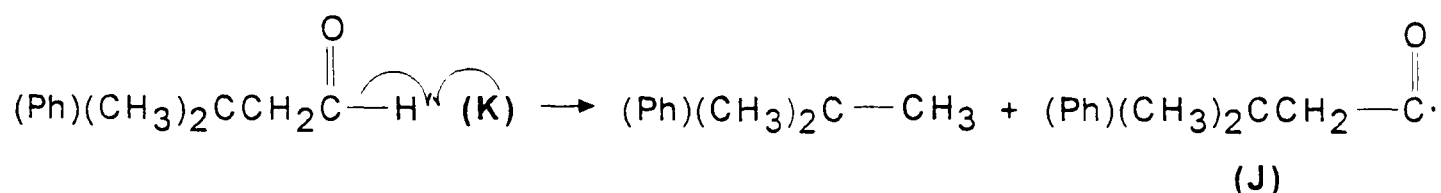


(c) Rearrangement is another possible propagation reaction available to radicals. By far the largest number of radical rearrangements are those where an aryl group moves position to the adjacent atom to form a more stable radical. Treatment of phenylisovaleraldehyde with peroxides gives the following set of reactions:

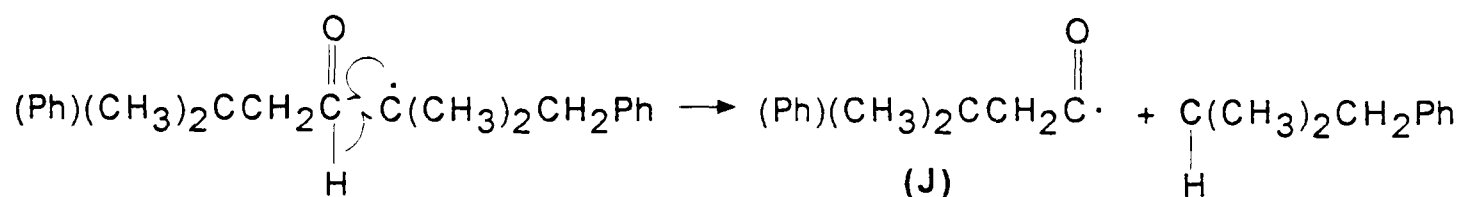




As well as rearranging, (K) can react with a molecule of aldehyde from which it was generated initially in a radical propagating step to form another radical (J), itself being terminated by hydrogen abstraction.



The tertiary radical can react similarly to yield a different termination product as well as (J). As shown above, (J) ultimately reverts to a termination product by hydrogen abstraction, via a primary or tertiary radical.

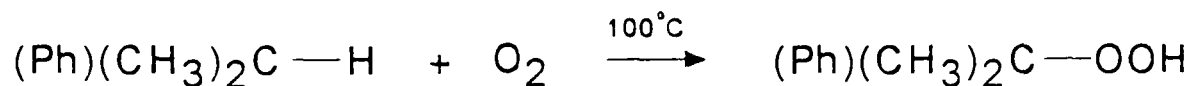


(d) Autoxidation is the slow oxidation of an organic compound by oxygen - "slow" meaning that oxidation is not accompanied by a flame and kept below 120°C, as in the hardening of paints and varnishes on drying, the deterioration of rubber and plastic materials in air, and many industrial oxidation processes in which oxygen is used as the oxidant.

The most common autoxidation is that where compounds with labile hydrogens react to form hydroperoxides.

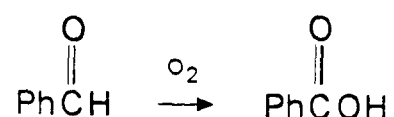


For example, the oxidation of isopropylbenzene:

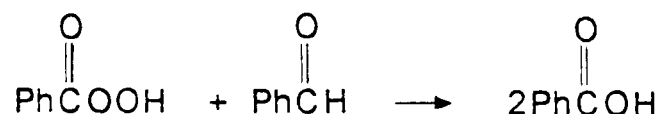
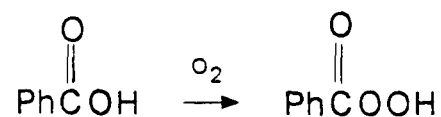


in 89% yield

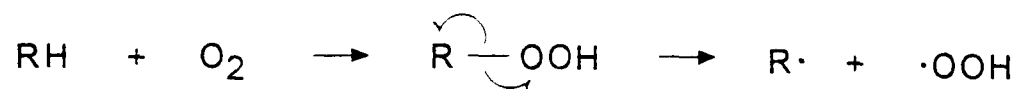
Sometimes, the product of autoxidation is not the hydroperoxide ROOH, but a molecule with the general formula ROH or ROOR. This is seen in the autoxidation of benzaldehyde to give benzoic acid.



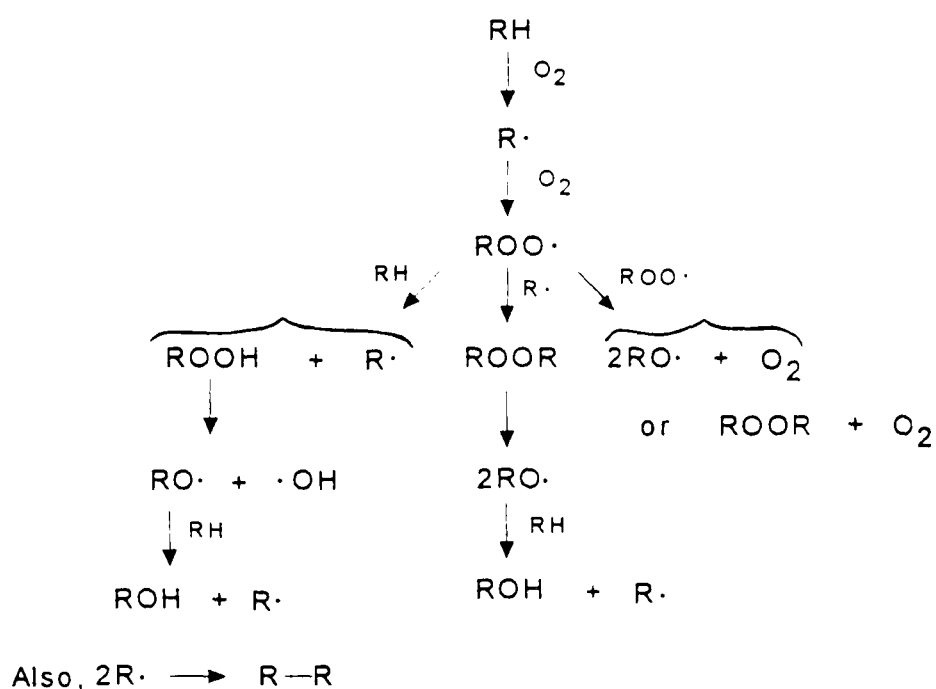
The mechanism involves the prior formation of the peroxyacid which then reacts with a molecule of benzaldehyde. (See this Chapter, 1.2.3 "Preparation of Peroxyacids".)



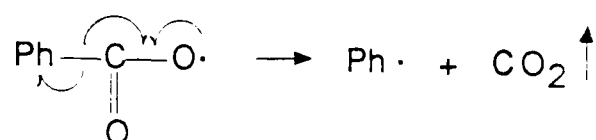
Autoxidations can be initiated by peroxides, hydroperoxides, azo compounds or any radical source. Initiation is often spontaneous due to the molecule-induced homolysis.



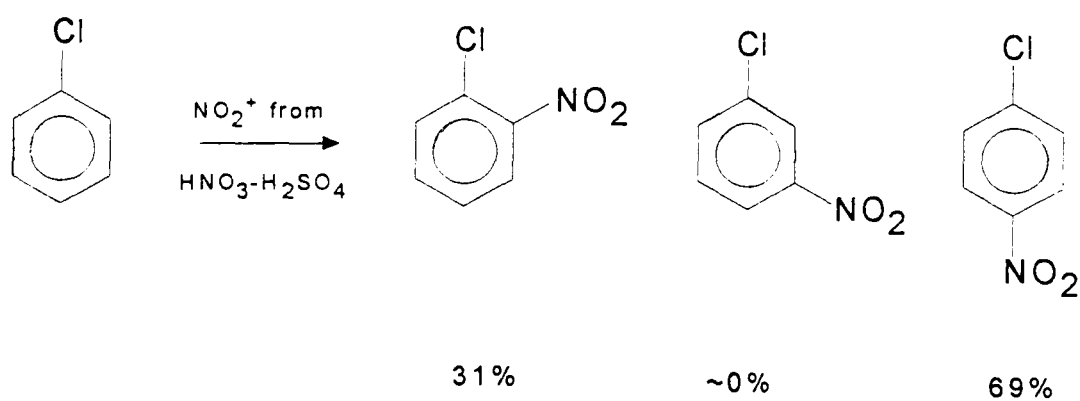
The type of reactions which occur in autoxidation systems are outlined below and incorporate hydrogen abstraction reactions^{66,67}.

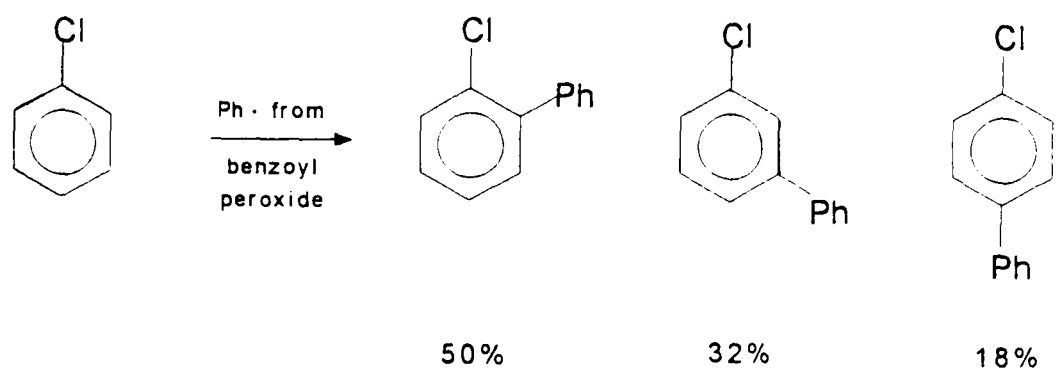


(e) A radical can also decompose to generate another radical and this is illustrated by the cleavage of the benzoyloxy radical.



Aromatic substitution by radical mechanisms gives different products to those obtained in the analogous ionic substitution (by an electrophile E^+). In the latter, electron-donating groups such as alkyl or alkoxy are ortho- and para- directing and lead to enhanced rates of substitution; electron-withdrawing groups such as nitro lead to meta-substitution products (except halogens, which are slightly deactivating, and are ortho-para directing) and deactivation of the ring. In the radical process these rules no longer hold. Homolytic substitution by phenyl radicals from benzoyl peroxide for example, is faster on either nitrobenzene or toluene than on benzene itself, and both are substituted mainly at the ortho position. For example, the nitration and phenylation of chlorobenzene:





Two possible mechanisms for aromatic substitution were first made by Hey in 1934, and in 1937 Hey and Waters outlined the ionic and radical mechanisms in detail and suggested the utility of the radical path. However, the mechanism of homolytic aromatic substitution is still not entirely clear.

1.4 *Principal Reactions of Peroxyesters, Hydroperoxides, Peroxyacids and Acyl Peroxides*¹⁷

The main reactions of organic peroxides unsurprisingly result from the presence of the peroxide bond, and usually involve O-O heterolysis or homolysis. The hydrolysis of peroxyesters⁷ does not involve O-O bond cleavage and is discussed separately. Acid- and base- catalysed decompositions of acyl organic peroxides do not result in heterolytic O-O bond breaking (except the acid-catalysed decomposition of hydroperoxides at the peroxy oxygen) but instead, attack on the acyl group - electrophilic attack on the carbonyl oxygen by H^+ , or nucleophilic attack on the carbonyl carbon by ^-OH or $X:$ (where X is an atom with a lone pair of electrons).

Recent reactions of hydroperoxides and alkyl peroxides have postulated intermediate protonated and alkylated peroxide structures. By mechanisms described later in this chapter, there is the potential of acylated peroxonium ions being formed from peroxyesters, as yet unknown.

The various types of organic peroxide reactions to be discussed are outlined below.

- 1.4.1 O-O Heterolysis:
 - 1.4.1.1 Intermolecular Nucleophilic Substitution at Oxygen;
 - 1.4.1.2 Intramolecular Nucleophilic Rearrangement;
 - 1.4.1.3 Other Redox Reactions:
 - (i) pH-dependent sulphite reduction of hydroperoxides;
 - (ii) Carbonyl-forming eliminations;
 - (iii) Base-catalysed elimination of oxygen from tertiary-alkyl hydroperoxides;
- 1.4.2 Acid-Catalysed Decomposition;
- 1.4.3 Base-Catalysed Decomposition;
- 1.4.4 Thermally Induced O-O Homolysis;
- 1.4.5 Hydrolysis of Peroxyesters;
- 1.4.6 Postulated Peroxide and Peroxonium Ion Intermediates.

1.4.1 O-O Heterolysis

1.4.1.1 Intermolecular Nucleophilic Substitution at Oxygen

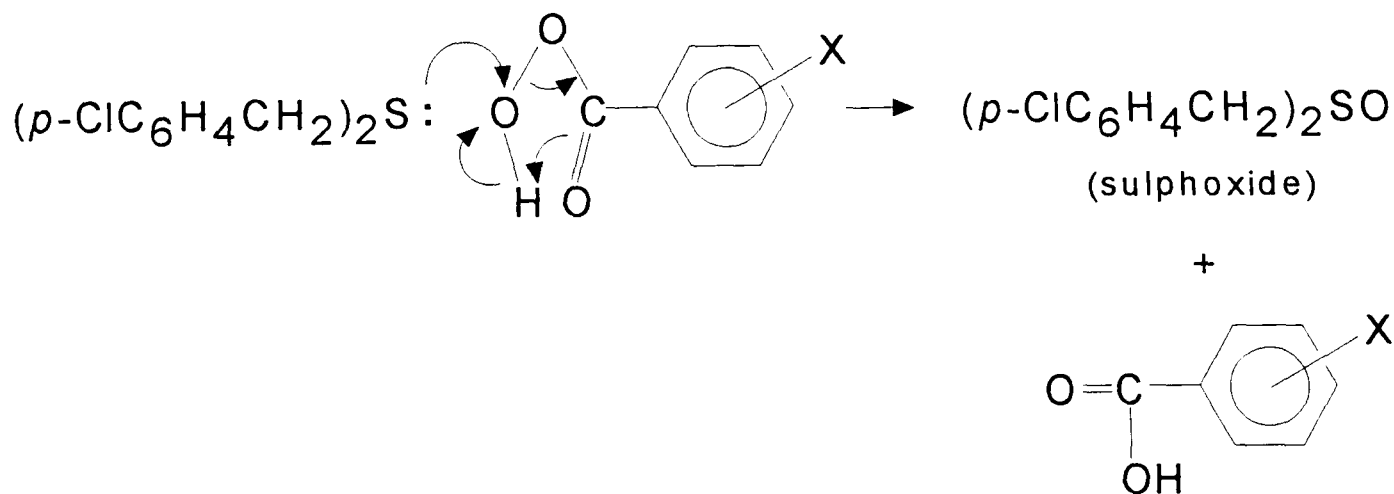
The bulk of the available evidence suggests that intermolecular nucleophilic substitution at oxygen in organic peroxides occurs by an S_N2 rather than an S_N1 mechanism⁷⁰.

Examples of this S_N2 process have been established where the nucleophilic reagent is taken from Groups IV, V, VI and VII of the Periodic Table (for example, carbon, nitrogen and phosphorus, oxygen and sulphur, and iodine), or where it is hydrogen or the π -electrons of a multiple bond.

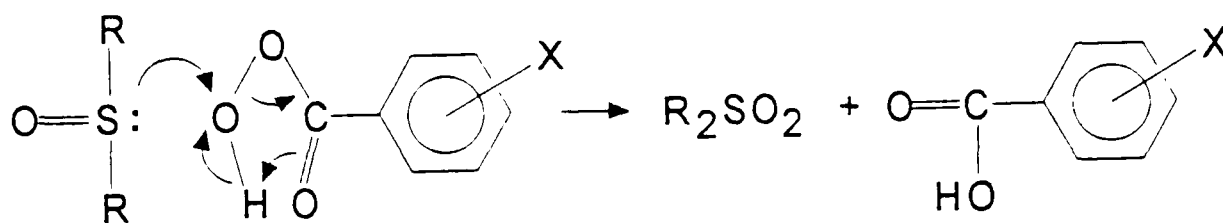
(a) By Sulphur⁷¹

(i) With peroxyacids

The S_N2 mechanism involved has been established most thoroughly in the case of the oxidation of sulphides and sulphoxides. The oxidation of bis (*p*-chlorobenzyl) sulphide with substituted peroxybenzoic acids is accelerated by electron-attracting groups X in the peroxyacid (making the peroxy oxygen more susceptible to attack by the nucleophile - making the peroxy oxygen more nucleophilic). A hydrogen atom is transferred intramolecularly in the process.

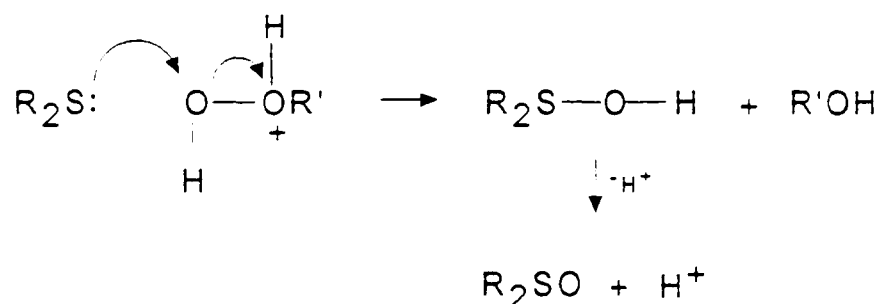


Sulphoxides are further oxidised to sulphones by a similar bimolecular process, and again probably involves nucleophilic attack of sulphur on oxygen⁷².



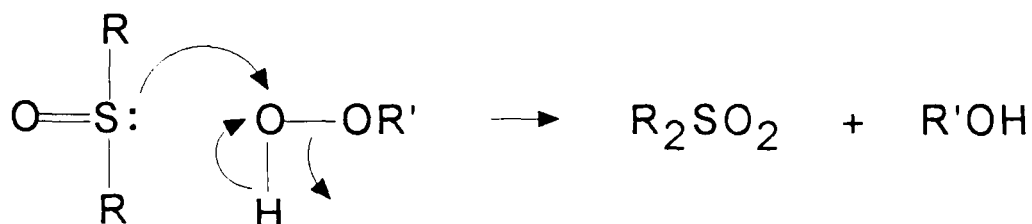
(ii) *With hydroperoxides and hydrogen peroxide*

The oxidation of sulphides by hydroperoxides and hydrogen peroxide follows a similar mechanism and is susceptible to acid catalysis. Hydrogen-bonding solvents (HY) (or in their absence a second molecule of the hydroperoxide) appear to assist in the fission of the O-O bond.



Electron-releasing substituents in the aromatic rings of for example, methyl phenyl sulphide and diphenyl sulphide, increase the rate of reaction.

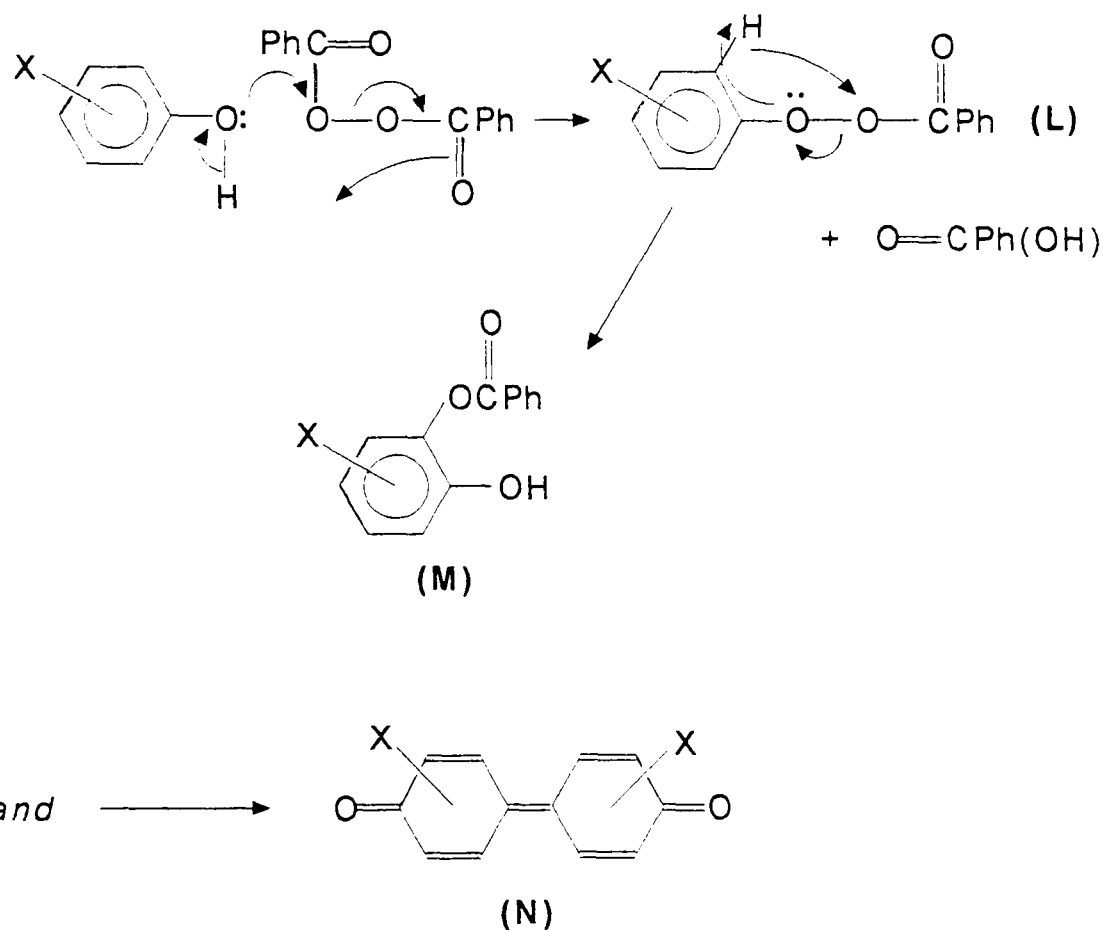
Similarly to the reaction with peroxyacids, the further oxidation of sulphoxides to sulphones by hydroperoxides is bimolecular⁷². Vanadium and molybdenum⁴² ions catalyse the further oxidation of sulphoxides to sulphones by hydroperoxides.



(b) By Oxygen

With acyl peroxides

The nucleophilic power of oxygen for oxygen would be expected to be low. The strongest evidence of this reaction comes from Walling and Hodgdon's work on the decomposition of benzoyl peroxide in the presence of phenols⁷³. The reaction is accelerated by electron-releasing groups in the phenol, and retarded by bulky ortho groups⁷⁴. It is assumed then, that the phenolic oxygen attacks nucleophilically on the peroxide bond. The reaction is not susceptible to acid- or base- catalysis, but hydrogen-bonding solvents depress the rate.



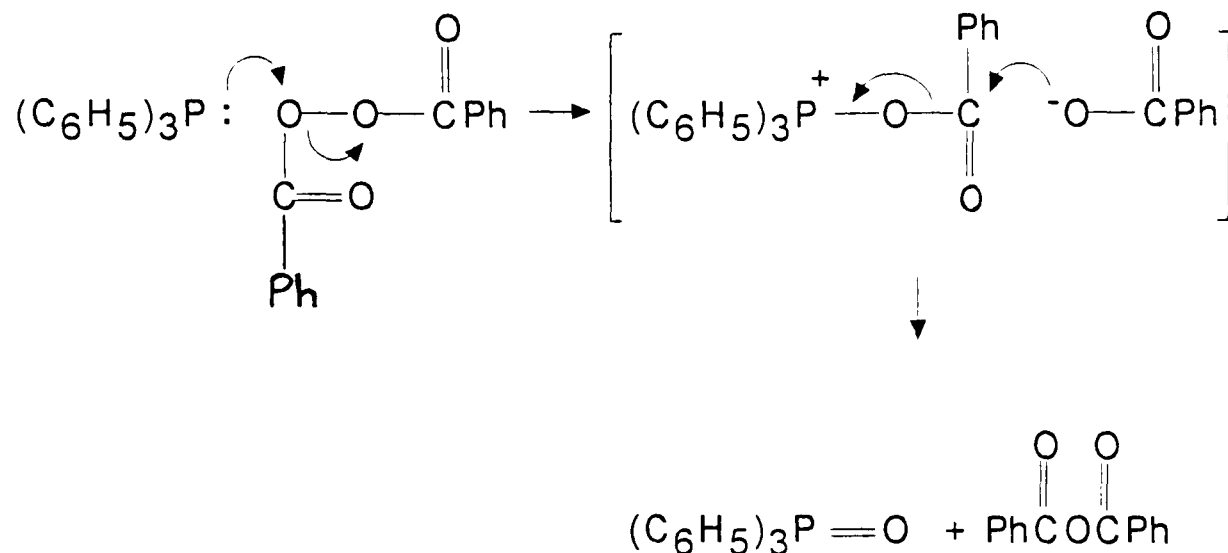
The aryl peroxyesters (L) then decompose rapidly by a Claisen-type rearrangement to *o*-hydroxyphenyl benzoate (M) or oxidise a second phenol

molecule giving a quinonyl dimer (N).

(c) By Phosphorus

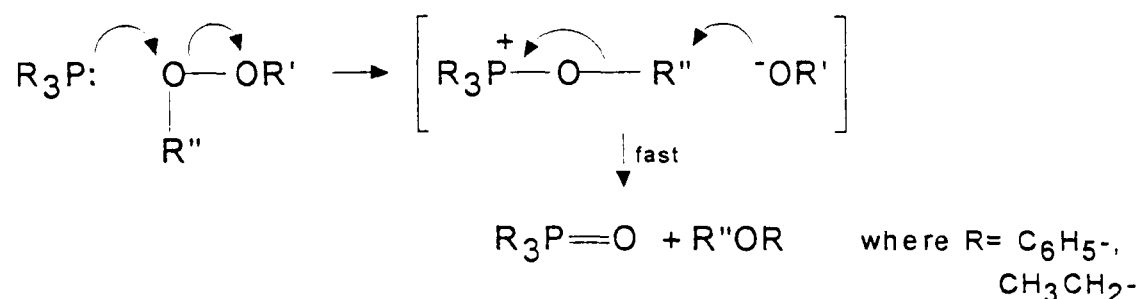
(i) With acyl peroxides

Challenger and Wilson⁷⁵ showed in 1927 that benzoyl peroxide would oxidise triphenylphosphine to triphenylphosphine oxide, itself being reduced to benzoic anhydride.



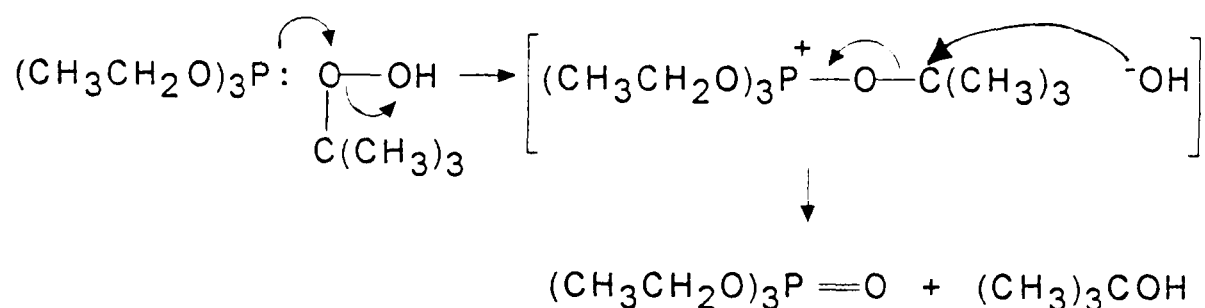
In 1955, Horner and Jurgeleit⁷⁶ studied the interaction of triphenyl and triethylphosphine with organic peroxides, and showed that irrespective of the structure of the peroxide ROOR', it was reduced to the oxide ROR'.

The reaction is considered to proceed by nucleophilic attack on oxygen to form an ion pair which then reacts to give the final product.

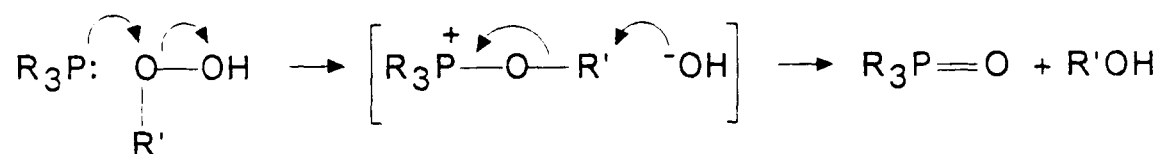


(ii) With hydroperoxides

A similar instantaneous and exothermic reaction occurs between tertiary-butyl hydroperoxide and triethylphosphite at 0°C, giving tertiary-butanol and triethylphosphate⁷⁷.



Similarly in the reduction of an alkyl hydroperoxide by a tertiary phosphine, the initial attack takes place on the α -oxygen atom which explains the products formed.



(d) By Nitrogen

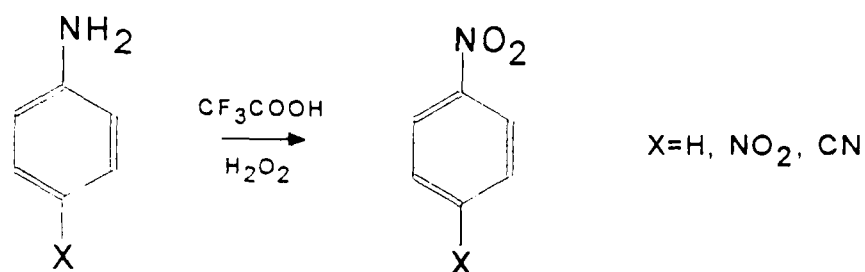
(i) With peroxyacids

The oxidation by peroxyacids^{71,78} of (a) primary amines to nitroso- and nitro- compounds, (b) tertiary amines to amine oxides, (c) azo- compounds to azoxy- compounds, and (d) nitrosamines to nitramines, clearly involves the nucleophilic attack of nitrogen on peroxidic oxygen. For example:

(a)(a) a solution of hydrogen peroxide in trifluoroacetic acid leads to the formation of peroxytrifluoroacetic acid in situ.

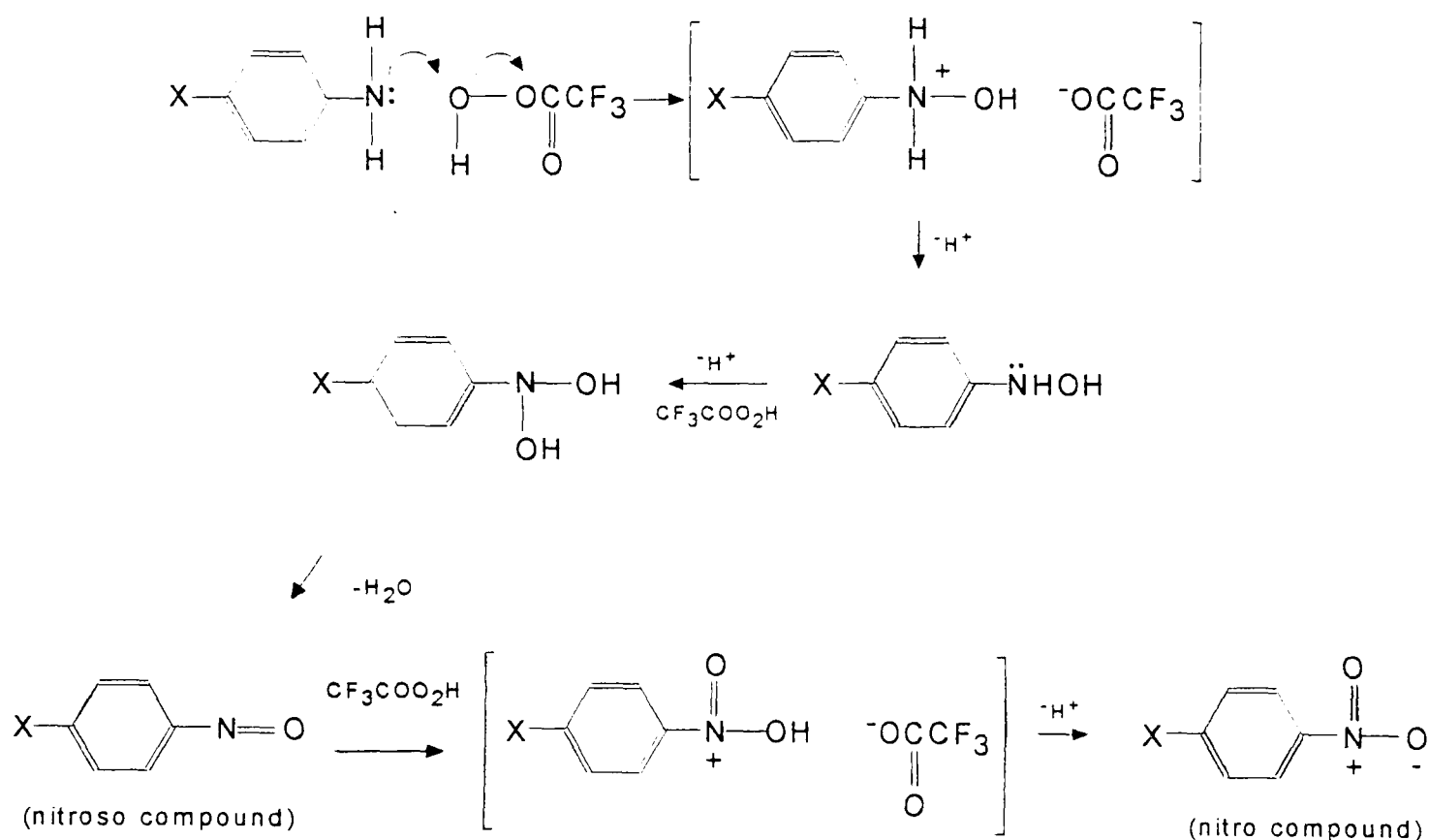


The reagent oxidises aniline and substituted anilines to nitrobenzenes in excellent yields^{78,79}. Aniline (X=H), *p*-nitroaniline (X=NO₂) and *p*-aminobenzonitrile (X=CN), were converted into nitrobenzene (79%), *p*-dinitrobenzene (86%) and *p*-nitrobenzonitrile (98%), respectively.

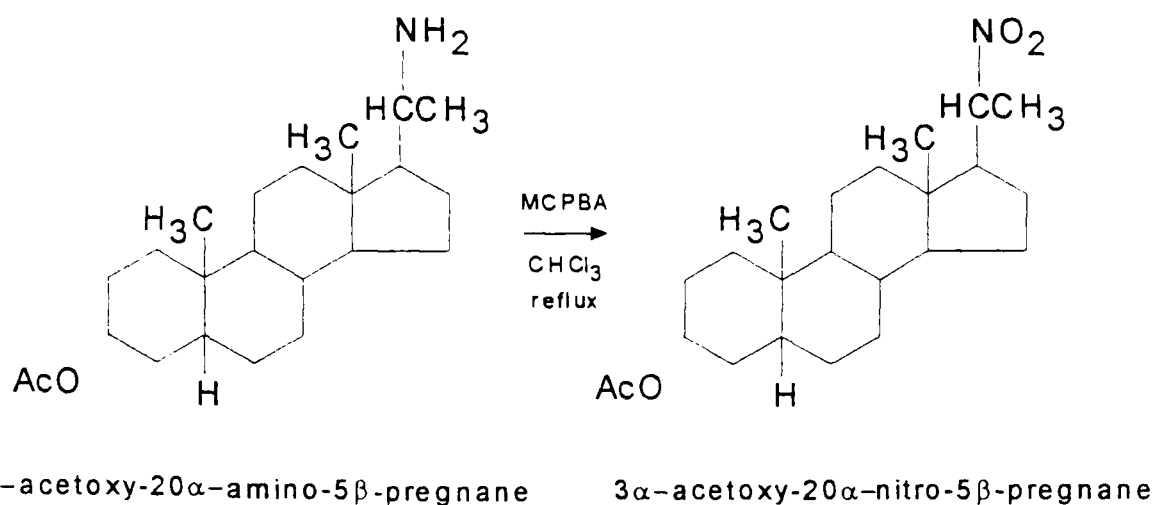


The amine is added slowly to a solution of seven equivalents of the peroxyacid in refluxing chloroform. The sequence of events is probably $\text{RNH}_2 \longrightarrow \text{RNHOH} \longrightarrow \text{RNO} \longrightarrow \text{RNO}_2$. The peroxyacid is in large excess to prevent accumulation and dimerisation of the nitroso compound (RNO) which can occur.

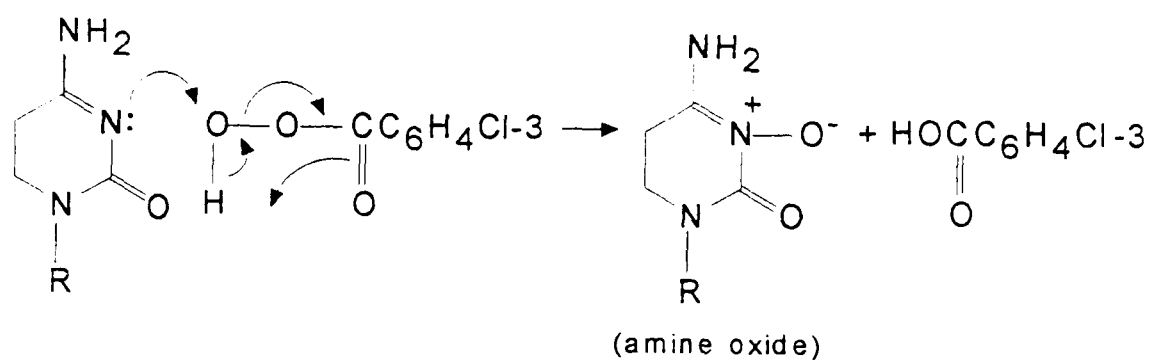
(In contrast, the peroxyacetic acid oxidation of aniline yields 11% nitrobenzene and 71% azoxybenzene⁸⁰.)



(B) MCPBA can oxidise steroid primary amines to nitrosteroids⁸¹.



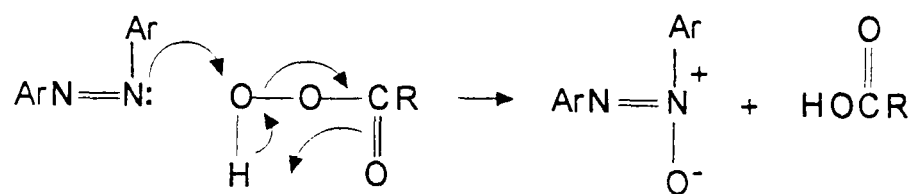
(b) Cytisine (O) and cytidine (P) have been converted by MCPBA into the corresponding 3-N-oxides in yields of 21% and 41% respectively⁸². In this case neither peroxyphthalic acid nor peroxytrifluoroacetic acid proved satisfactory.



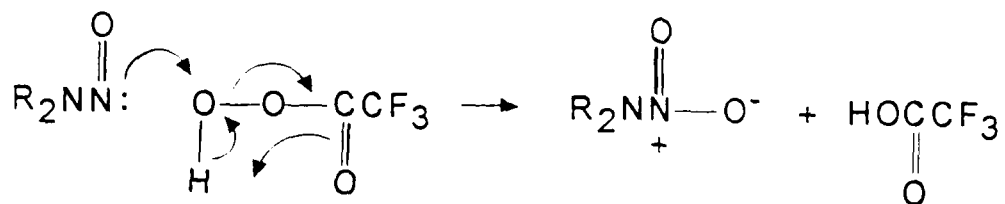
(O), R=H

(P), R=β-D-ribofuranosyl

(c) Azo compounds can be oxidised to azoxy compounds by peroxyacids and hydroperoxides^{19a}.



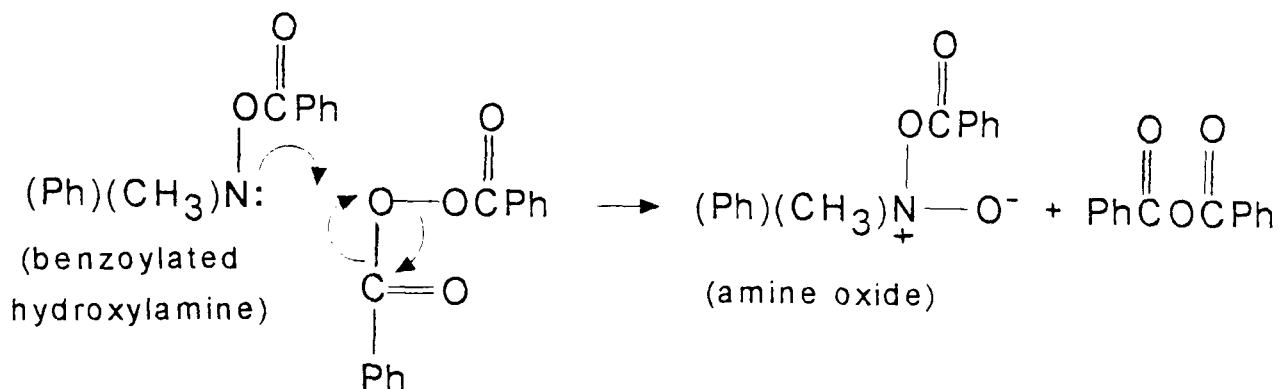
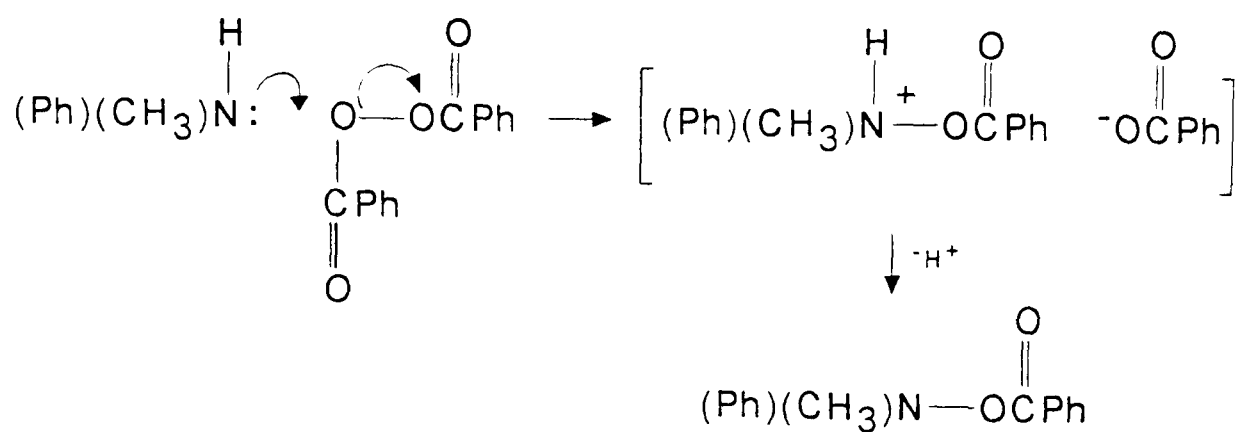
(d) Nitrosamines have also been oxidised to nitramines with trifluoroperoxyacetic acid.



Diethylnitrosamine and dibutylnitrosamine were converted into the corresponding nitramines in 76% and 77% yield, respectively^{78,83}.

(ii) With acyl peroxides

The first stage of the reaction with a tertiary amine, involves the formation of a substituted hydroxylamine, which reacts with a second molecule of acyl peroxide to give an amine oxide. Electron-repelling substituents in the amine, and electron-attracting substituents in the benzoyl peroxide, accelerate the reaction.



(iii) With hydroperoxides

When heated in the presence of amines, tertiary hydroperoxides are converted almost exclusively into the corresponding alcohols⁸⁴. The mechanism is uncertain, but it is known that no amine oxide is formed with only some of the amine being utilised - instead, much is recovered. Also, water is formed in an amount corresponding to the oxygen lost by the peroxide. Vanadium and molybdenum ions can act as catalysts.



The ease of the reaction is usually the greatest with tertiary amines and least with primary. The reaction gives a useful method for reducing tertiary-alkyl hydroperoxides preparatively, but with secondary and primary compounds, the basic conditions also give rise to carbonyl-forming elimination products⁸⁵. (See this Chapter, 1.4.1.3(ii) "Other Redox Reactions, Carbonyl-Forming Eliminations".) Carbonyl compounds are also formed with primary and secondary peroxyesters as they too are base-sensitive.

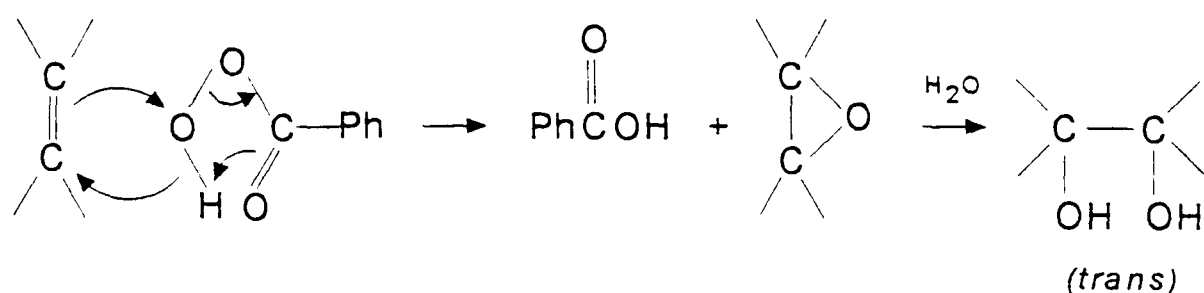
(e) By Carbon

This will involve the nucleophilic attack by the π -electrons of a multiple bond to carbon.

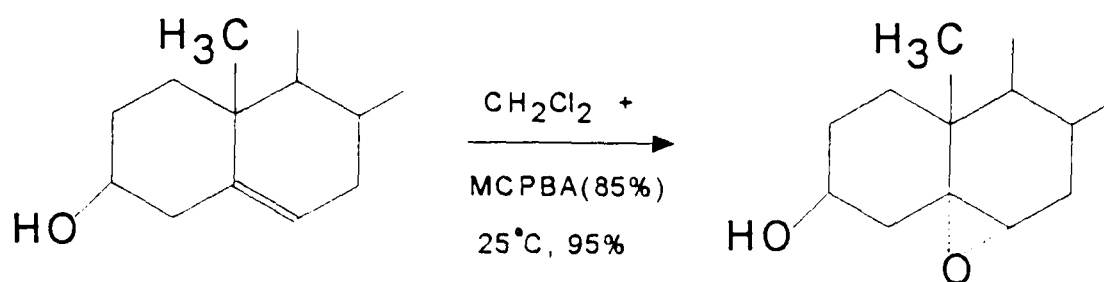
(i) The epoxidation of alkenes

(a) By peroxyacids

In 1909, Prileshajew⁸⁶ showed that peroxybenzoic acid would readily oxidise an alkene to an epoxide, and on hydrolysis yield a glycol.



For example^{22,87}



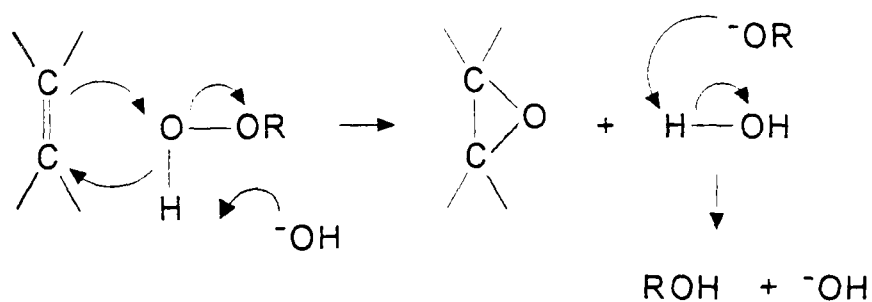
The epoxide is always formed by *cis* addition to the alkene. In the alkene, electron-releasing substituents accelerate and electron-attracting substituents decelerate the reaction.

The higher aliphatic peroxyacids, such as peroxyoctanoic acid, are more stable than the aromatic peroxyacids. Trifluoroperoxyacetic acid is much more reactive than the reagents derived from weaker carboxylic acids; it is particularly useful for the epoxidation of alkenes carrying electron-withdrawing substituents.

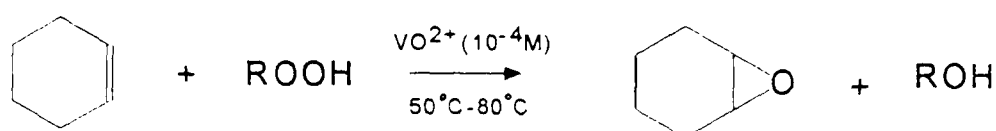
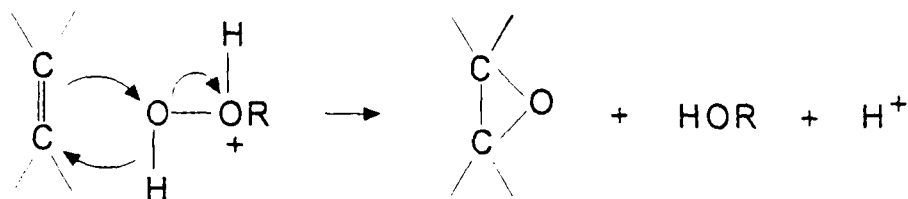
The peroxyacid mechanisms are described by Swern⁷¹.

(b) By hydroperoxides

In alkaline conditions hydroperoxides can also oxidise alkenes to epoxides. The tertiary compounds only undergo alkali-catalysed decomposition at elevated temperatures. (See this Chapter, 1.4.4 "Thermally Induced O-O Homolysis".) In addition to epoxide formation, use of tertiary-butyl hydroperoxide yields tertiary-butanol and oxygen.



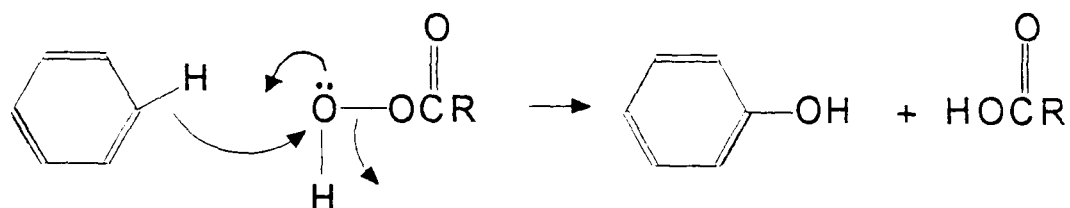
Epoxidation by hydroperoxides can be catalysed by boric acid and also by complexes or salts of vanadium, chromium, molybdenum⁸⁸ or tungsten⁸⁹. The presence of these ions produces virtually quantitative yields of epoxide from any hydroperoxide.



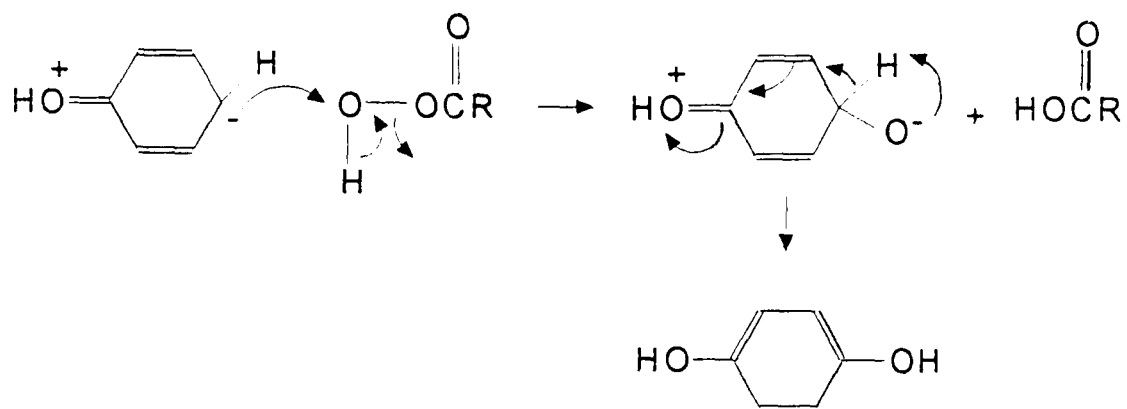
(ii) *The hydroxylation of aromatic compounds*

By peroxyacids

The relative reactivity of aromatic compounds towards peroxyacids and the position of attack on the aromatic ring, imply that the peroxyacid behaves as an electrophilic reagent.



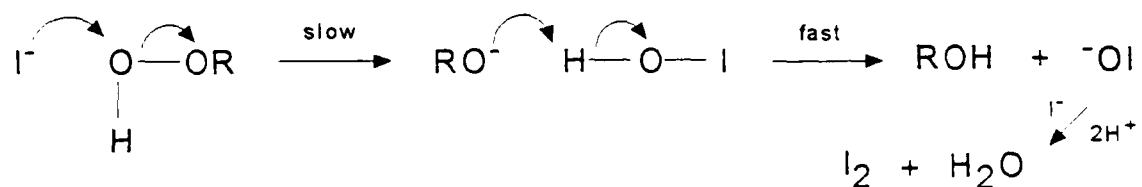
Sometimes the primary hydroxylated compound can be isolated. However, because of the activating effect of the HO- group which has been introduced, further substitution frequently occurs in the ortho or para positions sometimes displacing an electronegative group.



(f) By Iodine

(i) *With hydrogen peroxide and hydroperoxide*

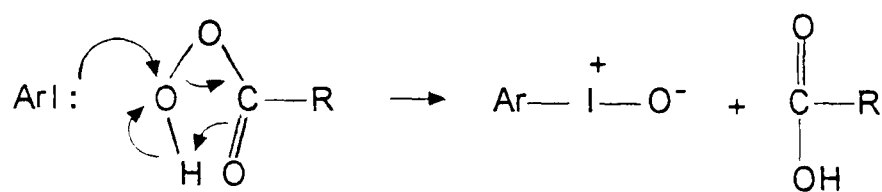
Reaction occurs between aqueous iodide ion and H_2O_2 , ROOH = methyl, ethyl, tertiary-butyl, or 2-phenyl-2-propyl hydroperoxide. The initial stage of the reduction involves nucleophilic attack on the β -oxygen atom.



(i) *With peroxyacids*

The oxidation of bromide ion by peroxyacetic acid is similarly a bimolecular reaction. The relative rates for different halide ions are $I^- > Br^- > Cl^-$.

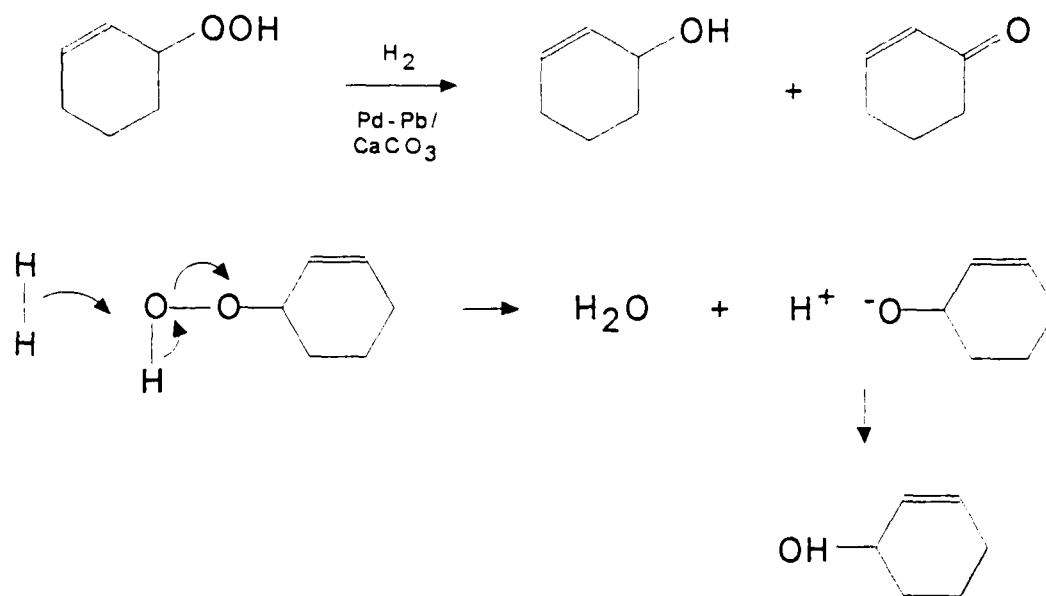
The oxidation of aryl iodides to iodoso compounds by peroxyacids similarly involves nucleophilic attack of iodine upon oxygen.



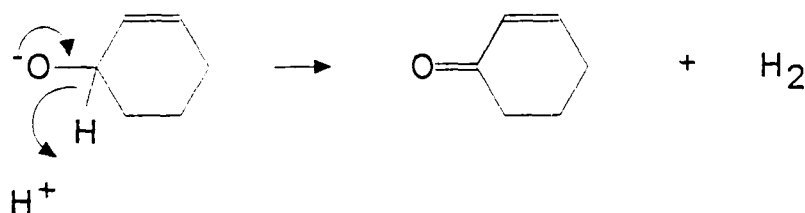
(g) By Hydrogen

With hydroperoxides, acyl peroxides and peroxyesters

Catalytic hydrogenation reduces hydroperoxides to the corresponding alcohol. Allylic hydroperoxides can be reduced with the double bonds remaining unaffected⁹⁰.



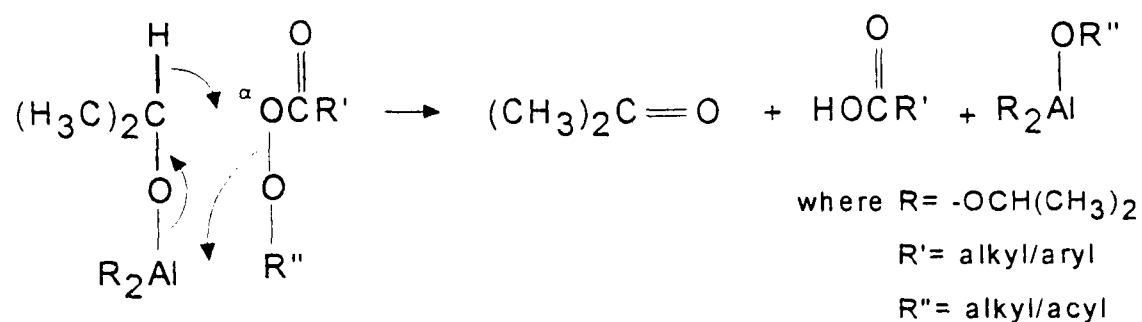
and,



With some reducing agents however, it is apparent that the reduction involves the transference of nucleophilic hydrogen. Lithium aluminium hydride will readily reduce hydroperoxides⁹¹, acyl peroxides⁹², and ozonides. The mechanism most probably involves nucleophilic attack by hydrogen on oxygen.

Hydroperoxides, acyl peroxides (but not alkyl peroxides) and peroxyesters, can also be reduced with aluminium isopropoxide ($\text{Al}[\text{O}-\text{CH}(\text{CH}_3)_2]_3$) in dioxan or isopropanol between 70°C and 75°C ; acetone is slowly distilled off (from the aluminium isopropoxide). As seen in the Meerwein-Ponndorf-Verley reaction⁹³, it is assumed that the peroxides are again reduced by the transfer of nucleophilic hydrogen (hydroperoxides to

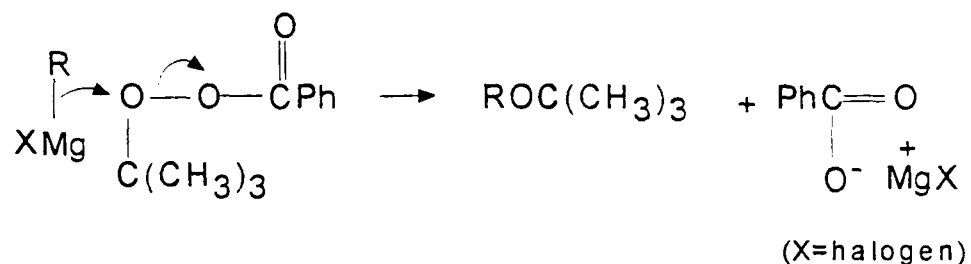
alcohols; peroxyesters and acyl peroxides to carboxylic acids). For example,



(h) Miscellaneous

Aryl Grignard reagents with tertiary-butyl peroxyesters

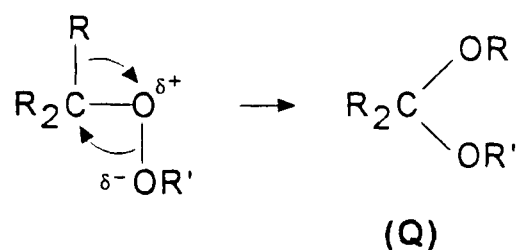
Aryl Grignard reagents are highly reactive nucleophiles, and have been shown to react with tertiary-butyl peroxybenzoate to give good yields of tertiary-butyl ethers and benzoic acid⁹⁴. The mechanism probably includes nucleophilic attack of the potential carbanion at the peroxy oxygen attached to the tertiary-butyl group, and the carboxylate anion acting as leaving group.



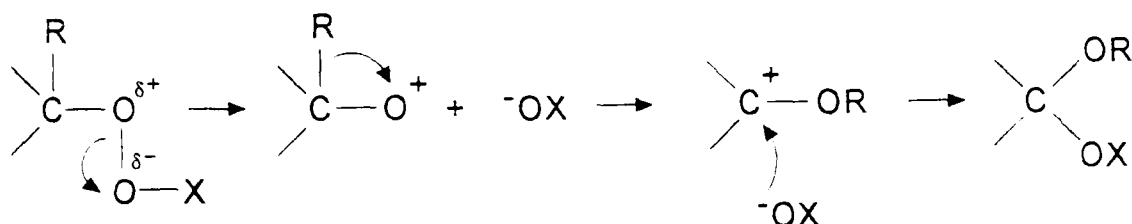
Tertiary-butyl peroxyacetate can be used instead of tertiary-butyl peroxybenzoate.

1.4.1.2 Intramolecular Nucleophilic Rearrangement

The fission of an O-O bond in an organic peroxide is often accompanied by cleavage of a C1-C2 bond to give an acetal derivative (Q) by a redox rearrangement.

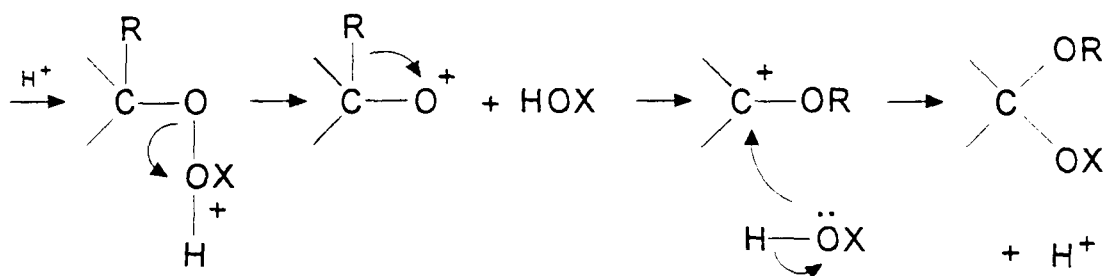


Familiarity with the homolysis of the peroxide bond delayed the recognition that the above reaction is often heterolytic, involving a nucleophilic 1,2-rearrangement of an alkyl or aryl group from carbon to oxygen. The three electronic shifts, some or all of which may in fact be synchronous, are depicted below.



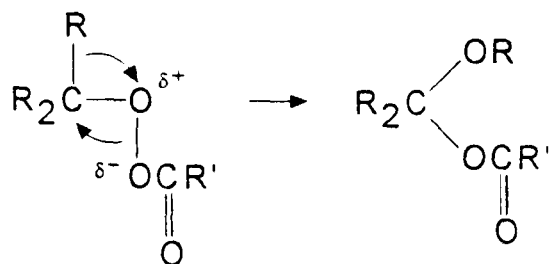
Evidence indicates that the migration of the alkyl or aryl group is synchronous with the fission of the O-O bond, the migration of R and of OX taking place in a concerted process as in the formation (Q).

This heterolytic mechanism would be expected to be promoted by electronically dissimilar substituents on the peroxide group (that is, promoting a dipole in the peroxide bond: $-\delta^+\text{O}-\delta^-\text{O}-$) and by a polar medium, and should be susceptible to acid catalysis⁹⁵.



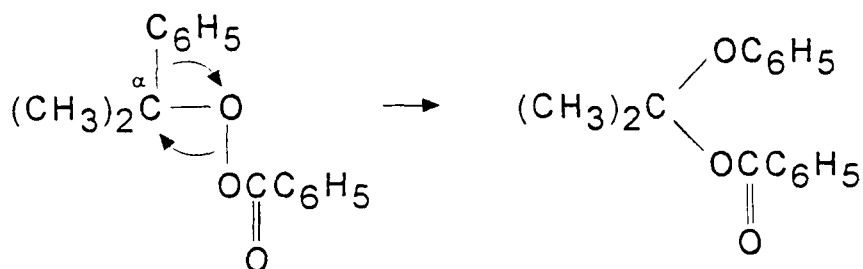
(a) Peroxyesters

In the case of peroxyesters, the reaction is known as the Criegee rearrangement (ionic thermal decomposition) and affects mainly tertiary peroxyesters. Some peroxyesters are difficult to prepare because of the inherent instability of the peroxyesters themselves towards this redox rearrangement. Thus on standing, a peroxyester may be converted to an acylal:

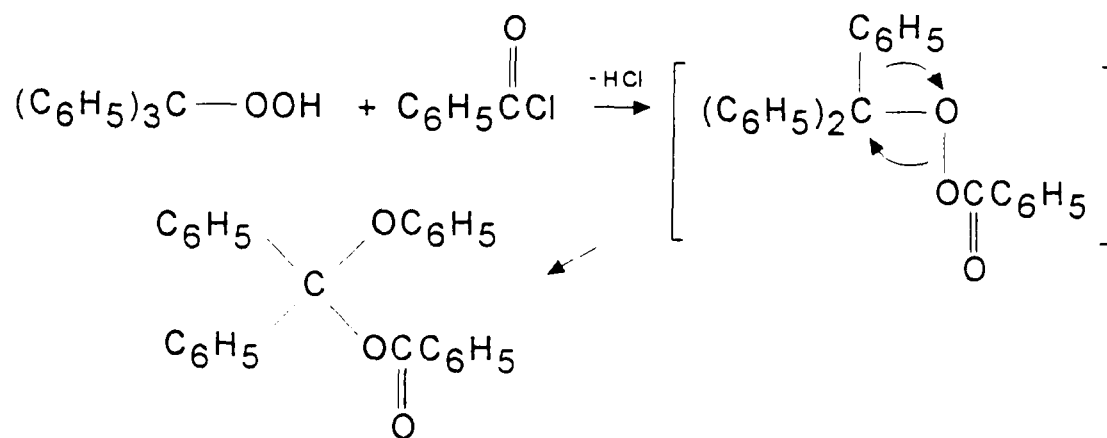


The reaction is facilitated by strong electron attraction in the acyloxy group $R'CO_2-$, by a high migratory aptitude in the alkyl or aryl group R (a phenyl group migrates in preference to a methyl group or a hydrogen atom), and polar media (to stabilise the charged molecule), as shown by Criegee and Kaspar⁹⁶.

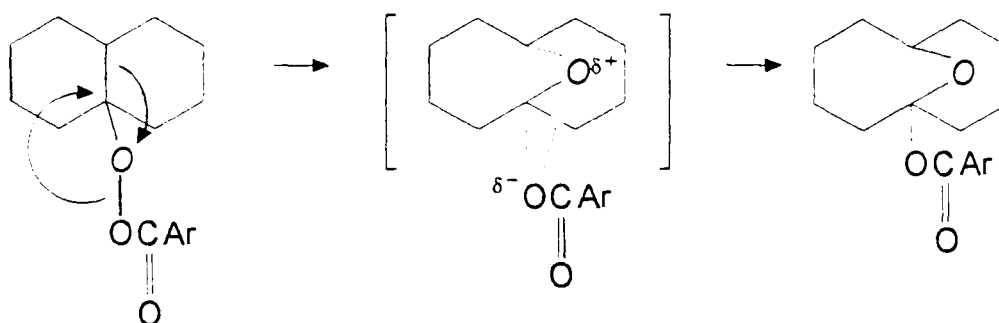
Simple peroxyesters derived from tertiary-alkyl hydroperoxides generally do not undergo the Criegee reaction. However, when a phenyl group is present at the α -position, a rearrangement is observed, as is the case for cumene peroxybenzoate⁹.



The peroxybenzoate of triphenylmethylhydroperoxide is so labile that only the rearrangement product can be isolated⁹⁷.



Esters of decahydro-9-naphthyl hydroperoxide also rearrange on standing, to form esters.

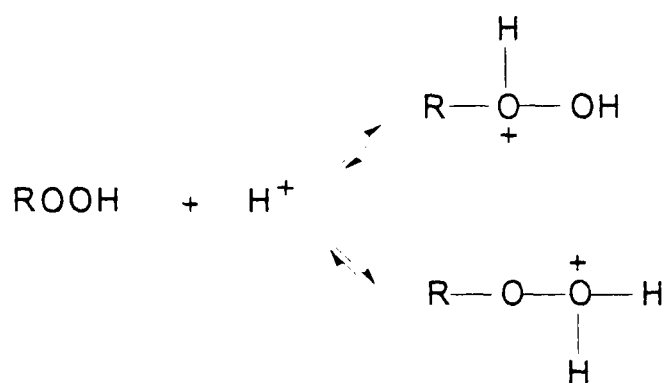


Although primary and secondary peroxyesters too may undergo the Criegee reaction, a competitive reaction may also occur involving carbonyl formation. (See this Chapter, 1.4.1.3 "Other Redox Reactions, Carbonyl-Forming Eliminations".)

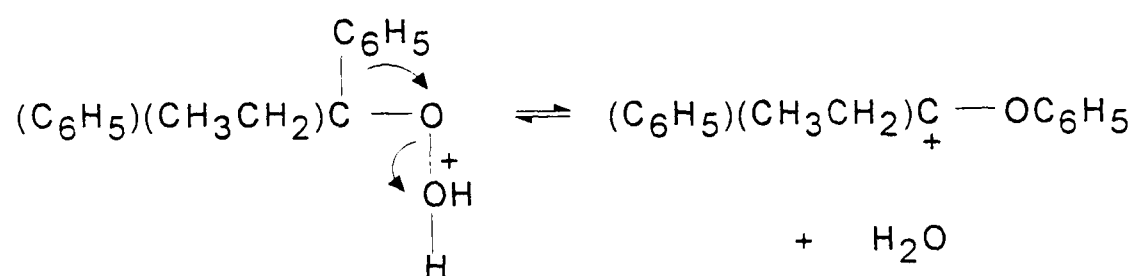
(b) Alkyl Hydroperoxides

The products obtained by their acid-catalysed decomposition have long been known, and since 1948⁹⁶, the nucleophilic rearrangement understood.

The proton may electrophilically attack either oxygen of a hydroperoxide.

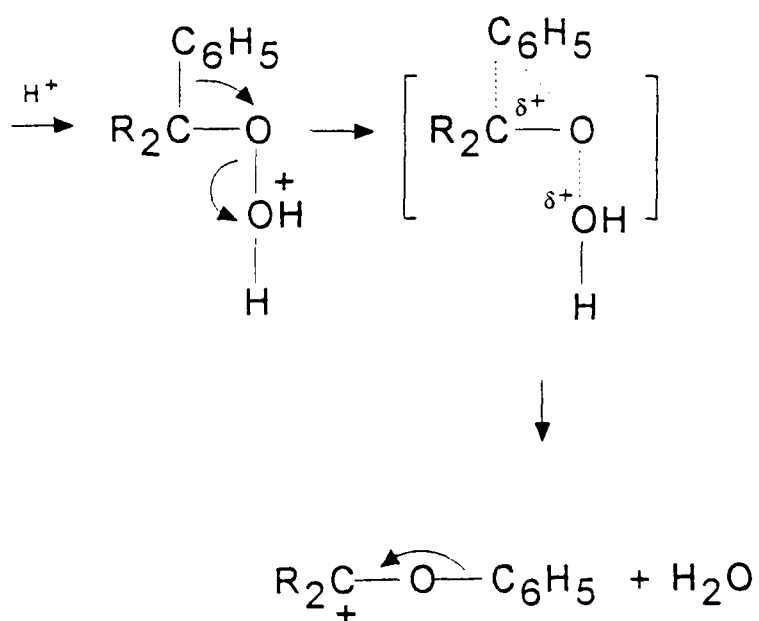


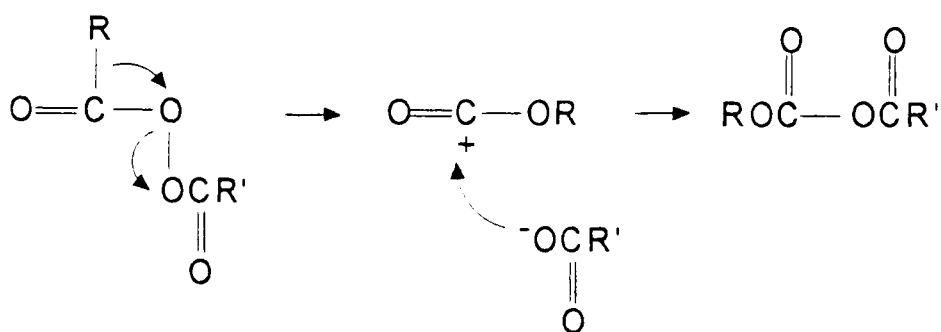
(1) If there is protonation of the peroxy hydroxylic oxygen, O-O heterolysis occurs accompanied by rearrangement. For example:



A transition state with the migrating group partially bonded to both carbon and oxygen is postulated. That is, the two processes involved - removal of water and migration of the phenyl group - occur synchronously.

Then, under acid-catalysed decomposition, the carbon from which the group migrates forms a carbonyl, and the migrating group forms an alcohol.

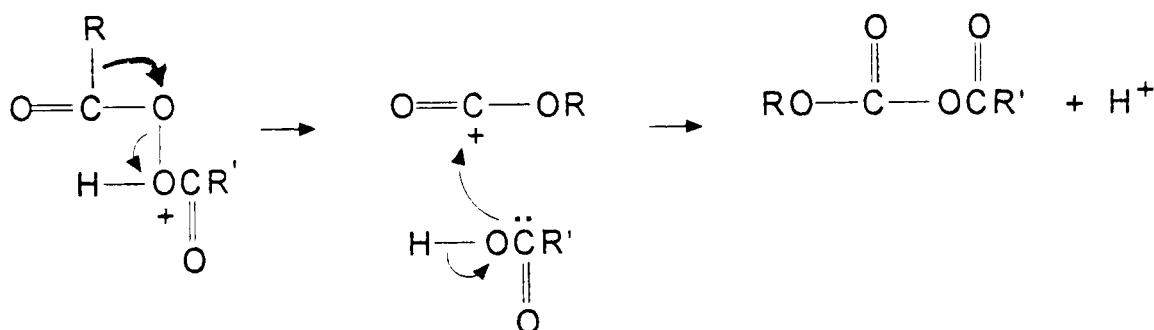




where $\text{R}=\text{4-OCH}_3\text{-C}_6\text{H}_4\text{-}$ and $\text{R}'=\text{4-NO}_2\text{-C}_6\text{H}_4\text{-}$

The reaction is subject to acid catalysis (with a mechanism as shown for the peroxide below). Homolytic decomposition on the other hand can be induced by heating in a non-polar solvent like benzene, as is the case for benzoyl peroxide, which homolytically decomposes and is insensitive to the nature of the solvent and the presence of acids. (See this Chapter, 1.4.4 "Thermally Induced O-O Homolysis".)

4-Methoxy-3',5'-dinitrobenzoyl peroxide undergoes a similar rearrangement which is acid-catalysed and is very sensitive to the polarity of the system.



where $\text{R}=\text{4-OCH}_3\text{-C}_6\text{H}_4\text{-}$ and $\text{R}'=\text{3',5'-NO}_2\text{-C}_6\text{H}_3\text{-}$

(d) Peroxyacids and the Peroxide Oxidation of Ketones and Aldehydes

(i) Ketones - The Baeyer-Villiger Reaction

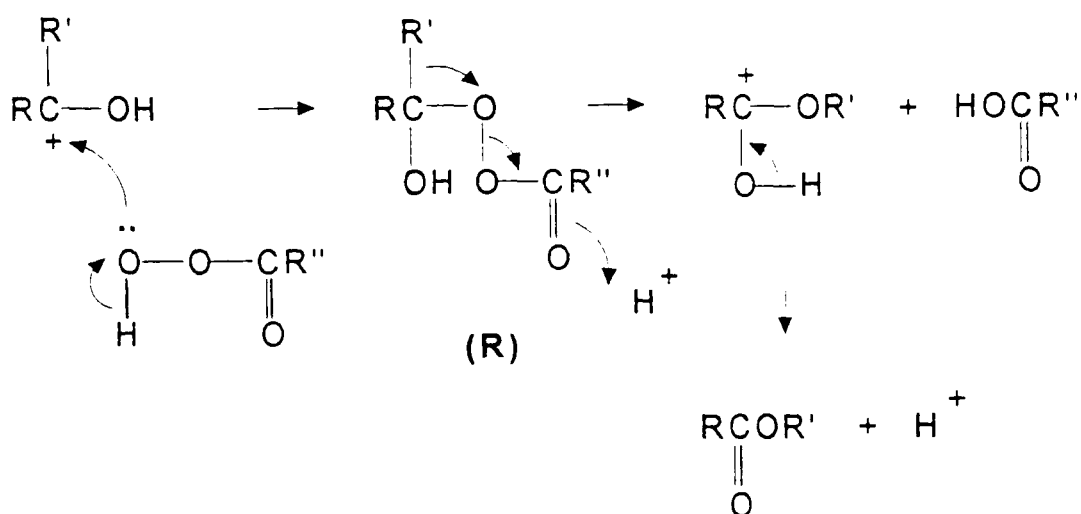
The oxidation of ketones to esters by peroxidic reagents, was first



demonstrated by Baeyer and Villiger in 1899⁹⁸. Peroxyacids were used which usually gave good yields of the esters. Trifluoroperoxyacetic acid is readily prepared and exothermically oxidises even simple dialkyl ketones in CH_2Cl_2 at or below room temperature, frequently as fast as the reagents are mixed, to give almost quantitative yields of esters.

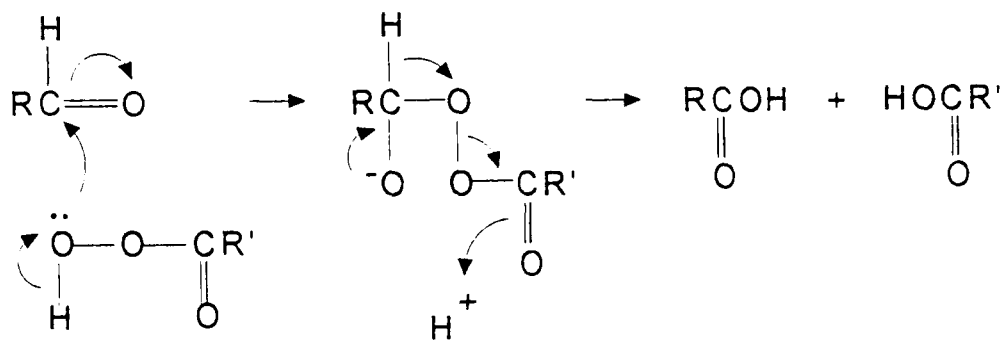
The reaction involves the formation of a ketone-peroxy acid adduct (R), which then breaks down heterolytically by nucleophilic rearrangement.

The relative migratory aptitude of different alkyl groups is the in following order²⁶: $\text{R}(\text{tertiary}) > \text{Ar-R}(\text{secondary}) > \text{R}(\text{primary}) > \text{CH}_3-$ and electron-releasing substituents are seen to increase the mobility of the aryl groups. The reaction is facilitated by polar solvents (to stabilise the charged species), and subject to acid catalysis.



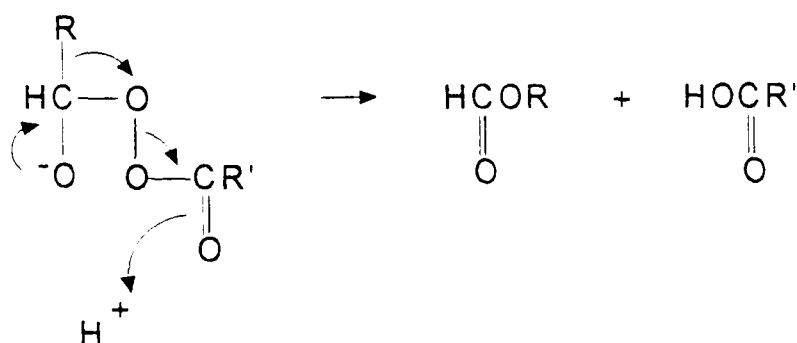
(ii) Aldehydes

By a similar mechanism to the peroxide reacting with a ketone, a peroxyacid (or alkaline H_2O_2) usually oxidises an aldehyde to the corresponding acid.



By the above mechanism, benzaldehyde is quantitatively oxidised to benzoic acid by peroxyacetic acid for example.

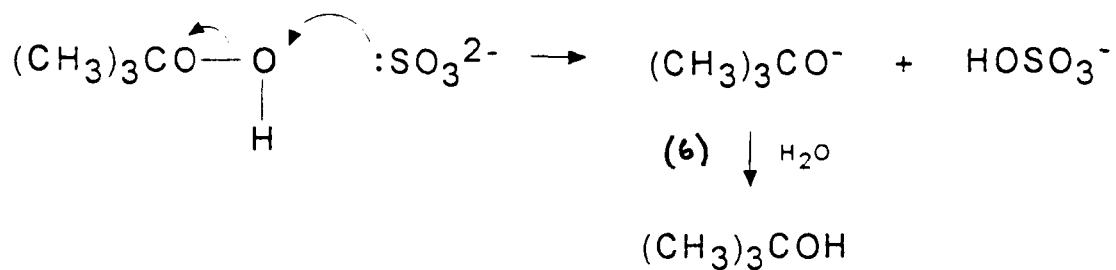
If the mobility of the alkyl or aryl group R is large however, it may migrate preferentially giving an alkyl or aryl formate as below.



1.4.1.3 Other Redox Reactions

(i) pH dependent sulphite reduction of hydroperoxides

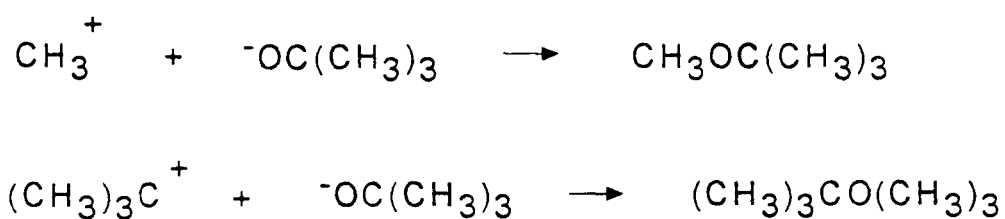
Sulphites can also be used to reduce hydroperoxides, with the solution pH determining the reaction route undertaken. For example, use of aqueous sodium sulphite (pH=9.5) yields the corresponding alcohol in good yield by intermolecular nucleophilic substitution at oxygen:



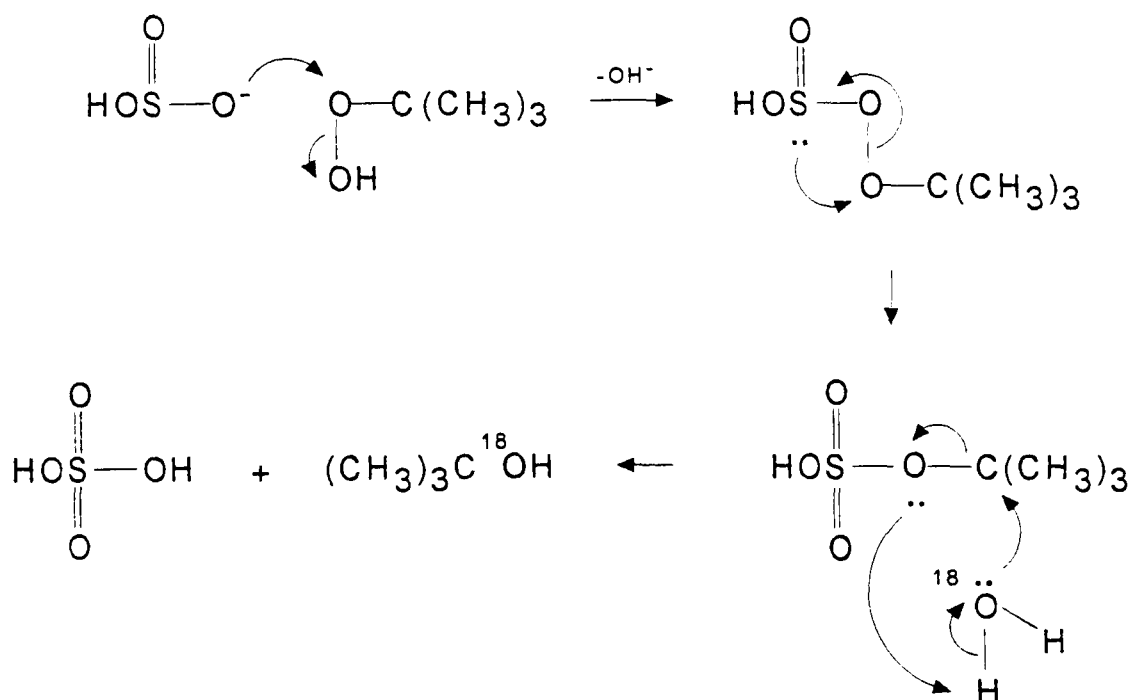
More acidic conditions however, mean the reaction becomes more complex, with ketones, alkenes and ethers forming at the expense of alcohol⁹⁹.

In the presence of acid, ketones and alkenes form via intramolecular nucleophilic rearrangements. (See this Chapter, 1.4.1.2 "Intramolecular Nucleophilic Rearrangement".)

Ether formation occurs when the anion combines with the carbocation (from intramolecular nucleophilic rearrangement) formed with the carbonyl compound and/or the carbocation formed by the loss of H₂O₂. For example,

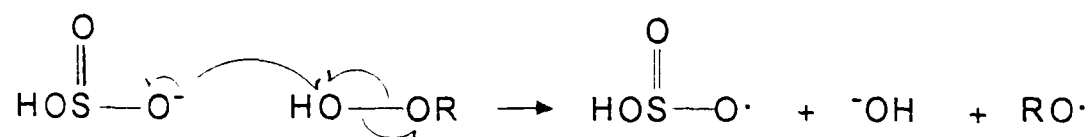


[¹⁸O]-Aqueous sodium hydrogen sulphite (pH≈5) reduces tertiary-butyl hydroperoxide giving tertiary-butanol which has derived about half its oxygen content from the solvent, as half the reaction seems to proceed by the intramolecular rearrangement of a peroxysulphurous ester to a sulphuric ester.



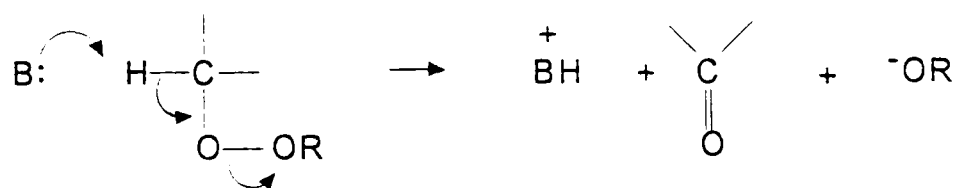
(This is unlike the related reaction of the hydrolysis of carboxylic esters, where there is instead bond cleavage between the oxygen and acyl group. Here, the other half of the reaction to tertiary-butanol presumably proceeds by normal intermolecular nucleophilic substitution at oxygen as seen above in route (6) above.)

At lower pH(0-1) levels, the system can induce radical formation⁹⁹ as the homolytic reaction becomes dominant:



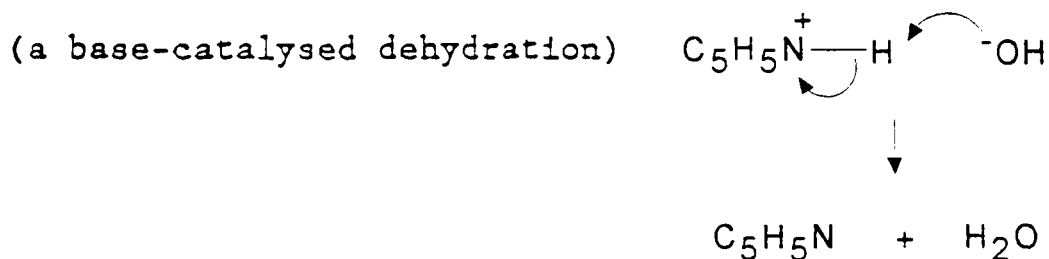
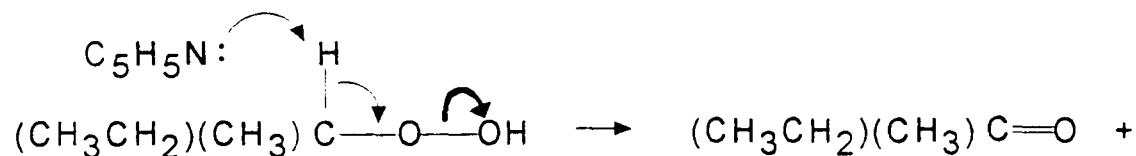
(ii) carbonyl-forming eliminations⁴²

These usually occur when a base abstracts a proton from a primary or secondary (a) hydroperoxide or (b) peroxyester. The primary peroxides yield aldehydes and the secondary yield ketones.



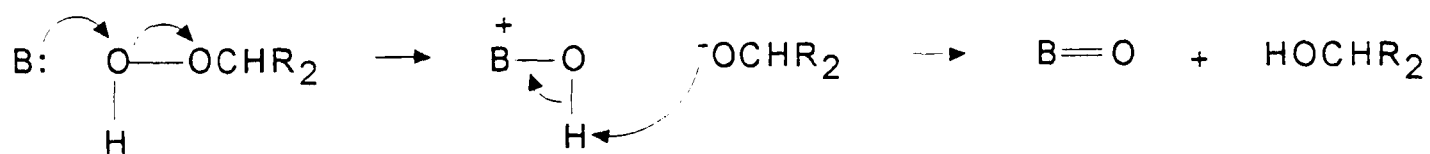
where R=H or an acyl group

(a) For example,



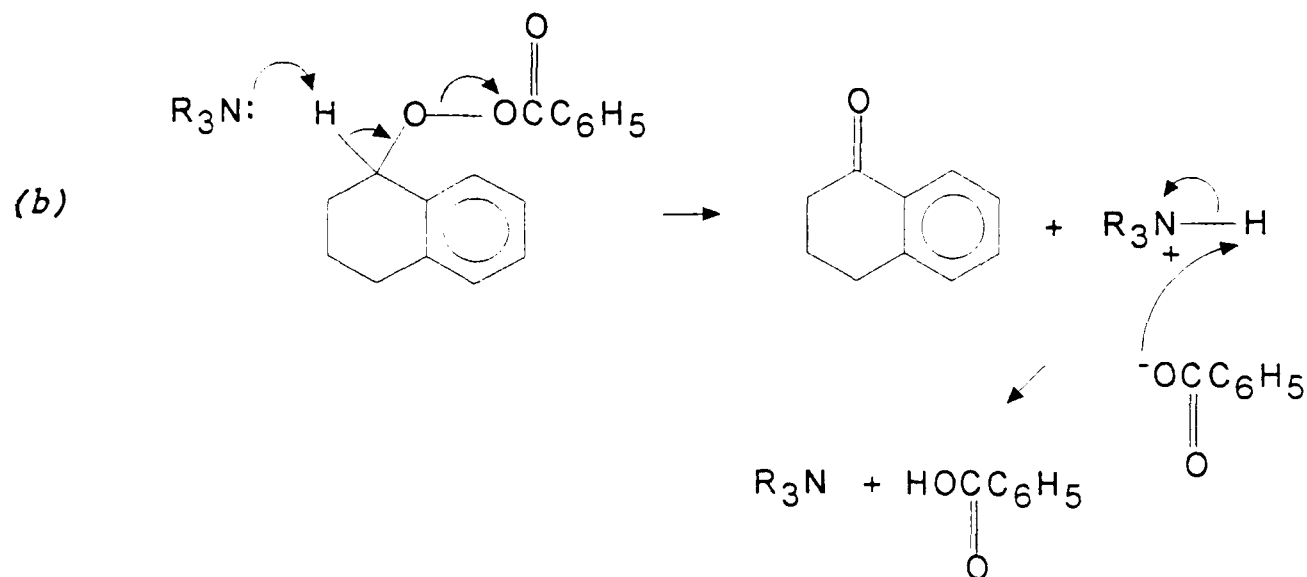
However, in most reactions of this type, alcohols and C-C cleavage products are generally prepared as well, as the base attacks the β oxygen to give rise to intermolecular substitution at oxygen. (See this Chapter,

1.4.1.1 "Intermolecular Nucleophilic Substitution at Oxygen".) For example,

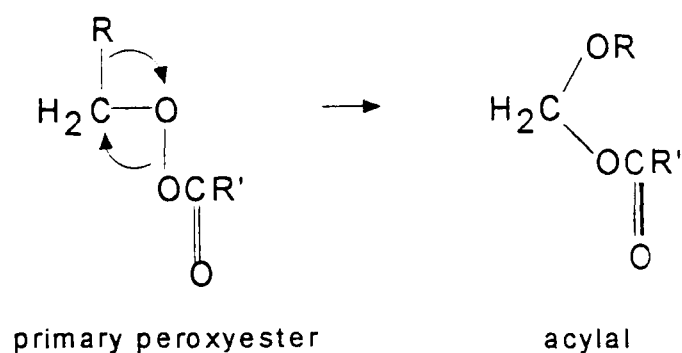


Primary and secondary hydroperoxides yield primary and secondary alcohols, respectively. As mentioned previously, tertiary hydroperoxides although not forming carbonyl compounds, can with heating, react with bases to yield tertiary alcohols and water.

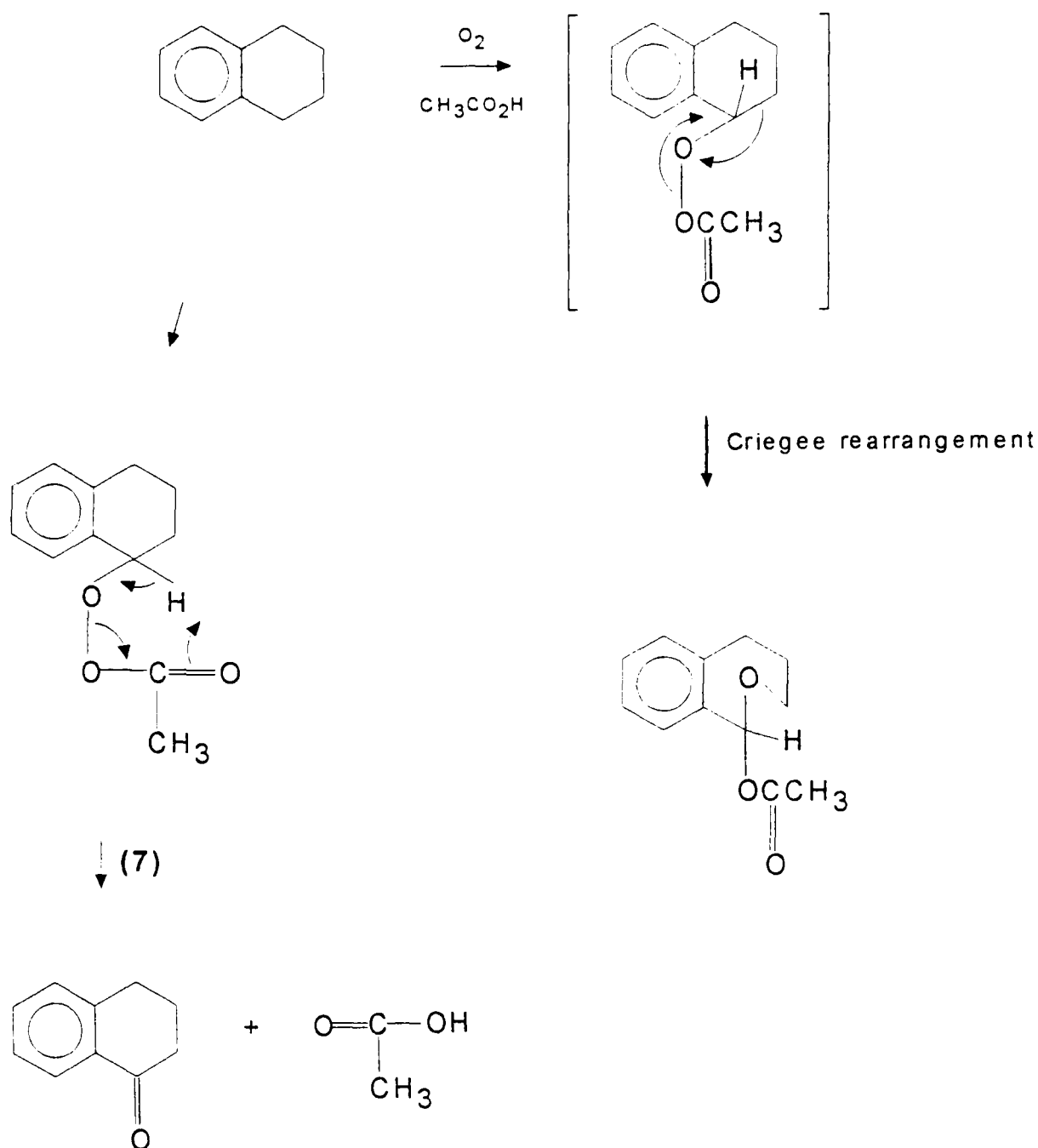
The carbonyl-forming decompositions may occur only very slowly or not at all without heating¹⁰⁰, whereas primary and secondary peroxyesters react more readily to yield an aldehyde and ketone, respectively, as well as an acid. For example,



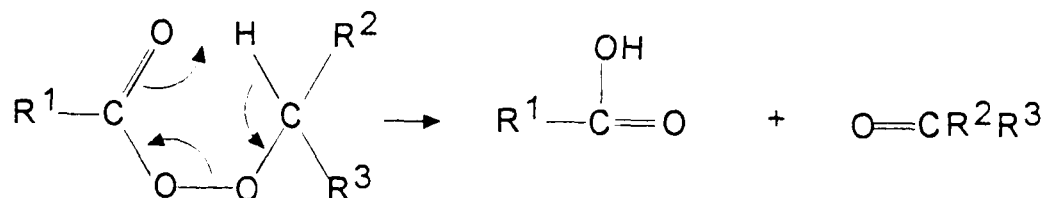
For primary and secondary peroxyesters under non-basic conditions, the Criegee rearrangement may compete with the carbonyl-forming elimination (though usually constrained to tertiary peroxyesters). (See this Chapter, 1.4.1.2 "Intramolecular Nucleophilic Rearrangement".)



For example,

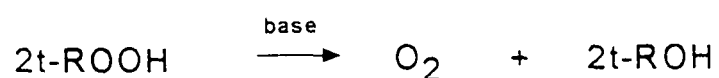


The mechanism of route (7) to the carbonyl compound and acid without the presence of base, is in fact a modification of the standard base-catalysed elimination, where the carbonyl oxygen instead acts as a base to abstract the hydrogen atom as shown above. The mechanism is an O-O heterolysis with intramolecular hydrogen abstraction. This has been proposed to explain the uncatalysed decomposition of the particularly unstable primary and secondary peroxyesters, for example n- and s- butyl peroxyacetate. These decompose very easily and so are synthesised only rarely using especially mild conditions. Unsurprisingly, tertiary peroxyesters are more stable to this reaction.

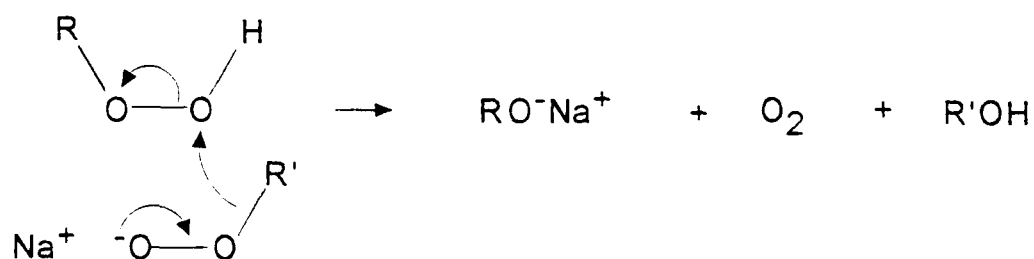


(iii) base-catalysed elimination of oxygen from tertiary-alkyl hydroperoxides

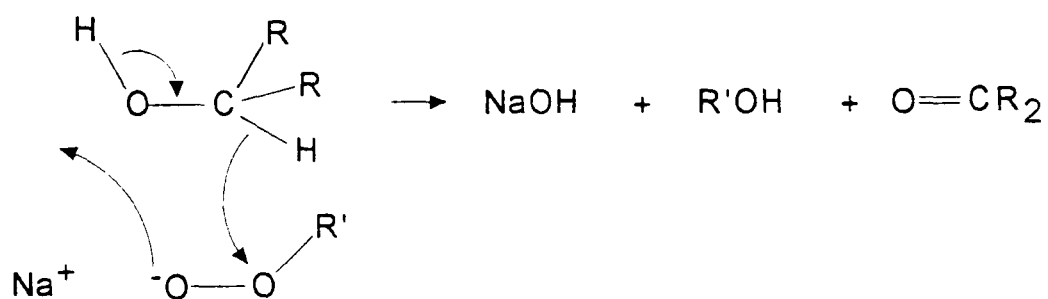
Although tertiary hydroperoxides are generally stable to alkali, cleavage under certain conditions liberates oxygen and the corresponding alcohol, although the decomposition is slow in an excess of aqueous alkali.



Their decomposition is most rapid when equimolar amounts of hydroperoxide and sodium salt are present. (Esters and nitriles catalyse the reaction by complexing with the hydroperoxide.)



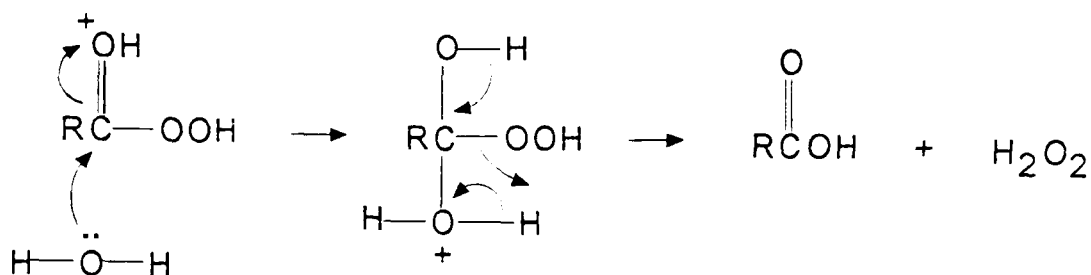
Addition of primary or secondary alcohols can suppress the evolution of O_2 , as they are oxidised to aldehydes or ketones respectively, by the hydroperoxide.



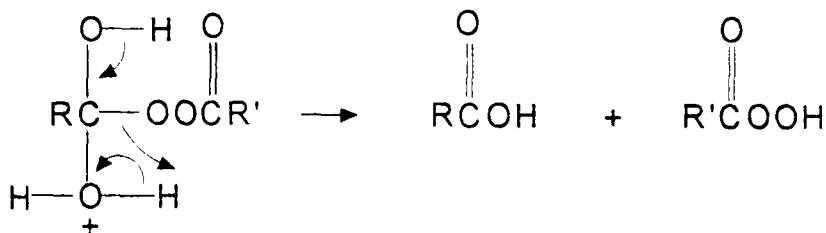
1.4.2 Acid-Catalysed Decomposition

Some acid-catalysed decompositions of organic peroxides have been discussed previously and incorporated within this Chapter (1.4.1.2 "Intramolecular Nucleophilic Rearrangement") when discussing *p*-methoxy-*p*'-nitro-benzoyl peroxide and 4-methoxy-3',5'-dinitrobenzoyl peroxide.

With the exception of these two substituted benzoyl peroxides, all acyl peroxy compounds yield the corresponding normal carboxylic acid when decomposed by acid. Price and Krebs¹⁰¹ found that acidifying *p*-nitrobenzoyl peroxide yielded the carboxylic acid. Later, Swern⁷¹ found that in the presence of acids, peroxybenzoic acid rapidly disappeared.

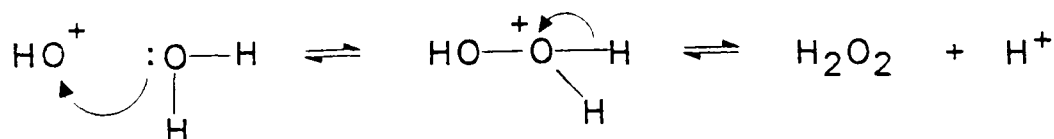


Similarly for acyl peroxides,



The peroxyacid decomposes as shown above.

By a similar mechanism, peroxyesters yield carboxylic acids and hydroperoxides. Susceptible hydroperoxides decompose to ketones by rearrangement or alkenes by elimination (see this Chapter, 1.4.1.2 "Intramolecular Nucleophilic Rearrangement"), unless anions are available. (See this Chapter, 1.4.1.3(i) "Other Redox Reactions, pH-Dependent Sulphite Reduction of Hydroperoxides".) Hydrogen peroxide would be in an equilibrium reaction:



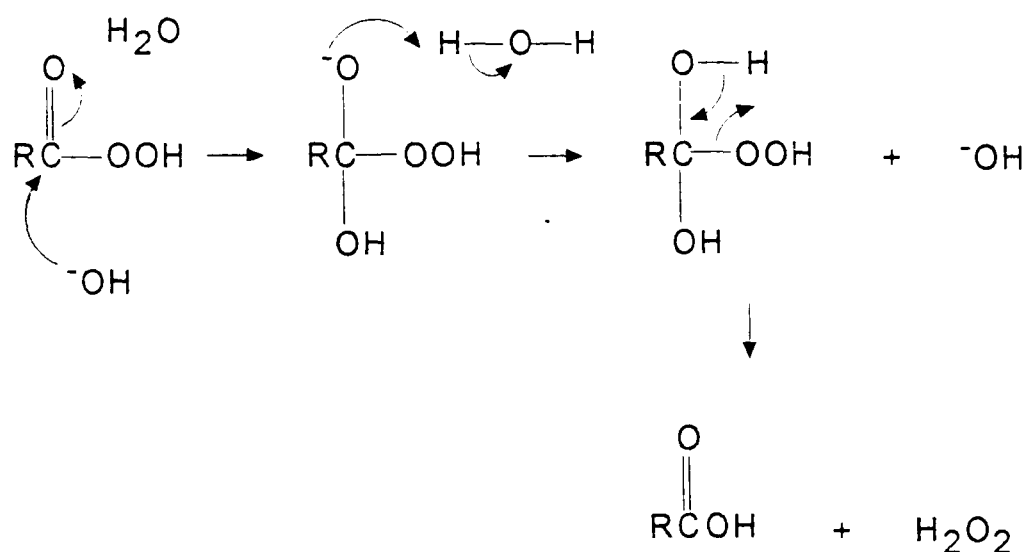
1.4.3 Base-Catalysed Decomposition

Organic peroxides may also be susceptible to alkali- or base-catalysed decomposition [- the base-catalysed reactions being discussed previously within this chapter (1.4.1.1 "Intermolecular Nucleophilic Substitution at Oxygen")] by the lone pairs of sulphur; oxygen; phosphorus and nitrogen. Hydroperoxides yield the corresponding alcohol, and the acyl peroxy compounds (other than primary and secondary peroxyesters) revert to the acid, unless reaction is with phosphines, when they are reduced to their acid anhydrides. (Tertiary peroxyesters are not reactive.)

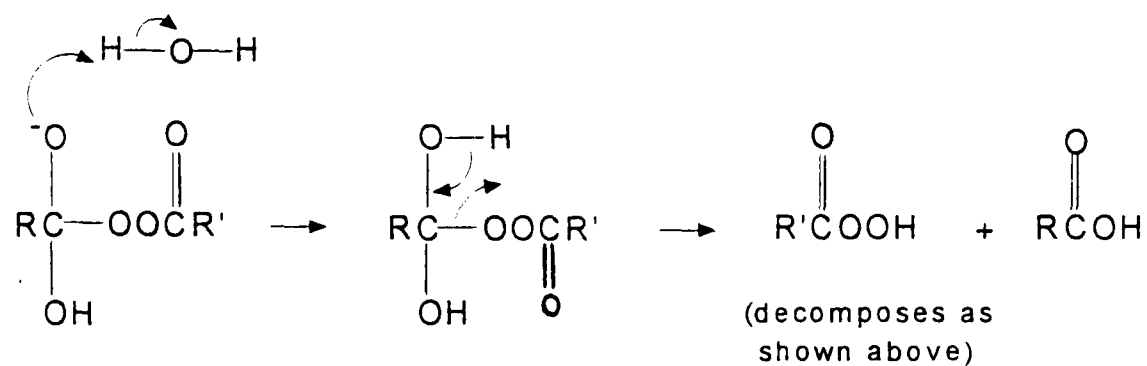
The reaction of a base on primary and secondary hydroperoxides and peroxyesters as mentioned previously (1.4.1.3(ii) "Other Redox Reactions, Carbonyl-Forming Eliminations") forms aldehydes from the primary peroxides and ketones from the secondary. The hydroperoxides additionally yield primary and secondary alcohols, whereas peroxyesters yield an acid.

The hydrolysis of peroxyesters also involves base catalysis and is discussed separately below. (1.4.5 "Hydrolysis of Peroxyesters".)

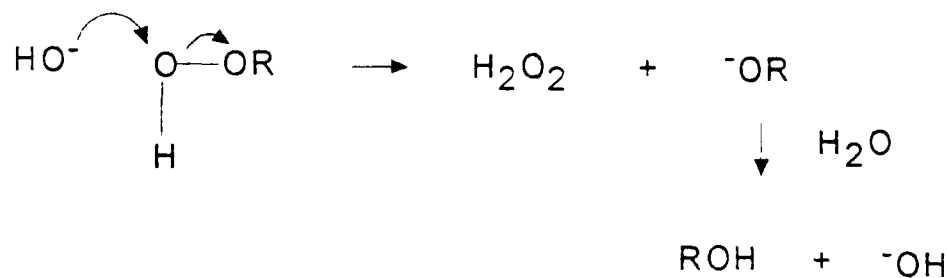
Considering then the effect of alkali (OH^-), it can be seen that the susceptible acyl peroxy compounds yield acids, as with acid catalysis.



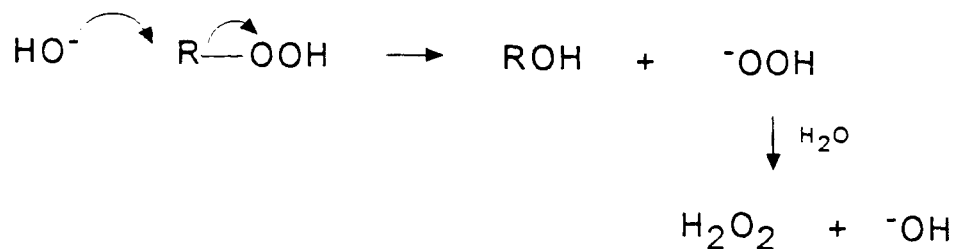
Similarly for acyl peroxides:



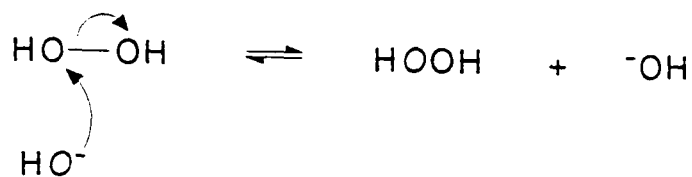
By a similar mechanism peroxyesters yield carboxylic acids and hydroperoxides. Susceptible hydroperoxides yield the corresponding alcohol.



or



As in aqueous acid, hydrogen peroxide would be in an equilibrium reaction:



1.4.4 Thermally Induced O-O Homolysis^{66,102,103}

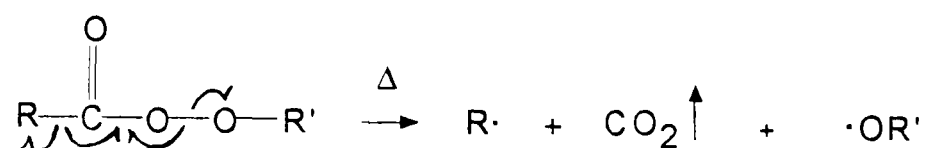
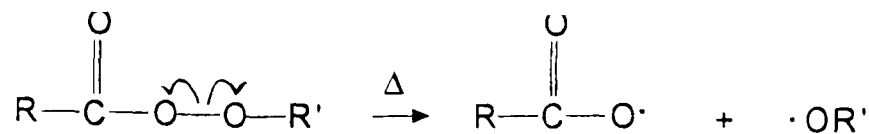
In particular, the lower aliphatic peroxyacids, alkyl peroxides, alkyl acyl peroxides and alkyl hydroperoxides are prone to explosion when in a pure state or relatively pure state. Their preparations are carried out at low temperatures (ice), and if the pure products are isolated, they must be kept free from shock or friction and should be stored in the cold. In most cases, solutions of these peroxides are prepared for immediate use.

In the next section, 1.5 "Physical Properties of Organic Peroxides", a summary of reaction products as a result of thermal decomposition are detailed. Here, the conditions and corresponding reaction mechanisms involved will be discussed.

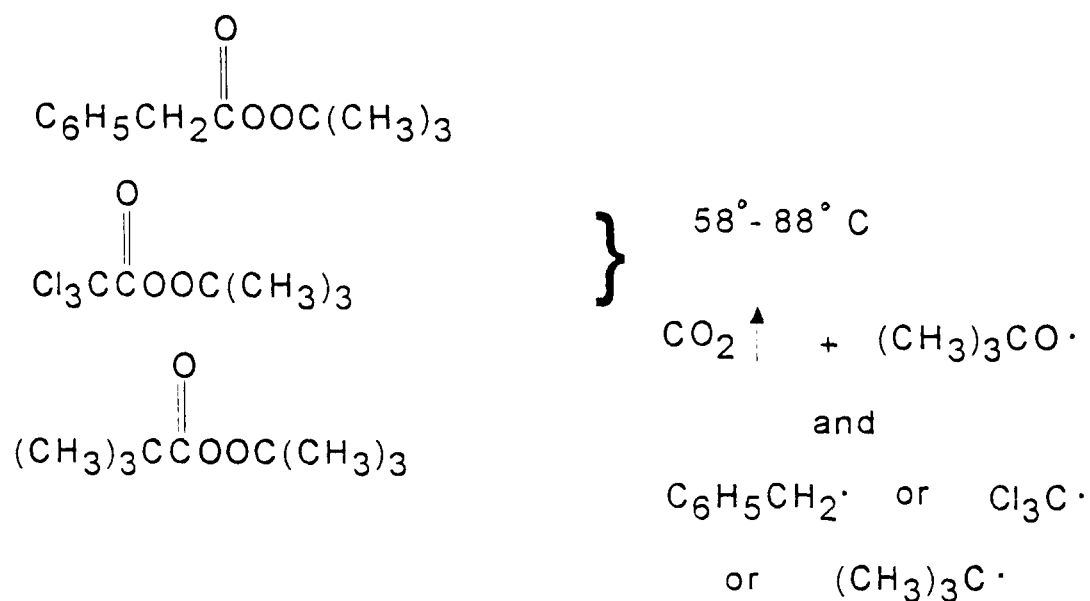
The dissociation energy⁶⁸ of the O-O bond in organic peroxides is about 125-167kJmol⁻¹. As mentioned previously, if there is sufficient stability of R· and the applied thermal energy is sufficient, the concerted homolysis of a C-C bond (dissociation energy⁶⁸ ~348kJmol⁻¹) and the O-O bond will occur. R· needs to be constituted so as to have a degree of stabilisation considerably exceeding that of the methyl or phenyl radical¹⁰⁴. When the peroxide carries electronically dissimilar groups (for example, if the alkyl group carries α -substituents as in peroxyesters of strong acids like trifluoroperoxyacetic acid), or when the nucleophilic migratory aptitudes of the α -position are high, then the heterolytic mechanism of decomposition may compete. (See this Chapter, 1.4.1.2 "Intramolecular Nucleophilic Rearrangement".)

Peroxyesters

The primary products of thermal decomposition of tertiary peroxyesters are acyloxy and alkoxy radicals, but if R· is stable enough under the conditions then the alkyl or aryl radical and carbon dioxide will be formed by a concerted reaction:

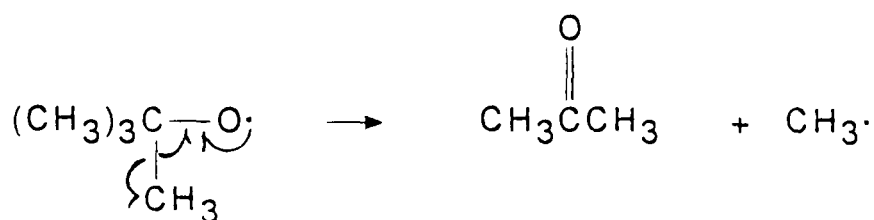
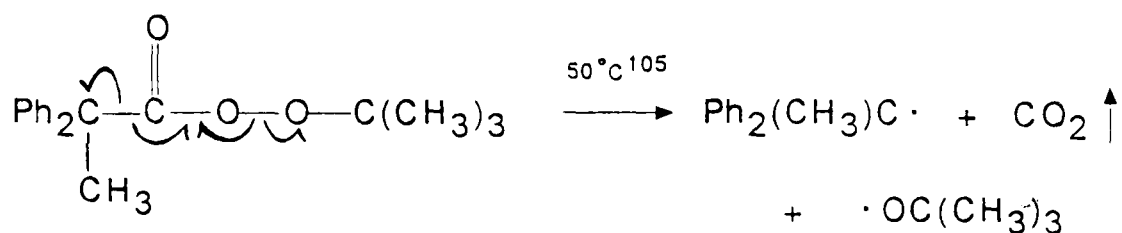


In the thermal decomposition of tertiary-butyl peroxyphenylethanoate, peroxytrichloroethanoate and peroxy-2,2-dimethylpropanoate¹⁰⁴, carbon dioxide is formed by the mechanism as described above.



Both the tertiary-butyl and trichloromethyl radicals are stabilised by a resonance energy of 50kJmol⁻¹, relative to a methyl or phenyl radical. The benzyl radical has a corresponding resonance stabilisation energy¹⁰⁴ of 102kJmol⁻¹.

In the case of the peroxyester tertiary-butyl α,α -diphenylperpropionate ($\text{Ph}_2(\text{CH}_3)\text{CCO}_3\text{C}(\text{CH}_3)_3$, carbon dioxide, tertiary-butyl alcohol, 1,1-diphenylethane, 1,1-diphenylethylene, acetone, and by combination, 2,2,3,3-tetraphenylbutane and tertiary-butyl α -methylbenzhydryl ether are formed.

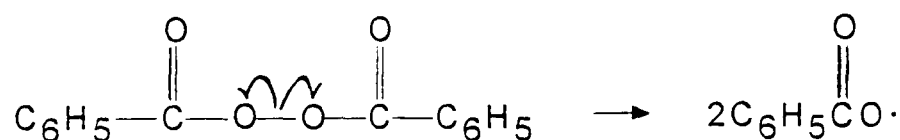
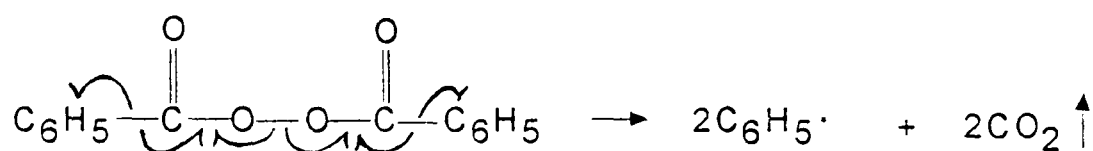


Unlike most tertiary peroxyesters, primary and secondary ones can decompose by a non-radical mechanism because of their generally high instability. (See this Chapter, 1.4.1.3(ii) "Other Redox Reactions, Carbonyl-Forming Eliminations".)

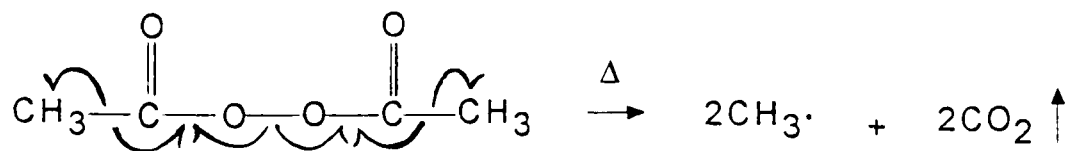
Acyl Peroxides

As with tertiary peroxyesters, simple O-O bond scission of acyl peroxides gives acyloxy radicals, or carbon dioxide and alkyl/aryl radicals. Hey and Waters¹⁰⁶ were the first to suggest the thermal decomposition of benzoyl peroxide as being a homolytic reaction.

In the absence of a solvent containing abstractable hydrogen radical donors, carbon dioxide, biphenyl and some phenyl benzoate and benzene are formed¹⁰⁷.

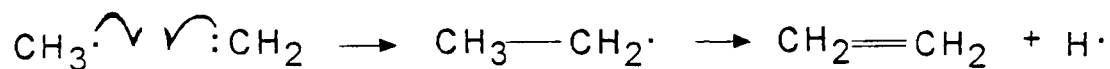
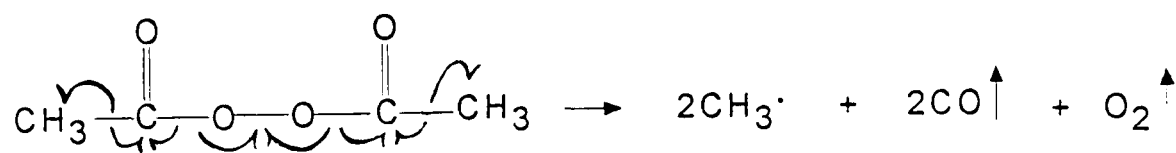


When hydrocarbons having easily abstractable hydrogen atoms are used (for example, cyclohexane) as solvents during the decomposition of acetyl peroxide, formation of methane takes place as well as of carbon dioxide. The hydrocarbon radicals left after the abstraction of hydrogen usually dimerise.



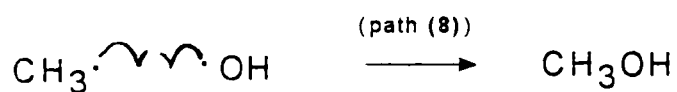
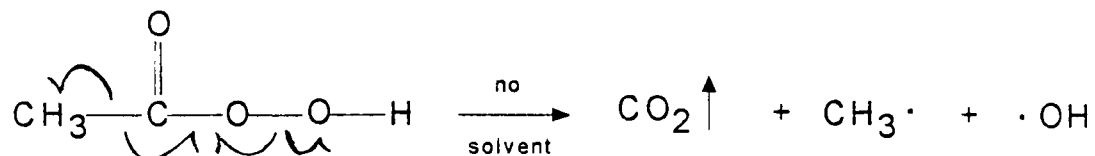
In the absence of solvents, acetyl peroxide yields carbon dioxide (60%), methane (29-34%), ethane (3.5-4.5%), ethylene (1.1-1.6%), oxygen (ca.2%) and carbon monoxide (1.6-3%). In UV light, decomposition yields carbon dioxide and ethane¹⁰⁸ as the major products.

Additional mechanisms:

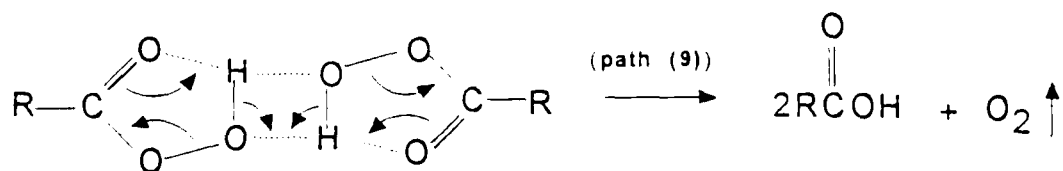


Peroxyacids

As with the previous two types of acyl peroxide, carbon dioxide can be formed by a similar mechanism from peroxyacids. Between 60° and 80°C, peroxyethanoic acid yields carbon dioxide and methanol.



The carboxylic acid may also be formed for example. This is seen for peroxybenzoic acid between 80° and 100°C in the absence of a solvent where oxygen is also formed. The reaction follows a non-radical cyclic concerted mechanism⁶⁶.



For example, when heated alone above its melting point, peroxydodecanoic acid yields undecanol (30%) (path (8)) and dodecanoic acid (60%) (path (9)). Heating in petrol or cyclohexane for example at 50°C, gives by slow decomposition (90 hours) dodecanoic acid (path (9)) exclusively. (Similarly, peroxybenzoic acid gives benzoic acid at 25°C³⁴). In boiling solvent, rapid decomposition (half an hour, 70°C; 2 hours, 41°C) gave mainly undecanol (80%) (path (8)) and dodecanoic acid (15%) (path (9)).

In storage, induced decomposition may occur, the rates varying with the compound. For example, the active oxygen content of the sample may be lost on standing after a few days or months. Table (B) follows the decomposition of solid peroxybenzoic acid to benzoic acid³⁴.

Table (B) - Stability of Peroxybenzoic Acid at 25°C

Weeks	Percentage
0	100
1	81
2	63
4	34
6	11
8	2.5

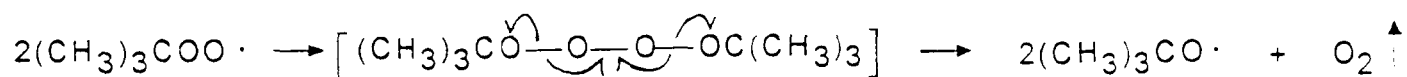
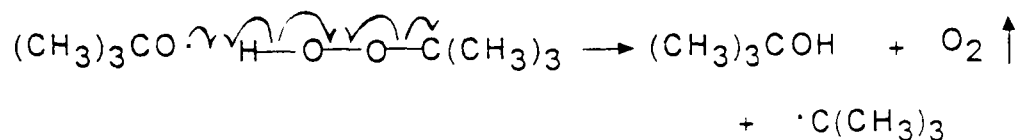
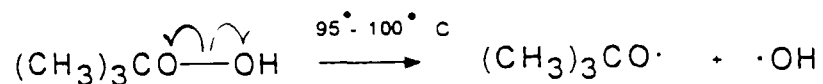
Hydroperoxides^{97,109}

The thermal decomposition of primary, secondary and tertiary hydroperoxides leads to various carbonyl and hydroxy compounds via the alkoxy and hydroxy radicals (primary products) as seen in tertiary peroxyester decomposition above. Alkanes (via combination of alkyl radicals), oxygen, carbon dioxide, carbon monoxide, hydrogen and carboxylic acids can also be formed.

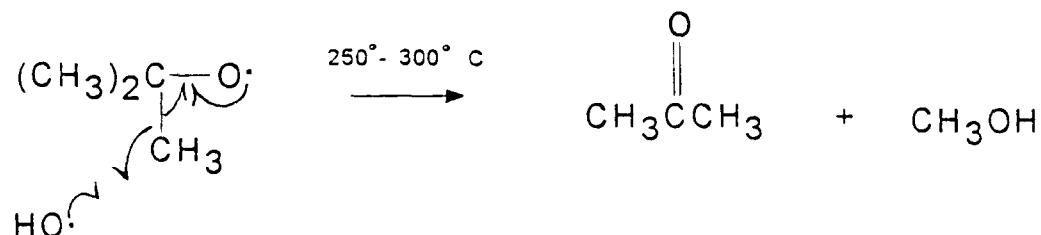
In the presence or absence of light and at low or elevated temperatures, there can be spontaneous decomposition dependent on the hydroperoxide involved.



The fate of the radicals depends on the environment and conditions. At low temperatures the corresponding alcohols and oxygen are formed as seen with for example, tertiary-butyl hydroperoxide.

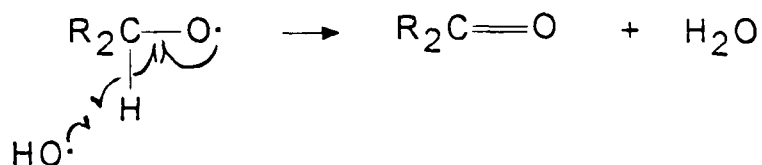


At elevated temperatures, acetone and methanol are formed from the breakdown of the tertiary-butoxy radicals, with less oxygen and tertiary-butanol being formed.

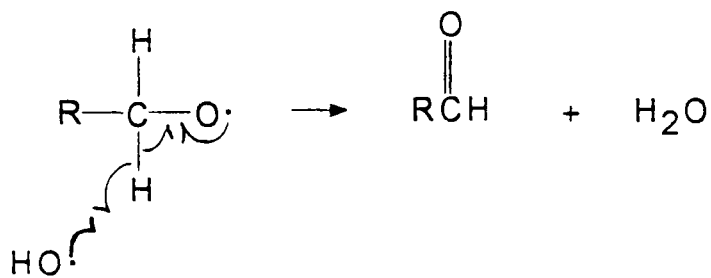


Minor products at elevated temperatures include methanal (oxidation of methanol), methane (hydrogen abstraction by $\text{CH}_3\cdot$) and water (hydrogen abstraction by $\cdot\text{OH}$).

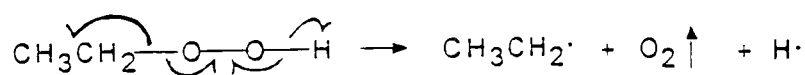
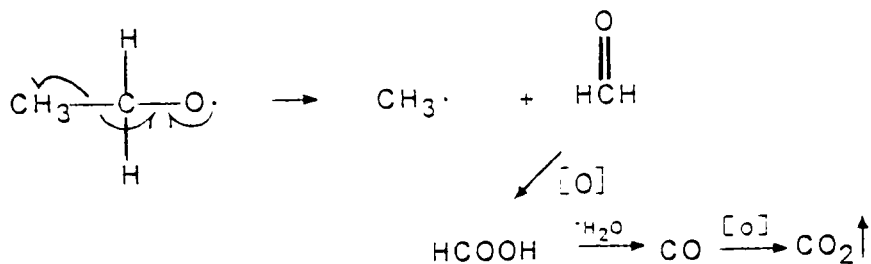
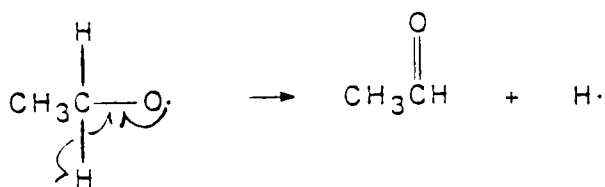
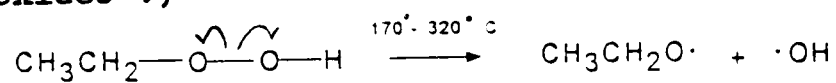
Correspondingly, the major products of secondary hydroperoxides at elevated temperatures are ketones and water,



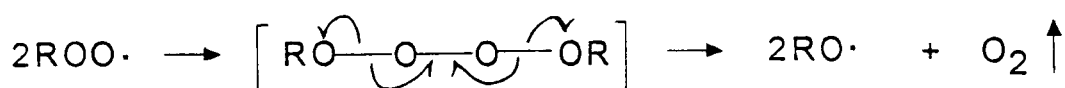
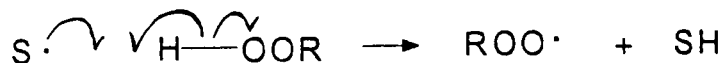
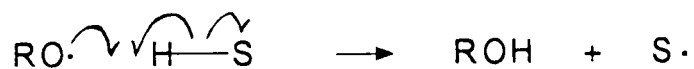
whereas primary hydroperoxides yield mainly aldehydes and water.



Also at elevated temperatures, ethyl hydroperoxide in addition to ethanal and water, yields methanal, hydrogen, carbon dioxide, carbon monoxide and alkanes. (See this Chapter, 1.5 "Physical Properties of Organic Peroxides".)



Use of solvents with a labile hydrogen (SH) can enhance the rate of hydroperoxide decomposition, as the solvent readily forms radicals which take part in the induced decomposition.

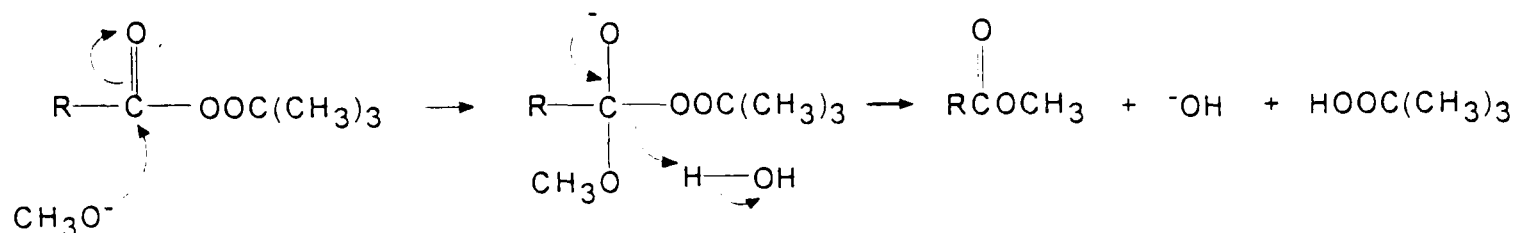


1.4.5 Hydrolysis of Peroxyesters

Although peroxyesters are hydrolysed more readily than the analogous nonperoxidic esters (which require acid or base catalysis), it is an underused method of hydroperoxide formation.

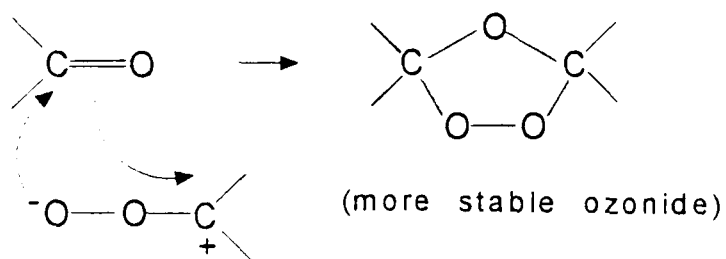
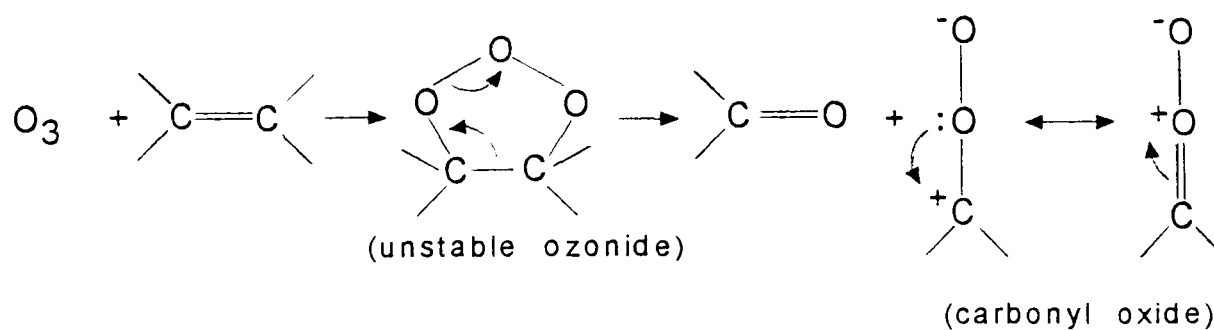


Tertiary-butyl hydroperoxide is obtained in 71% yield by the alkaline hydrolysis of tertiary-butyl peroxybenzoate using sodium methylate⁷.

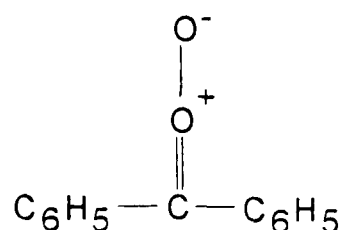


1.4.6 Postulated Peroxide and Peroxonium Ion Intermediates

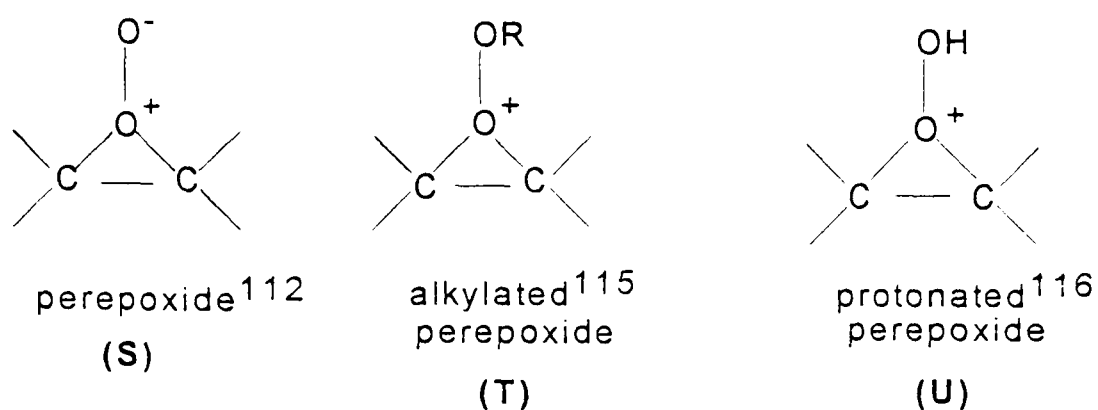
Positive oxygen species have been recognised as intermediates in the ozonolysis of alkenes for many years¹¹⁰, but up until 1988 carbonyl oxides were only observed at low temperatures of around -100°C .



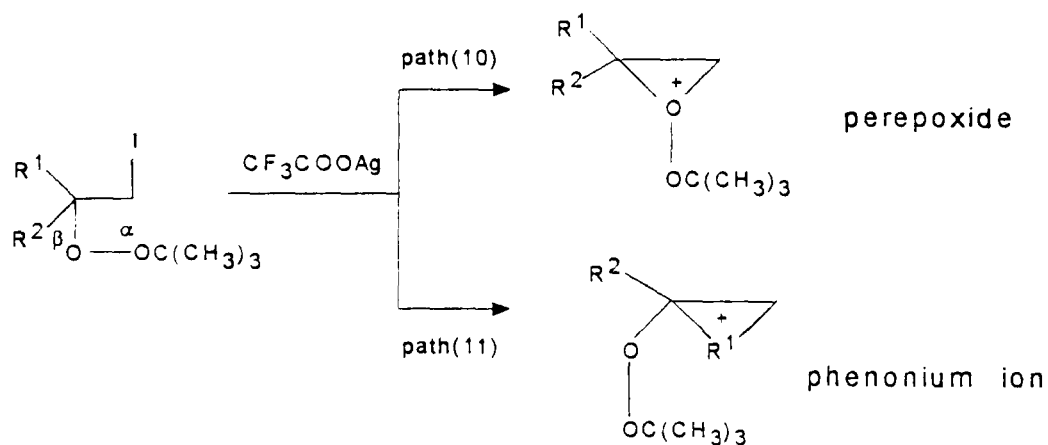
Scaiano *et al.*¹¹¹ have at room temperature recently observed that diaryl-substituted carbonyl oxides have absorption maxima in the 400-450nm region, including the parent benzophenone oxide at 410nm in acetonitrile.

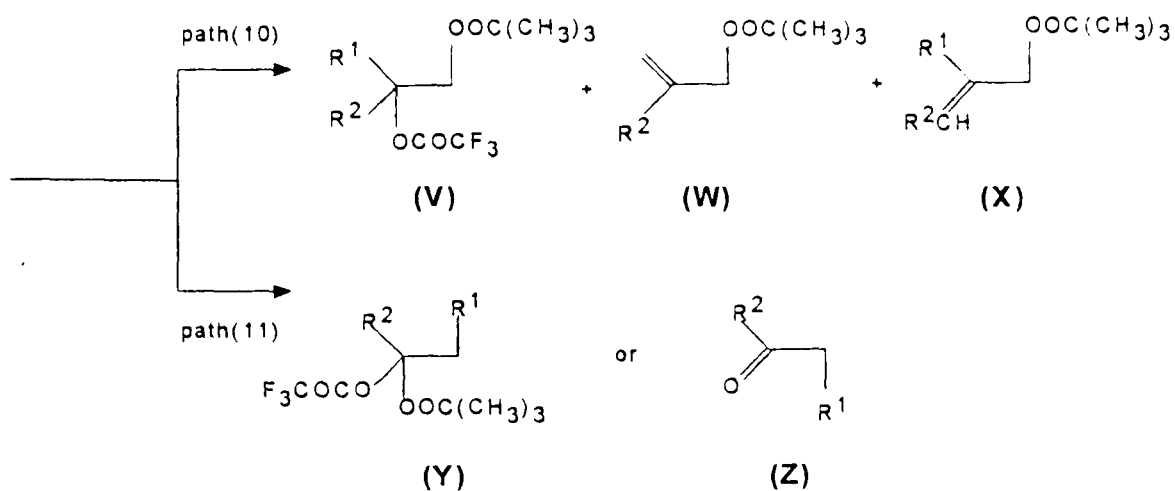


Only recently has the reactivity of the unstable but structurally related dioxygen ylides come to be recognised (experiments at 20°C)¹¹².



The formation of perepoxides (S) as intermediates has been postulated in the singlet oxygenations of alkenes¹¹⁷ and in the base-induced reactions of β-hydroperoxybromides¹¹⁴. Bloodworth *et al.*^{115a} postulated the previously unknown alkylated perepoxide structure (T) in reactions of suitable β-haloalkyl tertiary-butyl peroxides with silver trifluoroacetate. However, where possible, phenonium intermediates were formed, preferentially where the positive charge was distributed in the aromatic group.



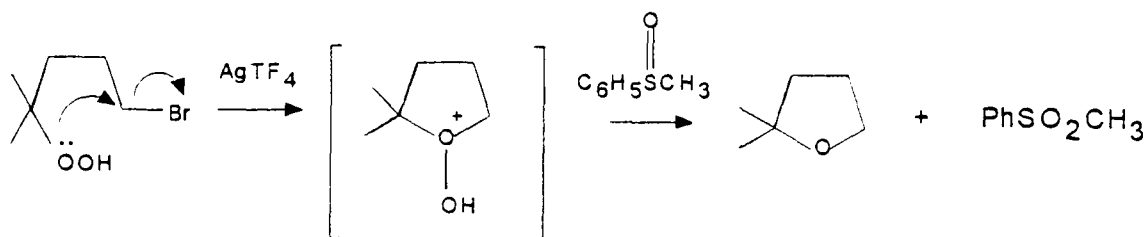


For example, as seen in Table (C):

Table (C)

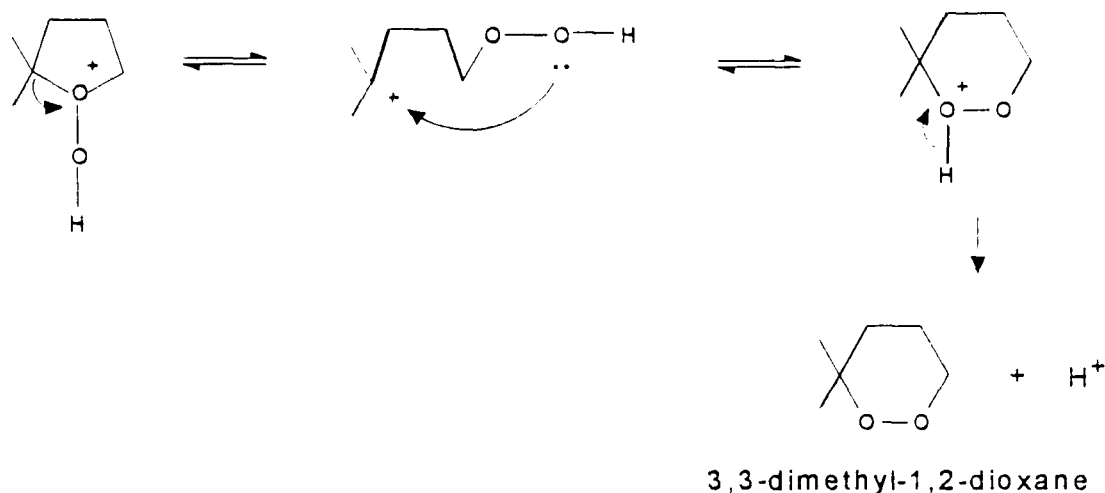
R ¹	R ²	path	products (yields, %)
CH ₃	CH ₃	(10)	(V)(57) + (W)(16)
CH ₃	CH ₃ CH ₂	(10)	(V)(35) + (W)(6) + (T)(12)
C ₆ H ₅	H	(11)	(Y)(96)
C ₆ H ₅	C ₆ H ₅	(11)	(Z)(72)

The intermediacy of the corresponding dialkylperoxonium ions has also been postulated as relating to (U). Bloodworth *et al.*^{116a} prepared the positive oxygen species by reaction of β -haloalkyl hydroperoxides and silver trifluoroacetate. In the presence of a reducing agent the subsequent products could be observed to indicate the transfer of oxygen only possible by intermediate dialkylperoxonium ions via paths (10) and (11). For example:

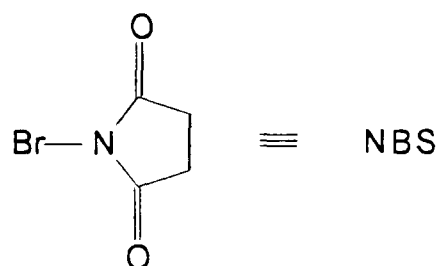


The above reaction provided further evidence of oxygen-transfer capability of species (U), with the incorporation of methyl phenyl sulphoxide into the silver trifluoroacetate-mediated ring closure of 1-bromo-4-methyl-4-hydroperoxypentane, to yield the cyclic ether and an equimolar amount of sulphone.

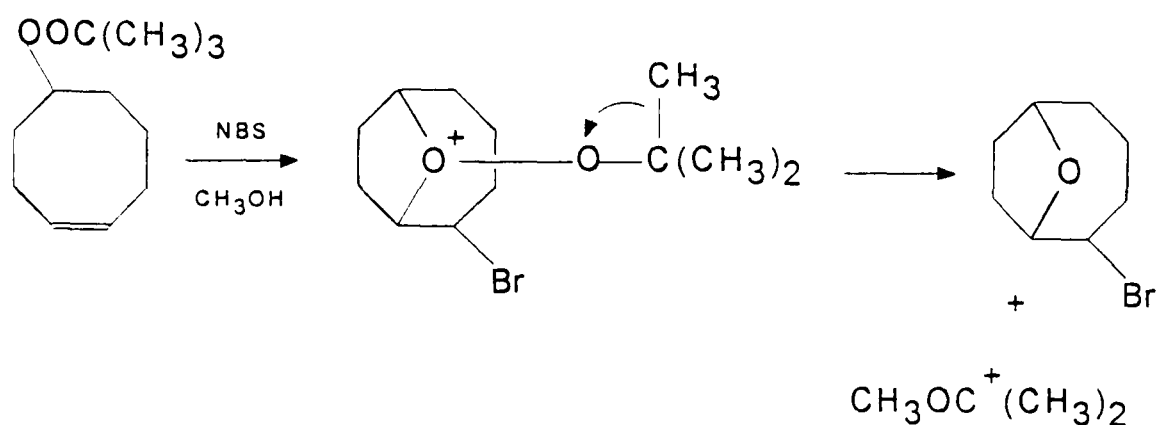
In the absence of sulphoxide, the cyclisation product was 3,3-dimethyl-1,2-dioxane, which is believed to arise by a different mechanism involving the peroxonium intermediate¹¹⁷.



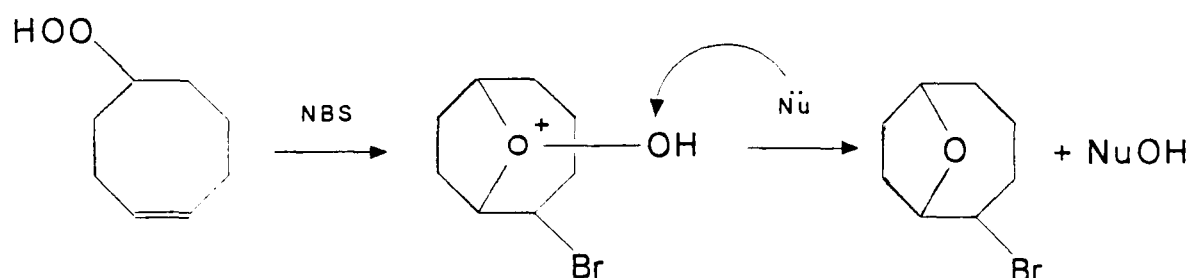
Another reaction postulating positive oxygen species involves the electrophilic attack on the alkylperoxyalkene 5-tertiary-butyl peroxyoctene, and the hydroperoxyalkene 5-hydroperoxyoctene by N-bromosuccinimide (NBS) or bromine in carbon tetrachloride.



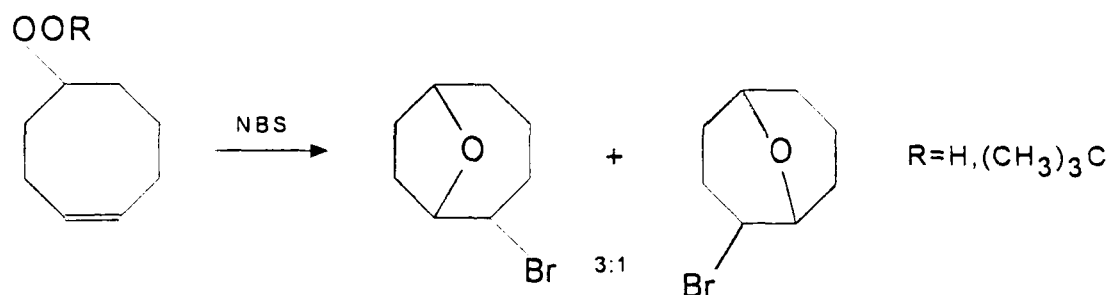
The mechanism involves the formation of peroxonium ion types (T) and (U) respectively, as seen above. In the former case, it is reported to be electrophilic attack on the double bond, followed by intramolecular alkylation of the peroxide and subsequent methyl migration to produce the ether product and 2-methoxy-2-propyl carbocation¹¹². (Compare with 1.4.1.2 "O-O Heterolysis, Intramolecular Nucleophilic Rearrangement" in this chapter, for the acid-catalysed decomposition of hydroperoxides.)



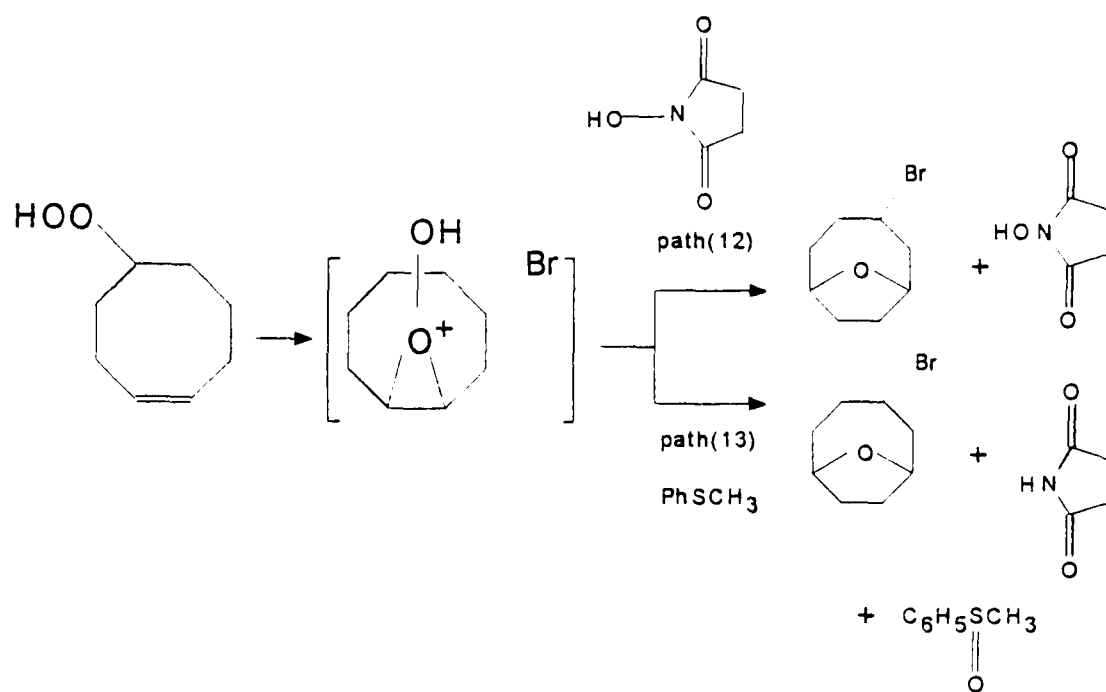
In the reaction with the hydroperoxyalkene, it was shown that internal nucleophilic attack on oxygen was not necessary to cleave the O-O bond in peroxonium ions. Intermolecular nucleophilic attack was also suitable^{112,116}. (Compare with other reactions involving "O-O Heterolysis, Intramolecular Nucleophilic Substitution at Oxygen" discussed in this Chapter, 1.4.1.2.)



There were in fact two bicyclic ethers formed in each case:



If the only nucleophile present was the succinimide anion, then as well as the bicyclic ethers, N-hydroxysuccinimide would form (path (12)). When methyl phenyl sulphide ($\text{C}_6\text{H}_5\text{SCH}_3$) was present, equimolar amounts of succinimide and methyl phenyl sulphoxide were obtained at the expense of N-hydroxysuccinimide (path (13)).



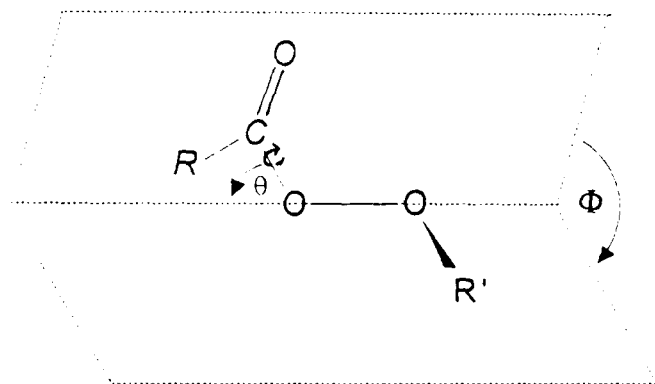
This shows how the bicyclic peroxonium ion can transfer oxygen to suitable nitrogen- and sulphur-centred nucleophiles¹¹⁶.

1.5 Physical Properties of Organic Peroxides

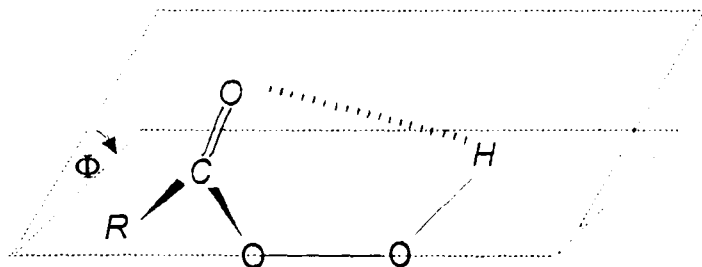
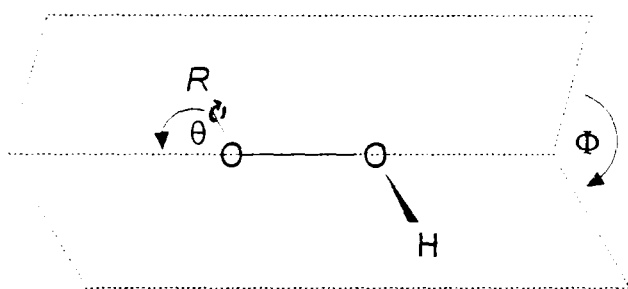
Differences and similarities between the organic peroxides can be seen further by examination of their physical properties, for which spectroscopy in particular remains perhaps the most practical and informative method. NMR and IR are also best for differentiation between peroxides and their non-peroxidic analogues. The following properties will be discussed.

- 1.5.1 Structure
- 1.5.2 Stability
- 1.5.3 Spectroscopic Data
 - (i) IR
 - (ii) ^1H NMR
 - (iii) ^{13}C NMR

1.5.1 Structure¹¹⁸



there is restricted oscillation of the acyl group out of the plane of the peroxide grouping¹¹⁹.



where R=aryl group;
 R'=alkyl [(CH₃)₃C-], aralkyl or aroyl group;
 ϑ=oscillating twist;
 θ=oscillating twist angle;
 ϕ=dihedral angle.

Table (D) - Penny-Sutherland¹¹⁹ structures

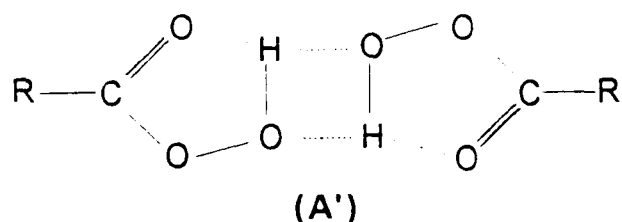
Peroxide	ϕ	θ	Examples	O-O distance (Å)	Comments
Peroxyesters ¹²⁰	100°-150°	-35°	C ₆ H ₅ CO ₃ C(CH ₃) ₃	-	Carbonyl group is orientated towards peroxide oxygen - cis to (CH ₃) ₃ C group ¹²⁰ .
Aroyl Peroxides ^{121,122}	91°-100°	-	(C ₆ H ₅ CO ₂) ₂	1.46 ±0.015	Carbonyl groups face inward ¹²¹ .
Peroxyacids	-72° ^a	-	C ₆ H ₅ CO ₃ H	-	Carbonyl group is orientated towards peroxide oxygen - cis to the hydrogen.
Hydroperoxides ¹²³	100°	-	(CH ₃) ₃ COOH	-	-

^a The angle, although significantly smaller than in most other organic peroxides, is due to the strong intramolecular hydrogen bonding (the barrier to rotation of the acyl group). The conformation also allows for greater stability, where the lone-pair electrons in hybridised orbitals on each oxygen atom are now *trans* (as for the other peroxides) rather than *cis* (where repulsive forces are at a maximum).

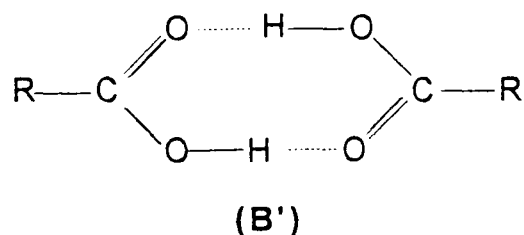
In polar solvents peroxyacids exist solely as five-membered monomer rings.



In inert solvents like benzene and carbon tetrachloride and in the solid state, the dimer also exists with additional intermolecular hydrogen bonding - presumably with a similar dihedral angle to that of the monomer.



Infrared, X-ray structure analysis and molecular weight studies¹²⁴ have been used to confirm the presence of intramolecular and intermolecular hydrogen bonding in the various states of peroxyacids. In nearly all cases the melting points of the parent aromatic carboxylic acids are higher than those of the corresponding aromatic peroxyacids. In the solid state, an aromatic carboxylic acid takes on the form of a nearly planar intermolecularly hydrogen-bonded, eight-membered ring (B'). Its planarity permits a closer packing arrangement than that permitted by the skewed dimer (A'). This in turn allows for a stronger influence of van der Waal's forces, whereas the skewed dimer (A') indicates a less dense packing arrangement. For example, the van der Waal's attractions of the phenyl rings are less than in peroxybenzoic acid than in benzoic acid, borne out by the melting points of 42°C and 122°C, respectively. In general, the aromatic acids melt between 50 and 100°C higher than the corresponding peroxyacids³⁴. This is despite the fact that the peroxycarboxyl group contains an additional electronegative oxygen, which might be expected to have more of an effect in raising the melting point than the skewed conformation has in lowering it such that the corresponding peroxy carboxyl group-containing compound has a higher melting point. This is not seen however, and instead the molecular packing arrangement is the dominant force for determining the melting point in the normal and aromatic peroxyacid.



By contrast, in the aliphatic series up to and including C₁₄, the peroxyacids have higher melting points than the parent acids. For the shorter aliphatic chains, the higher polarity of the peroxy carboxyl group is sufficiently dominant to exert a more positive effect on the melting point than the now weakened (relative to the aromatic series) van der Waal's attractions. With increasing aliphatic chain lengths of C₁₅

and higher, the van der Waal forces become sufficiently strong to outweigh the effect of the peroxy-carboxyl group presence.

In polar solvents, the structures of peroxyacids and carboxylic acids greatly influence their degree of acidity. The intramolecular hydrogen bonding and the reduced resonance stabilisation reduces the acidities of peroxyacids compared with the corresponding carboxylic acids. Typical pKa values lie between 7.1 and 8.2 for peroxyacids compared with 2.6 and 4.9 for the corresponding carboxylic acids.

1.5.2 Stability^{19,32,94,105,118}

Although the reaction conditions employed in this work did not actually reach temperatures that would promote thermal homolysis of organic peroxides, a brief discussion of product types will be included for completion.

Rates of decomposition, course of reaction and amount of each product type formed depend on the temperature and stabilisation of the free radical, as well as on whether or not solvent is present¹⁰³ and if there are efficient hydrogen donors present¹⁰⁵.

Generally within each organic peroxide classification, the higher the molecular weight the more stable the compound⁹⁴. With homolytic rupture of the O-O bond, the primary products are acyloxy, alkoxy and hydroxy radicals. In the case of acyl-containing compounds, a sufficient stability of R· would encourage the concerted homolysis of a C-C bond and the O-O bond to yield CO₂ and alkyl or aralkyl radicals. Table (E) below lists the most common endproducts formed via thermal homolytic decomposition and subsequent elimination, combination, disproportionation and hydrogen abstraction processes. The conditions, reaction mechanisms and product types are reviewed earlier in this Chapter in 1.4.4 "Thermally Induced O-O Homolysis".

Table (E) - Products of Thermally Induced Homolysis

Organic Peroxide	Examples	Examples of Products formed
R-O-O-H	$\text{CH}_3\text{-CH}_2\text{-OOH} \xrightarrow{170^\circ\text{-}320^\circ\text{C}}$	$\begin{array}{c} \text{O} \quad \text{O} \\ \quad \\ \text{HCH}, \text{CH}_3\text{CH}, \text{H}_2, \\ \text{CH}_3\text{CH}_2\text{OH}, \text{O}_2, \text{CO}_2, \\ \text{CO, alkanes, for example} \\ \text{CH}_3\text{CH}_2\text{CH}_3 \text{ and } \text{CH}_3\text{CH}_2\text{CH}_3\text{CH}_3 \end{array}$
	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{-C-OOH} \\ \\ \text{CH}_3 \end{array} \xrightarrow{95^\circ\text{-}100^\circ\text{C}}$ $\xrightarrow{250^\circ\text{-}300^\circ\text{C}}$	$\text{O}_2 + (\text{CH}_3)_3\text{COH: a simple mixture.}$ $\begin{array}{c} \text{O} \\ \\ \text{CH}_3\text{CCH}_3, \text{CH}_3\text{OH}, \text{H}_2\text{O}, \\ (\text{CH}_3)_3\text{COH}, \text{HCH}, \text{CH}_4 \end{array}$
$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{O}-\text{H}$	$\begin{array}{c} \text{O} \\ \\ \text{CH}_3\text{C-OOH} \\ \text{(no hydrogen donors)} \end{array} \xrightarrow{60^\circ\text{-}80^\circ\text{C}}$ $\begin{array}{c} \text{O} \\ \\ \text{C}_6\text{H}_5\text{C-OOH} \\ \text{(no hydrogen donors)} \end{array} \xrightarrow{80^\circ\text{-}100^\circ\text{C}}$	$\text{CO}_2 + \text{CH}_3\text{OH}$ $\text{O}_2 + \text{C}_6\text{H}_5\overset{\text{O}}{\parallel}{\text{C}}\text{OH}$
$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{R}$	$\begin{array}{c} \text{O} \quad \text{O} \\ \quad \\ \text{C}_6\text{H}_5\text{C-OO-C-C}_6\text{H}_5 \end{array} \xrightarrow[\text{solvent}]{\text{no}}$ $\begin{array}{c} \text{O} \quad \text{O} \\ \quad \\ \text{CH}_3\text{-C-OO-C-CH}_3 \end{array} \xrightarrow[\text{from solvent}]{\text{abstractable H atoms}}$	$\text{CO}_2, \text{C}_6\text{H}_5\text{-C}_6\text{H}_5 \text{ and some}$ $\text{C}_6\text{H}_5\overset{\text{O}}{\parallel}{\text{C}}\text{OC}_6\text{H}_5 \text{ and benzene.}$ $\text{CO}_2, \text{CH}_4, \text{CH}_3\text{CH}_3$
$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{O}-\text{R}'$	$\begin{array}{c} \text{O} \\ \\ (\text{C}_6\text{H}_5)_2(\text{CH}_3)\text{CC-OO-C}(\text{CH}_3)_3 \end{array} \xrightarrow{\text{in chlorobenzene at } 50^\circ\text{ }^{105}}$	$\text{CO}_2, (\text{C}_6\text{H}_5)_2\text{C}=\text{CH}_2,$ $(\text{C}_6\text{H}_5)_2\text{CHCH}_3,$ $\begin{array}{c} \text{O} \\ \\ \text{CH}_3\text{CCH}_3, (\text{CH}_3)_3\text{COH, and} \\ \text{some } [(\text{C}_6\text{H}_5)_2(\text{CH}_3)\text{C-}]_2 \text{ and} \\ (\text{C}_6\text{H}_5)_2(\text{CH}_3)\text{C-OC}(\text{CH}_3)_3 \end{array}$

The Criegee rearrangement of tertiary peroxyesters is detailed earlier in the chapter in 1.4.1.2 "O-O Heterolysis, Intramolecular Nucleophilic Rearrangement", as are the possibilities of primary and secondary

peroxyester elimination products in 1.4.1.3(ii) "Other Redox Reactions, Carbonyl-Forming Eliminations".

1.5.3 Spectroscopic Data

To conclude the study of the physical properties of organic peroxides, a number have their characteristic spectroscopic details tabulated below and compared with those of their non-peroxidic analogues. To determine the identity of the compound and its functional groups conclusively, hydrogen-1 and carbon-13 NMR proved most useful.

(i) Infrared Spectroscopy

Although infrared does show the O-O stretch, it is often a weak peak and can be difficult to determine. Other vibrational peaks can be used to assign other covalent bonds, and used in conjunction with NMR, a compound's unique structure can be elucidated.

notes accompanying table (F): the author recorded the spectra of the peroxyester oils and the hydroperoxide and alkyl peroxide liquids, directly on potassium bromide discs.

Table (F) - Infrared Absorption Bands of Characteristic Functional Groups^{118,125,126,127,128}

Compound	O-O stretch/cm ⁻¹	C=O stretch/cm ⁻¹	O-H stretch/cm ⁻¹	C-O stretch/cm ⁻¹	Comments
Peroxyester $\begin{array}{c} \text{O} \\ \parallel \\ \text{RCOOR}' \end{array}$	930-915(w) broad band and 870, 845(g), for alip. 129, 130 and arom. 129, 130 The band at ~850 is attributed to the peroxy group rather than peroxide group ^{129,131}	1783-1750(s) aliph. and 1771-1758(s) arom. tertiary-butyl ¹³² peroxyesters	-	Presumably two peaks because of the C-O-C link. Similar frequency to that for esters	Considering the O-O stretching, tertiary-butyl esters have a similarly positioned doublet at 948(m) and 845(w) broad peak. Tertiary-butyl esters and peroxyesters are distinguishable from normal alkyl esters which show only a trace of a doublet in this region
Ester $\begin{array}{c} \text{O} \\ \parallel \\ \text{RCOR}' \end{array}$	-	1735-1712(s) aliph. tertiary-butyl ^{129,133} esters 1750-1735(s) saturated, acyclic 1730-1717(s) α,β -unsaturated and aryl 1820-1735(s) lactones	-	1300-1000(s) two or more bands, one usually stronger and broader than the other (higher values for aryl conjugated and saturated systems)	As shown, conjugation in R group adjacent to carbonyl group moves absorption to the right; conjugation with O in the R' part moves absorption to the left
Peroxyacid $\begin{array}{c} \text{O} \\ \parallel \\ \text{RCOOH} \end{array}$	873-846(w) in o-, m- and p- (-Cl, -Br, -F and -NO ₂) substituted peroxybenzoic acids. PBA has a band at 880	1760-1710(s): singlet for aliph.; doublet for arom. in solid, singlet in soln.	~3300 sharp peak (intramolecularly hydrogen-bonded monomers) (as distinguished from carboxylic acids) 3270-3250 arom. solns. 3260-3232 solid aroms.	~1200(s) (coupled to OH deformation) in solids or solns. generally accompanied by one or two weaker bands on the higher frequency side	Except for o-nitro- and p-fluoro- peroxybenzoic acids, peroxybenzoic acids have narrower O-H bands in soln. than in the solid state
Carboxylic Acid $\begin{array}{c} \text{O} \\ \parallel \\ \text{RCOH} \end{array}$	-	1725-1700(s) saturated, acyclic 1705-1690(s) α,β -unsaturated 1700-1680(s) aryl conjugated	3560-3500(m) free, in very dilute soln. 3300-2500(w) bonded, very broad (variable absorptivities because of equilibrium between free monomers and intermolecularly hydrogen-bonded dimers)	1320-1210(s)	Conjugation moves the C=O stretch to the right of the range. The O-H is usually very broad and often interferes with C-H absorptions

Compound	O-O stretch/cm ⁻¹	C=O stretch/cm ⁻¹	O-H stretch/cm ⁻¹	C-O stretch/cm ⁻¹	Comments
Acyl Peroxide ¹²¹ $\begin{array}{c} \text{O} \\ \parallel \\ \text{RCOOCR} \end{array}$	892(m) semibroad band for long-chain acyl peroxides	Doublet in carbonyl absorption (due to coupling) 1820-1811 and 1796-1784 in aliph. 1805-1780 and 1783-1758 in arom.	-	For example, benzoyl peroxide has its doublet at 1225(s) ¹²⁸ and 1000(s)	Average splitting due to carbonyl group: 25cm ⁻¹ aliph. 22cm ⁻¹ arom. 24-33cm ⁻¹ asymmetrical with an aryl and alkyl group attached to opposing carbonyls
Acid Anhydride $\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ \text{RCOCR} \end{array}$	-	1850-1800(s) and 1790-1740(s) but variable relative intensities. Unsaturation moves absorption to the right; ring strain (cyclic, 5-membered ring) to the left	-	1300-1200(s) cyclic 1170-1050(s) acyclic. For example, benzoyl anhydride is near 1275(s)	The splitting of the carbonyl groups is 60cm ⁻¹ (compare with acyl peroxides)
Alkyl Peroxide ROOR	Calculated, ^{132b} being at 985-819(s)	-	-	Similar to ethers	-
Ether ROR	-	-	-	1300-1000(s)	Phenyl and vinyl ethers give two strong bands at each end of the range; aliph. give one strong band to the right. Absence of C=O and O-H is required to be sure that C-O is not from alcohol or ester
Hydroperoxide ROOH	~883 (calculated) weak absorption experimentally found at 877-847 (region of corresponding aliph. alcohol absorption of OH deformation)	-	Hydroperoxides do not exhibit specific O-H stretching or vibrations that distinguish them from other hydroxy containing compounds (see alcohols)	~1200, C-O stretching coupled with O-H deformation. As for O-H stretch, the region is not uniquely characteristic but in the range for alcohols	Bands around 880-700 are a result of the non-planar deformational vibrations of the O-H group. These have only been observed for H ₂ O ₂ and isopropylbenzene hydroperoxide

Compound	O-O stretch/cm ⁻¹	C=O stretch/cm ⁻¹	O-H stretch/cm ⁻¹	C-O stretch/cm ⁻¹	Comments
Alcohol ROH	-	-	3650-3600(m) sharp peak, no hydrogen-bonding (only in dilute soln.) 3500-3200(m) broad	1250-1000(s) phenols, ~1200 tertiary, ~1150 secondary, ~1100 primary, ~1050	The broad O-H stretch sometimes overlaps with C-H stretch absorptions primary, ~3640 secondary, ~3630 tertiary, ~3620 phenols, ~3610
Tertiary-butyl peroxybenzoate (spectrum A) <chem>C6H5CO3C(CH3)3</chem>	935(w) and 831(m)	1757(s)	-	1236(s) and 1055(s)	Peak at 863(m) is possibly due to the butoxy group
Tertiary-butyl 3-chloro-peroxybenzoate (spectrum B) <chem>3-Cl-C6H4CO3C(CH3)3</chem>	900(w) and 846(m)	1762(s)	-	1234(s) and the other doublet peak is split into a doublet at 1054 and 1074(m)	The peak at 869(vw) may be that of the butoxy group or one of the O-O doublets
Allylic metachloro-peroxybenzoate (spectrum C) <chem>3-Cl-C6H4CO3CH2CH=CH2</chem>	903(w) and 837(w)	1774(s)	-	1225(m) and 1052(m) (latter is of lower intensity)	-
Tertiary-butyl hydroperoxide <chem>(CH3)3COOH</chem>	886(vw) and 845(m)	-	~3700-3100(s) very broad (incorporating water peak, and is in range of OH stretch for alcohols)	1194(m) (in range of alcohol absorption ~1200(s))	Commercial sample used (70% hydroperoxide and 30% water)
Tertiary-butyl peroxide <chem>(CH3)3COOC(CH3)3</chem>	878(s) (874 ¹¹⁸)	-	-	1194(s) (pear) 1200(s)	-

s=strong; m=medium; w=weak; vw=veryweak; aliph.=aliphatic; arom.=aromatic; soln.= solution

(ii) ¹H Nuclear Magnetic Resonance Spectroscopy

From table (G) below, it can be seen that it is possible to distinguish peroxyacids from hydroperoxides by proton NMR, not only from the differences in their chemical shift values but also by the effect of dilution¹³⁵. It is only with hydroperoxides and their corresponding non-peroxidic analogues alcohols that the difference can be seen in the rather different chemical shift values for the hydroxy group, whereas the hydroxy chemical shifts of peroxyacids and carboxylic acids are in the same range.

The labile acidic proton of a peroxyacid shows little or no shift with dilution, a result consistent with its intramolecular structure (whereas many carboxylic acids will shift upfield on dilution). In the case of hydroperoxides, the shift to high field that occurs on dilution presumably results from a decrease in intermolecular hydrogen-bonding (as for carboxylic acids). In comparison with alcohols hydroperoxides are not extensively hydrogen-bonded. The large downfield shift of the signal of the hydroperoxy proton compared with its non-peroxidic analogue, is due to the large deshielding effect of the peroxy group although the mechanism of the effect is not clear¹³⁵.

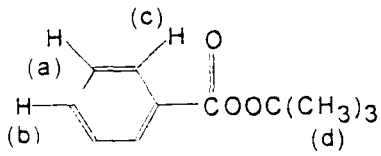
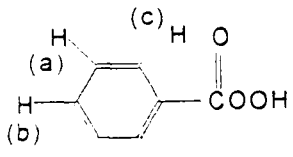
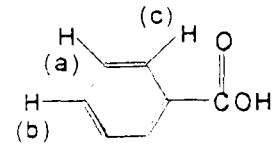
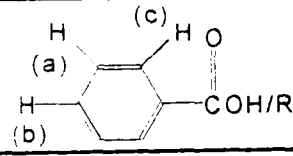
In peroxides without acidic protons, proton chemical shift values are generally not significantly different from those of their non-peroxidic analogues¹³⁵, except for protons on α - and β - carbons of the -OOR group in peroxyesters. The aliphatic and aromatic protons of acidic peroxides too have very similar shifts to their non-peroxidic analogues.

notes accompanying table (G): unless otherwise stated, CDCl₃ is used as solvent and TMS as internal standard.

s=singlet; d=doublet; t=triplet; m=multiplet; fs=fine splitting; tfs=triplet fine splitting; ns=no splitting; b=broad; vb=very broad; sp=sharp peak; Ph=aromatic ring; R=aliphatic group; per.an.=peroxidic analogue; non-per.an.=non-peroxidic analogue; concn.=concentration; conc.=concentrated; dep.=dependent; indep.=independent

Table (G) - Characteristic Proton Chemical Shifts^{126,134,135,136,137}
Standard Proton Chemical Shifts

Type of Proton	Chemical Shift / ppm
C-CH ₃	0-2
CH ₂ =	4.6-4.9
C=C-H; CH=	4.6-5.9; 5.1-5.6
R-OH	0.5-5.0(b, unless in dilute soln.)
PhCO ₂ -CH ₂	3.5-4.5
RCO ₂ H; PhCO ₂ H	10.2-12.0
RCO ₃ H; PhCO ₃ H	10.90-11.75(concn. indep.)
$\begin{array}{c} \\ \text{HCOR (ether)} \\ \end{array}$	3.3-4
H ₃ CCR ₂ -OOR	as for non-peroxidic analogue
HC-OH	3.4-4.0
H ₃ CCR ₂ OOH	as for non-peroxidic analogue

Peroxides and their Non-Peroxidic Analogues	Chemical Shift / ppm [integrals]
 <p>(spectrum D)</p>	(a) 7.47; 7.44; 7.42 (t; fs) [2H] (b) 7.60; 7.57; 7.54 (t; tfs) [1H] (c) 7.95; 7.92 (d; fs) [2H] (d) 1.38 (s) [9H] (1.36 ¹³⁵)
 <p>(spectrum F) (CD₂Cl₂)</p>	(a) 7.54; 7.51; 7.49 (t; fs) [2H] (b) 7.70; 7.67; 7.64 (t; tfs) [1H] (c) 8.00; 7.97 (d; fs) [2H] (d) 11.70 (vb) [1H]
	(a) 7.47; 7.44; 7.42 (t; fs) [2H] (b) 7.62; 7.59; 7.56 (t; fs) [1H] (c) 8.12; 8.09 (d) [2H] (d) 11.44-11.67 (vb) [1H]
	(a) 7.42 (b) 7.47 (c) 8.07

Peroxides and their Non-Peroxidic Analogues	Chemical Shift / ppm [integrals]
<p>(spectrum H)</p>	(a) 7.53; 7.50; 7.48 (t; fs) [2H] (b) 7.68; 7.65; 7.63 (t; tfs) [1H] (c) 8.09; 8.06 (d; fs) [2H]
	(a) 7.52; 7.49; 7.47 (t; fs) [2H] (b) 7.67; 7.65; 7.63 (t; tfs) [1H] (c) 8.15; 8.12 (d; fs) [2H]
<p>(spectrum E) (CD₂Cl₂)</p>	(a) 7.46; 7.43; 7.40 (t; fs) [1H] (b)/(c) 7.60; 7.57 (d; fs) [1H] (b)/(c) 7.86; 7.83 (d; tfs) [1H] (d) 7.92 (s; tfs) [1H] (e) 1.40 (s) [9H]
	peak at 7.30 [2H] = t for (a) and one of d's for (b)/(c) peak at 7.70 [1H] = other d for (b)/(c) peak at 7.85 [1H] = s for (d) (e) 4.65; 4.75 (d; fs) [2H] (f)/(g) 5.05 (d; fs) [1H] / [2H] (f)/(g) 5.25; 5.35 (d; fs) [1H] / [2H]
<p>(spectrum G) (CD₂Cl₂)</p>	(a) 7.50; 7.48; 7.45 (t; ns) [1H] (b)/(c) 7.67; 7.63 (d; fs) [1H] (b)/(c) 7.90; 7.87 (d; tfs) [1H] (d) 7.98 (s; tfs) [1H] (e) 11.41 (b) [1H]
	(a) 7.46; 7.43; 7.40 (t; ns) [1H] (b)/(c) 7.61; 7.58 (d; fs) [1H] (b)/(c) 8.02; 7.99 (d; tfs) [1H] (d) 8.10 (s; tfs) [1H] (e) 9.66-8.13 (vb) [1H]
$(\text{CH}_3)_3\text{COOH}$ (a) (b)	(a) 1.10 (s) (b) 9.38 (sp)
$(\text{CH}_3)_3\text{COH}$ (a) (b)	(a) 1.25 (s) (b) 3.42 (sp)
$(\text{CH}_3)_3\text{COOC}(\text{CH}_3)_3$ (a)	(a) 1.22 (s) (1.17 (s) ¹³⁵)
$(\text{CH}_3)_3\text{COC}(\text{CH}_3)_3$ (a)	(a) as for peroxidic analogue
	(a) 1.28 (b) 2.00 ± 0.02 ¹³⁴
	(a) 1.95 (b) 2.00 ± 0.02 ¹³⁴

(iii) ¹³C Nuclear Magnetic Resonance Spectroscopy

From table (H) of ¹³C chemical shifts, it can be seen that the peroxides and their non-peroxidic analogues can best be distinguished by the difference in the chemical shift of the carbon directly attached to the peroxygen or oxygen bond, in the case for peroxyesters and esters; hydroperoxides and alcohols; and alkyl peroxides and ethers. The aryl and aliphatic carbon values (other than those of a carbon attached to an oxygen atom) are very similar and are thus not useful for characterisation. Peroxyacids and carboxylic acids have different carbonyl carbon peaks, with the former further upfield by about 4ppm relative to the latter. Acyl peroxides and acid anhydrides have extremely similar chemical shifts for carbon, with the only real difference being the carbonyl carbon shift value. However, this difference is very small, with the acyl peroxide having a shift value less than 1ppm greater than its non-peroxidic analogue.

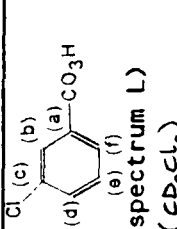
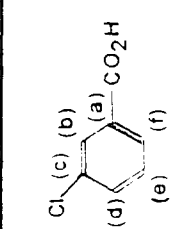
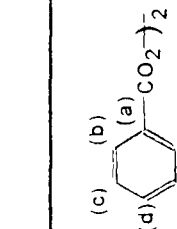
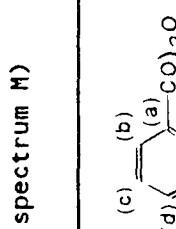
Although the aryl peaks of a peroxidic compound and its corresponding non-peroxidic analogue are very similar, it is possible to distinguish individual compounds in a mixture once the carbonyl carbon, ether/alcohol carbon, or the peroxy carbon have been identified.

notes accompanying table (H): unless otherwise stated, CDCl₃ is used as solvent and TMS as internal standard.

qc=quaternary carbon; sqc=small quaternary carbon; saqc=small aromatic quaternary carbon.

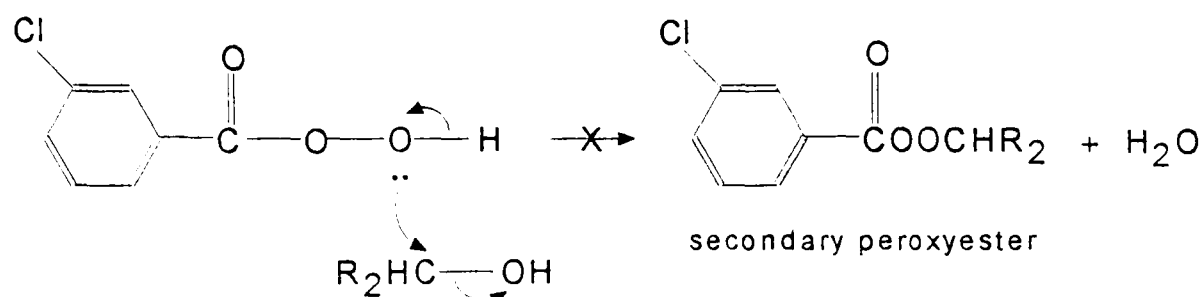
Table (H) - Characteristic ¹³C Chemical Shift Values ^{134,136,138}

Type of Carbon	Alkynes (sp ³)	-C-O	-C-O-O	Aryl C	O R-COOH	O R-COOH	O R-COOH	O R-COOH'	O R-COOH'	C=O
Chemical Shift/ppm	0-40	40-90	see below	120-155	160-18 5	see below	160-180	see below	160-180	160-180
(a) (d) (b) CO ₃ C(CH ₃) ₃ (c) (f) (spectrum I) (CD ₂ Cl ₂)	(a) 26.28	-	84.02 (sqc(b))	(c) 128.12 (saqc) (d)/(e) 128.98 (d)/(e) 129.30 (f) 133.66 (c) is - half intensity of (b), both qc	-	-	-	164.40	-	-
(e) (d) (b) CO ₂ C(CH ₃) ₃ (c) (f) Pelletier 139	(a) 28.2	(b) 80.7	-	(c) - (f) {128.1; 129.4; 132.1; 132.3}	-	-	165.6	-	-	-
Cl (e) (d) (b) CO ₃ C(CH ₃) ₃ (c) (f) (g) (h) (spectrum J)	(a) 26.20	-	84.26 (sqc(b))	(d)/(f)/(g)/(h) {127.22; 129.09} (c)/(e) 129.35 (saqc) (d)/(f)/(g)/(h) {130.02; 133.43} (c)/(e) 134.77 (saqc)	-	-	-	163.15	-	-
(c) (b) (a) CO ₃ H (d) (spectrum K) (CD ₂ Cl ₂)	-	-	-	(a) 125.78 (saqc) (b)/(c) 129.31 (b)/(c) 129.59 (d) 134.79	-	168.32	-	-	-	-
(c) (a) (b) CO ₂ H (d)	-	-	-	(a)/(c) 128.33 (b) 129.13 (saqc) (a)/(c) 130.02 (d) 133.67	172.06	-	-	-	-	-

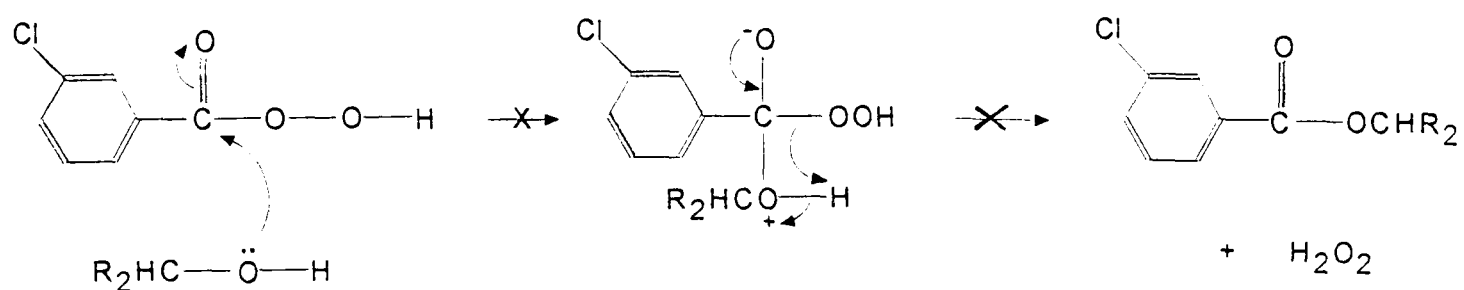
Type of Carbon	Alkynes (sp)	-C-O	-C-O-O	Aryl C	$\begin{array}{c} \text{O} \\ \\ \text{R-COOH} \end{array}$	$\begin{array}{c} \text{O} \\ \\ \text{R-COOH} \end{array}$	$\begin{array}{c} \text{O} \\ \\ \text{R-COOR} \end{array}$	$\begin{array}{c} \text{O} \\ \\ \text{R-COOR} \end{array}$	C=O
 (a) (b) (c) (d) (e) (f) CO ₂ H (spectrum L) (CD ₂ Cl ₂)	-	-	-	(a)/(c) 127.32 (saqc) (b)/(d)/(e)/(f) {127.70; 129.51; 130.68; 134.79} (a)/(c) 135.34 (saqc)	167.15	-	-	-	-
 (a) (b) (c) (d) (e) (f) CO ₂ H	-	-	-	(b)/(d)/(e)/(f) {128.32; 129.86; 130.24} (a)/(c) 130.97 (saqc) (b)/(d)/(e)/(f) 133.89 (a)/(c) 134.68 (saqc)	170.77	-	-	-	-
 (a) (b) (c) (d) (CO ₂) ₂ (spectrum M)	-	-	-	(a) 125.56 (saqc) (b)/(c) 128.86 (b)/(c) 129.78 (d) 134.32	-	-	-	-	163.08
 (a) (b) (c) (d) (CO) ₂ O	-	-	-	(a) 128.62 (saqc) (b)/(c) 128.73 (b)/(c) 130.37 (d) 134.43	-	-	-	-	162.21
(CH ₃) ₃ COOH	25.49	-	80.66	-	-	-	-	-	-
(CH ₃) ₃ COH	31.22	69	-	-	-	-	-	-	-
[(CH ₃) ₃ CO] ₂	26.59	-	78.29	-	-	-	-	-	-
[(CH ₃) ₃ C] ₂ O	0-40	40-90	-	-	-	-	-	-	-

CHAPTER 2 – RESULTS AND DISCUSSION

In 1970, Magelli and Sheppard *et al.*¹ claimed that peroxyesters could not be prepared by alkylation of peroxyacids or their salts. In 1989, Crich *et al.*¹⁴⁰ attempted the former by reacting MCPBA with secondary alcohols. The method proved unfruitful. The hope was that the nucleophilic centre of the peroxyacid, the peroxy oxygen, would have been nucleophilic and reactive enough to attack the carbon of the C-O bond of the alcohol. Ando's³ recent review of peroxide chemistry does not include this as a known route to peroxyesters either.



In the preparation of carboxylic esters (see Chapter 1, 1.2.2 "Preparation of Esters"), it is the O-H bond of the alcohol that is cleaved as the alcoholic oxygen is the reacting nucleophile, as opposed to the above mechanism where the C-O bond would have been broken, with the peroxy oxygen acting as the nucleophile instead. Neither did the attempted reaction of the peroxyacid and secondary alcohol yield a carboxylic ester.



This indicates the unreactivity of the lone pair of the alcoholic oxygen towards the carbonyl carbon of the peroxyacid. Perhaps in the presence of acid, the carbonyl carbon could have been more favourable for attack by protonation of the carbonyl oxygen. However, there may then have been the problem of acid-catalysed decomposition of the peroxyacid (see Chapter 1, 1.4.2 "Acid-Catalysed Decomposition"), and it has also

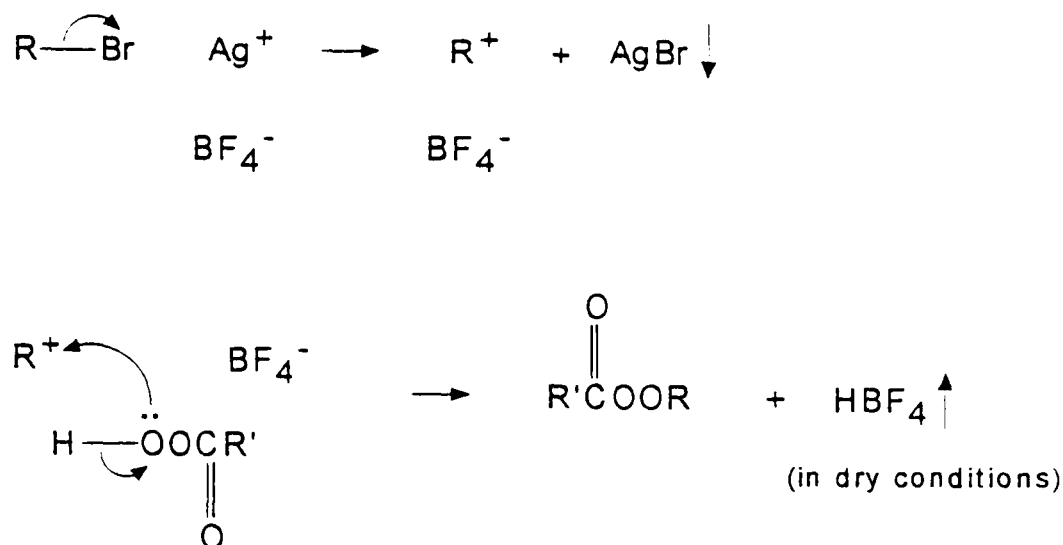
been found that the reaction of alcohols and peroxyacids in acidic conditions yield hydroperoxides¹⁸ rather than peroxyesters. Up to now, peroxyesters have therefore been stated to be derived from carboxylic acids and hydroperoxides rather than peroxyacids and alcohols, because their hydrolysis yields the former products and not the latter¹⁰³. This is stated although peroxyacids and alcohols on reaction have been shown to yield hydroperoxides rather than peroxyesters (compare with the reversible reaction of the esterification of carboxylic acids and the hydrolysis of esters). The experimental work of this thesis was to disprove the claim by Magelli and Sheppard *et al.*¹ that alkylation of peroxyacids or their salts to peroxyesters was impossible. It is no surprise therefore that problems were initially encountered and a full discussion is given below.

We decided to pursue the use of peroxyacids knowing that the use of MCPBA as a nucleophile at sp^2 centres was well documented, for example in epoxidation reactions^{22,87}. As they are highly reactive, the use of carbocations to promote attack by peroxyacid seemed the surest way to peroxyester synthesis. Tertiary carbocations were initially used because of their stability (see Chapter 1, 1.3 "Carbocation and Organic Radical Intermediates") and thus the greater likelihood of reaction actually occurring.

As light, temperature, concentration, reaction time and order of reactant addition determined modifications at the various stages during the course of experiments, corresponding alterations to the experimental procedures were made as they became necessary.

It was also decided that the Lewis acid silver tetrafluoroborate would be used to promote the formation of R^+ from an alkyl bromide (see Chapter 1, 1.3.1.2 "Carbocation Formation"), and the silver halide precipitated out of solution. Dry dichloromethane (3Å molecular sieves) and oven-dried glassware were also used as well as a nitrogen atmosphere (flushing with dry nitrogen before the reaction too). This was to prevent an aqueous medium for the strong acid $H^+BF_4^-$ to exist, which could lead to the acid-catalysed decomposition of the peroxyacid as well as of the peroxyester. (See Chapter 1, 1.4.2 "Acid-Catalysed Decomposition".) Although HBF_4 would be prepared in the reaction as shown below, under dry conditions it would be released as an association of boron trifluoride and hydrogen fluoride gases¹⁴⁴ and not as a source of protons directly.

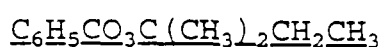
S_N1 mechanism:



A saturated solution of the mild base sodium bicarbonate was used at the end of the reactions to neutralise any tetrafluoroboric acid in the reaction mixture. Constant stirring was also employed to prevent local heating and ensure thorough mixing of reactants.

In all the reactions involving the attempted synthesis of the peroxyester 1,1-dimethylpropyl peroxybenzoate, the silver tetrafluoroborate was added to a solution of peroxybenzoic acid and the bromide with all reactants at 22°C. The relative number of moles of reactant were approximately: peroxyacid 1.0, alkyl bromide 1.0 and silver salt 1.2 (excess to balance any loss of Ag⁺ from the hydrolysis of the initial salt to silver hydroxide). For all these experiments, the recovery mass was less than 5% of the total reactant mass.

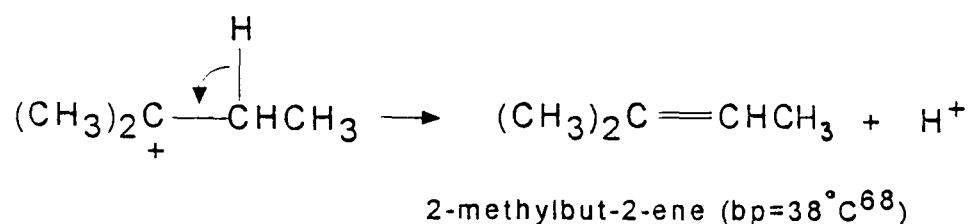
The preparation of 1,1-dimethylpropyl peroxybenzoate,



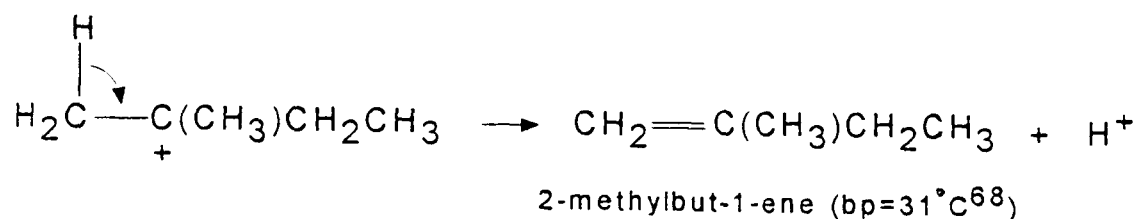
A. The first experiments were left to stir for 60 minutes once the silver salt had been added to a solution of peroxybenzoic acid and 2-bromo-2-methylbutane in 50ml of dichloromethane. After the workup, the product analysed by NMR was seen to consist largely of saturated hydrocarbons. (Comparing the proton spectra with those of saturated

aliphatic polymers¹⁴¹, the regions between 0 and 2ppm were very similar. For example, the spectrum of low molecular weight polyethylene in CDCl₃ showed a methyl absorbance band as a triplet at 0.89ppm. The methylene groups in the chain formed a broad singlet at about 1.27ppm. The spectrum of polypropylene in CDCl₃ had its methylene and methine multiplet resonances centred at about 1.1ppm and 1.6ppm, respectively. Its methyl group's doublet resonated at about 0.84ppm.) There were peaks in the proton NMR around δ 0.9 (RCH₃); δ 1.3 (R₂CH₂); δ 1.5 (R₃CH)¹²⁶, possibly indicating the result of different types of polymerisation. For example, as shown below, the initially formed carbocation may eliminate a proton in either of two ways and then react with a further carbocation (see Chapter 1, 1.3 "Carbocation and Organic Radical Intermediates") as seen in alkene polymerisation catalysed by electrophiles.

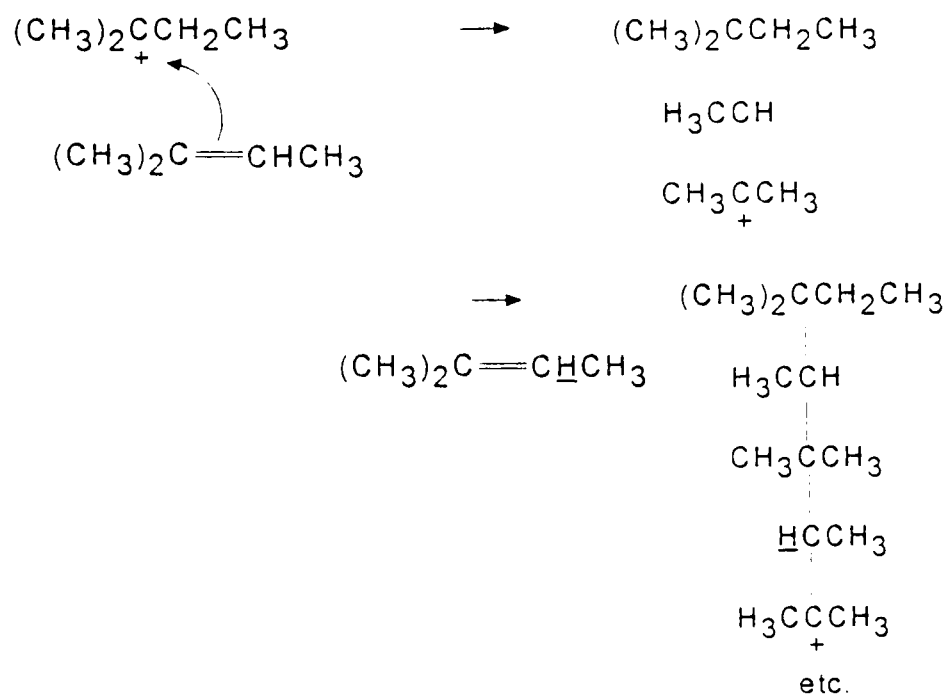
(1)(a)



(b)

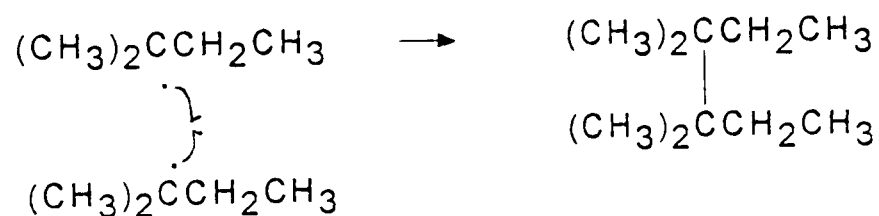


(ii)(a)



(b) The isomeric methylbutene could react similarly.

The ultimate fate of the tertiary carbocation from (ii)(a) and (b), would involve the elimination of a proton to yield a terminal alkene or a more substituted one. The ionic polymerisations shown above perhaps fully account for the proton NMR signals seen in the products. There may also have been the possibility of radical mechanisms arising from light-induced processes (see Chapter 1, 1.3 "Carbocation and Organic Radical Intermediates") (the average bond enthalpy at 25°C of C-Br⁶⁸ is 276 kJmol⁻¹):



The corresponding saturated carbon peaks that would result from the above mechanisms were seen in the ¹³C NMR spectrum^{126,134,136}: CH₃-C, 0-25ppm; C-CH₂-C, 18-40ppm; C-CH-C, 25-60ppm. Further observation of the ¹³C NMR also clearly showed peaks around 148 to 151ppm (aromatic carbons are found at about 120-140ppm¹²⁶), perhaps indicating the sp² carbons of an alkene(s) (found at about 100-165ppm¹²⁶). Proton type peaks for C=C-CH₃ (about δ1.7) and C=C-H (about δ4.5-7) were seen but were very small. This may therefore suggest that the possible polymerisation products were largely saturated hydrocarbons, with the peaks around 150ppm possibly

being those of alkenes, where the extent of polymerisation had been great enough, so that any protons or carbon atoms specific to the alkene(s) formed to terminate the polymerisation, would not be "seen", because of the relatively very large number of methyl peaks (about $\delta 5-25^{126}$) for example, obscuring them. Other peaks included were those of a trace of unreacted peroxybenzoic acid. There was no indication of unreacted 2-methyl-2-bromobutane (use of excess silver tetrafluoroborate) nor a possible hydrolysis product 2-methyl-2-butanol. The few peaks around 55-70ppm may have been due to other aliphatic alcohols (rearrangement, cyclization), for their values are very similar to some of those in the literature¹³⁸. Although the proton spectrum appeared very similar to that for bromobenzene, the corresponding ¹³C pattern of peaks was clearly not indicated.

Table (I) - ¹³C NMR/ppm

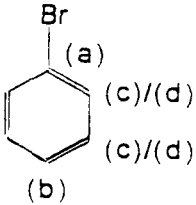
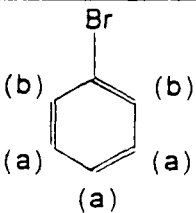
$(\text{CH}_3)_2\text{C}(\text{Br})\text{CH}_2\text{CH}_3$ (b)(d) (c)(a) (bp ¹³⁶ =108°C)	(a)10.55; (b)33.65; (c)40.08; (d)67.74 (CDCl ₃ , 90MHz) (in good agreement with literature in CDCl ₃ , 90MHz ¹⁴²)
(bp ^{68, 136} =156°C; 43°C, 18mmHg) <div style="display: inline-block; vertical-align: middle; text-align: center;">  </div>	(a)122.39; (b)126.67; (c)129.85; (d)131.33 ¹⁴² (CDCl ₃ , 90MHz)
$(\text{HO})\text{C}(\text{CH}_3)_2\text{CH}_2\text{CH}_3$ (d)(b) (c)(a) (bp ¹³⁶ =102°C; 50°C, 60mmHg)	(a)8.82; (b)28.71; (c)36.60; (d)70.95 ¹⁴² (CDCl ₃ , 90MHz)

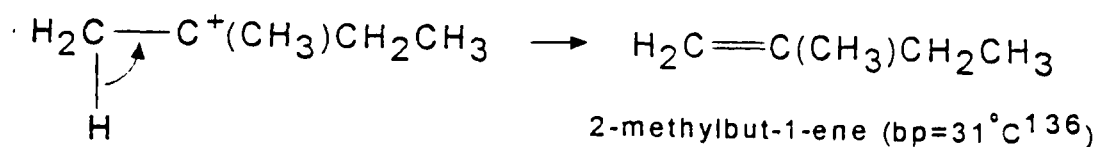
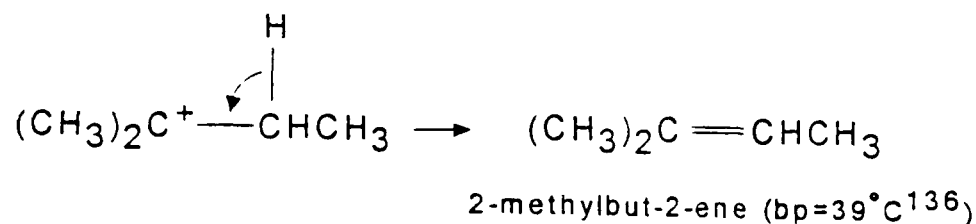
Table (J) - ^1H NMR/ppm

$(\text{CH}_3)_2\text{C}(\text{Br})\text{CH}_2\text{CH}_3$ (b) (c) (a)	(a) 1.03; 1.06; 1.09 (t) [3H]; (b) 1.74 (s) [6H] (c) 1.78; 1.80; 1.83; 1.86 (q) [2H] (CDCl_3 , 90MHz)
	(a) ca. 7.13 (m) [3H] ₁₃₇ (b) ca. 7.41 (m) [2H] (CCl_4 , 60MHz)

s=singlet; t=triplet; [] integrals

The low recovery mass needs also to be explained. The precipitated silver bromide (pale green) was readily and visibly formed. Its mass did not suggest that unreacted peroxyacid had been filtered off with it being of similar mass to that of silver tetrafluoroborate used. Thus, the most feasible explanation is that, because of strong acid (see Chapter 1, 1.4.2 "Acid-Catalysed Decomposition") or perhaps irradiation for example (see Chapter 1, 1.3 "Carbocation and Organic Radical Intermediates") some of the peroxyacid decomposed to benzoic acid. On addition of the saturated solution of sodium bicarbonate the benzoic acid was presumably lost into the aqueous layer on its reaction to form the sodium salt. Similarly for the peroxybenzoic acid, which would have then decomposed to the normal acid.

As silver bromide was seen to form, the loss in alkyl halide mass can most probably be attributed to the reaction conditions being too warm for the carbocation to be stable, and the volatile elimination product(s) being lost during the reaction and on reducing down the reaction mixture after neutralisation and drying, with a little being involved in polymerisation as described above. The low concentration of peroxyacid and carbocation is a possible explanation for this occurring - instead of being in close proximity to facilitate their reaction, elimination occurred at a greater rate than the desired nucleophilic attack by the peroxyacid upon the relatively unstable carbocation because of low concentration.



Perhaps the more favourable alkene would be the more substituted one, though neither was seen on the NMR spectra due to their volatility. This may explain the low product yield.

Table (K) - ^{13}C NMR/ppm

(d)(c) $(\text{CH}_3)_2\text{C}=\text{CHCH}_3$ (a), (e) (b) (bp=39 $^\circ\text{C}^{136}$)	(a)13.3; (b)17.1; (c)25.5; (d)118.7; (e)131.7 ¹³⁸ (dioxane, 60MHz)
(d) (b) (c)(a) $\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{CH}_2\text{CH}_3$ (e) (bp=31 $^\circ\text{C}^{136}$)	(a)12.46; (b)22.46; (c)30.86; (d)108.68; (e)147.63 ¹⁴² (CDCl ₃ , 90MHz)

Table (L) - ^1H NMR/ppm

$(\text{CH}_3)_2\text{C}=\text{CHCH}_3$ (a), (d)(c) (b)	(a), (b)1.5; (c)1.6; (d)5.1 ¹³⁷ (CCl ₄ , 60MHz)
$\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{CH}_2\text{CH}_3$ (d) (b) (c)(a)	(a)1.0; (b)1.7; (c)2.0; (d)4.6 ¹³⁷ (CCl ₄ , 60MHz)

B. It was now decided to exclude light to reduce the likelihood of radical processes. The other conditions were kept as in A.

(i) The first set of experiments excluding light saw white fumes of boron trifluoride together with hydrogen fluoride turning neutral water acidic, as well as possible polymerisation products again. Additionally however, ^1H NMR peaks were seen around 1.9 and 5.1ppm (CD₂Cl₂). These new peaks may

indicate the termination of polymerisation to yield alkene(s) as described above. Further indications were the additional sp^2 ^{13}C peaks around 133ppm ($-C=C-$ δ 80-166^{134,136}) (CD_2Cl_2). (The alkene peaks did represent those of the elimination product 2-methylbut-2-ene¹³⁸. Also it is important to note that the exclusion of light resulted in unreacted peroxybenzoic acid and benzoic acid (from decomposed peroxybenzoic acid after neutralisation) as the only aromatic compounds present.

(ii) As no success had yet been had, it was decided to increase the concentration of reactants two-fold – by using a total volume of 25ml – and reducing the time of reaction to 15 minutes. At this stage it seemed obvious to decrease the time of reaction because, as the formation of silver bromide was seen to occur within 30 seconds of the addition to the peroxyacid and halide solution, the carbocation would be formed instantaneously and its fate determined at the very most within a few seconds at the temperature employed.

The results were dramatically different to those of previous experiments. The low product mass was now seen to include the peroxyester, and the corresponding normal carboxylic ester (measurement of NMR integrals indicated 50% of each).

Comparing NMR details with those of commercial tertiary-butyl peroxybenzoate, it became apparent that the 1,1-dimethylpropyl peroxybenzoate had indeed formed. The results of tlc (5cm, Al_2O_3 plate, $R_F=0.8$ in CH_2Cl_2 ; UV light sensitive and peroxide positive, see Chapter 3, "Experimental") were positive, being very similar to those of tertiary-butyl peroxybenzoate as would be expected. Most of the experiments did indeed show peroxide positive spots. However, when sprayed with freshly prepared peroxide spray, they only became a very slight pink and there was no visible sign of the peroxyester after the work-up. This was due to the spray being highly sensitive, and many experiments had to be carried out before a workable mass of peroxyester was prepared.

This reinforced the belief that an increase in the reactants' concentrations would increase the likelihood of the peroxyacid and tertiary carbocation reacting together. Reducing the time of reaction apparently hindered polymerisation, unless this was also a direct result of concentration increase where the competing reaction of the carbocation with the peroxyacid came to the fore above that which involved the alkene. This was a better change than the exclusion of light, because polymerisation was still seen in that case.

carboxylic esters - a review of the utilised preparations is discussed in Chapter 1.

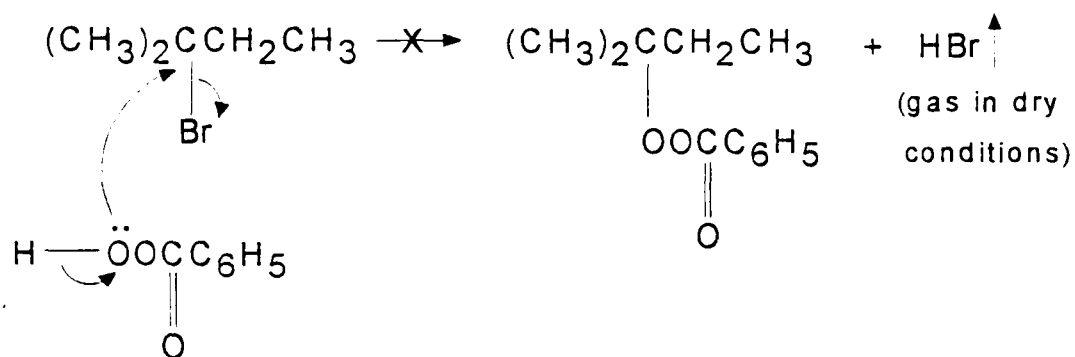
The reaction was again carried out at 22°C, under nitrogen and in the dark. Based on the positive results using higher reactant concentration and the fact that the hydroxy oxygen of the carboxylic acid is not as nucleophilic as the corresponding peroxyacid, concentrations were increased further. A total volume of 25ml was used (half that of the first set of experiments) and about three times the number of moles of benzoic acid and bromide, compared with the initial amounts of peroxyacid and bromide used. Thus, a twelvefold increase in reactant concentration was used. For reasons as described above, the reaction time was limited to 15 minutes.

The conditions proved unfruitful. Again there was visibly a low recovery mass and ¹H NMR spectroscopy indicated only benzoic acid (too little sodium bicarbonate solution must have been added) and saturated proton peaks. The region between 0 and 2ppm was extremely similar to that for the first and second set of reaction attempts to form the aforementioned peroxyester, where the carbocation did not react with the peroxyacid but essentially eliminated a proton to form volatile alkenes, with a relatively small amount possibly resulting in vinyl polymerisation products. The corresponding ¹³C peaks were at 8.40; 26.80; 27.35; 29.41 and 30.11ppm: there were a number of peaks within 0.2ppm of these values. These proton peaks were seen in A and B of the attempted syntheses of the peroxyester 1,1-dimethylpropyl peroxybenzoate, as were their corresponding carbon peaks.

The attempted preparation of 1,1-dimethylpropyl
peroxybenzoate, without the use of silver
tetrafluoroborate

It was then thought that perhaps the peroxyester could be formed if the peroxy oxygen of the peroxyacid was nucleophilic enough to displace the bromide of the original halide. Similar conditions to the successful procedure above were employed, except that the reaction time was extended to 60 minutes as there was no reactive intermediate.

S_N2 mechanism



However, there was no sign of peroxyester formation, and the materials isolated were the unreacted bromide with a little peroxyacid and benzoic acid. Peroxybenzoic acid readily decomposes in solution at 22°C. So, refluxing to try and increase its reactivity was not considered. The presence of benzoic acid after neutralisation was due to the partial decomposition of the unreacted peroxybenzoic acid.

It was now thought that perhaps use of a more stable peroxyacid and tertiary carbocation would increase the likelihood of reaction and subsequently yield a greater amount of a peroxyester.

MCPBA is known to be very stable, for example epoxidations require temperatures of 25°C in dichloromethane²², whereas peroxybenzoic acid decomposes under milder conditions as mentioned above. Also, it is well known that the tertiary-butyl carbocation (CH₃)₃C⁺ is less susceptible to elimination and is more stable than other C₄ carbocations, which usually rearrange to it⁵⁸.

The route to the peroxyester via the Milas and Surgenor⁷ preparation of 1946 provided the NMR spectra of authentic material that could be compared with our product. (See Chapter 3, "Experimental".)

The attempted preparation of tertiary-butyl meta-chloroperoxybenzoate, 3-Cl-C₆H₄CO₃C(CH₃)₃ with the late addition of silver tetrafluoroborate

Firstly, an attempt was made to see whether the peroxy oxygen of MCPBA was nucleophilic enough to react with tertiary-butyl bromide. Neither continuous stirring for 60 minutes or 3 days at 22°C, in the dark, under

nitrogen and with a threefold reactant increase compared with initial amounts, yielded any of the peroxyester. As for peroxybenzoic acid, the attempted reaction with MCPBA resulted in no conversion, nor did refluxing in 40-60 petroleum ether for 225 minutes. Adding silver tetrafluoroborate at this stage gave only unreacted MCPBA and silver bromide. The tertiary carbocation presumably eliminated a proton to form volatile alkene(s).

The preparation of tertiary-butyl 3-chloroperoxybenzoate

(i) By adding the silver salt to a solution of peroxyacid and alkyl bromide.

As in the attempted preparations of 1,1-dimethylpropyl peroxybenzoate, the silver salt was added to a solution of peroxyacid and bromide at 22°C, in the dark and under nitrogen. The reaction was carried out for 30 and 90 minutes and the reactant concentration eventually increased threefold compared with that used initially.

As for the previous peroxyester under the similar controls and environment, only a very small amount of peroxyester was formed. Again, a low total recovery mass was found, although as 3-chloroperoxybenzoic acid is more stable, it was not as low as for the peroxybenzoic acid experiment, -5%-10%. This can be accounted for once again by the elimination of a proton by the tertiary-butyl cation to form for example, the extremely volatile isobutylene (2-methylprop-1-ene, bp=-6.5°C⁶⁸), therefore not seen in the NMR spectra.

Also, some 3-chloroperoxybenzoic acid decomposes to the normal carboxylic acid, and is thus lost on reaction with saturated sodium bicarbonate solution. Times of reaction longer than 15 minutes had been decided upon because as the $(\text{CH}_3)_3\text{C}^+$ is more stable than $(\text{CH}_3)_2\text{C}^+\text{CH}_2\text{CH}_3$, it was thought that the tertiary-butyl carbocation may have been sufficiently less reactive to necessitate a longer reaction time. However, it was found that by maintaining a reaction time of 15 minutes and varying the temperatures, different amounts of peroxyester could be prepared. It became apparent therefore that the stability of the tertiary-butyl cation at 22°C was insufficient and its decomposition

accelerated giving a lower chance to react with the peroxyacid than at lower temperatures. By comparing the results when the addition rate of silver tetrafluoroborate caused the temperature to climb to 40°C and when maintaining the temperature between 12 and 15°C, it appears that lowering the temperature gave better results of peroxyester formation. Thus, reaction at 2°C gave better results still.

However, cooling the solution of 3-chloroperoxybenzoic acid and alkyl bromide to -12°C before addition of the silver tetrafluoroborate presented problems. Not only did the solubility of the peroxyacid decrease so that more dry dichloromethane had to be added (lowering the concentration of reactants), but the peroxyacid was not as reactive as at the higher temperatures and again little peroxyester was seen in the NMR spectra. Increasing the solution temperature to -4°C however (for 15 minutes as previously), gave a 10% recovery of essentially 3-chloroperoxybenzoic acid).

(ii) By adding the alkyl bromide to a slurry of silver salt in a solution of peroxyacid.

At similar temperatures, experiments were then attempted in which the alkyl halide was added to a mixture of the 3-chloroperoxybenzoic acid and silver salt over about 15 minutes. With temperatures of about -12°C and -4°C, only a little of the peroxyester was formed, as part of a low product mass. At 22°C whether total reaction times were 5, 30 or 60 minutes, no peroxyester at all was produced. (At this temperature, adding silver tetrafluoroborate last had led to some product, although very little.)

In summary, it was shown that under similar conditions, peroxyester formation was seen to occur in larger quantities when the silver tetrafluoroborate salt was added last, rather than the tertiary-butyl bromide. However, the product mass was still low and in need of improvement. It now seemed a logical step to attempt a set of reactions where a solution of 3-chloroperoxybenzoic acid was added dropwise at 22°C, to the reaction vessel containing the tertiary-butyl bromide and silver salt.

(iii) By addition of the peroxyacid to a mixture of the silver salt and alkyl bromide in solution, with the contents of the reaction flask at various temperatures.

Again, the reaction was carried out under nitrogen without the exclusion of light. This method also reduced the amount of silver tetrafluoroborate rendered useless in its ready conversion to silver hydroxide and tetrafluoroboric acid, whilst being previously added at a rate such that a particular temperature could be maintained in the reaction vessel. By a certain amount of cooling of the reaction flask to desired requirements, the dropwise addition of the 3-chloroperoxybenzoic acid solution could very comfortably be carried out within 15 minutes. As previously explained, there was no need to let the reaction stir after the addition was complete, because the tertiary carbocation had shown itself to be a highly reactive species, reacting immediately with the incoming peroxyacid solution.

Results confirmed that adding the 3-chloroperoxybenzoic acid solution over 15 minutes whilst the carbocation was initially at -2°C , produced virtually no peroxyester as the temperature rose too greatly. Cooling a solution of the bromide to -4°C and then adding the silver tetrafluoroborate such that the temperature was at -2°C , followed by the addition of 3-chloroperoxybenzoic acid solution over 17 minutes (the temperature climbed to 2°C), produced a yellow oil in a 17% crude yield (peroxyester and some 3-chloroperoxybenzoic acid).

Addition of the 3-chloroperoxybenzoic acid solution to the reaction vessel contents at 2°C and maintained at that temperature, resulted in a 53% crude yield - a pale yellow solid (3-chloroperoxybenzoic acid and some peroxyester).

Cooling a solution of the alkyl halide to -8°C before adding silver tetrafluoroborate to give a temperature of -6°C , gave a crude yield of 63% - a white, oily solid. The temperature was now too low for much of the peroxyacid to be reactive. As expected, more unreacted 3-chloroperoxybenzoic acid was seen in the NMR than in the reaction starting at 2°C .

The best results obtained involved the cooling of a solution of the tertiary-butyl bromide to -4°C , to which silver tetrafluoroborate was

added as quickly as possible (to minimise hydrolysis) such that the temperature rose to -2°C , followed by immediate addition of a 22°C solution of the peroxyacid over 15 minutes. Although light was not excluded, the reaction was not carried out under bright sunlight, but the reaction flask submerged within the ice-methanol bath. This reaction yielded a yellow oil (similar to commercial tertiary-butyl peroxybenzoate) of a 36% crude yield (yellow oil), and an actual yield of 25% (a less viscous, pale yellow oil).

These experimental conditions employed the minimum time that silver tetrafluoroborate was in contact with the relatively humid laboratory air. Very quick procedures followed as soon as the carbocation was formed at a low enough temperature to stabilise it over the 15 minutes required for reaction with the incoming meta-chloroperoxybenzoic acid solution, but not so low that the peroxyacid was unreactive and partially insoluble. The rate of neutralisation then proceeded such that the temperature did not rise too greatly – which would otherwise raise the reactivity of any possible unreacted strong fluoroboric acid present (from the acid dissolving in any trace of water) before neutralisation was complete – but quickly enough that any acid formed could be quenched – at a low temperature where a short time may not see a reaction occur, but a longer time may at that temperature. The reactant concentrations used were just greater than three times those of the first experiments with peroxybenzoic acid and 2-bromo-2-methylbutane.

The preparation of tertiary-butyl peroxybenzoate,
 $\text{C}_6\text{H}_5\text{CO}_3\text{C}(\text{CH}_3)_3$

Similarly, reaction of peroxybenzoic acid with tertiary-butyl carbocation using the most favourable conditions for the corresponding meta-chloroperoxybenzoate formed the corresponding peroxyester, tertiary-butyl peroxybenzoate in 20% yield (pale yellow oil) (crude yield, 30%). As described above, peroxybenzoic acid is not as stable as MCPBA and this probably accounts for the lower yield under the same reaction conditions. It is also very readily decomposed even in the presence of a trace of strong acid⁷¹. (See Chapter 1, 1.4.2 "Acid-Catalysed Decomposition".)

Unknowns including peroxides formed during the preparation of the
peroxyesters

The preparations also yielded white by-products and the ^1H and ^{13}C NMR spectra of the solids (see Chapter 3, "Experimental") revealed a

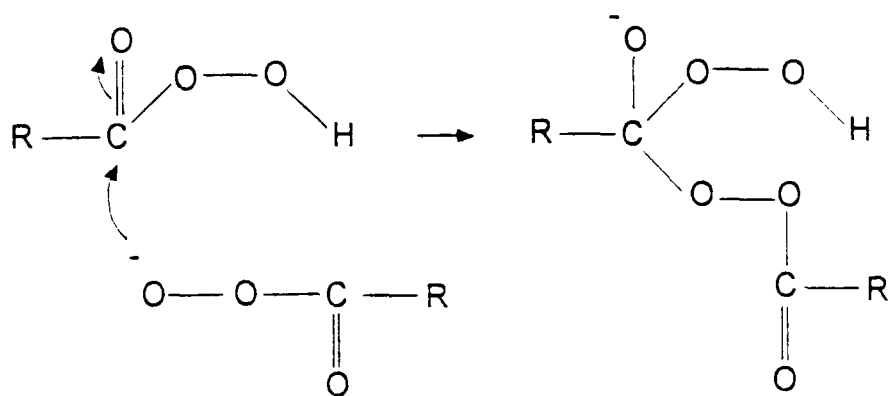
possibility of two compounds for each, as observation of the proton peak integrals suggested that the singlet at 1.79ppm was not related to the aromatic peaks (spectra P and Q). The ^{13}C NMR suggested aromatic peaks arising from $\text{C}_6\text{H}_5\text{CO}_3^-$ and $3\text{-Cl-C}_6\text{H}_4\text{CO}_3^-$ (spectra N and O, respectively).

In each case, the aromatic carbon ^{13}C NMR spectrum was clearly different to those of the corresponding peroxyacid, peroxyester and carboxylic acid, although all had very similar shift values. (The latter three have spectra as detailed in Chapter 1, 1.5.3 "Physical Properties of Organic Peroxides, Spectroscopic Data".) In addition, the carboxylic acids do not move on tlc in CH_2Cl_2 , 2% or 10% ethyl acetate in hexane. It was then thought that perhaps the aromatic compounds were the carboxylic esters. However, using the ^{13}C NMR database, an estimated spectrum was given for the ester:

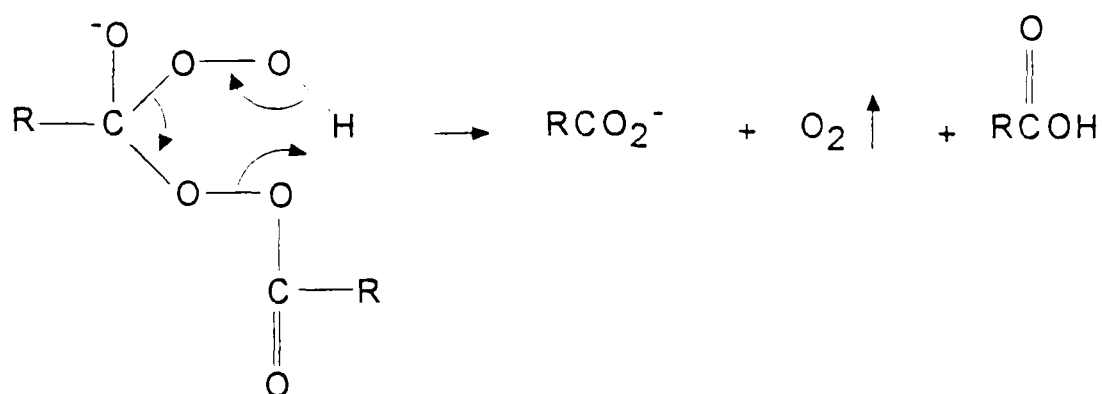
28.1(± 0.2), 81.8(± 0.6) (C-O), 129.7(± 1.2), 130.4(± 1.1), 131.9(± 2.7), 132.3(± 1.6), 132.9(± 0.6) or 127.9(± 0.1), 134.7(± 0.7), 162.8(± 0.0) (C=O) ppm.

The corresponding spectrum for tertiary-butyl benzoate is given by Pelletier¹³⁹. It was seen that the unknowns did not have a C-O peak at about 81ppm, so the ester idea was dismissed. This was in addition to the fact that they were peroxide positive unlike the carboxylic acids. Thus, their anhydrides were also dismissed. (See Chapter 1, 1.5.3 "Physical Properties of Organic Peroxides, Spectroscopic Data" where they are compared.)

Another possibility considered was the acyl peroxide, of which the ^1H and ^{13}C NMR spectra of the chloro compound are as yet unknown. In a recent article by James and Mackirdy^{23a}, it was mentioned that Swern originally reported how in certain pH regions where free peroxyacid is present, the acyl peroxide is formed, though in no more than 5% yield. In the mechanism proposed for decomposition, an intermediate is formed by the attack of the nucleophilic peroxyacid anion on the electrophilic carbonyl carbon of the unionized peroxyacid.

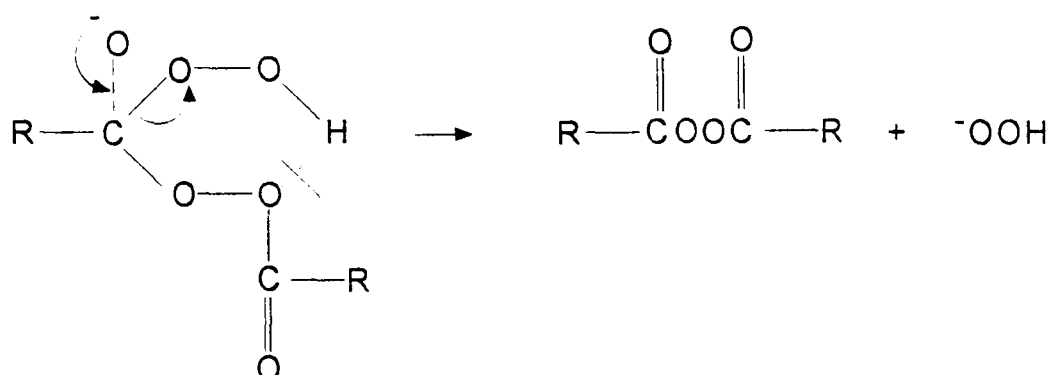


The intermediate decomposes immediately to the parent carboxylic acid and oxygen via a cyclic intramolecularly hydrogen-bonded form.



Thus, the presence of acidic water could very probably be the cause of the lower than expected crude product mass. (See Chapter 1, 1.4.2 "Acid-Catalysed Decomposition".)

The small quantities of aroyl peroxide may arise by the alternative breakdown of the intermediate:



Running a tlc of benzoyl peroxide, tertiary-butyl peroxybenzoate reaction mixture and the corresponding unknown peroxide, there appeared the slightest trace of benzoyl peroxide (the singlet barely being seen in ^1H NMR as well as the ^{13}C peaks) in the reaction mixture at a slightly greater R_f value than the unknown peroxide (0.5, compared with 0.3, in 10% ethyl acetate in hexane). On spraying with the peroxide spray, the unknown peroxide immediately became a deep red, whereas the benzoyl peroxide turned a pale pink. Although it is very well known that concentration can cause a variation in chemical shifts from sample to sample for ^{13}C and ^1H NMR¹²⁶, and the chemical shifts in the proton NMR especially are very similar for peroxybenzoic acid, benzoic acid, benzoyl peroxide, tertiary-butyl peroxybenzoate and the unknown peroxide - varying no more than 0.2ppm with the same splitting patterns - by careful examination of the NMR data, the unknown peroxide could be assigned to specific peaks, thus differentiating it from benzoyl peroxide. The acquired ^{13}C NMR data were extremely helpful, for although most of the

aromatic peaks were again very close in value, by singling out one of the two quaternary carbon peaks together with the compound's corresponding carbonyl carbon peak, they were sufficiently different that it was possible to determine the components in a reaction mixture by NMR.

The process was easier with the chlorinated compounds. The presence of the chlorine is presumably the cause for the very different ^{13}C spectral patterns seen for the meta-chloroperoxybenzoic acid, meta-chlorobenzoic acid, tertiary-butyl meta-chloroperoxybenzoate, and the corresponding unknown peroxide, where one of the two quaternary carbons shifts dramatically from compound to compound.

In the experiments to prepare the tertiary-butyl meta-chloroperoxybenzoate, tlcs and NMRs showed no aromatic compounds other than those of the chlorinated peroxyacid, carboxylic acid, peroxyester and unknown. Thus, there was no trace of the acyl peroxide as previously for the case with peroxybenzoic acid. (There are no spectral data in the literature for the chloro compound). This can be explained by the higher stability of the MCPBA compared with the parent peroxyacid which more readily reverts to the acyl peroxide, the mechanism as shown above.

The other possible unknown compound remained with the white solid peroxide (assumed, because of its aromatic structure, to have a greater RMM) even after 4 hours at 25°C , under a reduced pressure of 1mmHg. This implied a high boiling point compound, although it may have been locked in the other unknown's structure, or in fact been part of its structure. Several compounds containing a methyl group were considered to try and explain the ^{13}C peak around 21ppm.

Table (M) - ^1H NMR/ppm

s=singlet; []=integrals

(a) (b) $(\text{CH}_3)_2\text{C}=\text{CH}_2$ (2-methylpropene, bp=-6.5°C ⁶⁸)	(a)1.73(s);(b)4.60(s) ¹³⁷ (CDCl_3 ,60MHz)
(a) $(\text{CH}_3)_2\text{C}=\text{C}(\text{CH}_3)_2$ (2,3-dimethylbut-2-ene, bp=73°C ¹³⁶)	(a)1.62(s) ¹³⁷ (CDCl_3 ,60MHz)
(a) $(\text{CH}_3)_3\text{CBr}$ (tertiary-butyl bromide,bp=73°C ⁶⁸)	(a)1.79 (CDCl_3 ,270MHz)
(a) $(\text{CH}_3)_3\text{CCl}$ (tertiary-butyl chloride,bp=51°C ⁶⁸)	(a)1.61 ¹³⁷ (CCl_4 ,60MHz)
(a) $(\text{CH}_3)_2\text{CBr}_2$ (2,2-dibromopropane, bp=114°C ¹¹)	(a)-2.55 ¹¹ (CDCl_3)
$\begin{array}{c} \text{Br} \quad \text{Br} \\ \backslash \quad / \\ \text{C}=\text{C} \\ / \quad \backslash \text{(a)} \\ \text{H}_2\text{C} \quad \text{CH}_3 \\ \text{(cis-2,3-dibromo-} \\ \text{but-2-ene)} \end{array}$	(a)2.32 ¹³⁷ (CCl_4 ,60MHz)
$\begin{array}{c} \text{CH}_3 \quad \text{Br} \\ \backslash \quad / \\ \text{C}=\text{C} \\ / \quad \backslash \text{(a)} \\ \text{Br} \quad \text{CH}_3 \\ \text{(trans-2,3-dibromo-} \\ \text{but-2-ene)} \end{array}$	(a)2.40 ¹³⁷ (CCl_4 ,60MHz)
(a) (b) $(\text{CH}_3)_3\text{COH}$ (tertiary-butanol, bp=83°C ⁶⁸)	(a)1.25[9H]; (b)3.42(broad)[1H] (CDCl_3 ,270MHz)
(a) (b) $(\text{CH}_3)_3\text{COOH}$ (tertiary-butyl hydroperoxide, bp=33-34°C/17mmHg ⁴² mp=4.0-4.5°C ⁴²)	(a)1.10[9H]; (b)9.38(broad)[1H] (CDCl_3 ,270MHz)
(a) $(\text{CH}_3)_3\text{COOC}(\text{CH}_3)_3$ (tertiary-butyl peroxide, bp=110°C)	(a)1.22 (CDCl_3 ,270MHz)

Table (N) - ^{13}C NMR/ppm

(a) (b) (CH_3) ₃ CBr (tertiary-butyl bromide)	(a)36.41;(b)62.28(sqc) (CDCl_3 ,270MHz)
(a) $\begin{array}{c} \text{H}_3\text{C} \quad \text{Br} \\ \diagdown \quad / \\ \text{(b)C=C} \\ / \quad \diagdown \\ \text{Br} \quad \text{CH}_3 \end{array}$ (trans-2,3-dibromobut-2-ene)	(a)28.61;115.76 ¹⁴³ (CDCl_3 ,60MHz)
(a) (b) (CH_3) ₃ COH (tertiary-butanol)	(a)31.22;(b)69.00(sqc) (CDCl_3 ,270MHz)
(a) (b) (CH_3) ₃ COOH (tertiary-butyl hydroperoxide)	(a)25.49;(b)80.66(sqc) (CDCl_3 ,270MHz)
(a) (b) (CH_3) ₃ COOC(CH_3) ₃ (tertiary-butyl peroxide)	(a)26.59;(b)78.29(sqc) (CDCl_3 ,270MHz)

sqc=small quaternary carbon

Table (O) - Tlc: R_f values

Peroxide	10% ethyl acetate in hexane
(CH_3) ₃ COOH	≈0.3
(CH_3) ₃ COOC(CH_3) ₃	-(see note a)

Neither peroxide was sensitive to UV light.

a) Tertiary-butyl peroxide was not sensitive to the peroxide spray, probably due to symmetry (similarly, benzoyl peroxide is barely responsive to the peroxide spray, though it is UV light sensitive).

Tertiary-butyl- and methyl- tetrafluoroborate salts were considered, (CH_3)₃C⁺BF₄⁻ and CH₃⁺BF₄⁻, respectively, but it does not seem likely that either would have survived the neutralisation, been soluble in CH₂Cl₂, or have been stable at 25°C, as well as under a reduced pressure of 1mmHg for four hours at 25°C. The most stable of the simple alkyl carbocations is (CH_3)₃C⁺, and for example, the cation is stable at room temperature only when in "super acid"^{62a}. (See Chapter 1, 1.3

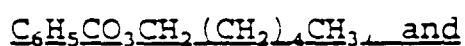
"Carbocation and Organic Radical Intermediates".) The ^{13}C NMR has been recorded at -20°C in "super acid"⁵⁷.

The salt, tertiary-butyl hypobromite $(\text{CH}_3)_3\text{CO}^-\text{Br}^+$, is destroyed by 5% sodium hydrogen carbonate solution^{144,19b} and so would not have survived the neutralisation employing a saturated solution.

Comparing the spectra of the two aliphatic and two aromatic unknowns with those of above, and those discussed in 1.5.3 "Physical Properties of Organic Peroxides, Spectroscopic Data", their identification could still not be identified.

With the successful formation of the two tertiary-butyl peroxyesters as described above, an attempt was made to prepare the corresponding primary peroxyesters n-hexyl peroxybenzoate and n-hexyl-3-chloroperoxybenzoate. Concentrations were similar and the time of reaction kept to 15 minutes for reasons as discussed in detail previously.

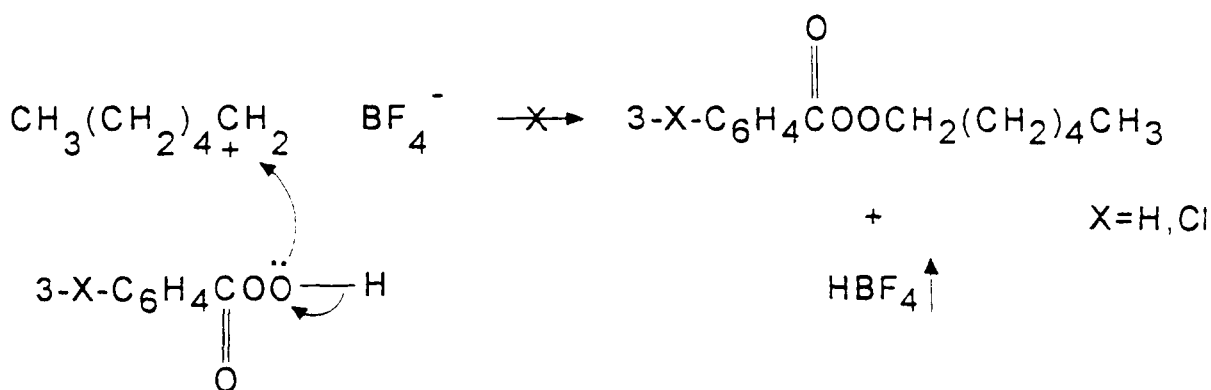
The attempted preparation of n-hexyl peroxybenzoate,



n-hexyl 3-chloroperoxybenzoate,

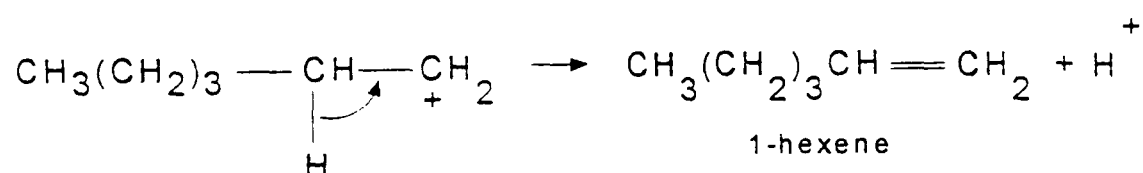
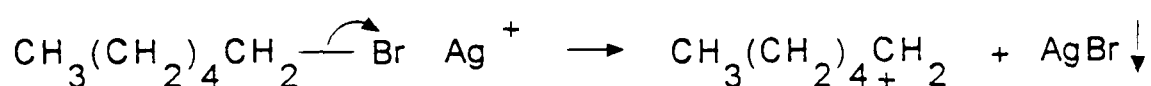


(i) By addition of the peroxyacid to a mixture of the silver salt and alkyl bromide in solution.



Initially, reactions involved the addition order that had given 20% and 25% yields of the tertiary-butyl peroxybenzoate and 3-chloroperoxybenzoate, respectively: the silver tetrafluoroborate and alkyl bromide were kept stirred and maintained at -1°C as the peroxyacid solution was added over 15 minutes before quenching. However, there was

no sign of peroxyester formation in either case. Initial indication would have been a relatively fast running peroxide-positive spot at about $R_f=0.6$ in 10% ethyl acetate in hexane. A C-OO peak at about 84ppm in $CDCl_3$ or CD_2Cl_2 , together with a change in the chemical shift for the protons of the new $-CH_2-OO-$ group (compared with the original $-CH_2Br$ group) would have indicated peroxyester formation. Instead there was only unreacted peroxyacid and normal carboxylic acid, and no unreacted alkyl bromide but green silver bromide had formed. After neutralisation and drying of the dichloromethane (bp= $40.2^\circ C^{68}$) solutions of the reaction mixtures there was incomplete evaporation, 1-hexene (bp= $64^\circ C^{68}$) was seen in the NMR spectra. This implied that at $-1^\circ C$, the primary carbocation was readily eliminating a proton as the temperature was too high for it to be stable enough to react with the peroxyacid.



Carrying out the reaction at $-12^\circ C$ resulted in no peroxyester formation either, instead only unreacted peroxyacid, carboxylic acid and green silver bromide precipitate again. This can be compared with the earlier and similar reaction involving the tertiary carbocation formation at $-12^\circ C$ of tertiary-butyl bromide, 3-chloroperoxybenzoic acid and the silver salt, which yielded only very little of the corresponding peroxyester, whereas reaction at $-1^\circ C$ yielded more (and more than at $-4^\circ C$).

At both $-12^\circ C$ and $-1^\circ C$ the tertiary carbocation is stable, but at the lower temperature the peroxyacid is at too low a temperature to be reactive towards it. In summary therefore, it is probable that in the case of the intermediate primary carbocation, $-1^\circ C$ is not low enough a temperature to stabilise it for long enough for the peroxyacid to react with it (although reaction did occur in the tertiary case). Instead, it eliminates a proton to form 1-hexene. Whereas $-12^\circ C$ may be a satisfactory temperature for the primary carbocation stability, it is too low for the peroxyacid to be reactive towards it. Thus, with the subsequent work-up,

the latter case gave rise to the same products seen in the experiment at -1°C , with the formation of 1-hexene as the temperature rises during neutralisation.

(ii) By addition of the silver salt to a solution of peroxyacid and alkyl bromide maintained at -1°C .

Rather than trying to prepare the primary carbocation first (although this method produced the higher yields of tertiary peroxyester), it was thought that perhaps stirring a solution of peroxyacid and alkyl bromide at -1°C (stable together, as they did not react) before adding the silver salt (the primary carbocation being available for potential immediate reaction with the peroxyacid) might prove fruitful. Previously, the tertiary case had produced a little peroxyester, but the primary case resulted only in peroxyacid and carboxylic acid (silver bromide was also seen).

(iii) By addition of alkyl bromide to a slurry of silver salt in a solution of peroxyacid maintained at -1°C .

Another order of reactant addition was attempted, again where the primary carbocation would form at -1°C and react immediately with a continuously stirred solution of peroxyacid so that it was not left to stand in the reaction flask. Again, peroxyacid and carboxylic acid resulted and the formation of silver bromide was seen. The tertiary case had led to very little peroxyester under these conditions.

(iv) By addition of a solution of peroxyacid and primary bromide to a slurry of silver salt in dichloromethane, with the temperature maintained at -1°C .

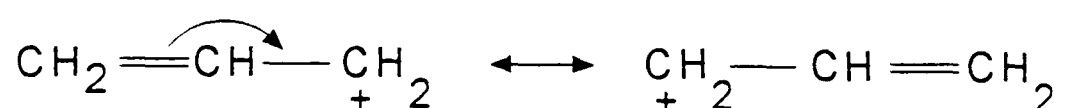
This also failed to form any of the primary peroxyester. With hindsight, it was perhaps obvious that the very low incoming concentrations of both peroxyacid and alkyl bromide would produce

virtually no chance of either finding the other in solution for reaction, before the highly reactive primary carbocation eliminated a proton to form 1-hexene.

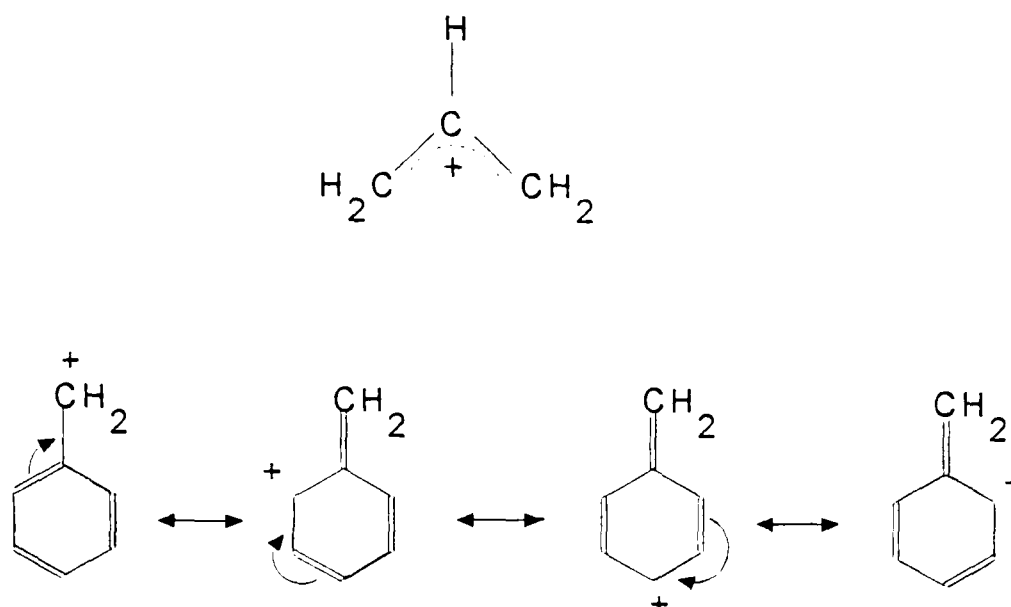
The relatively low resultant recovery masses in the primary bromide cases can again be attributed to some loss of peroxyacid, due perhaps to acidic decomposition or hydrolysis to carboxylic acid and subsequent reaction with saturated sodium bicarbonate solution. The peroxyacid itself may also have reacted. The loss of the high boiling 1-bromohexane (bp=154°-158°C⁶⁸) via the carbocation eliminating a proton to yield the relatively volatile 1-hexene (bp⁶⁸=64°C) as shown above, also contributed to the low recovery masses.

The preparation of prop-2-enyl meta-chloroperoxybenzoate and
benzyl meta-chloroperoxybenzoate

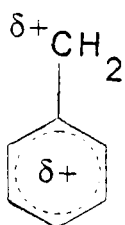
Although attempts failed to sufficiently stabilise the n-hexyl carbocation for its reaction with peroxybenzoic acid and meta-chloroperoxybenzoic acid, reactions were attempted with more stable primary allylic and benzylic carbocations (again, via their bromides). (These peroxyesters are unknown in the literature). By virtue of their various canonical forms¹⁹, the positive charge can be distributed over more than one carbon atom (involving π orbitals), making the resultant carbocation more stable than simple alkyl carbocations where there is a concentration of charge. (See Chapter 1, 1.3.1.1 "Structure and Stability of Carbocations".)



Resonance hybrid structure:



Resonance hybrid structure:



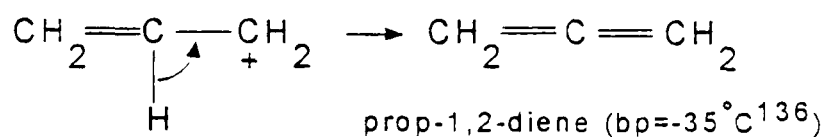
The greater the number of significant structures that can be written and the more nearly equal they are, the greater the stability of the carbocation formed. It could therefore be expected that the likelihood of the allylic and benzylic bromides yielding primary peroxyesters would be greater than that of 1-bromohexane under the conditions employed.

By addition of a solution of peroxyacid and primary bromide to a slurry of silver salt in dichloromethane.

In both attempts to prepare the primary peroxyesters, the experimental procedure involved dropwise addition of a solution comprising 3-chloroperoxybenzoic acid and the corresponding bromide to a slurry of silver tetrafluoroborate in dry dichloromethane. Time of reaction was again kept to 15 minutes, dry nitrogen gas used and the concentration of reactants was as for the tertiary-butyl peroxyesters. Although there was a low concentration of peroxyacid and carbocation in contact with each other, peroxyester formation was seen.

Reaction with allyl bromide

The peroxyacid and bromide solution at 22°C was initially added dropwise to the silver salt slurry at -8°C. The reaction mixture showed signs of peroxyester on tlc, but ¹H NMR indicated essentially the presence of unreacted peroxyacid and some carboxylic acid. Repeating the experiment but with the silver salt slurry at 5°C, gave rise to a 40% crude yield of quite a dark yellow oil. From the 60MHz ¹H NMR integration measurements, the crude product consisted of no more than half of the peroxyester. Unlike tertiary peroxyesters, primary peroxyesters often very readily decompose to carboxylic acid and carbonyl compounds as discussed in Chapter 1, 1.4 "Principal Reactions of Peroxyesters, Hydroperoxides, Peroxyacids and Acyl Peroxides". This is a possible explanation regarding the seemingly low yield, together with some of the allylic carbocation eliminating a proton to form the volatile prop-1,2-diene.

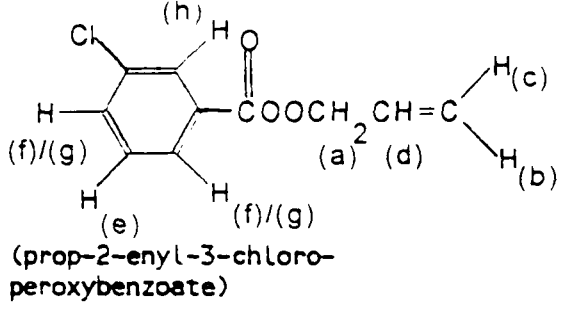
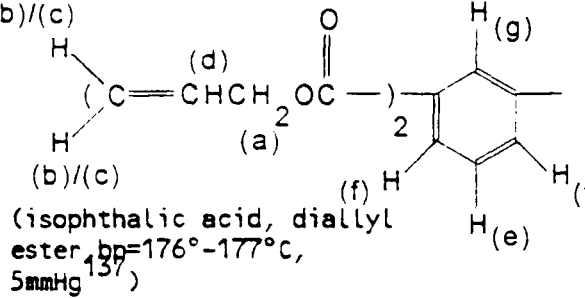
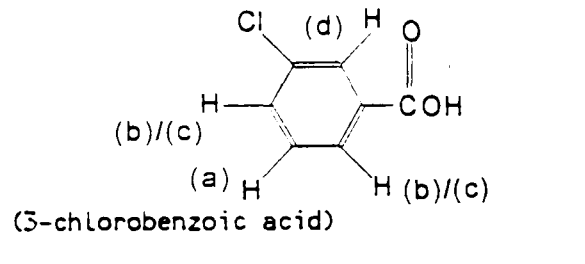


The 270MHz ¹H NMR of the peroxyacid, normal carboxylic acid and the tertiary-butyl peroxyester, and the 60MHz ¹H NMR of meta-chlorobenzoic acid, led to the peak assignment (seen below) for the allylic peroxyester.

Sadtler's¹³⁷ spectrum 2904 of isophthalic acid, diallyl ester, had a virtually identical proton NMR spectrum in the aliphatic allyl region to that of the newly prepared peroxyester. Comparing the peak assignments of allyl bromide and the prepared allyl peroxyester, it becomes very obvious that Sadtler's assignment for peaks (b) and (c) of the reference spectrum above, is not wholly correct. The peak at 5.31ppm in fact incorporates approximately half of each doublet for (b) and (c). The peak at about 5.4ppm is one of the doublets for (b), and correctly, the peak at 5.42ppm belongs to proton type (c) being one of its doublets. As seen for the allyl peroxyester, the splitting for one of the doublets (b)/(c) is greater than that for the other.

The new compound can be distinguished from a carboxylic ester therefore, by observation of the C-OO peak in the ¹³C spectrum and being peroxide positive, as the proton NMR spectra are similar.

Table (P) - ^1H NMR/ppm (CDCl_3)

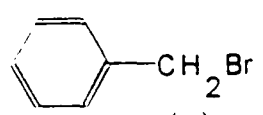
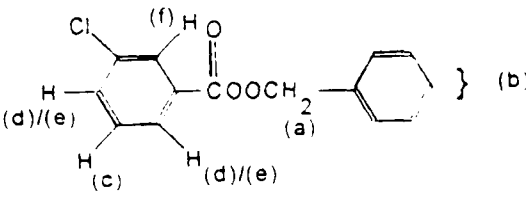
<p>H(c) \ (a) $\text{C}=\text{CHCH}_2\text{Br}$ / (d) H(b) (3-bromo-prop-1-ene, bp=70-71°C)</p>	<p>(a) 3.75; 3.85(d;ns)[2H] (b)/(c) 4.95; 5.05(d;dfs)[1H] (b)/(c) 5.10; 5.30(d;dfs)[1H] (d) 5.60-6.25(m;fs)[1H] (in accordance with the literature¹³⁷) (CDCl_3, 60MHz)</p>
 <p>(prop-2-enyl-3-chloro- peroxybenzoate)</p>	<p>(a) 4.65; 4.75(d;fs)[2H] (b)/(c) 5.05(d;fs) (b)/(c) 5.25; 5.35(d;fs) ((b)+(c) [2H]) (d) 5.50-6.20(m;fs)[1H] 7.30=t for (e) and d for (f)/(g)[2H] 7.70=d for (f)/(g)[1H] 7.85=s for (h)[1H] (CDCl_3, 60MHz)</p>
 <p>(isophthalic acid, diallyl ester, bp=176°-177°C, 5mmHg¹³⁷)</p>	<p>(a) 4.88(d;ns); (b) 5.31(s;fs) (c) 5.42(s;fs); (d) 6.01(s); (e) 7.55(s); (f) 8.25(s); (g) 8.78(s) (CDCl_3, 60MHz¹³⁷)</p>
 <p>(3-chlorobenzoic acid)</p>	<p>7.35=t for (a); and one of d peaks for (b)/(c); 7.75=one of the other d peaks for (b)/ (c); and s for (d); 7.90=other d peak for (b)/(c) (CDCl_3, 60MHz)</p>

s=singlet; d=doublet; t=triplet; m=multiplet; ns=no splitting; dfs=doublet fine splitting; tfs=triplet fine splitting; [] integrals

Reaction with benzyl bromide

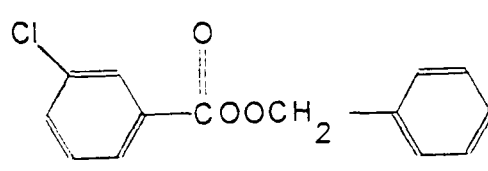
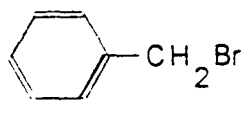
Similarly, preparation of the benzylic peroxyester was attempted, via the even more stable benzylic carbocation. Reaction was carried out using the same method as for allyl bromide, with the silver tetrafluoroborate at 6°C and gave an 8.5% crude yield of a dark brown-yellow viscous oil. The actual mass of the peroxyester gave a 2% yield of a slightly yellow tinted oil. Although there was apparently too little an amount of the peroxyester for a ^{13}C NMR spectrum, its ^1H NMR, as well as its tlc values, were recorded and compared with that of α -bromotoluene.

Table (q) - ^1H NMR/ppm

<p>(b) {  }</p> <p>(bp⁶⁸=201°C)</p>	<p>(a)-4.42(s)[2H] (b)-7.25(s, with broad base)[5H] (CDCl₃, 90MHz)</p>
<p> (b)</p>	<p>(a)5.36(s)[2H]; (b)7.36(s, with broad base); (c)7.43; 7.39;7.36(t) ((b)+(c)[6H]) (d)/(e)7.53;7.50(d)[1H] (d)/(e)7.97;7.94(d)[1H] (f)8.04(s)[1H] (CDCl₃, 90MHz)</p>

s=singlet;d=doublet;t=triplet;[] integrals

Table (R) - Tlc:R_f values

Compound	10% ethyl acetate in hexane	dichloromethane
	<p>≈0.7^a</p>	<p>≈0.9^a</p>
	<p>≈0.85^b</p>	<p>≈0.9^b</p>

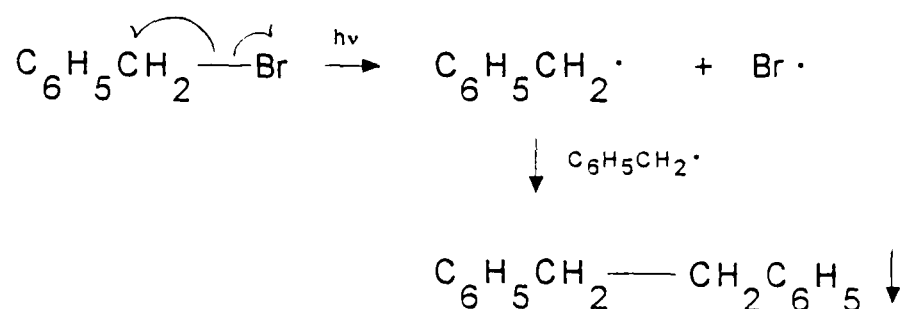
^aThe peroxyester was UV light and peroxide spray-sensitive

^bBenzyl bromide was UV light-sensitive

The tlc values of the peroxyester were similar to those of the other peroxyesters prepared. (See Chapter 3, Experimental.)

Comparing proton (a) of the allyl bromide and its corresponding peroxyester, an approximately 1ppm downfield shift was seen for the peroxyester. This was also the case for the benzylic compound.

The very low recovery mass for the benzylic case can be attributed to the brown tar that was filtered off after neutralisation. Rather than the formation of a volatile diene as in the allylic case, a reaction forming an insoluble product as shown below may have occurred.



(Average bond enthalpy of C-Br⁶⁸=276kJmol⁻¹)

It has been shown that allylic and benzylic primary peroxyesters can be made, even with reactants in very low concentration. With their stability, it is probable that by carrying out the reactions in the same way that the highest yields of tertiary peroxyesters were formed, that is, by adding the peroxyacid solution to a "cold" solution of carbocations (once a suitable temperature had been established), satisfactory yields of these peroxyesters could also be had.

Conclusion

The various experiments have shown the effect of light, temperature, concentration, time of reaction and order of reactant addition upon the type and amount of products.

In the case of the tertiary-butyl carbocation, maintaining a temperature of -1°C ensured its stability for 15 minutes and allowed the reaction with the peroxyacid, to form the corresponding peroxyester.

For the primary n-hexyl carbocation, -1°C was too high causing the elimination of a proton to give 1-hexene. Lower temperatures rendered the

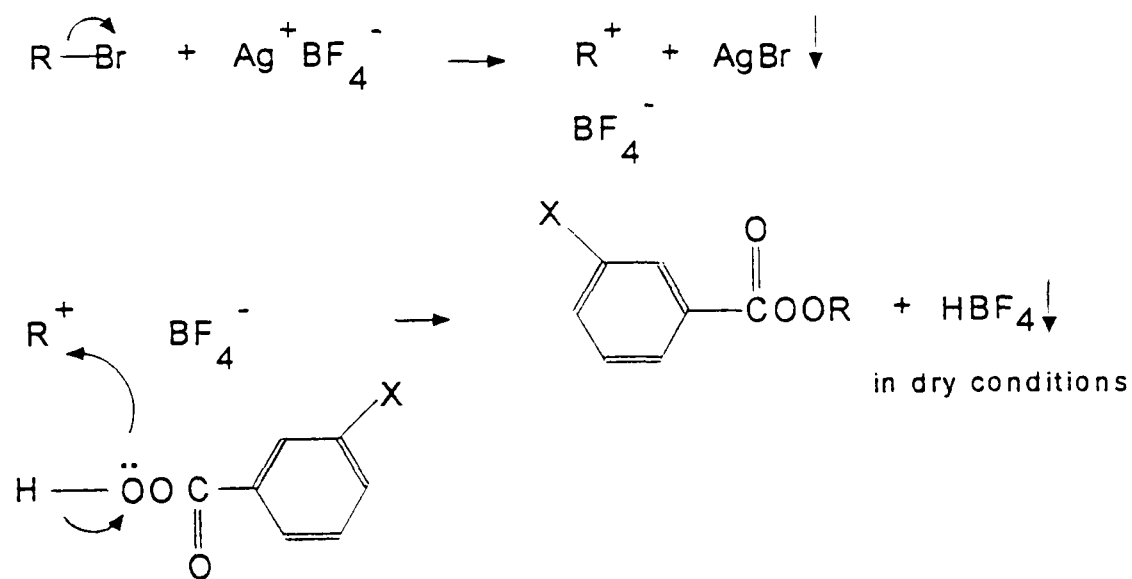
peroxyacid unreactive and the reactants in lower concentration, as more solvent was added because of the solubility decreases.

The allylic and benzylic primary chloroperoxyesters were prepared with a slurry of silver salt in dichloromethane at -8°C ; 5°C and 6°C , respectively. It seems most probable that a temperature of around -1°C would have been stable enough for the allylic and benzylic carbocations to react with the incoming peroxyacid over 15 minutes as for the tertiary case.

For all the reactions, as long as the reaction vessel was not in direct sunlight, there did not appear to be any substantial amount of radical induced decomposition. If all the glassware had been completely devoid of any light entering, then there would have also been the exclusion of any decomposition of the peroxides by radical routes, which may have led for example to some of the loss of carboxylic acid (via peroxyacid) in the work up. This may have largely contributed to lower yields than expected.

Also, as long as the reactant concentration was high enough and the temperature kept low enough, the carbocation could react with the peroxyacid at the expense of elimination and possible ionic polymerisation. Dry conditions also prevented the formation of aqueous acid which could otherwise decompose the peroxyacid or peroxyester.

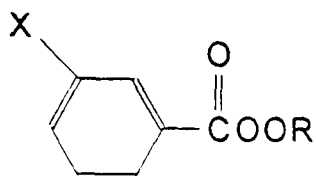
Summary of the successful reactions



Where R=(a) $(\text{CH}_3)_3\text{C}-$; (b) $(\text{CH}_3)_2(\text{CH}_2\text{CH}_3)\text{C}-$; (c) $\text{CH}_2=\text{CHCH}_2-$; (d) $\text{C}_6\text{H}_5\text{CH}_2-$
 X=H when R is (a) and (b)

X=Cl when R is (a), (c) and (d)

All of the successful reactions occurred out of direct sunlight, in a dry nitrogen atmosphere with continuous stirring and in a total volume of 25ml dry dichloromethane. The reactions were carried out for 15 minutes and quenched with an equal volume of saturated sodium bicarbonate solution, and except for the reaction with 2-bromo-2-methylbutane, such that the temperature did not rise higher than 10°C (the latter maintained at 22°C). All of the reactions used approximately molar equivalents of peroxyacid and bromide to a 1.2 molar equivalent of silver tetrafluoroborate.



R	X	Mass of reactants in 25ml CH ₂ Cl ₂ for 15 mins; temp of reaction	Crude Yield %	Actual Yield%
(CH ₃) ₃ C-	H	tertiary-butyl bromide, 0.79g(5.77x10 ⁻³ moles); PBA, 0.80g(5.79x10 ⁻³ moles); silver salt, 1.35g(6.93x10 ⁻³ moles); -1°C	30	20 (pale yellow oil)
(CH ₃) ₂ (CH ₂ CH ₃)C-	H	2-bromo-2-methylbutane, 0.24g(1.59x10 ⁻³ moles); PBA, 0.25g(1.81x10 ⁻³ moles); silver salt, 0.38g(1.95x10 ⁻³ moles); 22°C	3	see crude yield
(CH ₃) ₃ C-	Cl	tertiary-butyl bromide, 0.79g(5.77x10 ⁻³ moles); MCPBA, 1.00g(5.79x10 ⁻³ moles); silver salt, 1.35g(6.93x10 ⁻³ moles); -1°C	36	25 (pale yellow oil)
CH ₂ =CHCH ₂ -	Cl	allyl bromide, 0.81g(6.70x10 ⁻³ moles); MCPBA, 1.13g(6.55x10 ⁻³ moles); silver salt, 1.52g(7.86x10 ⁻³ moles); 5°C	40	6 (slightly yellow tinted oil)
C ₆ H ₅ CH ₂ -	Cl	benzyl bromide, 0.99g(5.79x10 ⁻³ moles); MCPBA, 1.07g(6.20x10 ⁻³ moles); silver salt, 1.35g(6.93x10 ⁻³ moles); 6°C	8.5	2 (slightly yellow tinted oil)

Order of reactant addition

When $R=(CH_3)_3C-$, the silver salt was added to a solution of the bromide (maintaining a temperature of $-2^\circ C$), then a solution of the peroxyacid was added.

When $R=(CH_3)_2(CH_2CH_3)C-$, the silver salt was added to a solution of the peroxyacid and bromide.

When $R=CH_2=CHCH_2-$ and $C_6H_5CH_2C-$, a solution of the peroxyacid and bromide were added to a slurry of silver salt.

Future Work

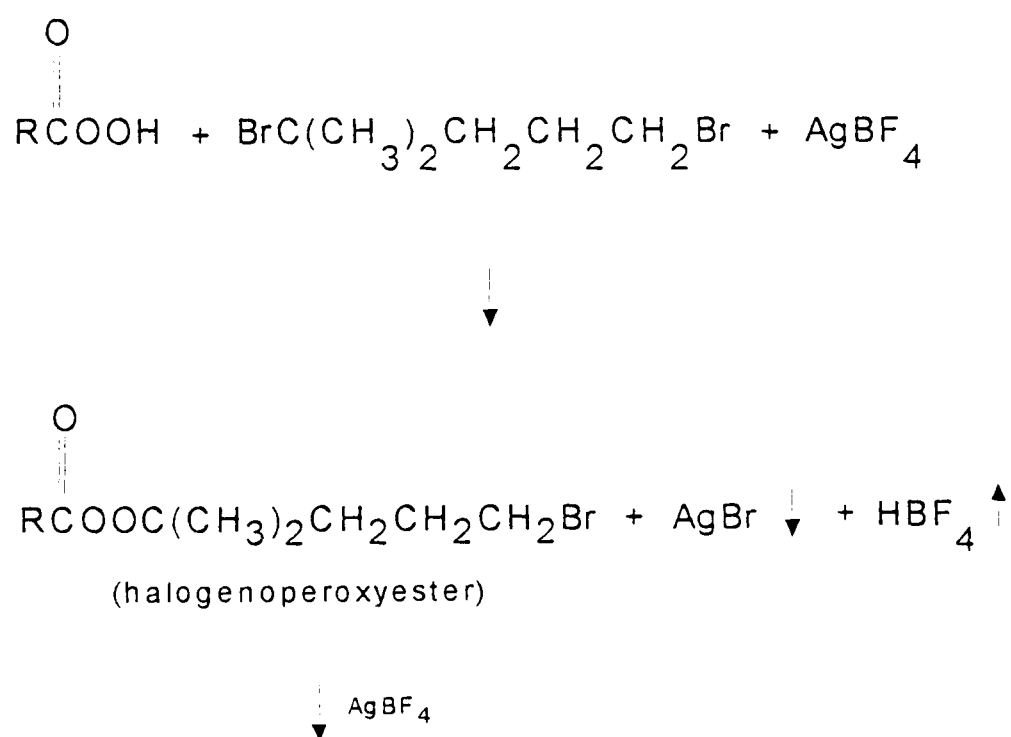
Most methods of peroxyester preparation described in the literature involve the acylation of hydroperoxides under alkaline conditions. This poses a problem in cases of primary and secondary peroxyesters which are sensitive to base as described previously (see Chapter 1, 1.4.3 "Base-Catalysed Decomposition"), and so very few are known relative to the number of tertiary ones. An alternative route to peroxyester synthesis is thus required, utilising a milder and easier laboratory procedure. The use of silver tetrafluoroborate in the experiments of this thesis, has shown how the milder route has been successful in the preparation of tertiary and allylic peroxyesters in particular. There was also evidence of a benzylic peroxyester being formed. Further work controlling temperatures, concentrations, times of reaction and order of reactant additions, could utilise this new preparation via carbocations to include secondary peroxyester formation. Although no success has been found in attempts to prepare a normal primary peroxyester, use for example of a more polar solvent could perhaps lead to an improvement, as well as encouraging secondary formation. Total exclusion of water vapour may also see higher yields.

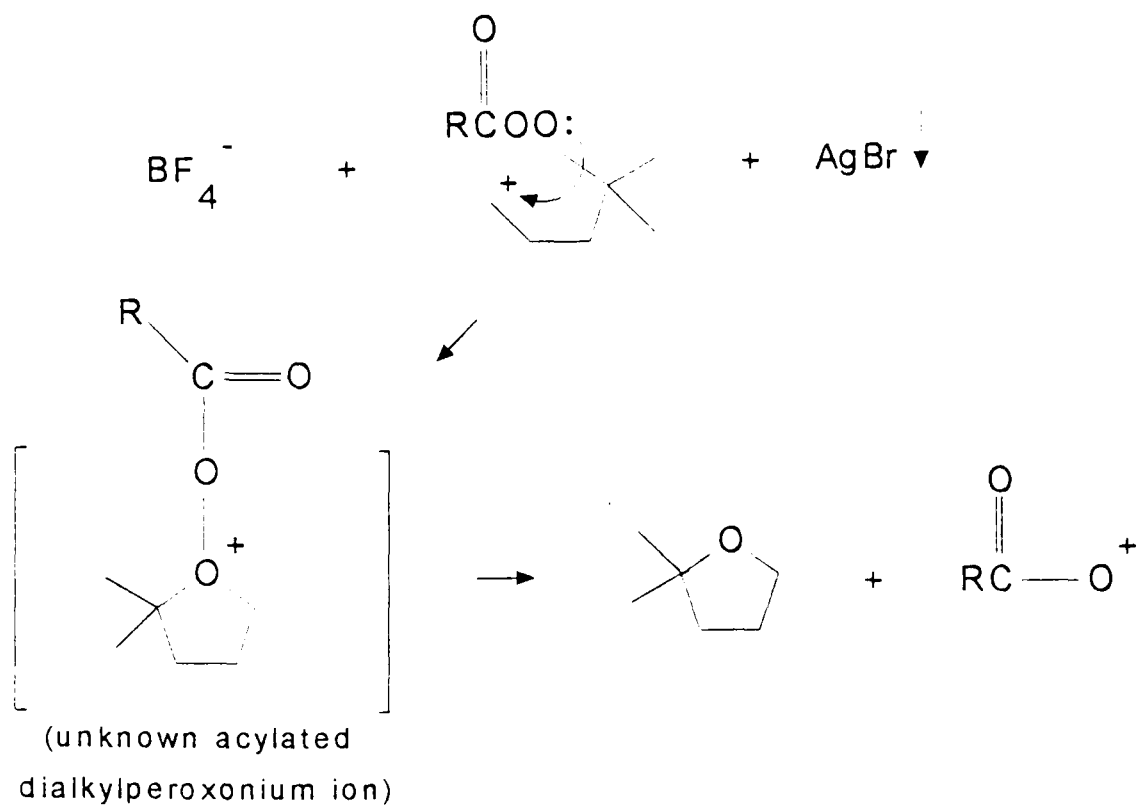
With the lack of availability of primary and secondary peroxyesters, corresponding hydroperoxides are at present very little known. However, by careful hydrolysis of peroxyesters via the new route, previously unknown hydroperoxides could be prepared, for example benzyl hydroperoxide ($C_6H_5CH_2OOH$). Most hydroperoxides are prepared from organic compounds by the action of molecular oxygen, ozone or hydrogen peroxide. Because of the problems arising from the limited number of products

formed, low yields or the potential detonability of solutions, the hydrolysis of peroxyesters⁷ offers a very favourable alternative. Hiatt⁴² may then be proved wrong when stating as a general rule, that if a particular hydroperoxide can be prepared easily by one method, it can be prepared by other methods, and vice versa with difficulty of preparation. He did not discuss the preparation by hydrolysis, shown above to have much potential.

There is little known about heterolytic oxygen-oxygen bond cleavage or formation. Chemical knowledge still suggests that most reactions involving oxygen proceed via oxygen radical species rather than ionic oxygen species. This is despite the fact that there are reactions that cannot be explained successfully by radical chemistry. As mentioned in Chapter 1, 1.4.6 "Postulated Perepoxy Intermediate", carbonyl oxides have long been recognised as intermediates in the ozonolysis of alkenes¹¹⁰, and recently work has involved postulating the existence of the structurally related but unstable, dioxygen ylides: perepoxy¹¹², protonated perepoxy¹¹⁶ and alkylated perepoxy¹¹⁵. Through examination of the end products of reactions postulating these intermediate structures, their possible existence is further substantiated.

On extending peroxyester formation to include halogenoperoxyesters containing a longer carbon chain, the as yet unknown acylated dialkylperoxonium ion may be prepared by intramolecular Lewis acid induced ring closure. As discussed previously, this has been seen for alkyl hydroperoxy bromides^{116a}, for example on use of silver trifluoroacetate (AgTFA) to yield cyclic ethers. (See Chapter 1, 1.4.6 "Postulated Perepoxy and Peroxonium Ion Intermediates".) Similarly therefore, a positive oxygen species may also form by reacting silver tetrafluoroborate with a halogenoperoxyester.





(In the above ring-closure, it is the peroxy oxygen that attacks the positive carbon centre, whereas with a similar hydroperoxide, it is instead the α -oxygen. [See Chapter 1, 1.4.6 "Postulated Peroxide and Peroxonium Ion Intermediates".])

Thus, the work covered by the thesis could be extended so as to add further to the knowledge of heterolytic oxygen-oxygen chemistry, where positive oxygen exists. New ideas may be promoted, and perhaps offer solutions to reactions not explained successfully by radical oxygen chemistry. The new route to peroxyesters could be extended to prepare peroxyesters otherwise difficult to form, and by suitable modification of Milas and Surgenor's method of hydrolysing peroxyesters⁷, their corresponding hydroperoxides could be made.

CHAPTER 3 - EXPERIMENTAL

Unless otherwise stated, ^1H NMR and ^{13}C NMR spectra were recorded with a Jeol JNM-GX270 Fourier Transform NMR Spectrometer using CD_2Cl_2 or CDCl_3 as solvent, as indicated. IR spectra were measured using a Perkin-Elmer 1710 Infrared Fourier Transform Spectrometer. Mass spectra were obtained using a Jeol JMS-DX300 Mass Spectrometer incorporating the Jeol Disc System. As peroxides are relatively unstable, a low electron voltage (15eV) was used to ensure the molecular ion (M^+) was detected.

Thin layer chromatography was carried out on Merck aluminium sheets (5cm), precoated with aluminium oxide 60 F_{254} neutral (type E) of 0.2mm thickness. The peroxide spray¹⁴⁴ used was prepared fresh, and is the most sensitive test known for peroxides, detecting as low as 0.001%. Peroxides convert the colourless ferrous thiocyanate to red ferric thiocyanate. It was found that the symmetrical acyl peroxide benzoyl peroxide did not respond as well as the unsymmetrical peroxides.

Peroxide Spray

1g ferrous sulphate [$\text{Fe}(\text{II})\text{SO}_4 \cdot 7\text{H}_2\text{O}$] was dissolved in 5.6ml 18% (concentrated is 36%) hydrochloric acid and a little granular zinc was added. 0.56g sodium thiocyanate ($\text{NaSCN} \cdot 2\text{H}_2\text{O}$) was added and once the transient red colour had faded, 1.33g more $\text{NaSCN} \cdot 2\text{H}_2\text{O}$ was added. The colourless solution was ready for immediate use.

Preparation of peroxybenzoic acid^{39,40,125}



The method described is that by Braun³⁹, with modifications suggested by Kolthoff *et al.*⁴⁰, as well as of the present author. To a 100ml 2-necked, round-bottomed flask containing 0.56g sodium methoxide, 15ml cold CH_3OH were slowly added. The resultant milky solution was cooled to -10°C (ice-methanol bath¹⁴⁴) and the magnetic stirrer switched on. 10.3ml of 0.5M H_2SO_4 , 25ml CH_2Cl_2 and an ice-water mixture were also cooled.

To 2.27g purified benzoyl peroxide^a were added 15ml CHCl_3 and the solution cooled. Without delay and behind a plastic blast shield, the CHCl_3 solution was added dropwise to the CH_3OH solution at such a rate that the temperature was kept below 0°C (on a larger scale, it would probably be necessary to add ice to the reaction vessel). 13ml ice cold water were added immediately and the mixture transferred to a 100ml separatory funnel to which another 13ml ice water were added. The mixture was swirled, and on settling, the denser CHCl_3 ^b layer was removed (containing the methyl benzoate). Any emulsion was discarded. The aqueous layer was then extracted with $2 \times 5\text{ml}$ cold CH_2Cl_2 ^c to remove completely any CHCl_3 introduced in the first part of the procedure. 10.3ml cold 0.5M

H₂SO₄^d were then carefully added to the separatory funnel to liberate the C₆H₅CO₃H from the sodium salt. The peroxyacid could be seen starting to precipitate out of the aqueous layer. The aqueous layer was extracted with 3×5ml cold CH₂Cl₂^e and the CH₂Cl₂ layers combined, then carefully washed with 2×3ml water and dried with anhydrous MgSO₄^f. After filtering, the CH₂Cl₂ was removed under reduced pressure to yield white crystals of C₆H₅CO₃H. The peroxyacid was then used for further reactions, unpurified. It was refrigerated if not used immediately.

The crude yield of peroxybenzoic acid was about 50% (0.65g) and the ¹H and ¹³C NMR recorded. (See Chapter 1, 1.5.3 "Physical Properties of Organic Peroxides, Spectroscopic Data".) Kolthoff et al.⁴⁰, obtained a yield of 82-86%, whereas Braun³⁹ obtained a yield of 82.5-86%. Iodometric titration can be used for an actual yield (as for MCPBA)¹²⁵.

Peroxybenzoic acid has a melting point of 41.3°-42°C³³.

^a It is assumed that Braun³⁹ used purified benzoyl peroxide as he obtained high yields.

^b Often emulsions form during the extraction of aqueous solutions by organic solvents, making good separation very difficult if not impossible¹⁴⁴. CHCl₃ posed a problem with vigorous shaking, so gentle but thorough mixing was carried out.

^c Braun's method used carbon tetrachloride.

^d A slight amount of excess acid is known to decompose C₆H₅CO₃H⁷¹.

^e Due to the stability of C₆H₅CO₃H in benzene, Braun used benzene as solvent. It was avoided in this preparation because it is a known carcinogen.

^f Braun used anhydrous sodium sulphate.

Table (S) - Tlc:R_f values

Peroxyacid	10% ethyl acetate in hexane	CH ₂ Cl ₂
C ₆ H ₅ CO ₃ H	0	0

The peroxyacid was UV light- and peroxide spray- sensitive.

Purification of benzoyl peroxide¹²⁵



Moistened benzoyl peroxide was dissolved in the minimum amount of CHCl₃^a at room temperature, and precipitated out as twice the volume of CH₃OH was added. It should not be recrystallised from hot CHCl₃, as a serious explosion may result. Like all peroxides, benzoyl peroxide should be handled with care behind shatterproof screens, and horn or moulded polyethylene (NOT nickel) spatulas used. Benzoyl peroxide is very shock sensitive. 99.75% purity was obtained by this method.

The ^1H and ^{13}C NMR were recorded. (See Chapter 1, 1.5.3 "Physical Properties of Organic Peroxides, Spectroscopic Data".) Benzoyl peroxide melts with decomposition at 106°C .

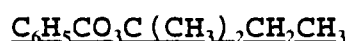
^a That is, until the obvious white colour changes to an opaque and wet looking solution (not clear and colourless which indicates too much CHCl_3 has been added, giving very little or no recovery).

Table (T) - Tlc: R_f values

Acyl Peroxide	10% ethyl acetate in hexane
$(\text{C}_6\text{H}_5\text{CO}_2)_2$	≈ 0.5

The acyl peroxide was UV light- and peroxide spray- sensitive (though not as strongly as unsymmetrical peroxides).

The attempted preparation of 1,1-dimethylpropyl peroxybenzoate



To a 100ml round-bottomed flask were added PBA (0.20g , 1.45×10^{-3} moles), dry dichloromethane (dried over 3\AA molecular sieves) (50ml) and 2-bromo-2-methylbutane (0.22g , 1.46×10^{-3} moles). At room temperature (22°C) and with continuous stirring (magnetic stirrer), silver tetrafluoroborate (0.34g , 1.75×10^{-3} moles) was added and the system purged with dry nitrogen for the 60 minutes of reaction. On addition of the silver salt, a fine, pale green-yellow precipitate formed and white fumes were seen (boron trifluoride and hydrogen fluoride which turned neutral water acidic). During the course of reaction, the reaction mixture became a green-grey colour.

After the 60 minutes, a saturated solution of sodium bicarbonate was added (10ml) and the organic layer became an opaque, light purple colour, and the aqueous layer an opaque white. A fine grey solid was seen at the bottom of the reaction vessel. The precipitate was filtered off using a sintered funnel and water pump. The organic layer was separated and the aqueous layer washed with dichloromethane ($2 \times 5\text{ml}$). The combined organic layers were dried over anhydrous magnesium sulphate and filtered to give a clear, light purple solution. Reducing down using a rotary evaporator (water bath at 20°C), gave a small amount of a viscous, dark brown liquid (crude mass 0.02g , percentage of reactant mass 2.5%).

The ^{13}C NMR (CDCl_3) showed many peaks at 5-45, 55-70, 120-135 and 145-155ppm within a complicated spectrum. A peak was also seen at 167.75ppm (carbonyl carbon of PBA).

The ^1H NMR (CDCl_3) was also a complicated spectrum, with peaks seen around 0.9, 1.3, 1.5 and 7.1-7.8ppm.

Preparation of 1,1-dimethylpropyl peroxybenzoate



To a 100ml round-bottomed flask covered with aluminium foil, were added PBA (0.25g, 1.81x10⁻³ moles), dry dichloromethane (dried over 3Å molecular sieves) (25ml) and 2-bromo-2-methylbutane (0.24g, 1.59x10⁻³ moles). At room temperature (22°C) and with continuous stirring (magnetic stirrer), silver tetrafluoroborate (0.38g, 1.95x10⁻³ moles) was added and the system purged with dry nitrogen for the 15 minutes of reaction. On addition of the silver salt, a fine, pale green-yellow precipitate formed and white fumes were seen (boron trifluoride and hydrogen fluoride which turned neutral water acidic).

After 15 minutes, a saturated solution of sodium bicarbonate was added (25ml) and after 1 minute, the precipitate was filtered off using a sintered funnel and water pump. The organic layer was separated and dried over anhydrous magnesium sulphate, filtered and reduced down using a rotary evaporator (water bath at 20°C) to give a small amount of a pale green tinted oil (crude mass 0.01g, crude yield 3%).

Table (U) - Tlc:R_f values

Peroxyester	CH ₂ Cl ₂	CHCl ₃
C ₆ H ₅ CO ₂ C(CH ₃) ₂ CH ₂ CH ₃	≈0.8	≈0.9

The peroxyester was UV light and peroxide spray-sensitive

The spots on tlc turned a slight pink when sprayed with freshly prepared peroxide spray.

The ¹³C NMR (CD₂Cl₂) and ¹H NMR (CD₂Cl₂) showed comparable peaks within complicated spectra, to those for tertiary-butyl peroxybenzoate. The proton spectrum integrals showed that there was half each of the peroxyester and carboxylic ester.

Table (V) - ¹H NMR in CD₂Cl₂ /ppm (270MHz)

	(a)/(a') 0.87; 0.84; 0.81 (t) [3H]
	(a)/(a') 1.00; 0.97; 0.95 (t) [3H]
	(b)/(b') 1.34 (s) [6H]
	(c)/(c') 1.43-1.53 (m) [2H]
	(c)/(c') 1.69-1.77 (m) [2H]
	(b)/(b') 2.11 (s) [6H]
	(d) and (d') 7.50; 7.47; 7.44 (t; fs) [4H]
	(e) and (e') 7.63; 7.61; 7.58 (t; fs) [2H]
	(f) 7.94; 7.92 (d; fs) [2H]
	(f') 8.08; 8.06 (d; fs) [2H]

s=singlet; d=doublet; t=triplet; m=multiplet; fs=fine splitting; [] integrals

Table (W) - ^{13}C NMR in CD_2Cl_2 /ppm (270Mz)

	(a) / (a') / (b) / (b') 24.62; 24.00; 28.74; 27.70 (c) / (c') 32.39; 31.94 (d) 86.62 (d') 78.04
	(e) / (e') 129.82/129.66; 128.58/128.20 (sqac) (f) / (f') / (g) / (g') 130.28; 129.39; 129.05; 128.79 (h) / (h') 133.76; 133.63 (i) 164.61 (sqac) (i') 169.74 (sqac)

saqc=small aromatic quaternary carbon.

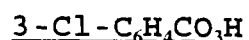
The attempted preparation of 1,1-dimethylpropyl benzoate



To a 100ml round-bottomed flask covered with aluminium foil, benzoic acid (0.51g, 4.18×10^{-3} moles) was dissolved in dry dichloromethane (dried over 3Å molecular sieves) (25ml) and 2-bromo-2-methylbutane (0.70g, 4.64×10^{-3} moles) added. At room temperature (22°C) and with continuous stirring (magnetic stirrer), silver tetrafluoroborate (1.06g 5.44×10^{-3} moles) was added, and after about 30 seconds a green precipitate was seen. Dry nitrogen was used throughout the reaction to purge the system.

After 15 minutes, a saturated solution of sodium bicarbonate was added (25ml). There was much fuming of white gas and the organic layer turned purple. With further mixing, the organic layer became opaque and a tinted green colour. The precipitate was then filtered off using a sintered funnel and water pump, the organic layer separated and the aqueous layer washed with dichloromethane (2x10ml). The combined organic layers were dried over anhydrous magnesium sulphate, filtered and reduced down using a rotary evaporator (water bath at 20°C). A small amount of white solid was seen (unweighed). ^1H NMR (CD_2Cl_2) indicated benzoic acid and saturated protons between 0 and 2ppm. ^{13}C NMR peaks besides those of benzoic acid, were most dominant at 8.40; 26.80; 27.35; 29.41 and 30.11ppm.

Purification of meta-chloroperoxybenzoic acid (MCPBA)¹²⁵



The commercial product was washed with a phosphate buffer of pH=7.5⁸⁷, and the residue dried under reduced pressure (this was done overnight in a vacuum oven). Based on 80-85% pure MCPBA (50-60% was used), 20ml buffer to 1g MCPBA was used. Washing was for 5 minutes, followed by filtering under vacuum to remove the residual water before vacuum oven drying. The

peroxyacid was assayed iodometrically before use. 99.96% purity was obtained and the ^1H and ^{13}C NMR were recorded. (See Chapter 1, 1.5.3 "Physical Properties of Organic Peroxides, Spectroscopic Data".) MCPBA melts at 92°C^{22} .

Table (X) - Tlc: R_f values

Peroxyacid	10% ethyl acetate in hexane	CH_2Cl_2
$3\text{-Cl-C}_6\text{H}_4\text{CO}_3\text{H}$	0	0

The peroxyacid was UV light- and peroxide spray- sensitive.

Preparation of tertiary-butyl meta-chloroperoxybenzoate



Following the method of Milas and Surgenor⁷, tertiary-butyl meta-chloroperoxybenzoate was prepared.

To a 100ml 2-necked, round-bottomed flask, was added 70% tertiary-butyl hydroperoxide (11.42g, 0.08870 moles). Simultaneously, and with vigorous stirring (magnetic stirrer), meta-chlorobenzoyl chloride (15.30g, 0.08742 moles) and 30% potassium hydroxide solution (21.10g, 0.11281 moles) were then added over 1 hour, with the temperature maintained between 10° and 20°C . The reaction mixture was stirred for a further 19 hours and on settling, the bottom organic layer was seen to consist of a fine white particulate suspension. 200ml of dichloromethane were added and the organic layer became clear and colourless. The organic layer was separated and washed with 10ml of 5% sodium carbonate solution, followed by 3x10ml washings with water before drying with anhydrous magnesium sulphate. The mixture was filtered and the filtrate reduced down using a rotary evaporator (water bath at 20°C), to give a pale yellow oil (crude mass 18.78g, crude yield 94%). The peroxyester was UV light- and peroxide spray- sensitive at $R_f \approx 0.8$ in CH_2Cl_2 .

Preparation of tertiary-butyl meta-chloroperoxybenzoate



Dry nitrogen gas was used throughout, together with continuous stirring by use of a magnetic stirrer. Oven-dried glassware was used, together with dry dichloromethane (dried over 3\AA molecular sieves). Cooling was by use of an ice-methanol bath. The reaction vessel was kept out of bright sunlight and kept below the level of the cooling mixture.

Tertiary-butyl bromide (0.79g, 5.77×10^{-3} moles) and 10ml dichloromethane

were added to a 100ml 3-necked, round-bottomed flask. The solution was cooled to -4°C and silver tetrafluoroborate (1.35g, 6.93×10^{-3} moles) added as quickly as possible via a glass funnel, but ensuring that the temperature did not rise above -2°C . Immediately, a dichloromethane solution (15ml) of MCPBA (1.00g, 5.79×10^{-3} moles) at 22°C was added dropwise over 15 minutes, with the contents of the reaction vessel maintained at -1°C . A yellow-orange solution was seen to appear shortly after the start of the addition of the peroxyacid solution, as well as a very fine green precipitate and white fumes (boron trifluoride and hydrogen fluoride which turned neutral water acidic). On completion of the peroxyacid addition, the reaction mixture was quenched with a saturated solution of sodium bicarbonate (25ml) as quickly as possible, with the resultant temperature at no more than 10°C . After stirring for 1 minute the precipitate was filtered off using a sintered funnel and water pump. The opaque, yellow organic layer was separated and the aqueous layer washed 5 times with 5ml dichloromethane. The combined organic layers were dried with anhydrous magnesium sulphate, filtered and reduced down (rotary evaporator, water bath at 20°C) to give a crude mass of 0.48g (crude yield 36%). The peroxyester was then purified using column chromatography with activated florisil and 10% ethyl acetate in hexane. About 30g of packing to 1g of material to be separated was used producing a column of 3cm diameter and a height of about 2cm with the quantities used. Very good separation was obtained. The solvent was removed under reduced pressure by use of a rotary evaporator followed by a vacuum pump at 23°C and at less than 9mmHg pressure for 120 minutes, to give a pale yellow oil (0.33g, yield 25%). The spectroscopic data were recorded. (See Chapter 1, 1.5.3 "Physical Properties of Organic Peroxides, Spectroscopic Data".)

Table (Y) - Tlc: R_f values

Peroxyester	10% ethyl acetate in hexane	2% ethyl acetate in hexane	CH_2Cl_2
$3\text{-Cl-C}_6\text{H}_4\text{CO}_2\text{C}(\text{CH}_3)_3$	≈ 0.6	≈ 0.4	≈ 0.9

The peroxyester was UV light- and peroxide spray- sensitive.

The mass spectrum of this previously unknown compound revealed a molecular ion (M^+) of 228.0553474 ($^{12}\text{C}_{11}\text{H}_{13}^{35}\text{Cl}^{16}\text{O}_3$ 228.0553152). The relative atomic masses used were as follows:

C	12.0000000,
H	1.0078246,
Cl	34.9688531,
O	15.9949141.

The (M⁺+2) peak was also seen. The ratio of (M⁺) to (M⁺+2) was about 3:1 due to the natural abundances of 75.77% and 24.23% of ³⁵Cl and ³⁷Cl, respectively¹⁴⁶.

Peak intensity ratio:

$$\frac{\text{Number of chlorine atoms} \times P(M^{+2}) \times 100\%}{P(M^{+})} = \frac{1 \times 24.23 \times 100\%}{75.77} \sim 31.98\%$$

The (M⁺+1) peak was also seen due to the presence of ¹³C.

Peak intensity ratio:

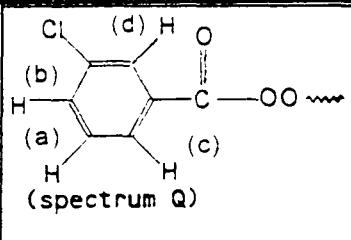
$$\frac{\text{Number of carbons} \times P(M^{+1}) \times 100\%}{P(M^{+})} = \frac{11 \times 1.108 \times 100\%}{98.892} \sim 12.32\%$$

Reducing down the latter fractions off the column, gave rise to a white solid by-product (0.0140g, 3% of the crude weight), with R_F≈0.2 in 2% ethyl acetate in hexane and R_F≈0.25-0.3 in 10% ethyl acetate in hexane. The spots on tlc were UV light sensitive and peroxide positive.

The addition of a little 2% ethyl acetate in hexane to the crude peroxyester, also resulted in a few "specks" of the white solid peroxide precipitating out.

The ¹H and ¹³C NMR spectra were taken of the solid and revealed a possibility of two compounds, as observation of the proton peak integrals suggested that the singlet at 1.79ppm was not related to the aromatic peaks seen (spectrum Q).

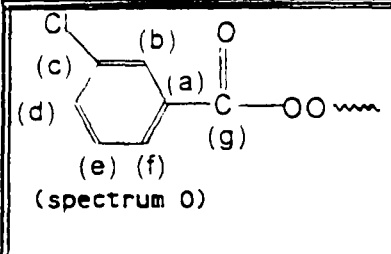
Table (Z) - ¹H NMR of aromatic protons in CDCl₃ / ppm (270MHz)

 <p>(spectrum Q)</p>	<p>(a)7.45;7.42;7.39(t;ns)[1H] (b)/(c)7.60;7.56(d;fs)[1H] (b)/(c)7.88;7.85(d;tfs)[1H] (d)7.95(s;tfs)[1H]</p>
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d=doublet;t=triplet;ns=no splitting;fs=fine splitting;tfs=triplet fine splitting;[] integrals

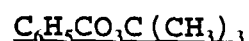
The ¹³C NMR suggested aromatic peaks arising from 3-Cl-C₆H₄CO₃- (spectrum O). The ¹³C NMR (CDCl₃) also showed peaks at: 21.09 and 112.16ppm. The lower value may indicate a methyl group and the larger value an sp² carbon.

Table (A1) - ^{13}C NMR of aromatic carbons in CDCl_3 / ppm (270MHz)

 <p>(spectrum 0)</p>	<p>(b)/(d)/(e)/(f)127.49 (a)/(c)128.60(saqc) (b)/(d)/(e)/(f){129.39; 130.07;133.80} (a)/(c)134.91(saqc) (g)162.57</p>
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saqc=small aromatic quaternary carbon

Preparation of tertiary-butyl peroxybenzoate



Dry nitrogen gas was used throughout, together with continuous stirring by use of a magnetic stirrer. Oven-dried glassware was used, together with dry dichloromethane (dried over 3Å molecular sieves). Cooling was by use of an ice-methanol bath. The reaction vessel was kept out of bright sunlight and kept below the level of the cooling mixture.

Tertiary-butyl bromide (0.79g, 5.77×10^{-3} moles) and 10ml dichloromethane were added to a 100ml 3-necked, round-bottomed flask. The solution was cooled to -4°C and silver tetrafluoroborate (1.35g, 6.93×10^{-3} moles) added as quickly as possible via a glass funnel, but ensuring that the temperature did not rise above -2°C . Immediately, a dichloromethane solution (15ml) of PBA (0.80g, 5.79×10^{-3} moles) at 22°C was added dropwise over 15 minutes, with the contents of the reaction vessel maintained at -1°C . A yellow-orange solution was seen to appear shortly after the start of the addition of the peroxyacid solution, as well as a very fine green precipitate and white fumes (boron trifluoride and hydrogen fluoride which turned neutral water acidic). On completion of the peroxyacid addition, the reaction mixture was quenched with a saturated solution of sodium bicarbonate (25ml) as quickly as possible, with the resultant temperature at no more than 10°C . After stirring for 1 minute the precipitate was filtered off using a sintered funnel and water pump. The opaque, yellow organic layer was separated and the aqueous layer washed 5 times with 5ml dichloromethane. The combined organic layers were dried with anhydrous magnesium sulphate, filtered and reduced down (rotary evaporator, water bath at 20°C) to give a crude mass of 0.34g (crude yield 30%). The peroxyester was then purified using column chromatography with activated florisil and 10% ethyl acetate in hexane. About 30g of packing to 1g of material to be separated was used producing a column of 3cm diameter and a height of about 2cm with the quantities used. Very good separation was obtained. The solvent was removed under reduced pressure by use of a rotary evaporator followed by a vacuum pump at 23°C and at less than 9mmHg pressure for 120 minutes, to give a pale yellow oil (0.22g, yield 20%). The spectroscopic data were recorded. (See Chapter 1, 1.5.3 "Physical Properties of Organic Peroxides, Spectroscopic

Data".)

Table (B1) - Tlc:R_f values

Peroxyester	10% ethyl acetate in hexane	2% ethyl acetate in hexane	CH ₂ Cl ₂
C ₆ H ₅ CO ₃ C(CH ₃) ₃	≈0.6	≈0.3	≈0.9

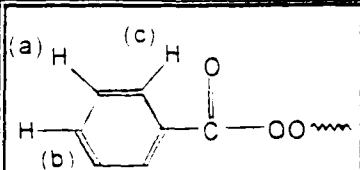
The peroxyester was UV light- and peroxide spray- sensitive.

Tertiary-butyl peroxybenzoate had NMR values in good agreement with the literature^{121,135,145}, and has a boiling point of 75°-77°C at 2mmHg⁷ and a melting point of 8.5°C¹.

Reducing down the latter fractions off the column, gave rise to a white solid by-product (0.0102g, 3% of the crude weight), with R_f≈0.14 in 2% ethyl acetate in hexane and R_f≈0.3 in 10% ethyl acetate in hexane. The spots were UV light sensitive and peroxide positive.

The ¹H and ¹³C NMR spectra were taken of the solid and revealed a possibility of two compounds, as observation of the proton peak integrals suggested that the singlet at 1.79ppm was not related to the aromatic peaks seen (spectrum P).

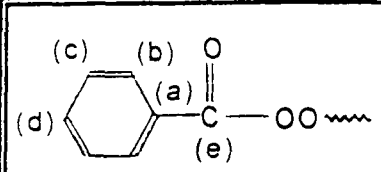
Table (C1) - ¹H NMR of aromatic protons in CDCl₃ / ppm (270MHz)

 <p>(spectrum P)</p>	(a)7.49;7.46;7.43(t;ns)[2H] (b)7.63;7.60;7.57(t;ns)[1H] (c)8.00;7.98(d;ns)[2H]
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d=doublet;t=triplet;ns=no splitting;fs=fine splitting;tfs=triplet fine splitting;[] integrals

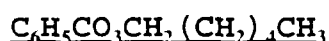
The ¹³C NMR suggested aromatic peaks arising from C₆H₅CO₃- (spectrum N). The ¹³C NMR (CDCl₃) also showed peaks at: 21.11 and 111.95ppm. The lower value may indicate a methyl group and the larger value an sp² carbon.

Table (D1) - ¹³C NMR of aromatic carbons in CDCl₃ / ppm (270MHz)

 <p>(spectrum N)</p>	(a)126.99(saqc) (b)/(c)128.69 (b)/(c)129.41 (d)133.66 (e)163.76
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saqc=small aromatic quaternary carbon

The attempted preparation of n-hexyl peroxybenzoate



(A) Dry nitrogen gas was used throughout, together with continuous stirring by use of a magnetic stirrer. Oven-dried glassware was used, together with dry dichloromethane (dried over 3Å molecular sieves). Cooling was by use of an ice-methanol bath. The reaction vessel was kept out of bright sunlight and kept below the level of the cooling mixture.

To a 100ml 3-necked, round-bottomed flask were added n-hexyl bromide (1.01g, 6.12×10^{-3} moles; 0.95g, 5.75×10^{-3} moles), dichloromethane (10ml) and silver tetrafluoroborate (1.41g, 7.24×10^{-3} moles; 1.34g, 6.88×10^{-3} moles). The contents of the reaction vessel were kept at -1°C ; -12°C while a dichloromethane solution (15ml) of PBA (0.79g, 5.72×10^{-3} moles; 0.80g, 5.79×10^{-3} moles) was added dropwise over 15 minutes. The reaction mixture became an opaque, white-grey and some white fumes were seen (boron trifluoride and hydrogen fluoride which turned neutral water acidic). Tlc of the reaction mixture showed a peroxide positive spot at $R_f=0$ in 10% ethyl acetate in hexane. 25ml of a saturated solution of sodium bicarbonate were added and the precipitate of silver bromide (grey-green) was filtered off using a sintered funnel and water pump. The organic layer was separated and reduced down (rotary evaporator, water bath at 20°C) to give a small amount of white solid (unweighed). The ^1H NMR (60MHz) indicated PBA, benzoic acid and 1-hexene.

(B) Dry nitrogen gas was used throughout, together with continuous stirring by use of a magnetic stirrer. Oven-dried glassware was used, together with dry dichloromethane (dried over 3Å molecular sieves). Cooling was by use of an ice-methanol bath. The reaction vessel was kept out of bright sunlight and kept below the level of the cooling mixture.

To a 100ml 3-necked, round-bottomed flask were added n-hexyl bromide (1.32g, 8.00×10^{-3} moles), dichloromethane (25ml) and PBA (1.10g, 7.96×10^{-3} moles). The contents of the reaction vessel were kept at -1°C and silver tetrafluoroborate (1.86g, 9.55×10^{-3} moles) added as quickly as possible via a glass funnel, but ensuring that the temperature was maintained at -1°C . The reaction mixture became an opaque, white-grey and some white fumes were seen (boron trifluoride and hydrogen fluoride which turned neutral water acidic) during the 15 minutes of reaction. Tlc of the reaction mixture showed a peroxide positive spot at $R_f=0$ in 10% ethyl acetate in hexane. 25ml of a saturated solution of sodium bicarbonate were added and the precipitate of silver bromide (grey-green) was filtered off using a sintered funnel and water pump. The organic layer was separated and reduced down (rotary evaporator, water bath at 20°C) to give a small amount of white solid (unweighed). The ^1H NMR (60MHz) indicated PBA and

benzoic acid.

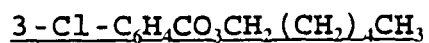
(C) Dry nitrogen gas was used throughout, together with continuous stirring by use of a magnetic stirrer. Oven-dried glassware was used, together with dry dichloromethane (dried over 3Å molecular sieves). Cooling was by use of an ice-methanol bath. The reaction vessel was kept out of bright sunlight and kept below the level of the cooling mixture.

To a 100ml 3-necked, round-bottomed flask were added PBA (1.75g, 0.01267 moles), dichloromethane (25ml) and silver tetrafluoroborate (0.35g, 1.80×10^{-3} moles). The contents of the reaction vessel were kept at -1°C while n-hexyl bromide (0.22g, 1.33×10^{-3} moles) was added dropwise over 7 minutes. The reaction mixture became an opaque, white-grey and some white fumes were seen (boron trifluoride and hydrogen fluoride which turned neutral water acidic). Tlc of the reaction mixture showed a peroxide positive spot at $R_f=0$ in 10% ethyl acetate in hexane. After the 15 minutes of reaction, 25ml of a saturated solution of sodium bicarbonate were added and the precipitate of silver bromide (grey-green) filtered off using a sintered funnel and water pump. The organic layer was separated and reduced down (rotary evaporator, water bath at 20°C) to give a small amount of white solid (unweighed). The ^1H NMR (60MHz) indicated PBA and benzoic acid.

(D) Dry nitrogen gas was used throughout, together with continuous stirring by use of a magnetic stirrer. Oven-dried glassware was used, together with dry dichloromethane (dried over 3Å molecular sieves). Cooling was by use of an ice-methanol bath. The reaction vessel was kept out of bright sunlight and kept below the level of the cooling mixture.

To a 100ml 3-necked, round-bottomed flask were added dichloromethane (10ml) and silver tetrafluoroborate (1.00g, 5.14×10^{-3} moles). The contents of the reaction vessel were kept at -1°C while a dichloromethane solution (15ml) of n-hexyl bromide (0.69g, 4.18×10^{-3} moles) and PBA (0.54g, 3.91×10^{-3} moles) was added dropwise over 15 minutes. The reaction mixture became an opaque, white-grey and some white fumes were seen (boron trifluoride and hydrogen fluoride which turned neutral water acidic). Tlc of the reaction mixture showed a peroxide positive spot at $R_f=0$ in 10% ethyl acetate in hexane. 25ml of a saturated solution of sodium bicarbonate were added and the precipitate of silver bromide (grey-green) filtered off using a sintered funnel and water pump. The organic layer was separated and reduced down (rotary evaporator, water bath at 20°C) to give a small amount of white solid (unweighed). The ^1H NMR (60MHz) indicated PBA and benzoic acid.

The attempted preparation of n-hexyl meta-chloroperoxybenzoate



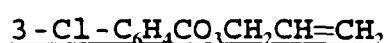
(A) Dry nitrogen gas was used throughout, together with continuous stirring by use of a magnetic stirrer. Oven-dried glassware was used, together with dry dichloromethane (dried over 3Å molecular sieves). Cooling was by use of an ice-methanol bath. The reaction vessel was kept out of bright sunlight and kept below the level of the cooling mixture.

To a 100ml 3-necked, round-bottomed flask were added MCPBA (2.00g, 0.01159 moles), dichloromethane (25ml) and silver tetrafluoroborate (0.60g, 3.08x10⁻³moles). The contents of the reaction vessel were kept at -1°C while n-hexyl bromide (0.20g, 1.21x10⁻³moles) was added dropwise over 7 minutes. The reaction mixture became an opaque, white-grey and some white fumes were seen (boron trifluoride and hydrogen fluoride which turned neutral water acidic). Tlc of the reaction mixture showed a peroxide positive spot at R_F=0 in 10% ethyl acetate in hexane. After the 15 minutes of reaction, 25ml of a saturated solution of sodium bicarbonate were added and the precipitate of silver bromide (grey-green) filtered off using a sintered funnel and water pump. The organic layer was separated and reduced down (rotary evaporator, water bath at 20°C) to give a small amount of white solid (unweighed). The ¹H NMR (60MHz) indicated MCPBA and meta-chlorobenzoic acid.

(B) Dry nitrogen gas was used throughout, together with continuous stirring by use of a magnetic stirrer. Oven-dried glassware was used, together with dry dichloromethane (dried over 3Å molecular sieves). Cooling was by use of an ice-methanol bath. The reaction vessel was kept out of bright sunlight and kept below the level of the cooling mixture.

To a 100ml 3-necked, round-bottomed flask were added dichloromethane (10ml) and silver tetrafluoroborate (0.68g, 3.49x10⁻³moles). The contents of the reaction vessel were kept at -1°C while a dichloromethane solution (15ml) of n-hexyl bromide (0.48g, 2.91x10⁻³moles) and MCPBA (0.51g, 2.96x10⁻³moles) was added dropwise over 15 minutes. The reaction mixture became an opaque, white-grey and some white fumes were seen (boron trifluoride and hydrogen fluoride which turned neutral water acidic). Tlc of the reaction mixture showed a peroxide positive spot at R_F=0 in 10% ethyl acetate in hexane. 25ml of a saturated solution of sodium bicarbonate were added and the precipitate of silver bromide (grey-green) filtered off using a sintered funnel and water pump. The organic layer was separated and reduced down (rotary evaporator, water bath at 20°C) to give a small amount of white solid (unweighed). The ¹H NMR (60MHz) indicated MCPBA and meta-chlorobenzoic acid.

Preparation of prop-2-enyl (allyl) meta-chloroperoxybenzoate



Dry nitrogen gas was used throughout, together with continuous stirring by use of a magnetic stirrer. Oven-dried glassware was used, together with dry dichloromethane (dried over 3Å molecular sieves). The reaction vessel was kept out of bright sunlight and kept below the level of the cooling mixture.

To a 100ml 3-necked, round-bottomed flask were added 15ml of dichloromethane and silver tetrafluoroborate (1.53g, 7.86×10^{-3} moles) and the slurry cooled (5°C, ice-water bath). Over 15 minutes a 22°C solution of MCPBA (1.13g, 6.55×10^{-3} moles) and allyl bromide (0.81g, 6.70×10^{-3} moles) in 15ml of dichloromethane was added dropwise to the silver salt slurry. Soon after the start of the addition of the solution (20 seconds), the reaction mixture became an opaque white with a purple colouration at the bottom. Copious white fumes were also seen (boron trifluoride and hydrogen fluoride which turned neutral water acidic). After a further 5 minutes, the reaction mixture was an opaque grey-green-purple colour. At the end of the 15 minutes of reaction (colourless solution with a dark green precipitate), 30ml of a saturated solution of sodium bicarbonate were added and more white fumes were seen. The precipitate was filtered off using a sintered funnel and water pump. The organic layer (pale yellow clear solution) was separated and the aqueous layer washed 5 times with 5ml dichloromethane. The combined organic layers were dried with anhydrous magnesium sulphate, filtered and reduced down (rotary evaporator, water bath at 20°C) to give a crude mass of 0.55g (crude yield 40%, dark yellow oil). The peroxyester was then purified using column chromatography with activated florisil and dichloromethane as eluant. The solvent was removed under reduced pressure by use of a rotary evaporator followed by a vacuum pump at 25°C and 0.3-0.5mmHg pressure for 30 minutes, to give a slightly yellow tinted oil (0.0810g, yield 6%) of the peroxyester.

The IR and ¹H NMR were taken of the compound. (See Chapter 1, 1.5.3 "Physical Properties of Organic Peroxides, Spectroscopic Data".)

Table (E1) - Tlc:R_f values

Peroxyester	10% ethyl acetate in hexane	CH ₂ Cl ₂
3-Cl-C ₆ H ₄ CO ₃ CH ₂ CH=CH ₂	≈0.7	≈0.9

The peroxyester was UV light- and peroxide spray- sensitive.

Preparation of benzyl meta-chloroperoxybenzoate



Dry nitrogen gas was used throughout, together with continuous stirring by use of a magnetic stirrer. Oven-dried glassware was used, together with dry dichloromethane (dried over 3Å molecular sieves). The reaction vessel was kept out of bright sunlight and kept below the level of the cooling mixture.

To a 100ml 3-necked, round-bottomed flask were added 15ml of dichloromethane and silver tetrafluoroborate (1.35g, 6.93x10⁻³ moles) and the slurry cooled to 6°C (ice-water bath). Over 15 minutes a 22°C solution of MCPBA (1.07g, 6.20x10⁻³ moles) and α-bromotoluene (0.99g, 5.79x10⁻³ moles) in 15ml of dichloromethane was added dropwise to the silver salt slurry. 2 minutes after the start of the addition of the solution, the reaction mixture became an opaque white, and copious white fumes were seen (boron trifluoride and hydrogen fluoride which turned neutral water acidic). After another 8 minutes, the reaction mixture was a dark red and after a total of 23 minutes, the reaction mixture was a black-red. 30ml of a saturated solution of sodium bicarbonate were added and more white fumes were seen. The precipitate (a brown gunge) was filtered off using fluted filter paper. The yellow organic solution was dried with anhydrous magnesium sulphate, filtered and reduced down (rotary evaporator, water bath at 20°C) to give a dark brown-yellow viscous oil (crude mass 0.13g, crude yield 8.5%). The peroxyester was purified using column chromatography with activated florisil and 10% ethyl acetate in hexane as eluant and secondly, with dichloromethane as eluant. The solvent was removed under reduced pressure by use of a rotary evaporator followed by a vacuum pump at 25°C and 0.3-0.5mmHg pressure for 30 minutes, to give a slightly yellow tinted oil (0.0324g, yield 2%) of the peroxyester.

The ¹H NMR was taken of the compound. (See Chapter 2, "Results and Discussion".)

Table (F1) - Tlc:R_f values

Peroxyester	10% ethyl acetate in hexane	CH ₂ Cl ₂
3-Cl-C ₆ H ₄ CO ₂ CH ₂ C ₆ H ₅	≈0.7	≈0.9

The peroxyester was UV light- and peroxide spray- sensitive.

Safety

In the interest of safety, the present author worked with a maximum of about 1g peroxide at any one time.

Organic peroxide decomposition can be initiated by light, heat, contamination, friction or mechanical shock. Commercial peroxides are often therefore formulated with desensitizing solvents. For example, benzoyl peroxide is moistened with water to reduce its burning characteristics. Solid peroxides should never be subjected to any grinding operation.

Within a series (that is, in one type of structure of the peroxy compound) the sensitivity increases with active oxygen concentration: the stability increases as the proportion of oxygen in the molecule decreases. Thus for example, methyl and ethyl hydroperoxides, as well as their barium salts, are extremely explosive in the dry state, and together with peroxyacetic acid, diacetyl peroxide and their peroxides, should be handled only with extreme caution and on a very small scale. The alkylidene peroxides derived from low molecular weight aldehydes and ketones are very sensitive and explode with considerable violence. Some peroxides usually regarded as being relatively innocuous, may become highly hazardous under certain conditions. For example, benzoyl peroxide dust may readily explode with friction, or in the presence of contaminants, or on recrystallisation from hot CHCl_3 . Also, mixtures of hydrogen peroxide and many organic compounds are potentially detonatable when hydrogen peroxide is present in more than 30% by weight¹⁴⁷. The dangers can be minimized by working on a small scale and by using protective glasses or a face mask and gloves, as well as an explosion screen and non-metallic spatulas of horn or plastic. Under no circumstances should metallic spatulas be used, especially for the lower molecular weight aliphatic peroxides.

A common but frequently disregarded hazard arises in working with organic solvents which may contain peroxides formed by autoxidation. Often solvents are distilled, concentrating the relatively involatile peroxides in the residue which may then detonate. This is especially seen for ethers and alkenes, though other solvents must not be disregarded.

Storing solvents in full air-tight amber glass bottles may reduce the peroxide formation. Effective inhibitors are polyhydric phenols, aminophenols and arylamines. Simple hydroperoxides can be removed for example, by treating the solvent with strong alkalis, sodium sulphite, stannous chloride, lithium aluminium hydride, triphenylphosphine and lead dioxide. The peroxides found in autoxidised ethers are much less readily attacked, but appear to be reduced by zinc and acid, or sodium and alcohol. Ferrous sulphate in 50% H_2SO_4 can also be used. The best general

physical method for removing peroxides from solvents, particularly on a small scale for peroxides resistant to reduction, is to pass the solvent down an alumina column when the peroxides are absorbed¹⁴⁸.

Health

All organic peroxides are classified as oxidising agents, though as a group of organic compounds they have a low order of toxicity. Not all physiological effects are known, and their irritating effects on skin, eyes, nose and throat, mean they should be handled with care.

The hazards of the diluents must also be considered. Benzene for example, can create a more serious hazard exposure than the peroxide as it is a known carcinogen¹²⁵.

Hydroperoxide solutions can produce pronounced skin irritations. Of those tested, benzoyl peroxide in general is considered to produce the least skin irritation and methyl ethyl ketone (MEK) peroxides the most. Ointments containing 5%-20% benzoyl peroxide are used in the treatment of acne.

Hydroperoxides and MEK peroxides are particularly injurious to the eyes, even in dilute solution. Inhalation of some organic peroxide vapours causes irritation of the eyes, nose and throat, and in high concentration causes inebriation similar to the effects of alcohol.

In the peroxide work detailed here, the more stable compounds were used in a ventilated fume cupboard. A plastic blast shield, plastic spatulas, safety glasses, a laboratory coat and disposable gloves were also used. Reactions were never carried out in direct, bright sunlight.

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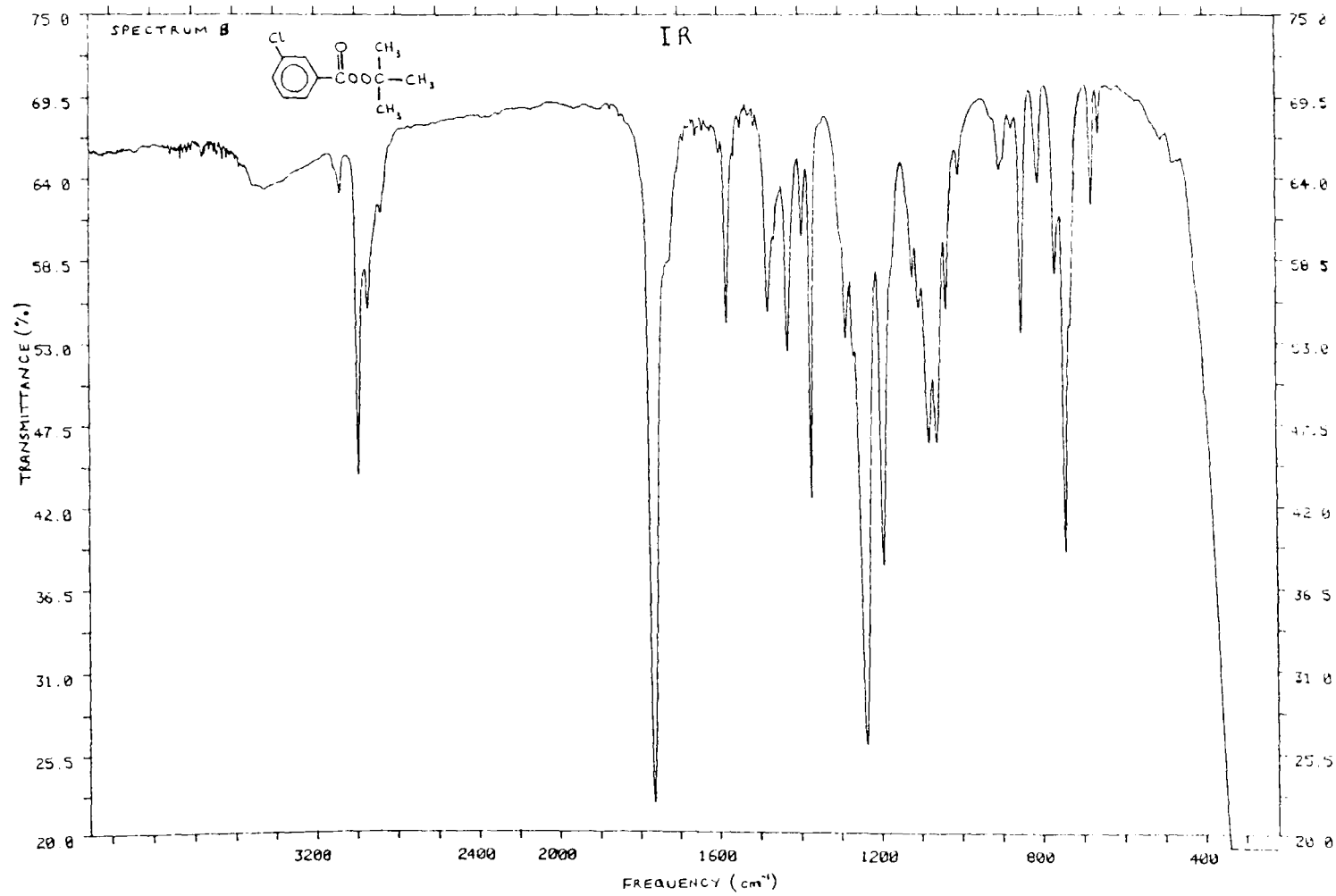
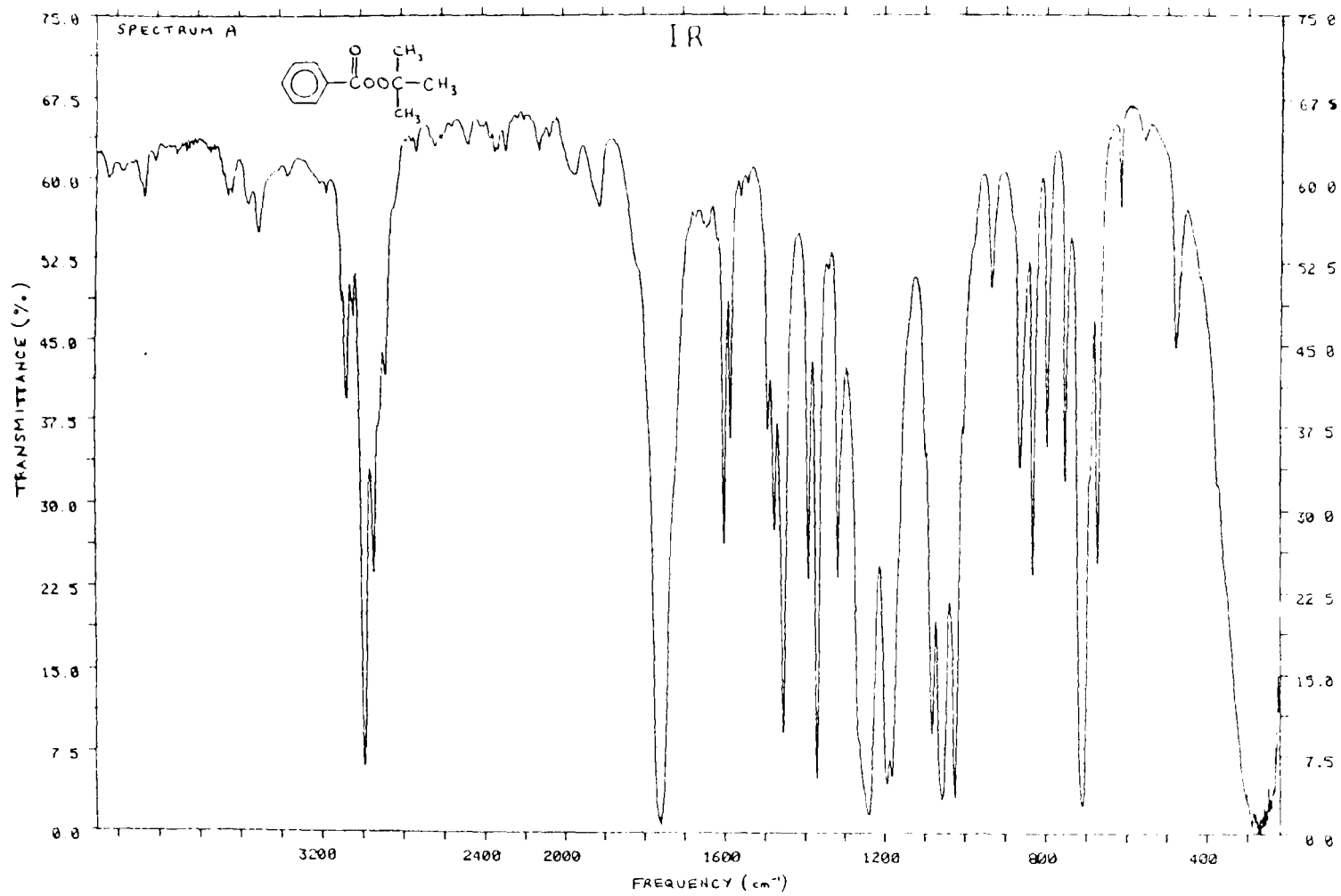
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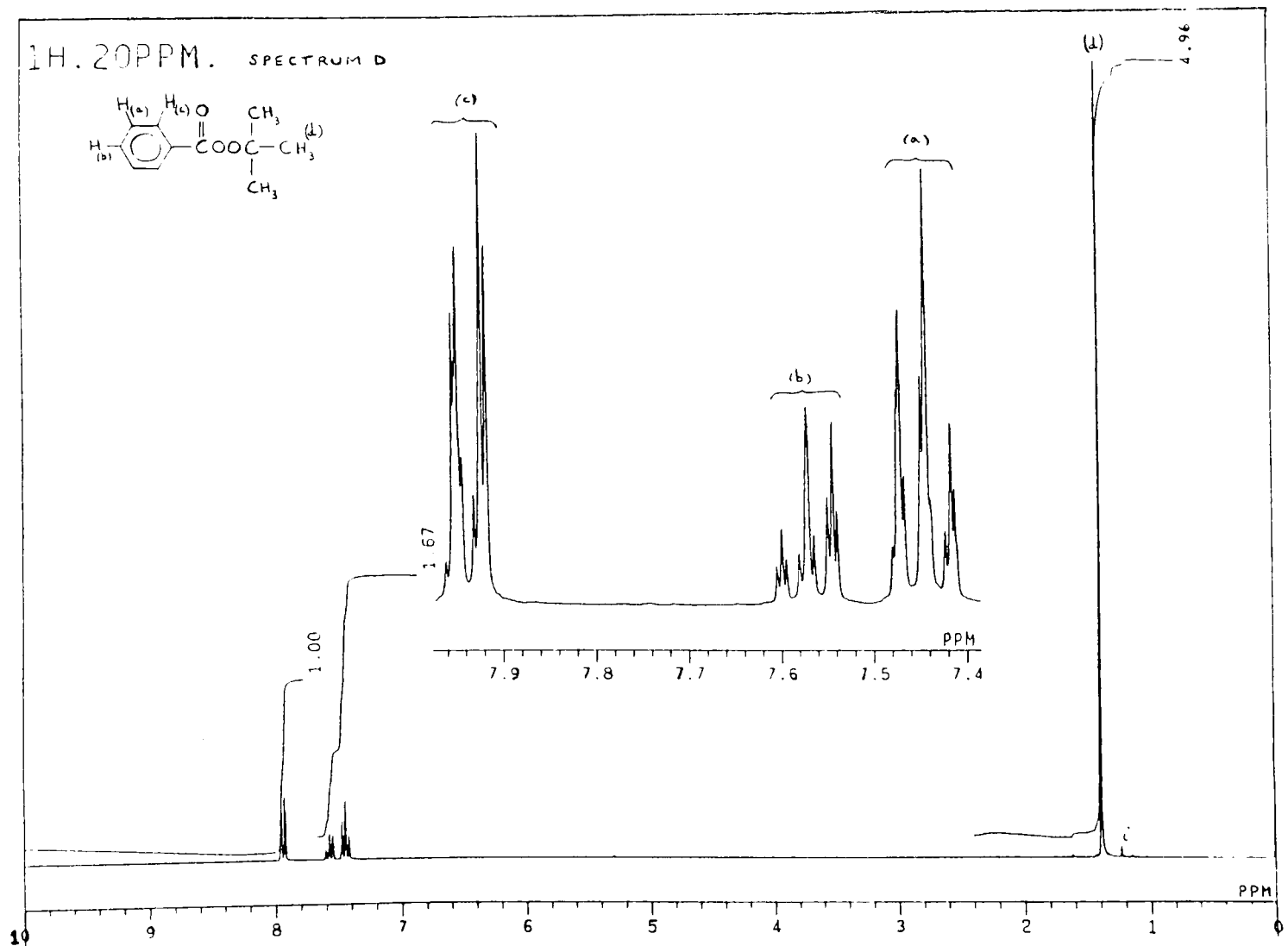
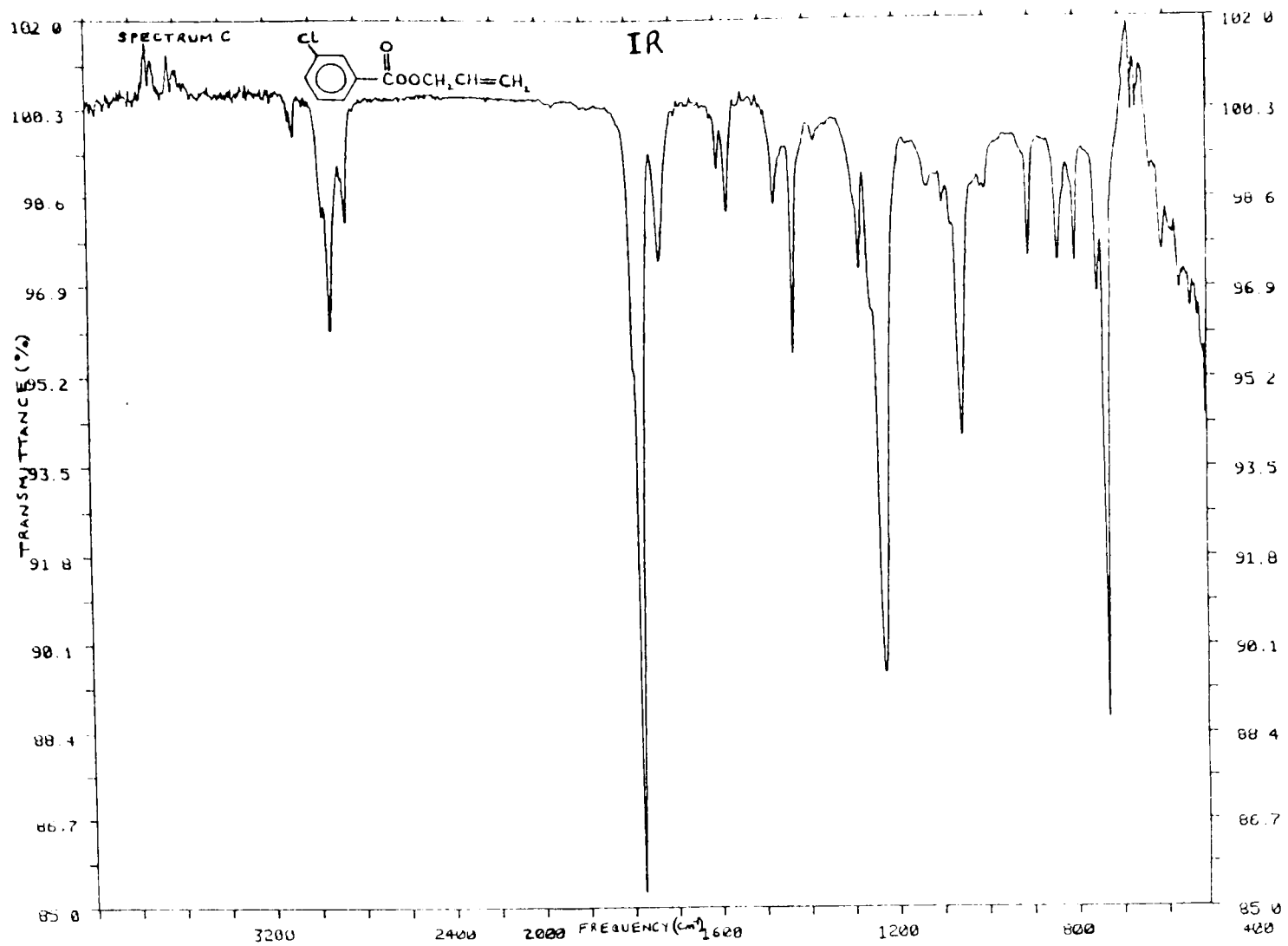
APPENDIX

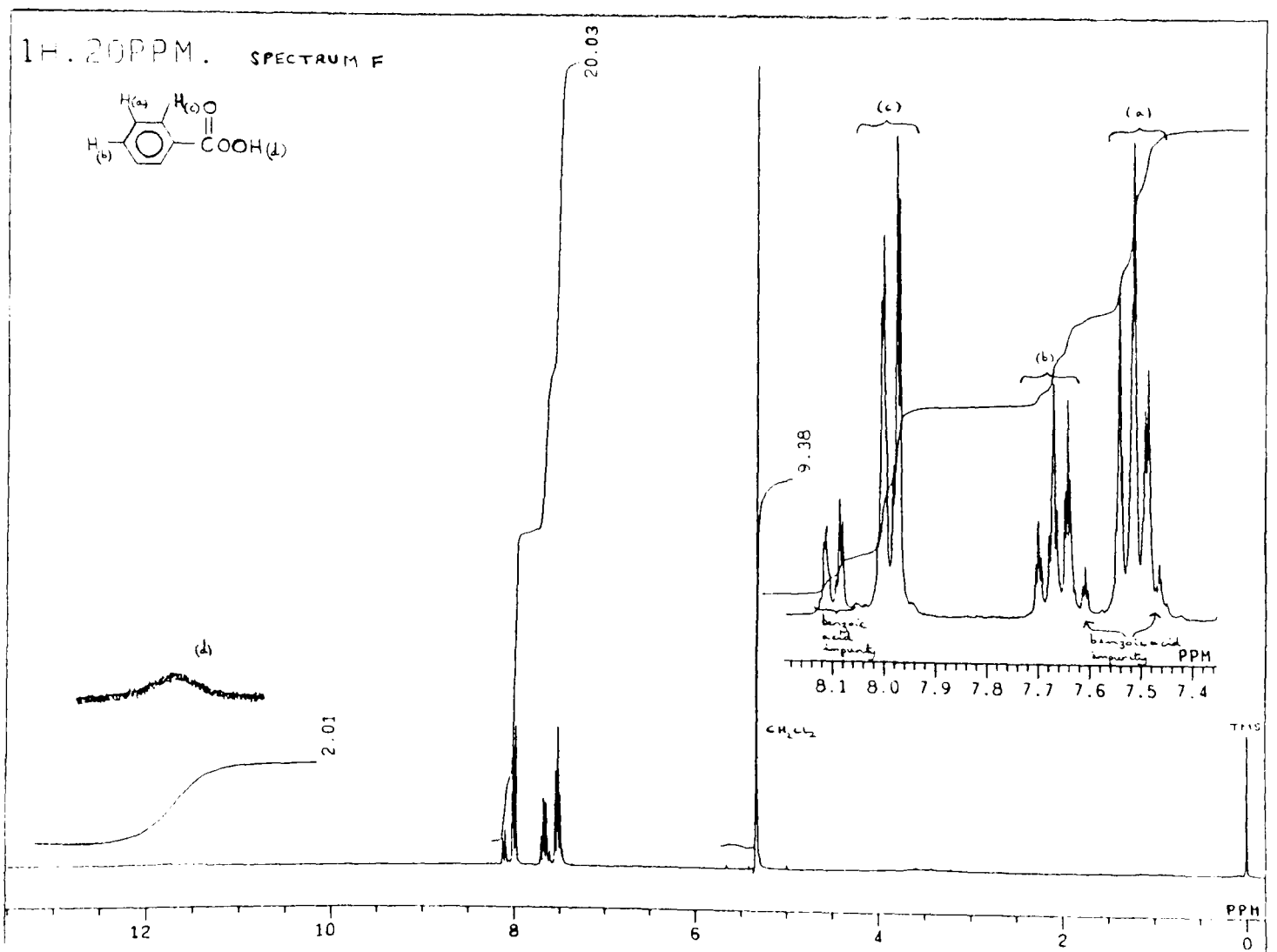
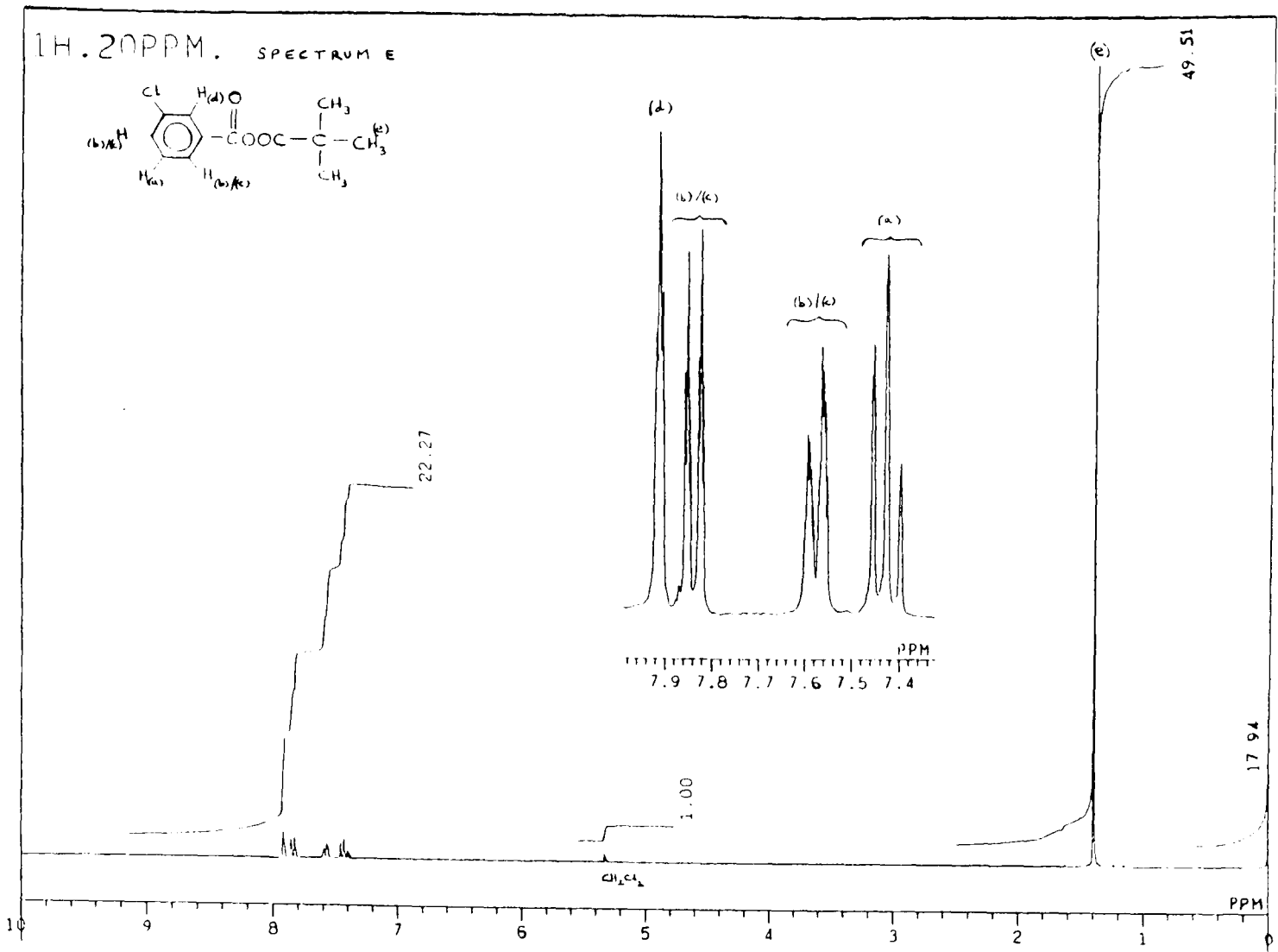
¹ Glassware was cleaned with a solution of the sodium salt of ethylenediaminetetraacetic acid (EDTA) $[\text{Na}_4(\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_8)]$ by forming stable complexes with any metal ions present. Distilled water was then used to rinse the glassware before being oven-dried.

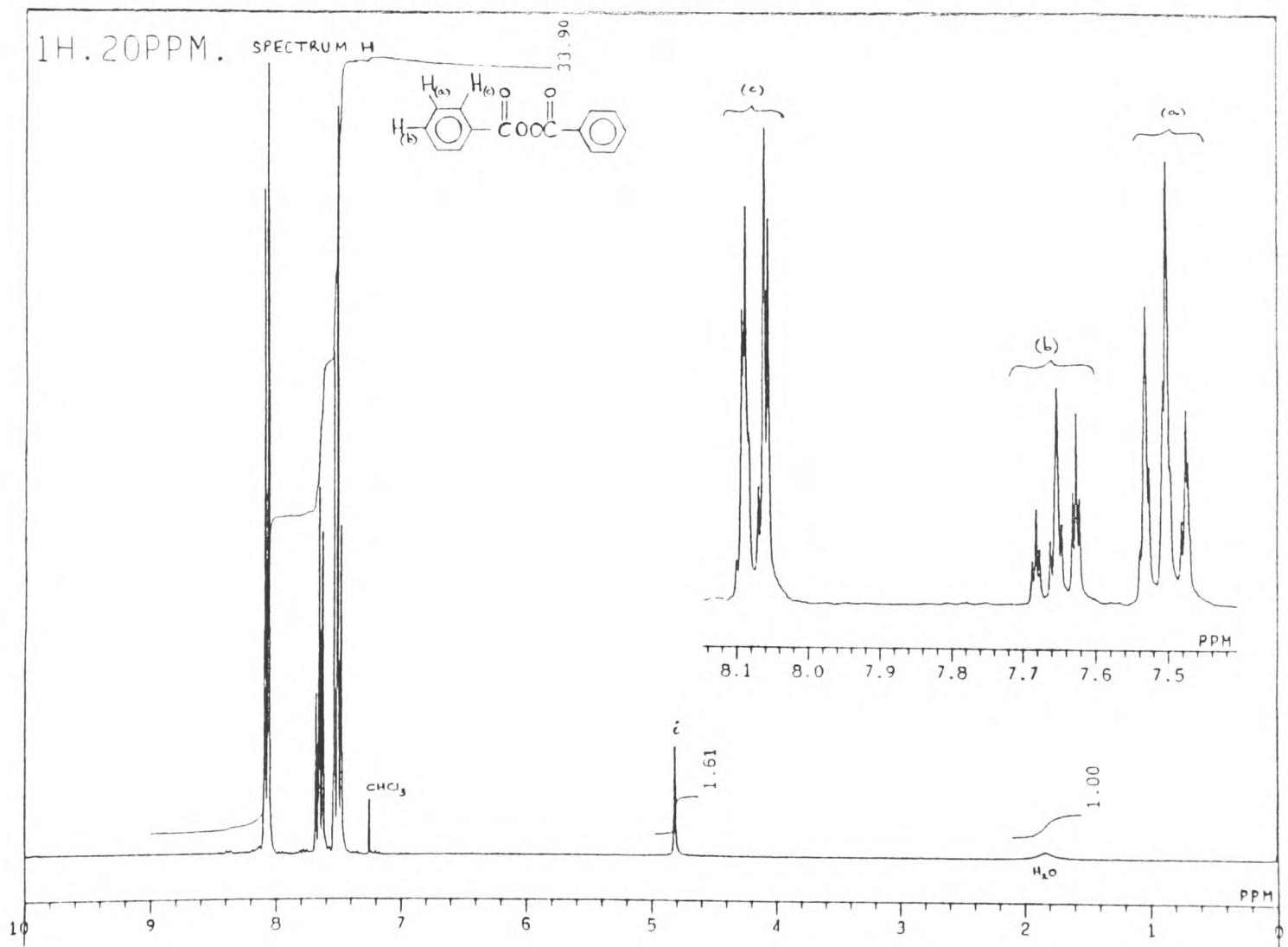
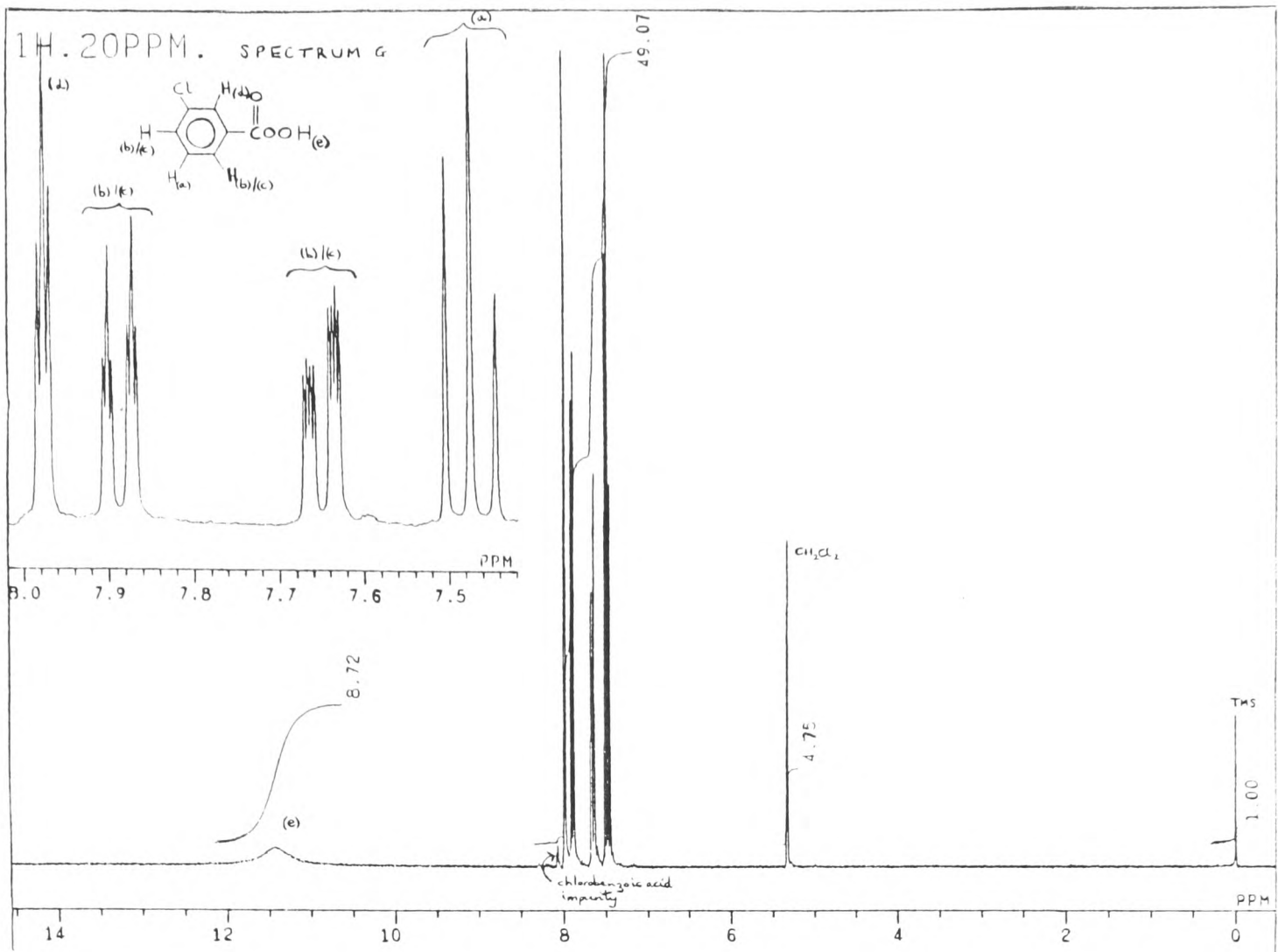
¹¹ Sent from Aldrich Chemical Co. Ltd., Gillingham, Dorset.

SPECTRA



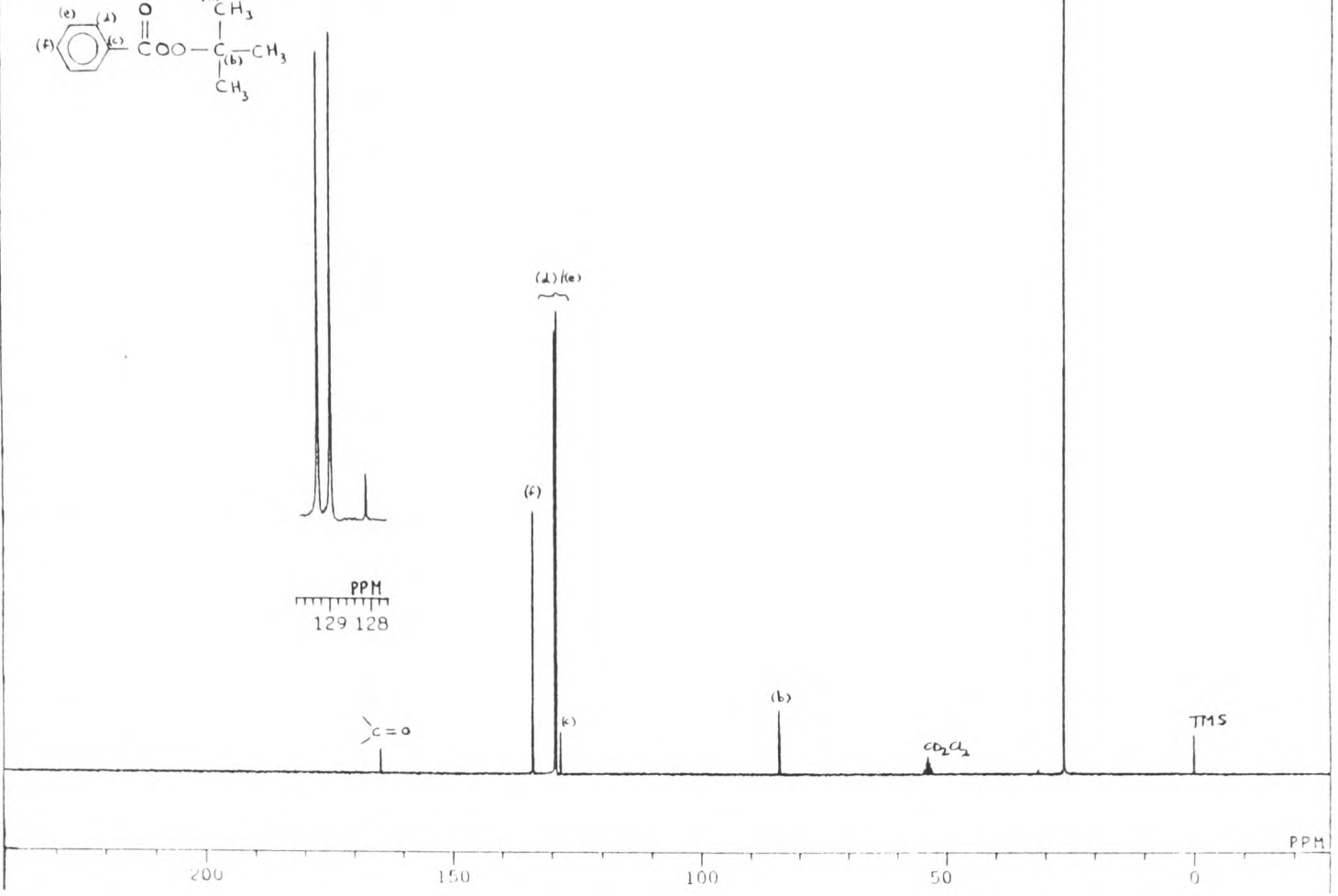
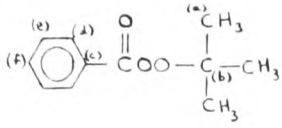




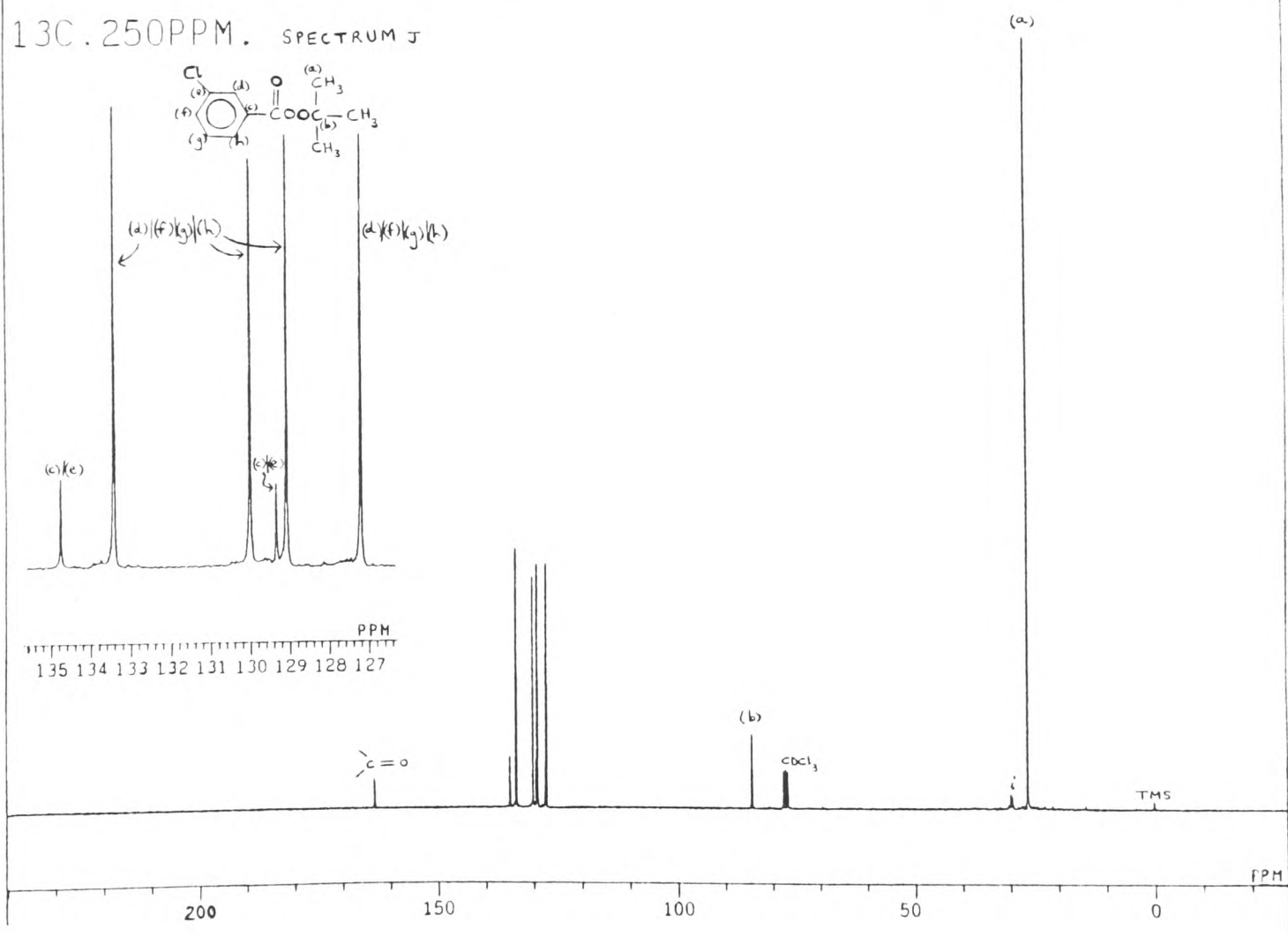
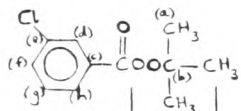


13C. 250PPM.

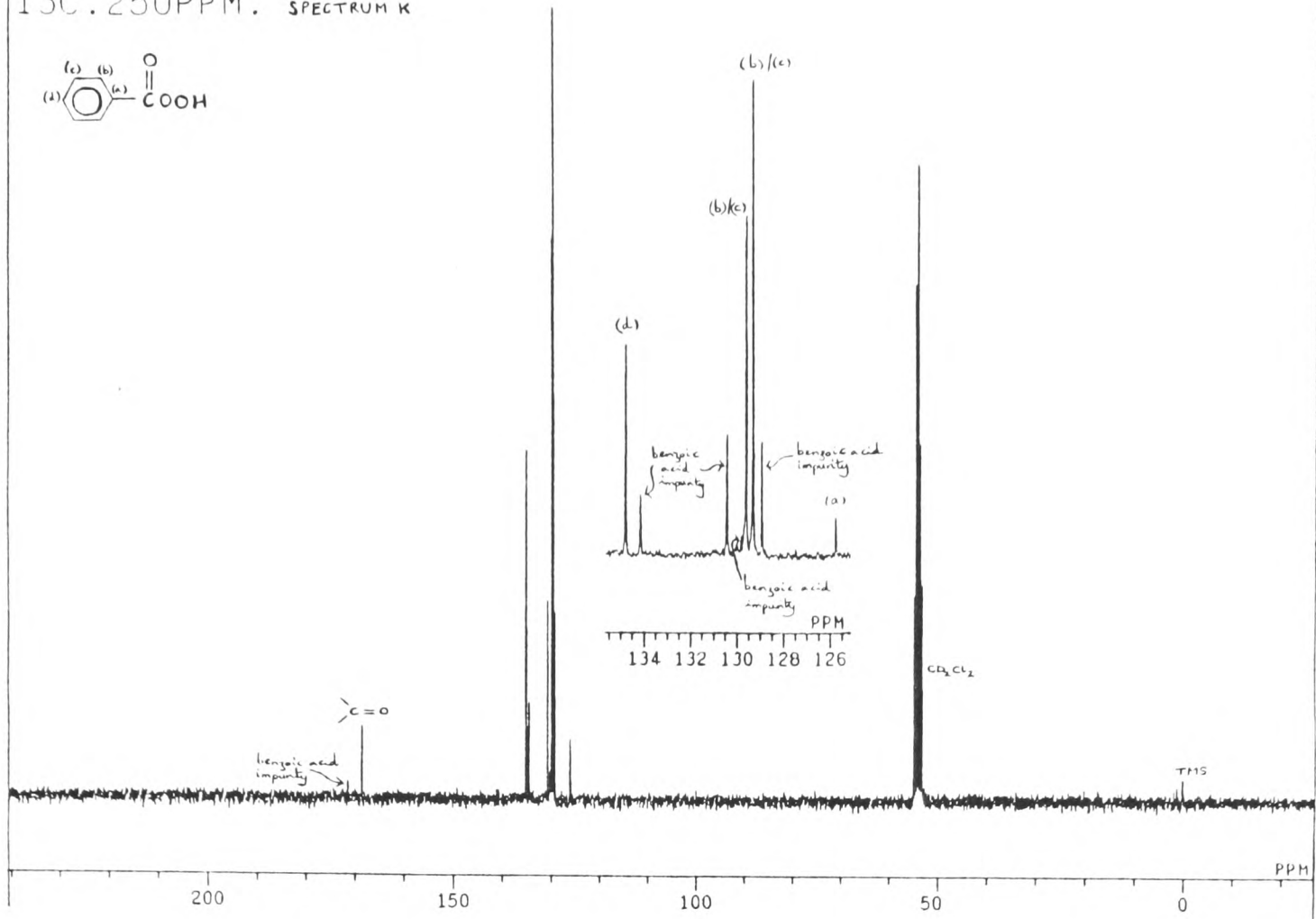
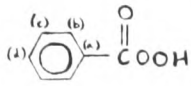
SPECTRUM I



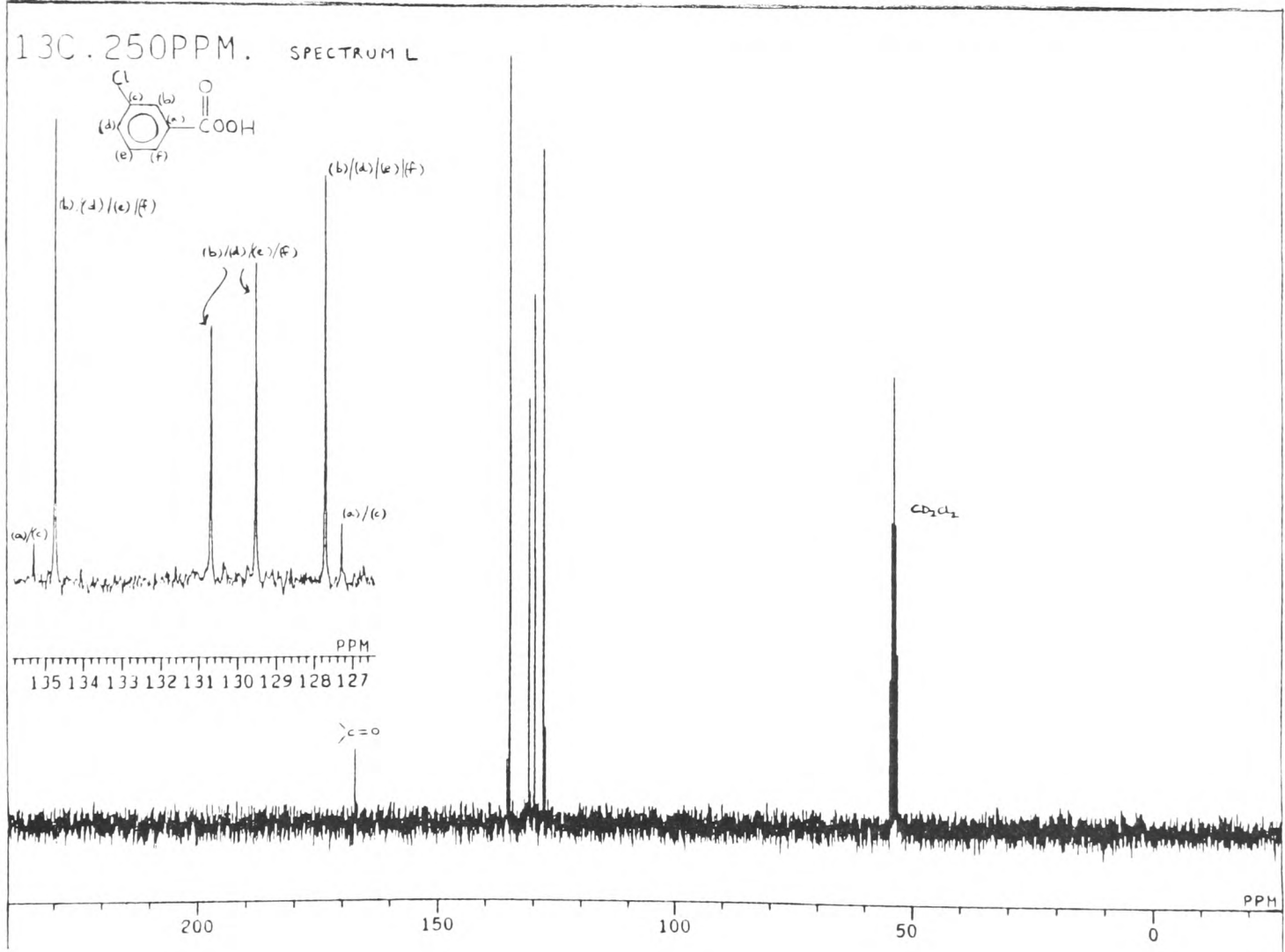
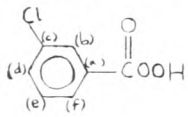
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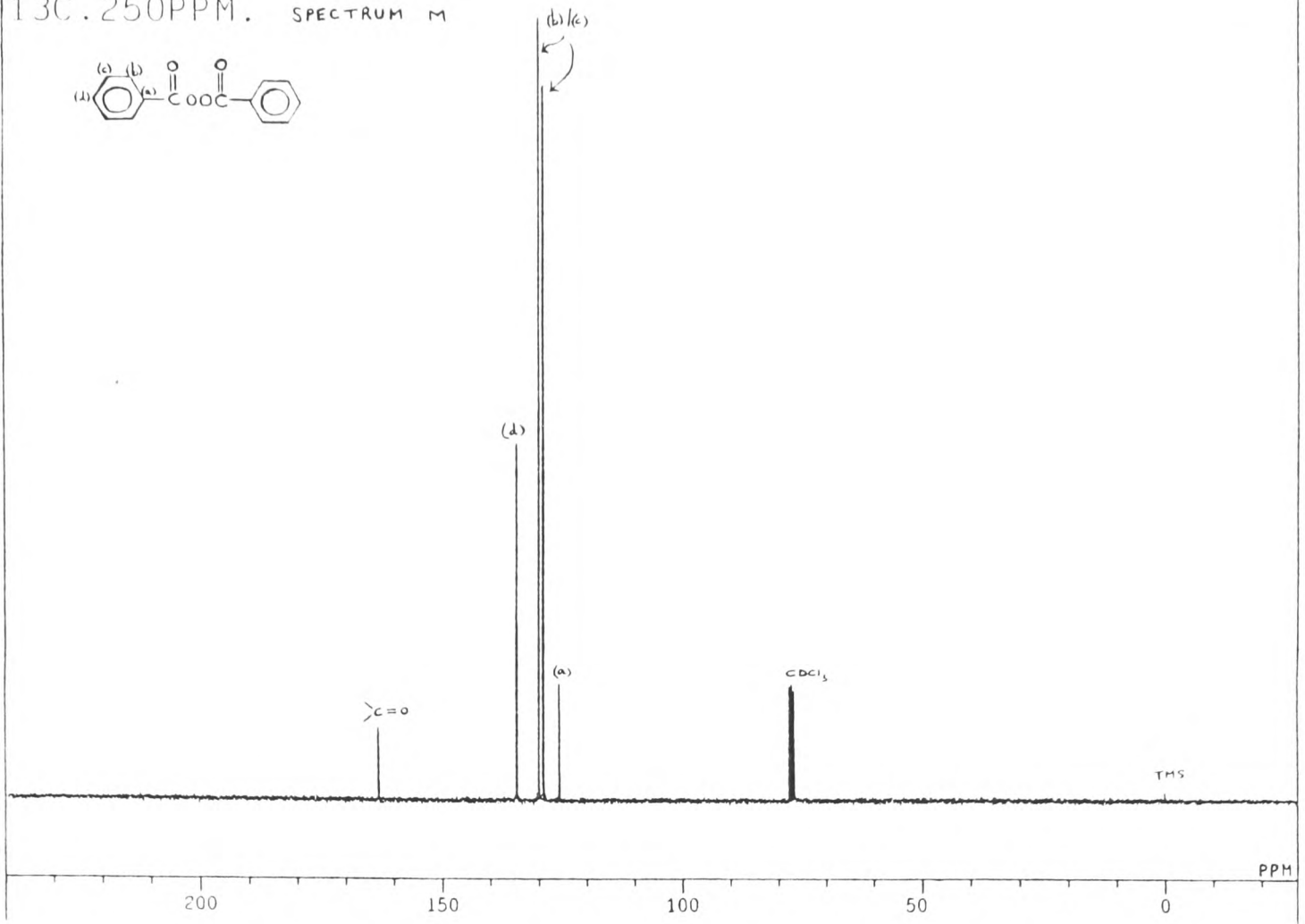
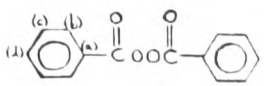
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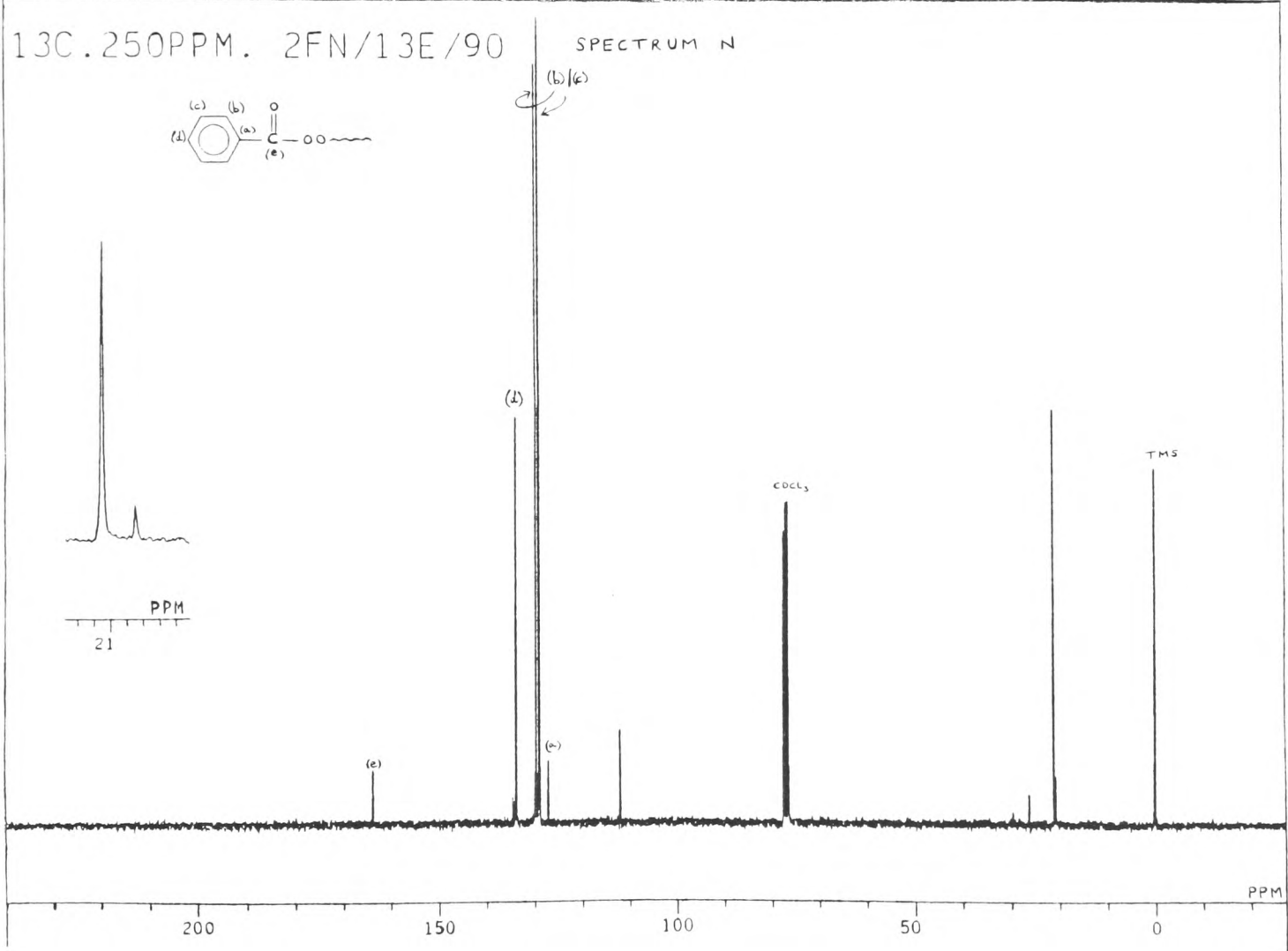
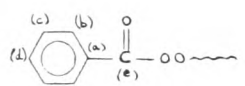
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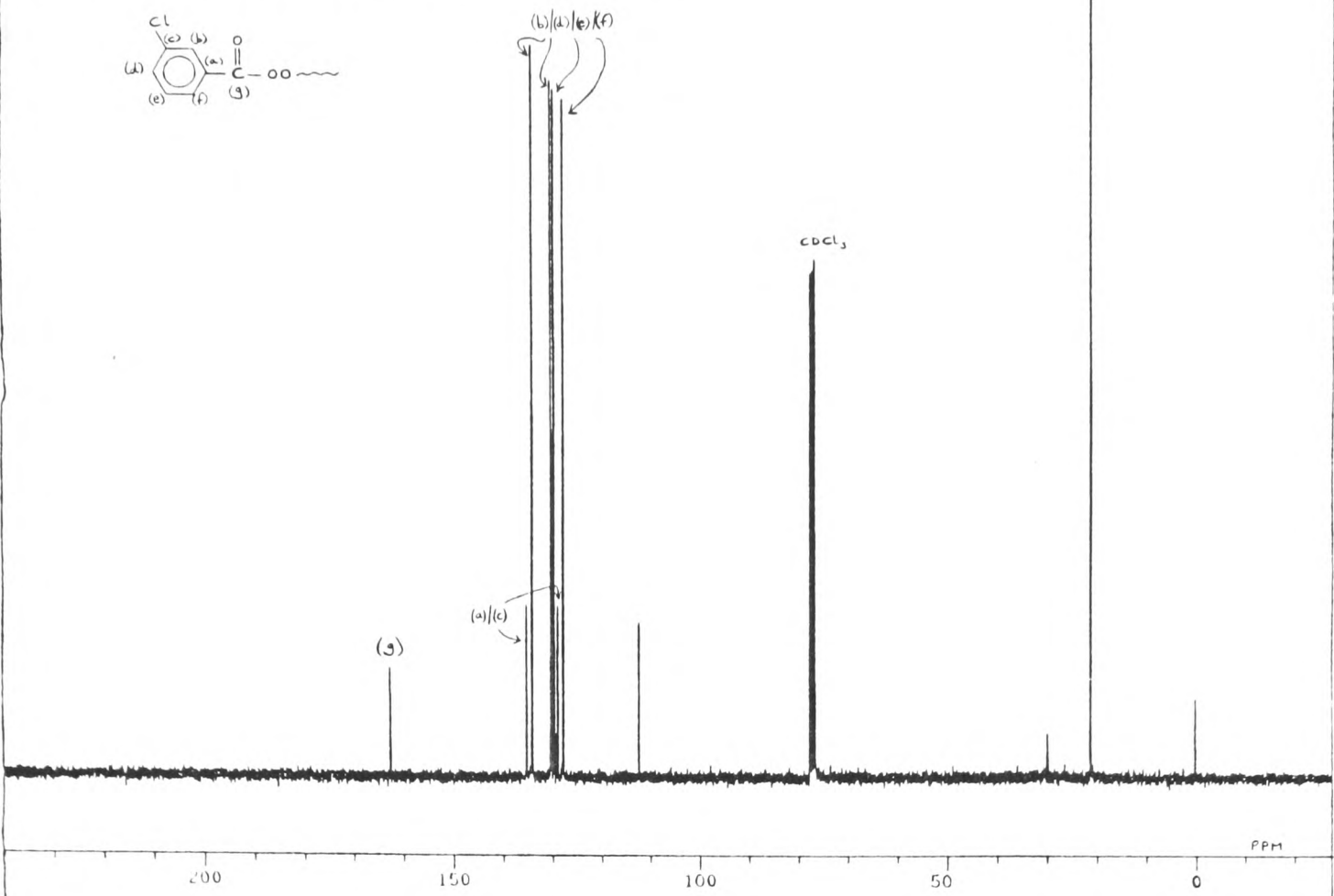
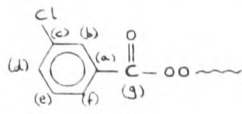
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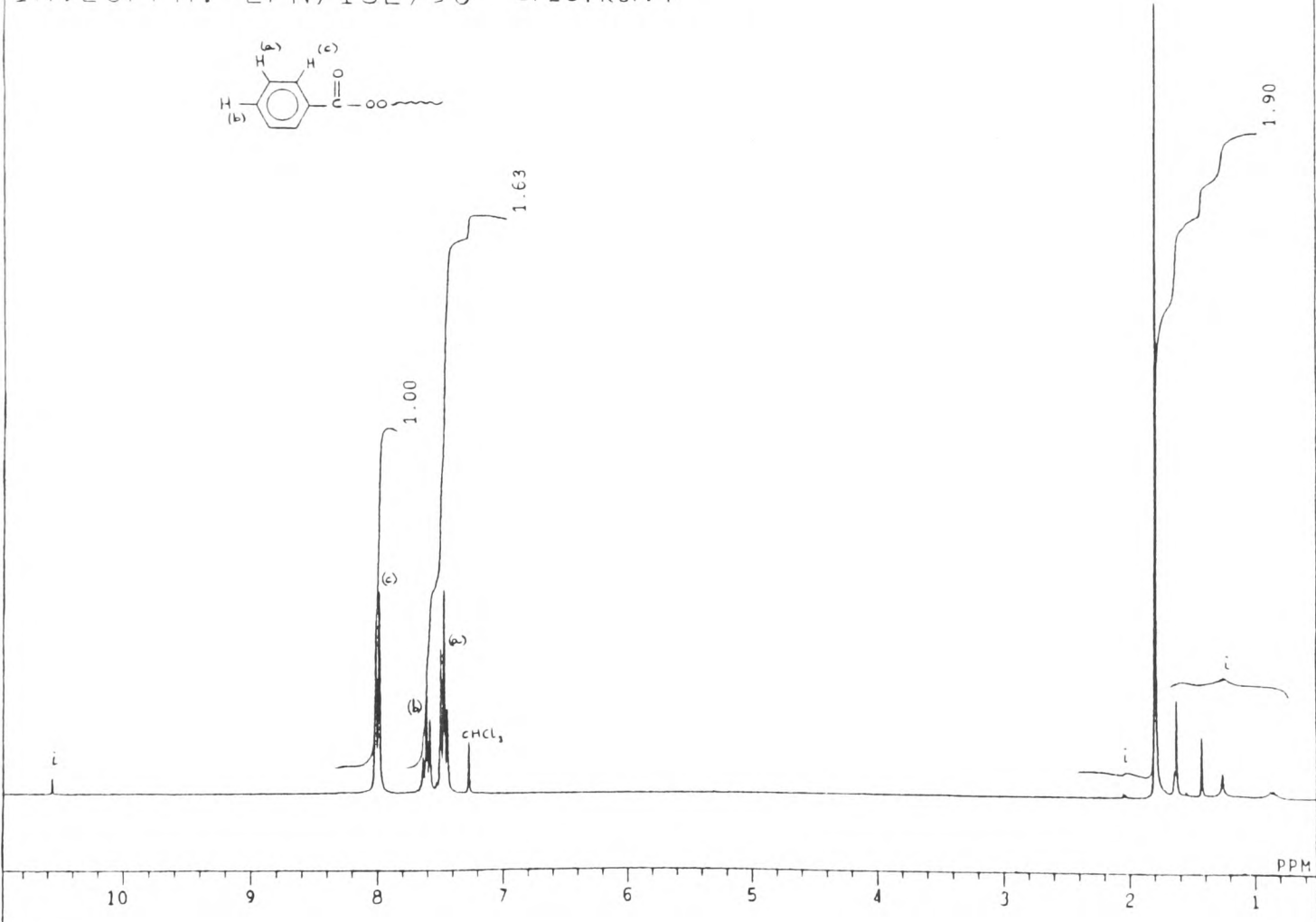
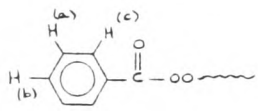
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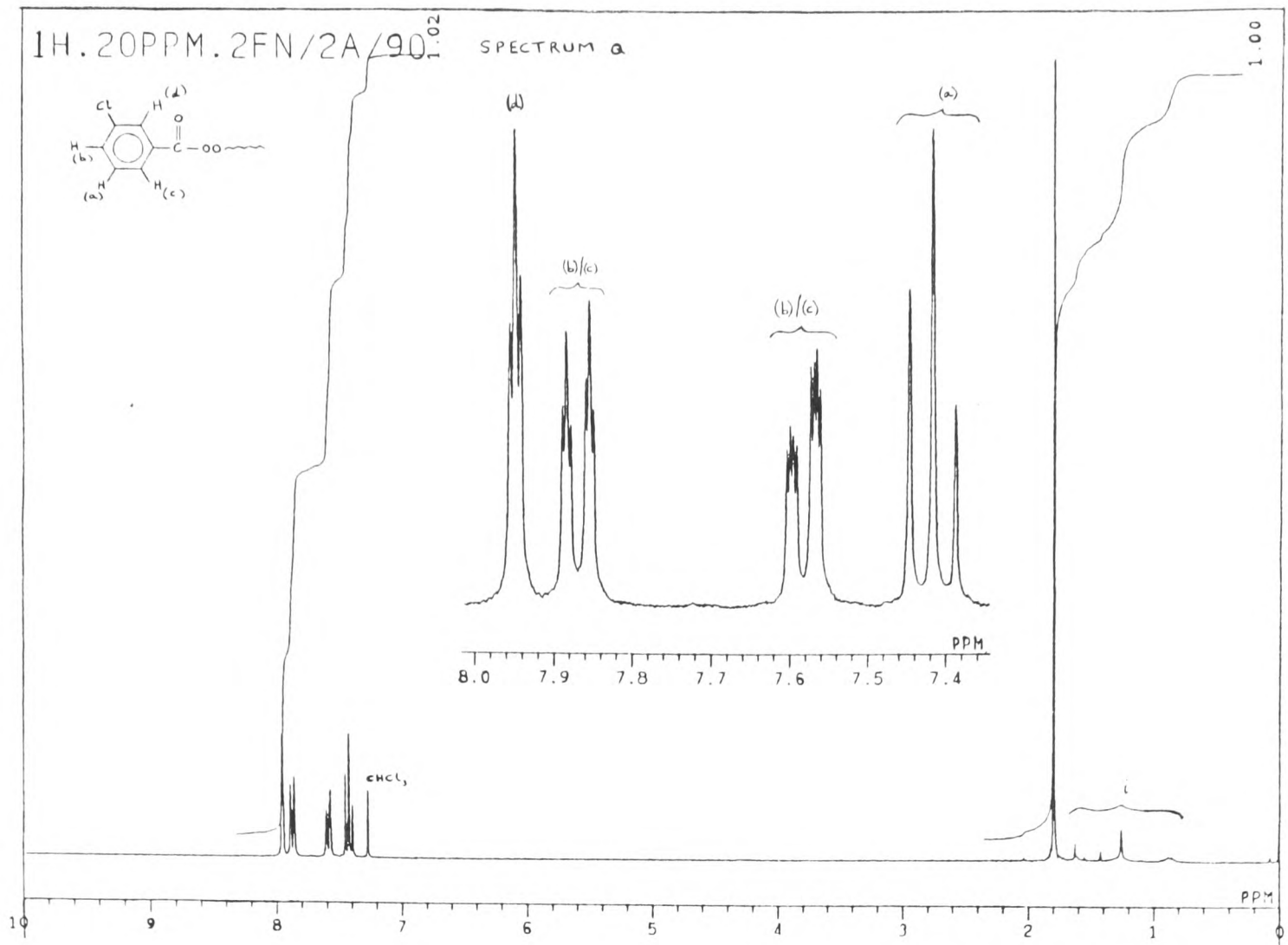


13C.250PPM.2FN/2A/90 SPECTRUM O



1H.20PPM. 2FN/13E/90 SPECTRUM P





i=impurity