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OXIDATIVE DESELENATION AND DESULPHURISATION AT PENTACOVALENT PHOSPHORUS

by

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A thesis submitted in fulfilment of the
requirements for the degree of
Doctor of Philosophy
of
The City University
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ABSTRACT

Oxidative deselenation and desulphurisation at pentacovalent phosphorus, using a variety of chemical oxidising reagents and photochemically generated species has been investigated.

Chapter 1 provides a general introduction to the photochemistry while chapters 2, 4 and 6 contain a discussion of oxidative deselenation at pentacovalent phosphorus with singlet oxygen, 1,2-dicarbonyl based initiators and a manganese III porphyrin in the presence of periodate ions and imidazole. Evidence for the involvement of singlet oxygen, in dye sensitised oxidative deselenation reactions, has been obtained from quenching studies and further inferred by examining the kinetic solvent isotope effect. The photooxidative deselenation reactions promoted by 1,2-dicarbonyl based initiators are thought to occur via the intermediacy of peroxy radicals. Possible mechanisms for these reactions have been postulated.

Chapters 3 and 5 report on the oxidative deselenation and desulphurisation at pentacovalent phosphorus by a number of photochemically generated species. These include a persulphoxide, excited N-oxides (or their photoproducts) and a carbonyl oxide.

In chapter 7 oxidative deselenation and desulphurisation at pentacovalent phosphorus, using a

large number of chemical oxidising reagents, has been reported. Various mechanisms have been proposed.

Finally, chapter 8 describes the experimental procedure for the preparation of organophosphorus compounds, in addition to the details of the various oxidation reactions and methods for analysing the products of these reactions.

CONTENTS

Dedicated to my parents for their
continuous support and neverending
encouragement throughout the years.

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Some of the work reported in here has been presented in the following publications:

(1) "Oxidative Desulphurisation and Deselenation at Pentacovalent Phosphorus by Photogenerated Peroxidic Species," Raj K. Bhardwaj and R.S. Davidson, Tetrahedron. (Accepted for publication.

(2) "The use of N-Oxides to Photoinduce the Oxidative Desulphurisation and Deselenation at Pentacovalent Phosphorus," Raj K. Bhardwaj and R.S. Davidson, J.Chem.Research. (Accepted for publication).

(3) "The Oxidative Desulphurisation and Deselenation at Pentacovalent Phosphorus catalysed by Metalloporphyrins," R.S. Davidson, M.D. Walker and (in part) Raj K. Bhardwaj, Tetrahedron Letters, 1987,28(26), 2981-2987.

Some of this work has also been presented at the 2nd European Postgraduate Symposium on Photochemistry, Mülheim, Germany, in October 1986.

CHAPTER 1

INTRODUCTION TO PHOTOCHEMISTRY

1.1 INTRODUCTION

Since several of the text books[1-6] have produced excellent reviews, regarding the creation of high energy electronic states and the detailed mechanistic investigations of the various complex decay processes that are open to these states, only a basic introduction to photochemistry is given here. Photochemistry is concerned primarily with the fate of the single photon of either ultra-violet or visible radiation by the molecule. The energy associated with these photons is proportional to the frequency (ν) of the respective radiations and is given by equation 1.1.

$$E = h\nu = hc/\lambda \tag{1.1}$$

where E is the energy of photons, h is the Planck's constant, c is the velocity of light, and λ the wavelength of incident light.

However, if these higher energy species or molecules are not utilised in the photochemical reactions they can then return to the stable ground state (S_0) by various photophysical processes which are available to them. These are illustrated schematically in fig.1.1. Such a schematic representation of the energy levels and photophysical processes which can occur in the excited molecule is commonly called a Jablonski diagram.[7] The electronic states are represented by the heavy horizontal lines while the vibrational states, associated with each electronic energy level or state, are depicted as narrow lines; the symbols S_0, S_1, S_2 and T_1 represent the ground state, first and second excited singlet states (electron spins antiparallel), and the first triplet state (electron spins parallel) respectively. These sets of energy levels are commonly referred to as the singlet and triplet manifolds.

The lowest triplet level (T_1) is usually placed at lower energy than the lowest excited singlet level (S_1), in accordance with Hund's rule. This states that the state of maximum multiplicity, i.e. with the highest number of unpaired electrons, lies at the lowest energy.

Upon excitation of a molecule, rapid transitions from the singlet ground state to the singlet excited states take place. The rate constant measurements have shown these absorptions to be extremely efficient i.e. in the general range $10^{15} - 10^{16}$ sec^{-1}.

The "activated molecule", apart from undergoing chemical reactions, may dissipate its acquired energy through intramolecular transitions from the vibrational levels of the upper electronically excited state to the higher vibrational levels of the lower excited state. These processes are known as Internal Conversions (IC) and are not as efficient as absorption transitions, but nevertheless they still have relatively high rate constants in the range ($S_2 \rightsquigarrow S_1$) $10^{11} - 10^{14}$ and ($S_1 \rightsquigarrow S_0$) $10^{6} - 10^{12}$ sec^{-1}.

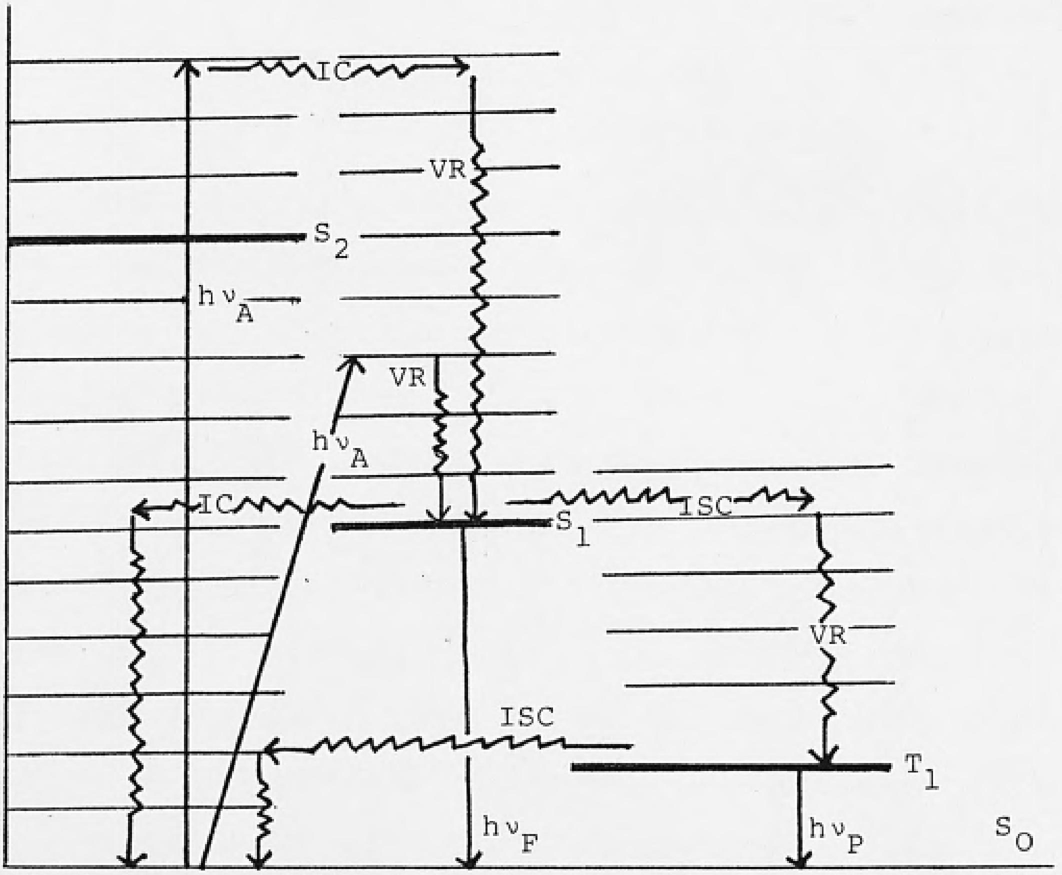


Fig.1.1; A modified Jablonski diagram showing both non-radiative and radiative processes available to molecules. Where IC = internal conversion; VR = vibrational relaxation; ISC = intersystem crossing; $h\nu_F$ = fluorescence; $h\nu_P$ = phosphorescence and $h\nu_A$ = absorption.

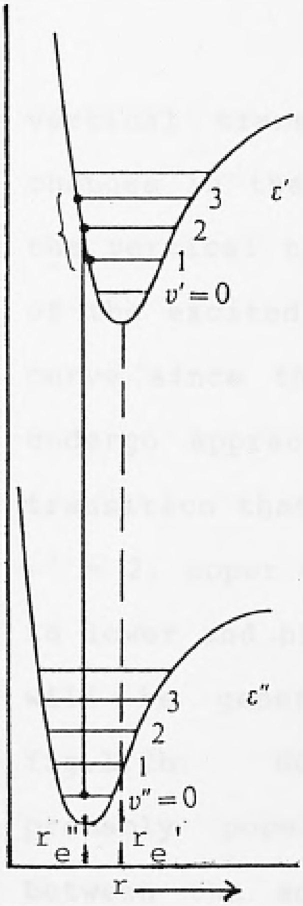
The internal conversions are followed immediately by further transitions, from higher to lower vibrational levels to eventually populate the lowest vibrational level of the excited state. These transitions occur within each excited state and are termed Vibrational Relaxation (VR). The VR processes enable the high energy molecule to transfer its excess vibrational quanta to other molecules by molecular collisions, involving a rate constant in the general range $10^{12}sec^{-1}$. Thus emissions from upper excited states are not observed under normal conditions. These two intramolecular (Internal Conversion and Vibrational Relaxation) transitions are known as radiationless or non-radiation processes.

The molecule may also lose its acquired energy by a third radiationless process called Intersystem Crossing (ISC). This involves electronic transitions between singlet and triplet states. Under the selection rules ISC is spin-forbidden and therefore should not occur. However, the singlet and triplet states are mixed, through the process of spin-orbital coupling. These intersystem crossing processes proceed relatively fast with rate constants in the region of 10^4-$10^{12}sec^{-1}$ for $S_1 \rightsquigarrow T_1$ transitions. They can be enhanced by internal and external heavy atom effects e.g. by incorporation of an Iodine atom into the molecule, by the presence of xenon in solution or the use of solvents containing heavy atoms.

Furthermore, transitions from the $T_1 \longrightarrow S_0$ states, Radiative Phosphorescence, are fairly slow with lower rate constants i.e. in the region of 10^{-1}-10^{+5}sec^{-1}. Consequently, the lowest triplet states are relatively long-lived in comparison to the lowest singlet states. Therefore the probability of photochemical reactions arising from the chemical reactivity of the triplet states is increased. In addition these triplet states are readily quenched by impurities in the solvents, and thus the radiative process of phosphorescence is prohibited. Decay processes such as vibrational relaxation, which occur immediately after intersystem crossing, and internal conversion operate in the triplet states as they do in the singlet states.

The excited molecule can also return to the ground state by the second radiative route, involving electronic transitions between states of same multiplicity i.e. $S_1 \longrightarrow S_0$. These processes are rapid and produce rate constants in the region of 10^6-10^9sec^{-1} and are accompanied by the emission of a quantum of light (h ν) from the excited state. This is a characteristic of radiative transitions. These emissions are known as Fluorescence and they may complete with radiationless processes.

1.1a Franck - Condon Principle; states that electronic transitions are so fast (10^{-15}sec), in comparison to nuclear motion (10^{-12}sec), that during the act of electronic transitions the nuclei do not alter appreciably their relative positions or their kinetic energies. Hence the initially formed excited state must have similar geometry to the ground state. This is illustrated by referring to Morse Curves such as those shown in fig.1.2a. The curves represent the potential energy of the electronic ground state (ε'') and of an excited state (ε') of a diatomic molecule as a function of the internuclear distance (r).



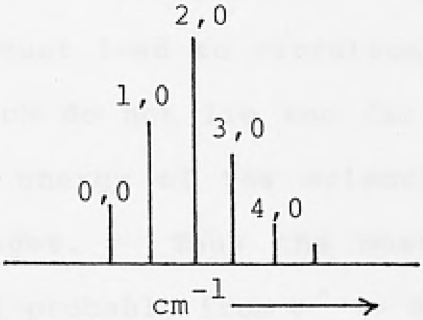


Fig.1.2(b); consequence of $r_e' > r_e''$.

Fig.1.2a; Schematic representation of potential energy curves of a diatomic molecule illustrating the application of the Franck-Condon principle.

This example represents a common situation where the equilibrium internuclear distance in the excited state is slightly larger than the corresponding distance in the ground state. This is to be expected since the excitation of an electron, from the bonding or non-bonding orbital to an anti-bonding orbital, results in a weakening of the bond.

Since at room temperature almost all of the molecules are in the lowest vibrational level ($\nu'' = 0$) of the ground state, excitation will occur from this level. According to the Franck-Condon principle, only vertical transitions are allowed since instantaneous changes in the bond distance cannot occur. Moreover, the vertical transition must lead to vibrational levels of the excited state which do not lie too far from the curve since the kinetic energy of the molecule cannot undergo appreciable changes. Thus the most intense transition that occurs is probably from $\nu'' = 0$ to $\nu' = 2$, upper vibrational state. Although transitions to lower and higher ν' states can also take place these will be generally weak in intensity, as shown in fig.1.2b. However, in general, the upper state most probably populated will depend on the difference between the equilibrium separations in the lower and upper state. For example when the upper state separation (r_e') is considerably greater than that in the lower state (r_e'') the vibrational level to which a transition takes place has a high ν' value. Further, transitions can occur to a state where the excited molecule has energy in excess of its own dissociation energy. From such states the molecule will dissociate without any vibration and, since the atoms which are formed may take up any value of kinetic energy, the transitions are not quantised and a continuum results, fig.1.3

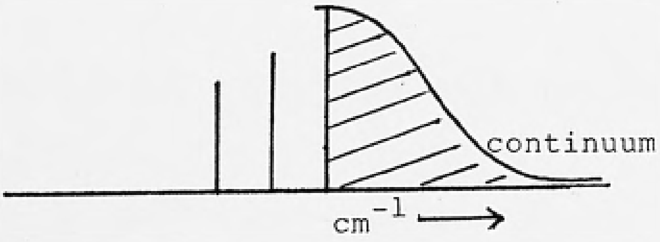


Fig.1.3; Showing the consequence of $r_e' \gg r_e''$.

Alternatively, for an ideal system with the same equilibrium internuclear distance in the excited and ground state i.e. $r_e' = r_e''$, the most intense and likely transition occurs from $\nu'' = 0$ to $\nu' = 0$. This is referred to as the (0,0) transition. In addition transitions to $\nu' = 1,2,$etc can also proceed, as shown in fig.1.4, but these diminish rapidly in intensity.

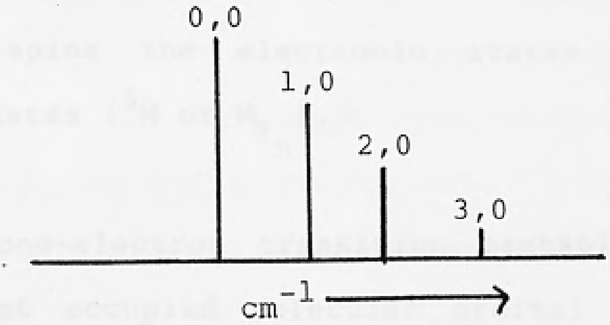


Fig.1.4; Showing the consequence of $r_e' = r_e''$.

1.1b Molecular Orbitals Involved in Electronic Transitions.

On absorption of ultra-violet or visible light by a molecule, as a first approximation, only one electron is promoted to a higher energy level while all others are unaffected. The initial excited state thus produced has a short lifetime, $10^{-6} - 10^{-9}$sec, and as a consequence of the time interval involved for an electronic transition, 10^{-15}sec, no change of electron spin can occur during this electronic excitation. These types of states where both electrons in the ground and excited states have antiparallel spins, are referred to as singlet states (^{1}M or M_{S_n} where n = 0 or a positive integer). Where the two electrons have parallel spins the electronic states are known as triplet states (^{3}M or M_{T_n}).

The one-electron transition probably occurs from the highest occupied molecular orbital to the lowest available unfilled orbital, but in several cases many transitions can proceed thus giving numerous absorption bands in the spectrum. However, not all transitions from filled to unfilled orbitals are allowed. In order to decide whether a transition is allowed or forbidden the following points must be taken into consideration:

(i) The geometry of the ground state molecular orbital

(ii) The geometry of the excited state molecular orbital

(iii) The orientation of the electric dipole of the incident light that might induce the transition.

Provided these three have an appropriate symmetry relationship with each other, the transitions will be allowed.

The appropriate electronic transitions in terms of σ (bonding), σ* (antibonding), π (bonding), π* (antibonding), and lone pair (nonbonding, designated by n) orbitals are shown in fig.1.5. In most organic molecules σ orbitals have the lowest energy, with the energies of π, π* and σ* orbitals being progressively higher. The energy of π orbitals is strongly influenced by the degree of conjugation.

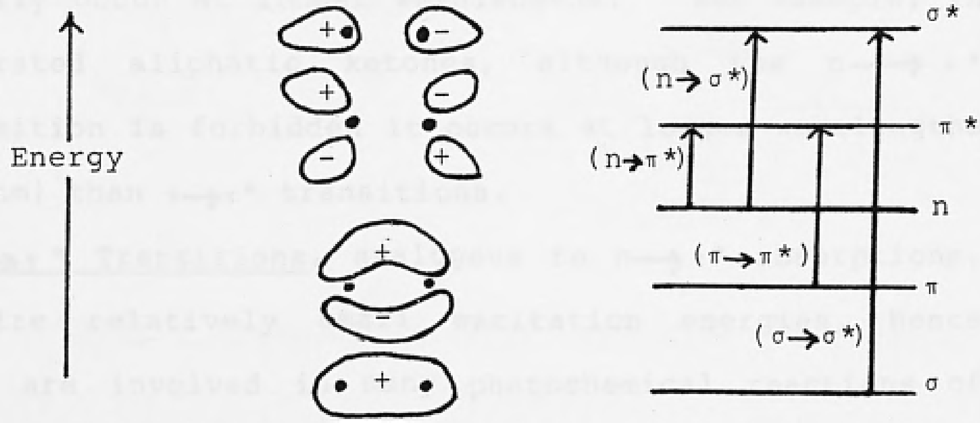


Fig.1.5;Orbitals involved in electronic transitions of Organic molecules and their relative energies.

The energy of n orbitals may lie above or below that of the π orbitals, although in the above example it is shown to be higher in energy than in the π orbital. The most common transitions encountered in organic molecules are: $n \longrightarrow \pi^*$, $\pi \longrightarrow \pi^*$, $n \longrightarrow \sigma^*$ and occasionally $\sigma \longrightarrow \sigma^*$, as shown in fig.1.5. Depending on which transition takes place a variety of molecular excited states is possible. For example an excited state derived from an $n \longrightarrow \pi^*$ transition is known as an n,π^* state, that from a $\pi \longrightarrow \pi^*$ transition as a π,π^* state and so on.

$n \longrightarrow \pi^*$ Transitions are very important since these are usually the lowest in energy and are characteristic of molecules possessing chromophores with multiple bonded heteroatoms, e.g. C = 0, C = N, C = S and N = 0. However, since the transitions are normally highly symmetrical in nature they are forbidden under the symmetry requirements discussed earlier. Hence, only low intensity absorptions can be produced. These usually occur at longer wavelengths. For example, in saturated aliphatic ketones, although the $n \longrightarrow \pi^*$ transition is forbidden it occurs at longer wavelengths (~280nm) than $\pi \longrightarrow \pi^*$ transitions.

$\pi \longrightarrow \pi^*$ Transitions, analogous to $n \longrightarrow \pi^*$ absorptions, require relatively small excitation energies, Hence they are involved in many photochemical reactions of organic molecules. However, since these transitions are symmetry allowed, intense broad absorptions in the vacuum ultra-violet may be produced. In simple alkenes, several transitions are available, but the lowest energy transition $\pi \longrightarrow \pi^*$ is the most important and occurs around 170-190nm. Furthermore, in conjugated alkenes this transition shifts to longer wavelengths. This occurs because the π orbitals of the separate alkene groups combine to form new orbitals, two bonding (π_1, π_2) and two antibonding (π_3^*, π_4^*), fig.1.6. The consequence of these orbital combinations is a reduction in the energy gap between the highest occupied molecular orbital and the lowest unoccupied molecular orbital. Hence the new $\pi \longrightarrow \pi^*$ transition, of very low energy ($\pi_2 \longrightarrow \pi_3^*$), becomes possible.

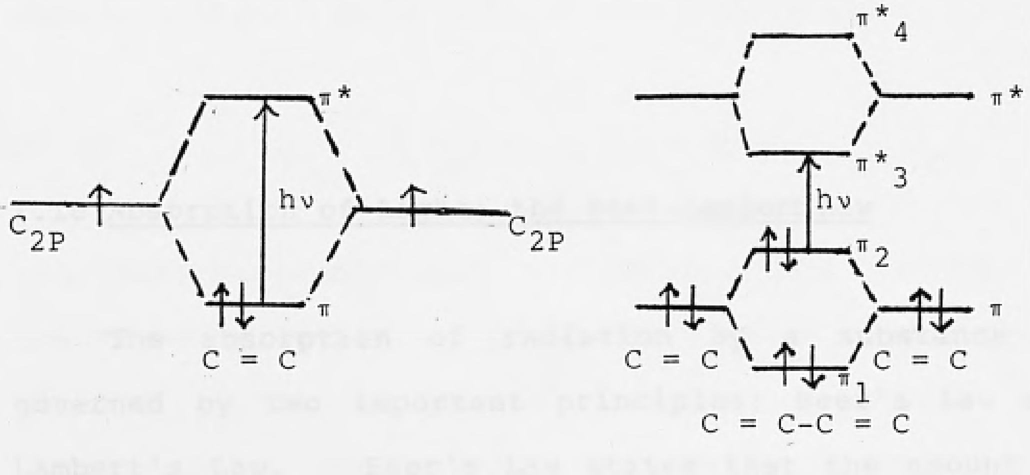


Fig.1.6;Orbital energies of ethene and buta -1, 3-diene.

$n \rightarrow \sigma^*$ Transitions are partially forbidden and hence give rise to low intensity absorptions. In the case of alkylhalides the excitation of a non-bonding halogen P-electron into the σ^* antibonding C-X orbital leads to the homolytic cleavage of the C-X bonds, relatively efficiently, to generate alkyl and halogen radicals.

Scheme 1.1 $$R - X \xrightarrow[\text{light}]{\text{ultraviolet}} R^{\cdot} + X^{\cdot}$$

$\sigma \rightarrow \sigma^*$ transitions are high energy absorptions and involve the promotion of an electron from the low-lying σ orbital to a high-energy σ^* antibonding orbital. These transitions occur at very short wavelengths of ultraviolet light, around 150nm, and are associated with saturated hydrocarbons.

1.1c Absorption of Light; the Beer-Lambert Law

The absorption of radiation by a substance is governed by two important principles: Beer's Law and Lambert's Law. Beer's Law states that the amount of light absorbed is proportional to the concentration of absorbing molecules in the light path, while Lambert's

Law states that the proportion of light absorbed by a medium is independent of the initial intensity (I_o).

These relationships are best expressed in terms of the combined Beer-Lambert Law, which is given by equation:

(1.2) $$\log(I_o/I_t) = \varepsilon Cl$$

Where I_o is the intensity of incident monochromatic light, I_t is the intensity of the transmitted light, ε is the molar absorptivity (formerly referred to as the molecular extinction coefficient, $mol^{-1}dm^3cm^{-1}$), C is the concentration of solute ($mol\ dm^{-3}$), l is the path length of the sample (cm) and $\log(I_o/I_t)$ is the absorbance (A) of the solution, formerly called optical density, which can be defined as shown in equation 1.3:

(1.3) $$A = \log(I_o/I_t) = \varepsilon Cl$$

Modern double-beam instruments can record the absorbance directly. Hence for a given concentration of the absorbing material, of known optical path length, molar absorptivity can easily be calculated. This will be constant for a particular compound at a given wavelength and is most commonly expressed as ε_{max}, the molar absorptivity at an absorption band maximum.

If there is more than one absorbing species present in the solution the total absorbance of the system is then given by the sum of the absorbances of the individual components i.e. $A = \sum \epsilon Cl$, provided that the components do not interact.

1.1d Quantum Yields

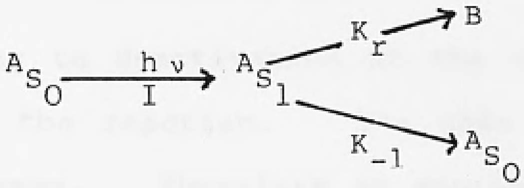
The efficiency of photochemical reactions and photophysical processes can be described by their quantum yield (ϕ). This is defined as the number of molecules undergoing a particular process divided by the number of photons absorbed:

$$(1.4) \qquad \phi = \frac{\text{number of molecules which react}}{\text{number of photons absorbed}} = \frac{\text{rate}}{I}$$

Where I is the rate (i.e. intensity) of absorption of radiation.

For a molecule (A) undergoing light absorption and the reaction from its lowest excited singlet state (S_1) to form a product (B) the following simple scheme can be written:

Scheme 1.2



$$\begin{tikzcd} & & B \\ A_{S_0} \arrow[r, "h\nu", "I"'] & A_{S_1} \arrow[ur, "K_r"] \arrow[dr, "K_{-1}"'] & \\ & & A_{S_0} \end{tikzcd}$$

The quantum yield (ϕ_B) for the product formation can now be given by:

(1.5) $$\phi_B = \frac{\text{rate of formation of product B}}{I} \equiv \frac{K_r [A_{S_1}]}{I}$$

using the steady state approximation for $[A_{S_1}]$,

$$\frac{d[A_{S_1}]}{dt} = 0 = I - (K_r + K_{-1})[A_{S_1}]$$

(1.6) $$[A_{S_1}] = I/(K_r + K_{-1})$$

Substitution of $[A_{S_1}]$ into equation 1.5 gives

1.7 $$\phi_B = \frac{K_r}{(K_r + K_{-1})}$$

where $K_{-1} = K_{ic} + K_{isc} + K_f$ - rate constants for internal conversion, intersystem crossing and fluorescence respectively.

Thus the efficiency of the reaction depends only upon the rate of reaction relative to the rates of all processes leading to deactivation of the excited state responsible for the reaction. The same is true for all other processes. Therefore an expression for the quantum yield for any particular process can be written without going through the above kinetics:

(1.8) $$\phi_f = \frac{K_f}{(K_r + K_{ic} + K_{isc} + K_f)}$$

(1.9) $$\phi_{isc} = \frac{K_{isc}}{(K_r + K_f + K_{ic} + K_{isc})}$$

where ϕ_f, ϕ_{isc} are quantum yields of fluorescence and intersystem crossing respectively.

For a reaction taking place in the triplet state, the quantum yield is not only dependent upon the relative rates of the process and other processes leading to deactivation of the triplet state but also on the efficiency with which the triplet state can be populated (θ_{isc}). Hence, the quantum yield of phosphorescence (ϕ_p) is given by:

(1.10) $$\phi_p = \theta_{isc} \left(\frac{K_p}{K_p + K'_{isc}} \right)$$

where K_p, K'_{isc} are rate constants for phosphorescence and intersystem crossing ($T_1 \rightsquigarrow S_0$) respectively: However, since

$$\theta_P = \left(\frac{K_P}{K_P + K'_{isc}}\right) \tag{1.11}$$

the quantum yield of phosphorescence becomes

$$\phi_P = \theta_{isc} \cdot \theta_P \tag{1.12}$$

where θ_{isc}, θ_P are the quantum efficiencies of intersystem crossing and phosphorescence respectively. Quantum efficiency is the ratio of the rate of a process involving an excited state to the rate of production of that state, hence it is distinct from quantum yield.

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CHAPTER 2

DYE SENSITISED PHOTO-OXIDATIVE DESELENATION OF PHOSPHINE SELENIDES

2.1 INTRODUCTION

The oxidation of organic and biological substrates in the presence of oxygen, light and a photosensitising dye was originally[1] believed to involve an activated substrate and not an activated form of oxygen. However, it is now generally accepted that an excited state of molecular oxygen ($^1O_2$) is involved in many of these processes.[2-5]

The apparent desire to study the behaviour of singlet oxygen has prompted much interest in its production and reaction mechanisms. In general singlet oxygen can be produced upon irradiation of highly coloured dyes such as Methylene blue and Rose Bengal, in the presence of molecular oxygen. These reactions are referred to as photosensitised and can be visualised as occurring by the following sequence of processes.

Scheme 2.1

$S_0 + h\nu \longrightarrow S_1$ (Light absorption)

$S_1 - h\nu \longrightarrow S_0$ (Fluorescence)

$S_1 \longrightarrow S_0$ (Internal conversion)

$S_1 \longrightarrow T_1$

(Intersystem crossing)

$T_1 \longrightarrow S_0$

$S_1 + {}^3O_2 \longrightarrow T_1 + {}^1O_2$

(Energy transfer)

$T_1 + {}^3O_2 \longrightarrow S_0 + {}^1O_2$

where S_0, S_1 and T_1 are the singlet ground state, lowest singlet excited state and the lowest triplet excited state, respectively, of the sensitiser or dye, and ${}^3O_2$ and ${}^1O_2$ are the ground and excited state, respectively, of molecular oxygen. This reaction scheme suggests that both singlet and triplet excited states of the sensitiser can transfer their energy to molecular oxygen. Indeed, oxygen has been known to reduce the fluorescence of many organic molecules[6] thereby generating singlet oxygen.

The mechanism of fluorescence, believed to involve the transient formation of a collision complex between the organic molecule and oxygen $O_2({}^3\Sigma_g^-)$, predominates when the collision complex has lower energy than the excited singlet of the sensitiser. The triplet state configuration of the molecular oxygen imparts to the whole complex a triplet multiplicity.

The excitation of one of the complex counterparts leads to several energy levels of excited states of the complex (fig.2.1).[11]

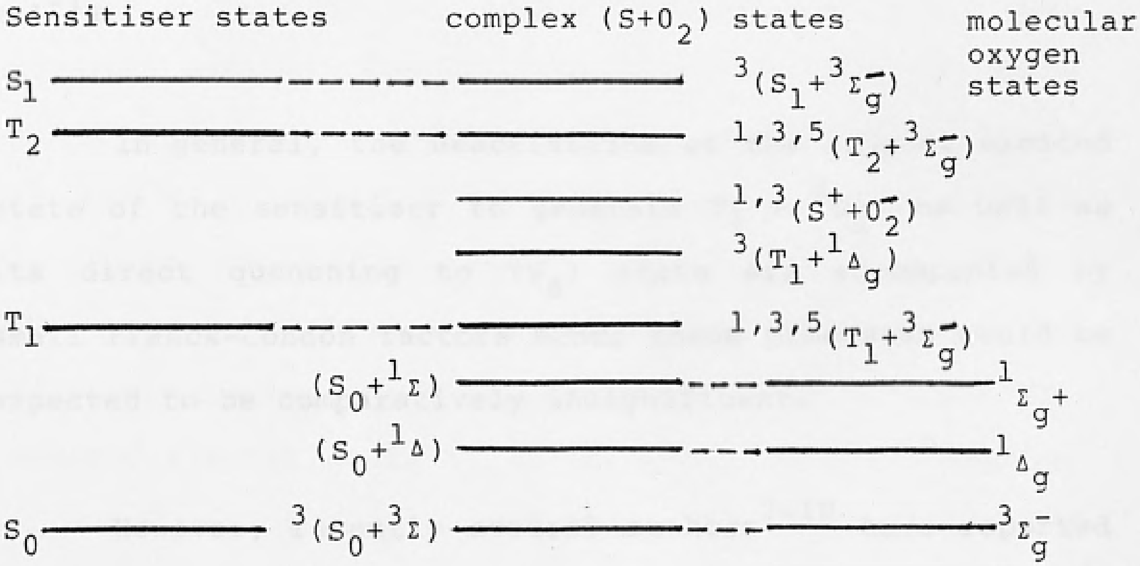


Fig.2.1; A diagram of the energy levels in the photosensitised generation of singlet oxygen.

From the point of view of singlet oxygen generation, the dissociation of the collision complex to T_1 + $^1O_2$ is definitely the most significant process.

Alternatively, a collision complex having higher energy than (S_1) state may dissociate via enhanced intersystem crossing followed by rapid vibrational relaxation to populate the lowest vibrational level $(\nu=0)$ of the first triplet state (T_1). The excess vibrational energy associated with this process can then be transferred to molecular oxygen to give singlet oxygen species, assuming the energy is greater or equal to the energy required to produce $^1O_2$ $(^1\Delta_g)$ from molecular oxygen (i.e. 7880cm^{-1} or 94.5KJ mol^{-1}).

In general, the deactivation of the singlet excited state of the sensitiser to generate $T_1 + {}^1O_2$, as well as its direct quenching to (S_0) state are accompanied by small Franck-Condon factors hence these processes would be expected to be comparatively insignificant.

However, recently several authors[7-10] have reported that the production of singlet oxygen, as a result of the quenching of the excited singlet states of aromatic hydrocarbons with vibrational energies in excess of 7880cm^{-1}, is an efficient and widespread phenomenon with quantum yields greater than unity. For example, rubrene[7a] ($\phi \sim 1.46$), rubrene[7b] ($\phi \sim 1.75$), 1,2-benzanthracene[7b] ($\phi \sim 1.4$), chrysene[7b] ($\phi \sim 1.2$), pyrene[8] ($\phi \sim 1.45$) and 9,10-dicyanoanthracene[9] ($\phi \sim 2.0$). Also kinetic analysis[10] of the self-sensitised photoperoxidation of anthracenes and other aromatic compounds has revealed the direct generation of singlet oxygen ($^1\Delta_g$) (with quantum yield efficiency of approximately unity) and the lowest excited triplet state by the oxygen quenching of the lowest excited singlet anthracenes or other aromatic compounds.

Although the lowest singlet excited states of organic molecules have higher energy than the lowest triplet excited states, the latter have generally longer lifetimes. This therefore, suggests that most of the photooxidation reactions observed for organic molecules presumably proceed via the triplet state. For instance the triplet state (T_1) of benzophenone is readily quenched by molecular oxygen, rather than the excited singlet state (S_1), to sensitise the formation of singlet oxygen[15]. The mechanism of sensitisation involves the formation of a collision complex of triplet sensitiser with ground state oxygen that can be formed with singlet, triplet and quintet multiplicity[11](fig.2.1). Since only the singlet complex can yield $^1O_2$ directly, it follows that the spin statistical factor for direct singlet formation is only 1/9, which is in full agreement with the experimentally observed rate constants for triplet quenching.

Alternatively the triplet - multiplicity complex may also dissociate to the ground state sensitiser and oxygen, via enhanced intersystem crossing. Although statistically favoured (1/3) it has a much smaller Franck-Condon factor and is therefore comparatively insignificant.

The fact that singlet oxygen generation is the major mechanism by which oxygen quenches triplet state molecules has been shown experimentally by direct detection of singlet oxygen emission, in energy transfer studies in the gas phase. Thus, Snelling[12] observed a 1.27 μm emission of $^1O_2$ which he assigned to the quenching of the benzene triplet state by oxygen; in addition the EPR studies showed that the quantum yield of conversion of the sensitiser triplet state to $^1O_2$ was close to unity.[13,14]

Kinetics of quenching and Product (AO_2) Formation in dye sensitised oxidation reactions.

The Kinetic Scheme for a dye-sensitised photooxidation of a $^1O_2$ acceptor (A) in the presence of another $^1O_2$ acceptor (B), e.g. β-carotene, can be represented as follows:

Scheme 2.2

$$^{3}D + {}^{3}O_2 \xrightarrow{K_0} D + {}^{1}O_2 \quad \text{(energy transfer reaction)}$$

$$A + {}^{1}O_2 \xrightarrow{K_1} AO_2 \quad \text{(singlet oxygen oxidation)}$$

$$A + {}^{1}O_2 \xrightarrow{K_2} A + O_2 \quad \text{(deactivation of singlet oxygen)}$$

$$B + {}^{1}O_2 \xrightarrow{K_3} BO_2 \text{ and/or } B + O_2$$

$$^{1}O_2 \xrightarrow{K_4} O_2$$

$$^{3}D + B \xrightarrow{K_5} D + B$$

$$^{3}D \xrightarrow{K_6} D$$

where D is a dye sensitiser (e.g. Methylene blue or Rose Bengal). The expression describing the quantum yield of product (AO_2) formation is given by equation:

2.1

$$\phi_{AO_2} = \left(\frac{\phi_T K_0[O_2]}{K_0[O_2] + K_5[B] + K_4}\right)\left(\frac{K_1[A]}{K_1[A]+K_2[A]+K_3[B]+K_4}\right)$$

where ϕ_T is the quantum yield of triplet dye-sensitiser (^{3}D) formation. Rewriting equation 2.1 as its reciprocal and rearranging gives equation 2.2:

2.2

$$[AO_2]^{-1} = K\phi_T^{-1}\left(1+\frac{K_5[B]+K_6}{K_0[O_2]}\right)\left(1+\frac{K_2}{K_1}+\frac{K_3[B]+K_4}{K_1[A]}\right)$$

where K is a proportionality constant relating the quantum yield of product and $[AO_2]$, the amount of AO_2 formed in a given time. A plot of $[AO_2]^{-1}$ vs. $[A]^{-1}$ gives:

2.3

$$\text{Intercept} = K\phi_T^{-1}\left(1+\frac{K_5[B]+K_6}{K_0[O_2]}\right)\left(1+\frac{K_2}{K_1}\right)$$

2.4

$$\text{Slope} = K\phi_T^{-1}\left(1+\frac{K_5[B]+K_6}{K_0[O_2]}\right)\left(\frac{K_3[B]+K_4}{K_1}\right)$$

The ratio of slope/intercept is the β-apparent value[16], and gives several different kinetic expressions that allow the

2.5

$$\beta = \frac{(K_3[B]+K_4)}{(K_1+K_2)}$$

convenient determination of $(K_1 + K_2)$, rate at which (A) removes $^1O_2$ from the system, under several conditions i.e. either in the absence or presence of $^1O_2$ acceptor (B). In the absence of β-carotene (where $K_3 = 0$) the slope/intercept ratio is given by:

2.6

$$\beta = \left(\frac{K_4}{K_1+K_2}\right)$$

For a known K_4 value in a given solvent, the sum of $(K_1 + K_2)$ can be calculated. However, the rate constant for product formation (K_1) is usually determined by competition studies against a well-defined $^1O_2$ acceptor such as 2-methyl-2-pentene (MP):

$$A + {}^1O_2 \xrightarrow{K_1} AO_2$$

$$MP + {}^1O_2 \xrightarrow{K_1'} MPO_2$$

Thus, the ratio K_1'/K_1, where K_1' is known, gives the

2.7

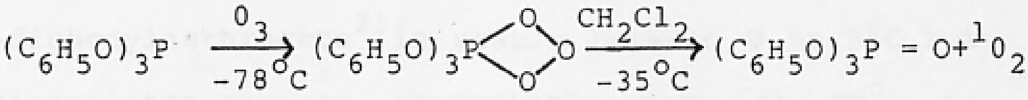
$$\frac{K_1'}{K_1} = \frac{[MPO_2][A]}{[AO_2][MP]}$$

value of K_1 (rate constant for product formation, AO_2).

Generation of singlet oxygen by thermal reactions

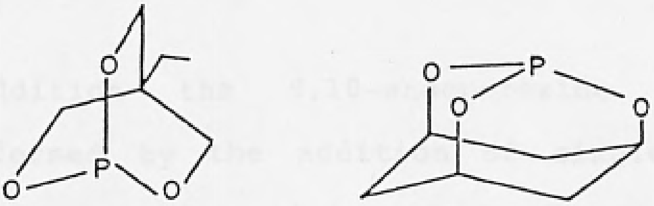
Alternatively singlet oxygen[17,18] can also be generated effectively and efficiently in good yields by the thermal decomposition of triaryl-phosphite-ozone adducts, which are produced by the reaction between a triarylphosphite and ozone at -78°C e.g.

Scheme 2.3



These ozonide adducts serve as a convenient thermal source for singlet oxygen and hence a large number of these adducts have been prepared. Among them, two bicyclic phospites have been reported to form ozonides possessing remarkable stability:

Fig.2.2

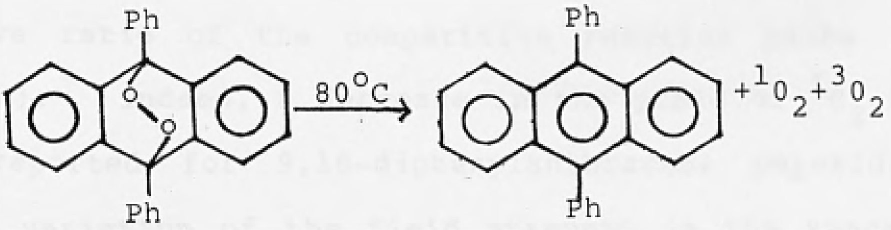


(A) (B)

Thus 4-ethyl-2,6,7-trioxa-1-phosphabicyclo [2,2,2] octane (A) produced singlet oxygen readily at temperatures above 0°C.[19] Similarly, the addition of ozone to 1-phospha-2,8,9-trioxa-adamantane (B) yields an adduct that is 1.4 times more stable than structure (A) at -5°C and still decomposes quantitatively to singlet oxygen.[20]

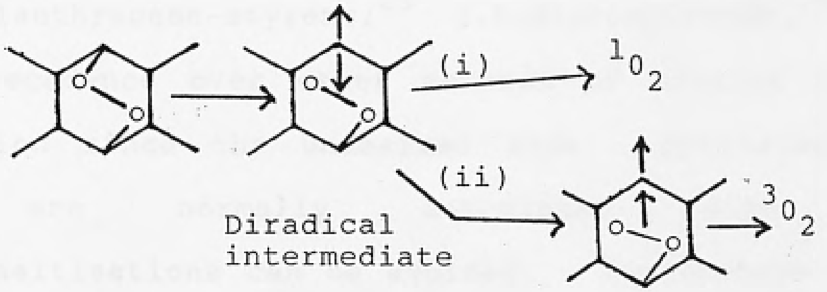
Thermolysis of polycyclic aromatic transannular peroxides can also provide an excellent source of singlet oxygen e.g. the endoperoxide of 9,10-diphenylanthracene[21] is stable between 0 to 5°C but it dissociates at an appreciable rate at 80°C to produce singlet oxygen.

Scheme 2.4



In addition the 9,10-endoperoxide has been initially formed by the addition of singlet oxygen, generated by self-sensitisation of the parent hydrocarbon, across the meso-positions of the aromatic ring. These thermolysis reactions have been proposed[22,23] as occurring via two path ways: (i) a concerted mechanism in which $^1O_2$ is formed quantitatively, and (ii) a diradical mechanism in which both $^3O_2$ and $^1O_2$ are generated.

Scheme 2.5



The evidence in support of the diradical intermediate has been provided by the observation of a magnetic field effect on these reactions.

Considering the above mechanism scheme 2.5, a variable external magnetic field may affect the relative ratio of the competitive reaction paths (i) and (ii). Indeed, a decrease in the yield of $^1O_2$ has been reported for 9,10-diphenylanthracene peroxide[21] with a variation of the field strength in the range 9,000 to 15,000G, thus indicating a diradical mechanism for the thermolysis process. Conversely, no magnetic field effect on the $^1O_2$ yield for thermolysis of 1,4-dimethyl-1,4 peroxide-9,10-diphenylanthracene has been observed since decomposition proceeds predominately via a concerted process.

The 9,10-diphenylanthracene peroxide and endoperoxides of other aromatics, rubrene,[21] alkylnaphthalenes,[24] a copolymer 9,10-di, p-styrylanthracene-styrene,[25] 2,5-diphenylfuran,[26] may take precedence over other methods of singlet oxygen generation since the undesired side - photoreactions that are normally associated with dye photosensitisations can be avoided. Furthermore there is no need to work at low temperatures as in the case of the thermolysis of triarylphosphite ozonides.

The decomposition of hydrogen peroxide (H_2O_2), in the presence of hypochlorites (e.g. NaClO) has also been reported,[27,32] to yield singlet oxygen successfully. For example the $^1O_2$ generated, in quantitative yields, in these reactions has been shown to be effective in the preparative peroxidation of alkenes.[28]

Detailed kinetic studies,[29,31] of the reaction H_2O_2 - HOCl, accompanied with radioactive labelling of the oxygen atoms in the H_2O_2, have shown that in these hypochlorite-hydrogen peroxide systems the singlet oxygen originates from the H_2O_2 and not from the ClO^- or H_2O:[30]

Scheme 2.6

$$H_2\bullet_2 + OCl^- \longrightarrow HOCl + H\bullet_2^-$$

$$H\bullet_2^- + HOCl \longrightarrow H\bullet\bullet Cl + OH^-$$

$$H\bullet\bullet Cl + OH^- \longrightarrow H_2O + Cl\bullet\bullet^-$$

$$Cl\bullet\bullet^- \longrightarrow {}^1\bullet_2 + Cl^-$$

● indicates ^{18}O Labelling

A variation in the hypochlorite-hydrogen peroxide system, bromine-H_2O_2[33] in alkaline solution, has provided a convenient peroxidation method for 9,10-disubstituted anthracenes to their corresponding endoperoxides.

Many other physical and chemical processes over the years have been reported to generate singlet oxygen. There are obviously far too many to be mentioned and discussed individually in this section. However, an extensive summary of these numerous miscellaneous methods has been compiled, in tabular form, by Frimer.[34a]

2.2 Results and Discussion

The oxidation of triphenylphosphine selenide has been investigated previously by Tamagaki and Akatsuka[34b] and reported to proceed in high yields (i.e. 92%) via the tentative involvement of singlet oxygen, generated by irradiation of Rose Bengal dye in chloroform: methanol (1:1 v/v). Similarly, photooxidation of triphenylphosphine sulphide and other trisubstituted phosphine sulphides has been attempted [34c]. However, no oxidation products were observed in these reactions. These observations suggest that the P=Se bond is more reactive towards singlet oxygen than its analogous P=S moiety.

In order to verify the involvement of singlet oxygen, as proposed in the oxidation reaction of triphenylphosphine selenide,[34b] the remainder of this chapter is concerned with the formation and ability of singlet oxygen to initiate oxidative deselenation reactions in a series of phosphine selenides. Furthermore the mechanisms involved in these oxygenations are also discussed.

The photochemical oxidative deselenation of phosphine selenides has been achieved by irradiating a mixture of phosphine selenide and a highly coloured dye e.g. Rose Bengal, meso-tetraphenylporphyrin or Methylene blue in either chloroform or chloroform:methanol (1:1 v/v), in the presence of oxygen. The results obtained are illustrated in table 2.1

Table 2.1 Product yields (%) for dye sensitised reactions of phosphine selenides (1-5).

Dye[a]	(%) oxidation of phosphine selenides[b]				
	Ph_3PSe (1)	$Ph_2PSe(OEt)$ (2)	$PhPSe(OEt)_2$ (3)	$(EtO)_3PSe$ (4)	$(MeO)_3PSe$ (5)
Rose Bengal[c]	97	23	6	1	0
Meso-tetraphenylporphyrin[d]	75	4	2	< 1	1
Methylene blue[d]	80	9	3	< 1	2
Methylene blue[c]	69	-	-	-	-
Meso-tetraphenylporphyrin[c]	68	-	-	-	-

a, Dye conc. 2.0×10^{-4}M.

b, Phosphine selenide (1-5) conc. 3.0×10^{-2}M, irradiated under oxygen for 5 hours through 2% $K_2Cr_2O_7$ solution with daylight fluorescent lamps.

c, Chloroform:methanol (1:1 v/v).

d, Chloroform.

The table shows that phosphine selenide (1) is by far the most reactive selenide in its reaction with singlet oxygen, as inferred from the percentage product yields, in comparison to phosphine selenides (2-5) which showed relatively lower yields of oxidation. In addition it appears that Rose Bengal is a more efficient producer of singlet oxygen under these conditions than either Methylene blue or meso-tetraphenylporphyrin. This is reflected in the percentage product yields obtained. Furthermore, it can be seen that the difference between the oxidative deselenation yields observed for the phosphine selenide (1) with Methylene blue and meso-tetraphenylporphyrin is negligible, although slightly higher deselenation occurred in the mixed solvent system.

These results on their own are not sufficient to suggest that the observed oxidative deselenation reactions involve singlet oxygen. Hence in order to provide positive evidence in favour of singlet oxygen, as the initial active intermediate responsible for the observed deselenations, typical efficient quenchers of singlet oxygen were employed in these studies. β -Carotene,[35] 1,4-diazabicyclo [2,2,2] octane[36] and 6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid are well known quenchers of singlet oxygen at concentrations that are sufficiently low to ensure that competitive quenching of the dye's excited triplet (T_1) does not occur.

It is assumed that over the concentration range of

Table 2.2

Product yields for the dye sensitised photooxidation of Triphenylphosphine selenide (Ph_3PSe)[a]

Dye 2×10^{-4}M in irradiated solution	Solvent system	Quencher (Q)[b]	Conc. of Q in irradiated solution	% $Ph_3P = O$
Rose Bengal	$CHCl_3$:MeOH (1:1 v/v)	DABCO	5×10^{-3}	37
		DABCO	2×10^{-2}	27
		-	-	98
		Trolox	2×10^{-3}	75
		Trolox	1×10^{-3}	39
		-	-	98
		β -carotene	3.3×10^{-4}	38
		β -carotene	1×10^{-3}	10
		-	-	99
Meso-tetraphenyl-porphyrin (TPP)	$CHCl_3$:MeOH (1:1 v/v)	DABCO	5.4×10^{-4}	38
		β-carotene	7.5×10^{-5}	46
		-	-	69
	$CHCl_3$	DABCO	2×10^{-2}	10
		β-carotene	3.3×10^{-4}	9
		-	-	77
Methylene blue (Mb)	$CHCl_3$:MeOH (1:1 v/v)	DABCO	1.3×10^{-3}	41
		β-carotene	1.0×10^{-4}	34
		-	-	51
	$CHCl_3$	DABCO	2×10^{-3}	13
		β-carotene	2×10^{-4}	21
		-	-	75

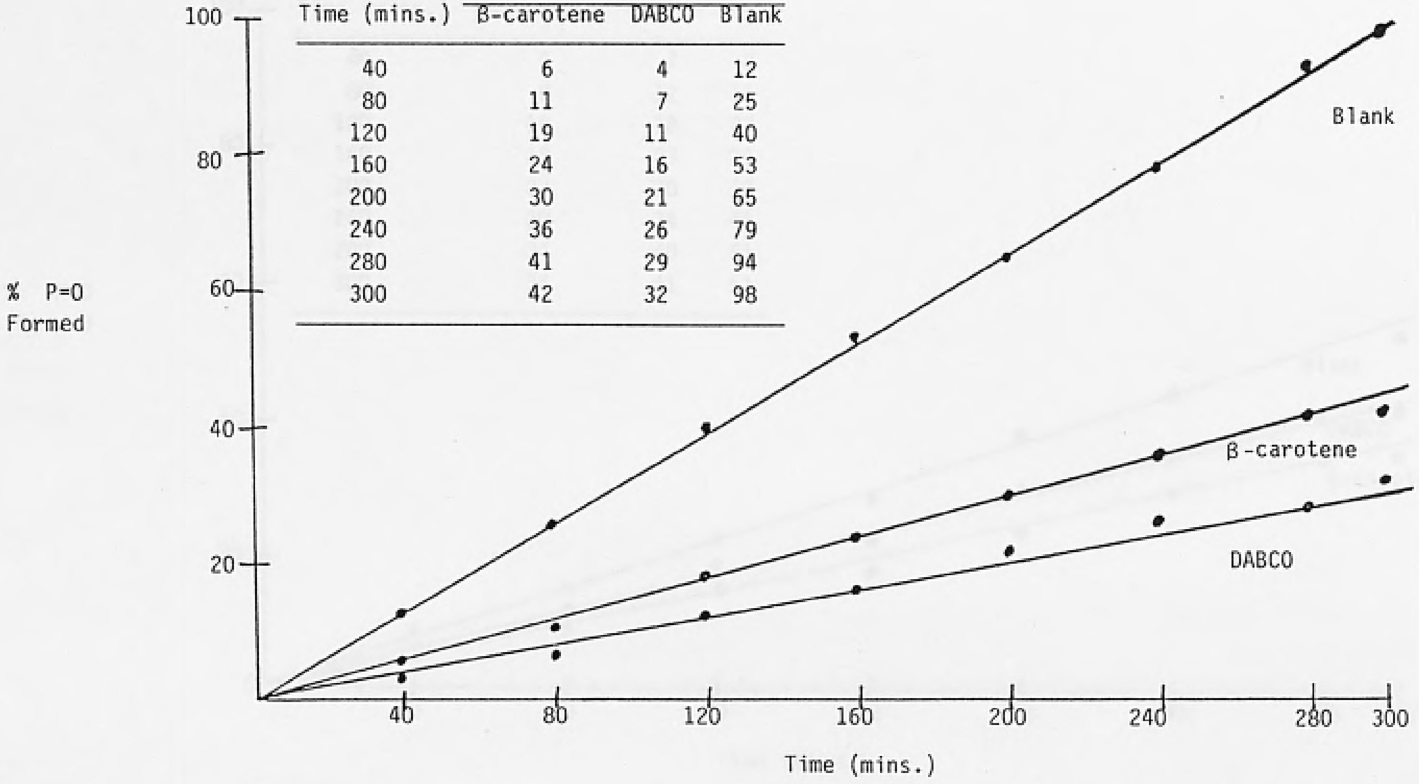
a, Ph_3PSe 3×10^{-2}M in irradiated solution, irradiation under oxygen for 5 hours through 2% $K_2Cr_2O_7$ solution.

b, quenchers were added to the solutions prior to irradiation to provide saturated solutions throughout the photolysis.

c, DABCO ≡ 1,4-diazabicyclo [2,2,2] octane.
Trolox ≡ 6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid.

these quenchers the triplet states of the three dyes were not quenched. The results for these oxidative deselenation reactions, in the presence of quenchers are illustrated in table 2.2

The table shows that Rose Bengal, Methylene blue and meso-tetraphenylporphyrin sensitised oxidations of the triphenylphosphine selenide (1) are lowered by the addition of singlet oxygen quenchers in chloroform:methanol (1:1 v/v) and chloroform solvent system. In the particular case of Rose Bengal dye, the triphenylphosphine selenide (1) was almost completely oxidised (98%) to its corresponding phosphine oxide in the absence of any quenchers. However, in the presence of quenchers, β-carotene ($1x10^{-3}$M), 1,4-diazabicyclo [2,2,2] octane (5×10^{-3}M) and 6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid (1×10^{-3}M) the yields of the triphenylphosphine oxide were reduced to 10, 37 and 39% respectively. Also for the case of meso-tetraphenylporphyrin dye in chloroform, 77% phosphine oxide was formed in the absence of any quenchers. On addition of β-carotene (3.3×10^{-4}M) and 1,4-diazabicyclo [2,2,2] octane (2×10^{-2}M) 9 and 10% yields of triphenylphosphine oxide were observed. Furthermore for the Methylene blue dye in chloroform, in the absence of any quenchers, 75%



Time (mins.)	Quenchers		
	β-carotene	DABCO	Blank
40	6	4	12
80	11	7	25
120	19	11	40
160	24	16	53
200	30	21	65
240	36	26	79
280	41	29	94
300	42	32	98

Fig.2.3: Ph$_3$PSe + Rose Bengal ± β-carotene (3.3 x 10^{-4}M) and DABCO (2 x 10^{-2}M)

	Quenchers		
Time (mins.)	β-carotene	DABCO	None
40	6	7	8
80	9	12	15
120	16	18	22
160	18	23	29
200	23	30	38
240	30	34	46
280	34	40	51
300	34	41	51

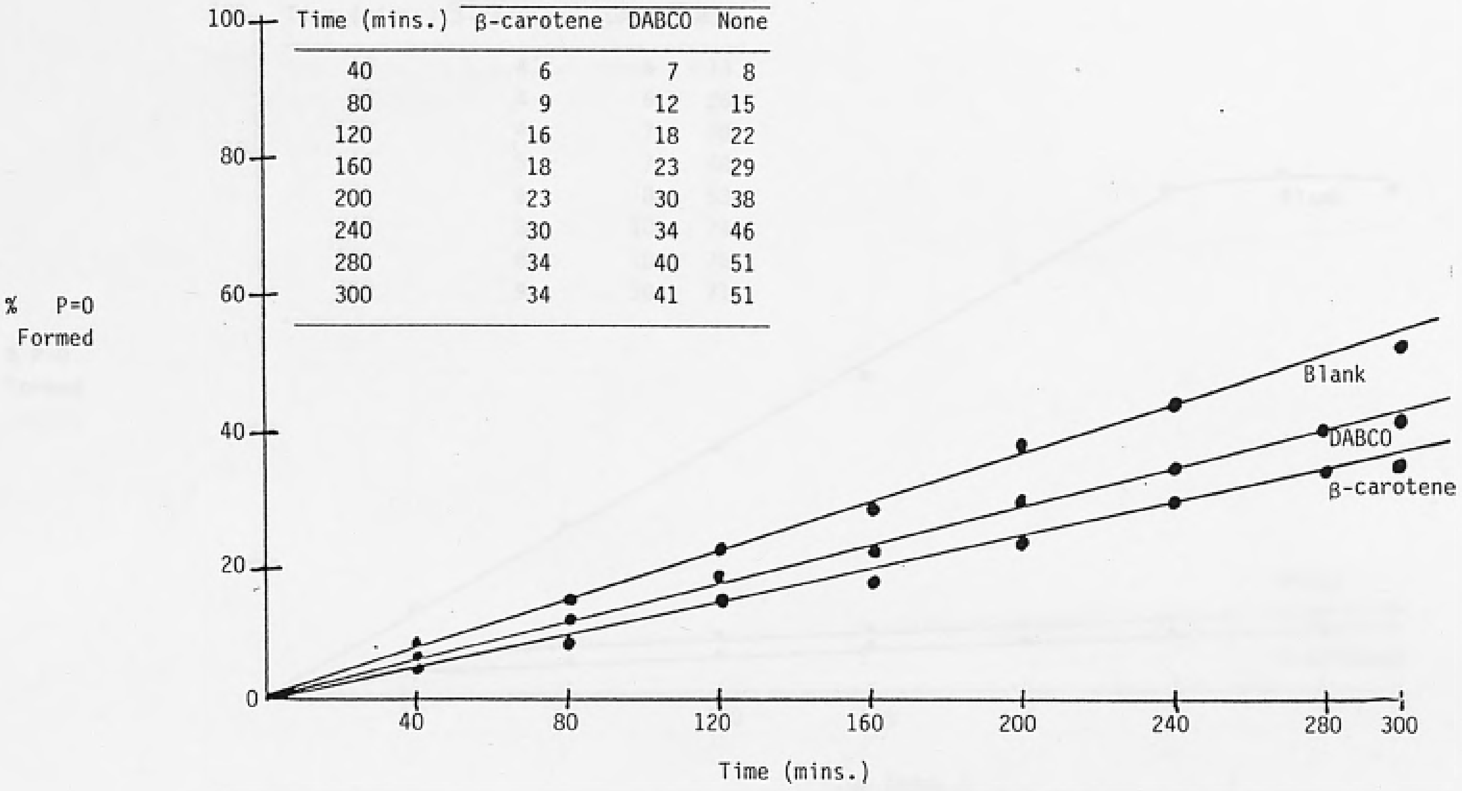
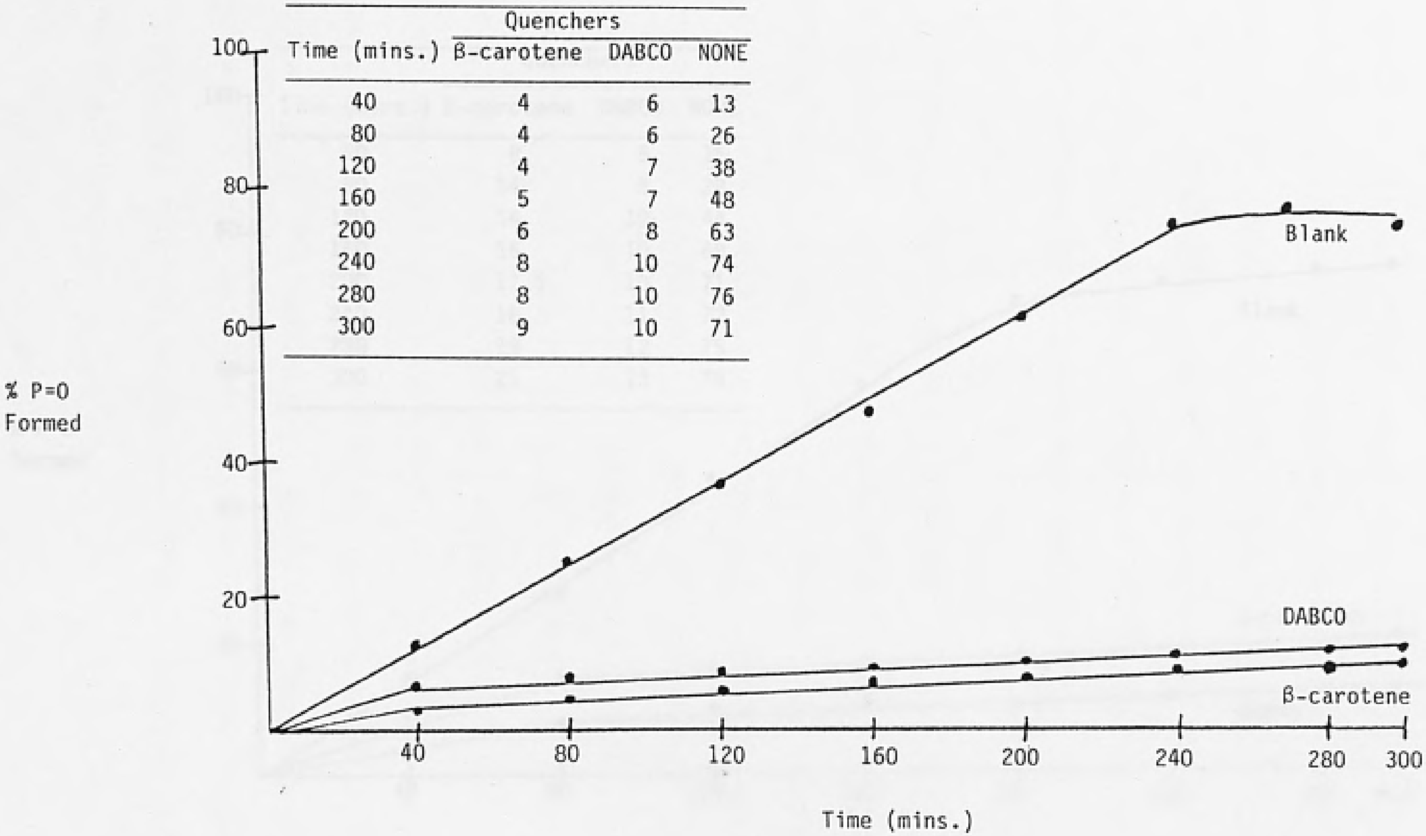
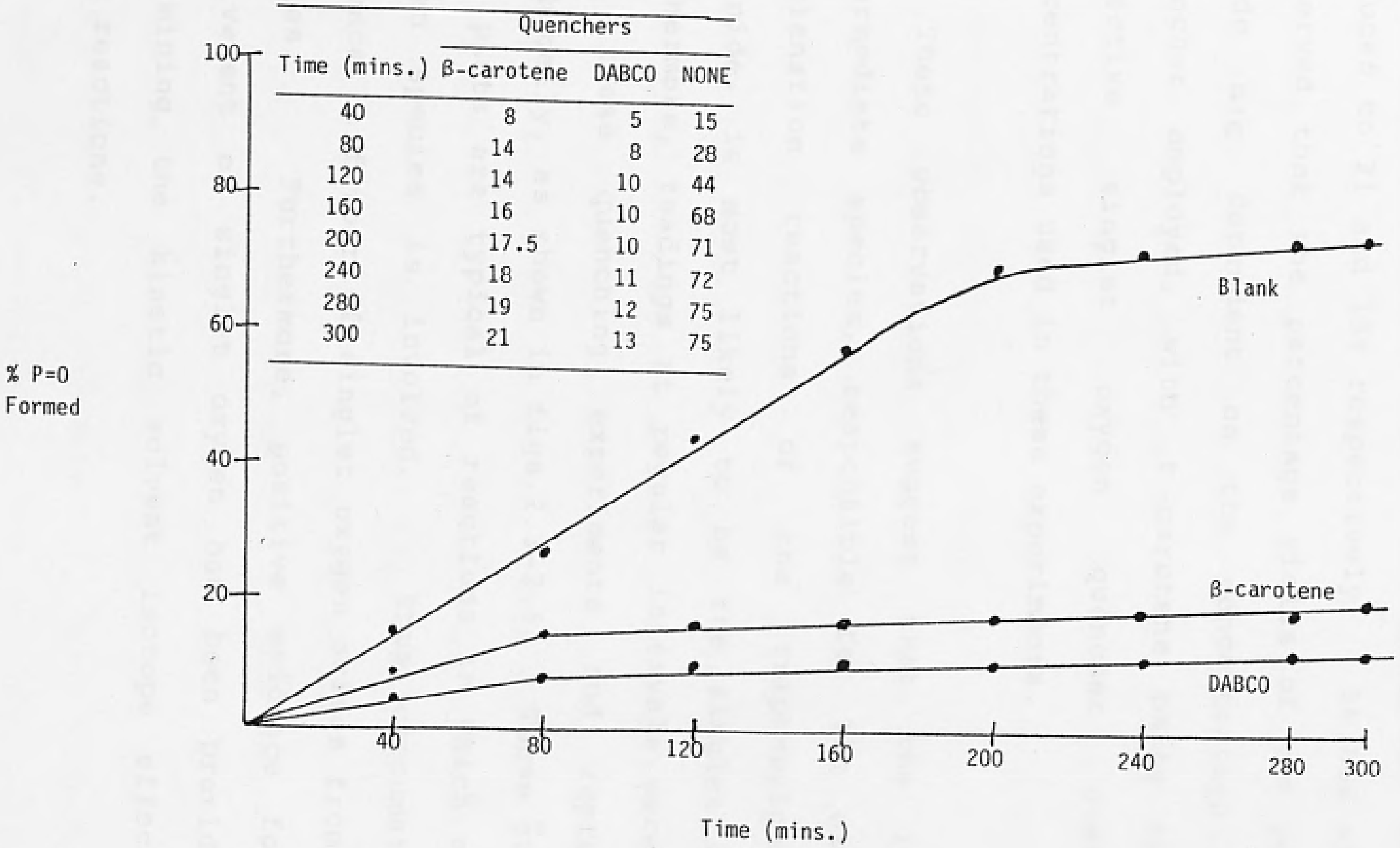


Fig.2.4: Ph$_3$PSe + Methylene blue, CHCl$_3$: MeOH, ± β-carotene (1 x 10^{-4}M) and DABCO (1.3 x 10^{-3}M)



Time (mins.)	Quenchers β-carotene	 DABCO	 NONE
40	4	6	13
80	4	6	26
120	4	7	38
160	5	7	48
200	6	8	63
240	8	10	74
280	8	10	76
300	9	10	71

Fig.2.5: Ph_3PSe + meso-tetraphenylporphyrin, $CHCl_3$, $\pm$ β-carotene (3.3×10^{-4}M) and DABCO (2×10^{-2}M)



Time (mins.)	Quenchers β-carotene	 DABCO	 NONE
40	8	5	15
80	14	8	28
120	14	10	44
160	16	10	68
200	17.5	10	71
240	18	11	72
280	19	12	75
300	21	13	75

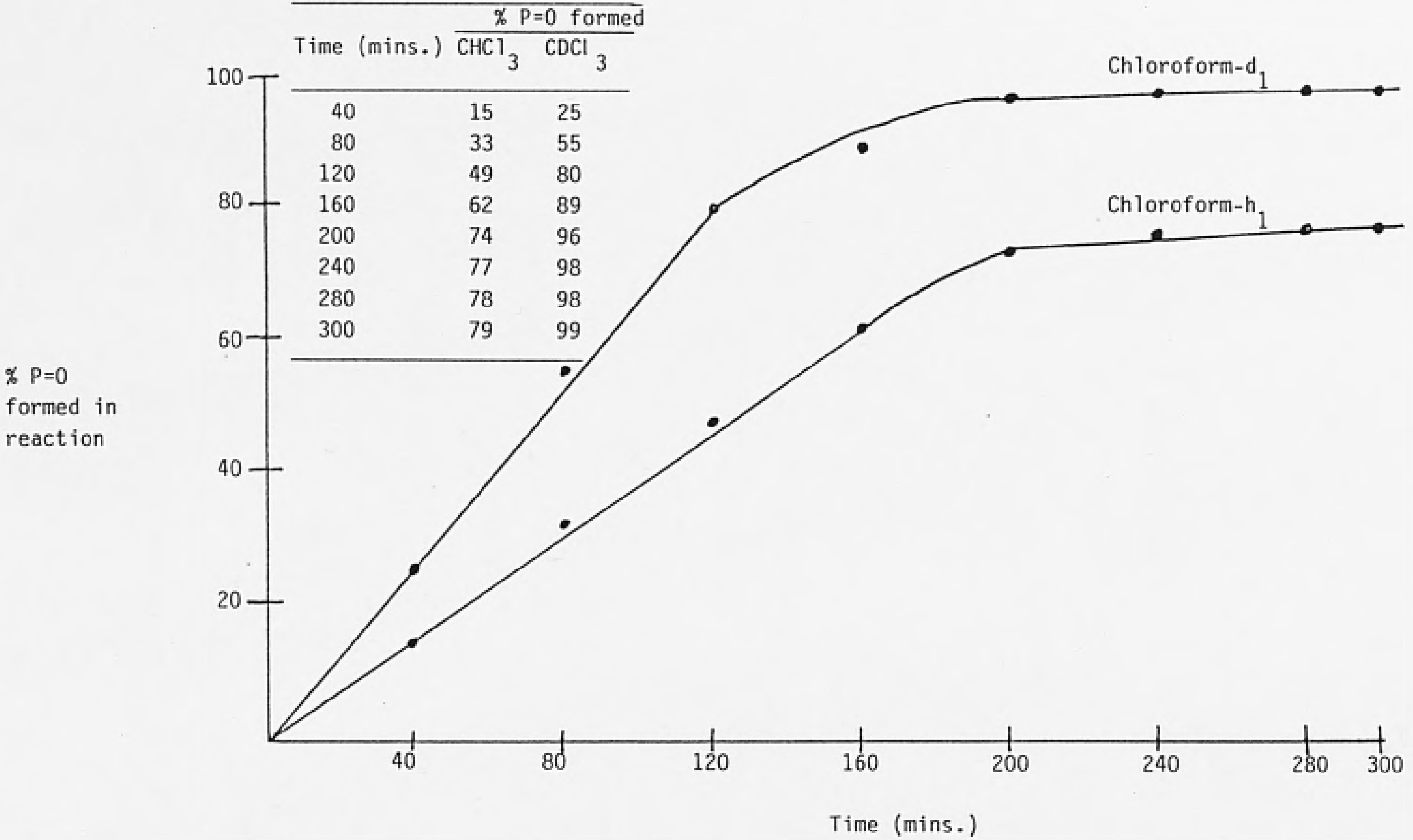
Fig.2.6: Ph_3PSe + Methylene blue, $CHCl_3$, $\pm$ β-carotene (2×10^{-4}M) and DABCO (2×10^{-3}M)

phosphine oxide was observed. However, on addition of β-carotene (2×10^{-4}M) and 1,4-diazabicyclo [2,2,2] octane (2×10^{-3}M) the yields of phosphine oxide were reduced to 21 and 13% respectively. It has also been observed that the percentage yields of the phosphine oxide are dependent on the concentration of the quencher employed, with β-carotene being the most effective singlet oxygen quencher over the concentrations used in these experiments.

These observations suggest that the reactive intermediate species, responsible for the oxidative deselenation reactions of the triphenylphosphine selenide, is most likely to be the singlet oxygen. Furthermore, readings at regular intervals were taken from these quenching experiments and represented graphically, as shown in figs.2.3-2.6. These straight line plots are typical of reactions in which singlet oxygen species is involved. Thus circumstantial evidence in favour of singlet oxygen arises from these studies. Furthermore, positive evidence for the involvement of singlet oxygen has been provided by determining the kinetic solvent isotope effects on these reactions.

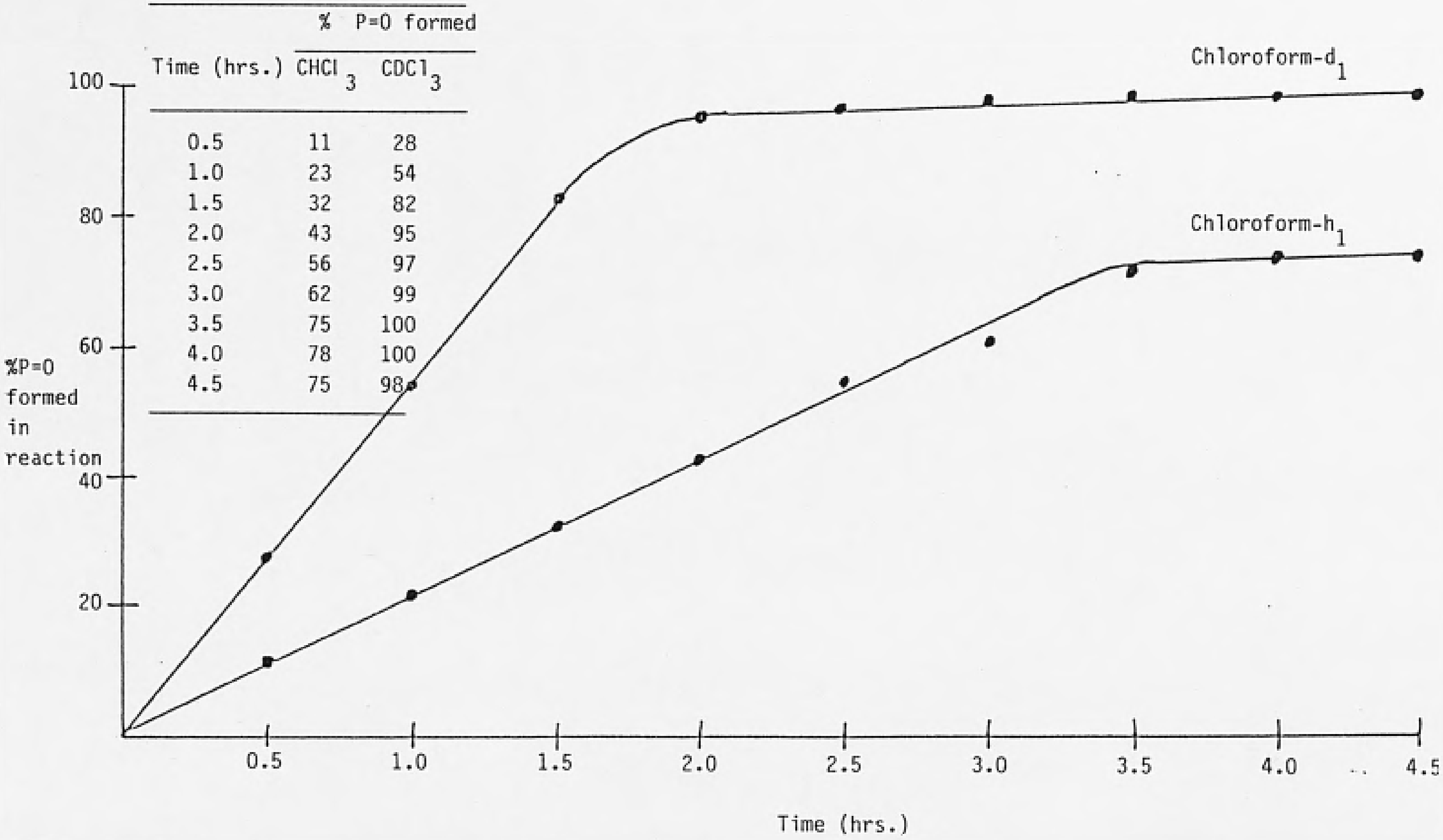
In recent years it has been reported that the life time of singlet oxygen in deuterated solvents is greater than in the corresponding non-deuterated[37,38] solvents.

This could be understood by considering the interactions between the solvent molecules and singlet oxygen. Most probably singlet oxygen doesn't lose its acquired excitation energy to the deuterated molecules as effectively as it does to molecules of non-deuterated solvents. Hence as a result singlet oxygen exists in deuterated solvents for a longer time period and can therefore participate in bimolecular reactions more effectively. This implies that if the photooxidation reaction involves singlet oxygen a change from non-deuterated to a deuterated solvent would be expected to cause an increase in the rate of photooxidation of the reaction. This increase in rate is referred to as the kinetic solvent isotope effect (SIE). The SIE of triphenylphosphine selenide, with Methylene blue and meso-tetraphenylporphyrin in chloroform - h_1, and chloroform - d_1, has been measured (figs.2.7 and 2.8). As expected the rate of deselenation in deuterated chloroform is much faster than in non-deuterated chloroform. Both figs.2.7 and 2.8 show a linear relationship to photooxidation, characteristic of singlet oxygen involvement. The ratios of the slopes, obtained from these graphical



Time (mins.)	% P=O formed	
	$CHCl_3$	$CDCl_3$
40	15	25
80	33	55
120	49	80
160	62	89
200	74	96
240	77	98
280	78	98
300	79	99

Fig.2.7: Methylene blue sensitised photooxygenation of triphenylphosphine selenide in chloroform-d_1 and chloroform-h.



Time (hrs.)	% P=0 formed $CHCl_3$	 $CDCl_3$
0.5	11	28
1.0	23	54
1.5	32	82
2.0	43	95
2.5	56	97
3.0	62	99
3.5	75	100
4.0	78	100
4.5	75	98

Fig.2.8: Meso-tetraphenylporphyrin sensitised photooxygenation of triphenylphosphine selenide in chloroform-d$_1$ and chloroform-h

representations, are referred to as the SIE and are given in table 2.3.

Table 2.3 Kinetic solvent isotope effect (SIE) for triphenylphosphine selenide with Methylene blue (Mb) and meso-tetraphenylporphyrin (TPP) in chloroform-h_1 and chloroform-d_1.

Phosphine selenide	Sensitisers[a]	
	Mb	TPP
Ph_3PSe[b]	1.65	2.60

a, 2.0 x 10^{-4}M.
b, 3.0 x 10^{-2}M.

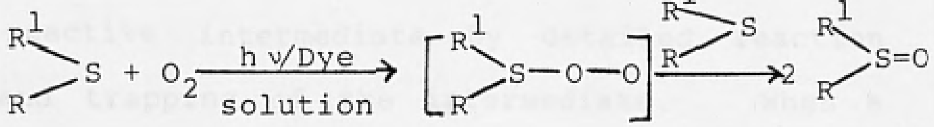
The present observations that the dye sensitised oxidations of triphenylphosphine selenide are significantly inhibited by the addition of typical singlet oxygen quenchers, under conditions where these quenchers are not inhibiting singlet oxygen formation, substantiates this claim.

Further support for this claim can be provided by the kinetic solvent isotope results. Hence it is now quite clear that the initial attack on the triphenylphosphine selenide occurs by the singlet oxygen. The result of this interaction presumably produces a reactive, "short-lived" intermediate species which then reacts further with another molecule of triphenylphosphine selenide to produce the triphenylphosphine oxide. However, in order to establish the structure of this intermediate species it is necessary to refer to the literature for analogous photosensitised oxidation reactions, in particular the reactions of dialkylsulphides.

The photooxidations of dialkylsulphides have been well studied and documented in the literature. However, the first photooxidation studies of these dialkylsulphides[40] were reported in 1962. The dialkylsulphides underwent oxygenation in high quantum yields in protic solvents, to produce the corresponding sulphoxides, which in turn reacted slowly producing the corresponding sulphones.

It was proposed that the oxygen first reacts with the sulphide to produce a highly reactive persulphoxide intermediate, which reacts at the diffusional rate with another molecule of the sulphide to produce stable sulphoxide.[41] This is shown below:

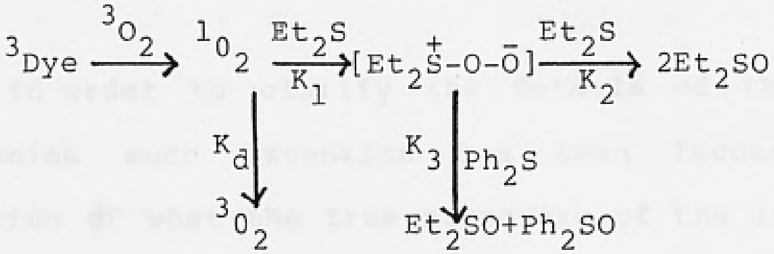
Scheme 2.7



The molecular oxygen was suggested to be in the excited singlet state,[42] as originally proposed by Kautsky[43,44] and later by Foote[45] and Wexler.

Foote and co-workers[45-49] have studied the dye sensitised oxidation reactions of many dialkylsulphides in order to propose a structure for the unstable oxidising species, formed initially in the reactions between dialkylsulphides and singlet oxygen. For the case of diethylsulphide it was suggested that the sulphide was oxidised by singlet oxygen to generate an unstable intermediate. This intermediate would then oxidise another diethylsulphide molecule (scheme 2.8)[46] to produce the diethylsulphoxide.

Scheme 2.8



$$\begin{tikzcd}
{}^3Dye \arrow[r, "{}^3O_2"] & {}^1O_2 \arrow[r, "Et_2S", "K_1"'] \arrow[d, "K_d"'] & {[Et_2\overset{+}{S}\text{-}O\text{-}\overset{-}{O}]} \arrow[r, "Et_2S", "K_2"'] \arrow[d, "K_3"', "Ph_2S"] & 2Et_2SO \\
& {}^3O_2 & Et_2SO+Ph_2SO &
\end{tikzcd}$$

The authors[47-49] have verified the existence of an unstable reactive intermediate by detailed reaction kinetics and trapping of the intermediate. When a mixture of diphenylsulphide and diethylsulphide was irradiated, in the presence of Rose Bengal in methanol, both corresponding sulphoxide products were found in comparable yields (1:2.5).[49] If scheme 2.8 is operative, a steady state kinetic equation (equation 2.8) may be derived for the trapping of the intermediate with diethylsulphide. The reported results showed that diethylsulphide was only four times more reactive towards the intermediate than diphenylsulphide, although it is 290[50] times more reactive than diphenylsulphide towards singlet oxygen.

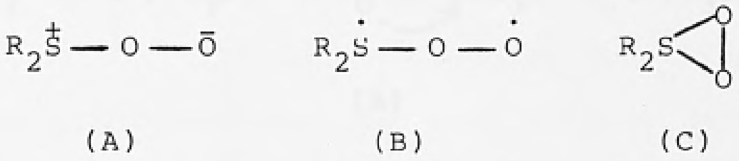
2.8

$$\frac{[Et_2SO]}{[Ph_2SO]} = \frac{2K_2\ [Et_2S]}{K_3\ [Ph_2S]} + 1$$

$$K_2/K_3 = 4$$

In order to clarify the details of the reaction mechanism much attention has been focused on the question of what the true structure of the intermediate might be. Although Foote and Peters[48,49] have tentatively assigned a zwitterionic "persulphoxide" structure (A), as the intermediate in the photooxidation of dialkylsulphides, Schenck[51] and co-workers suggested a biradical structure (B), while Cauzzo[52] and co-workers suggested a dioxathiirane structure (C).

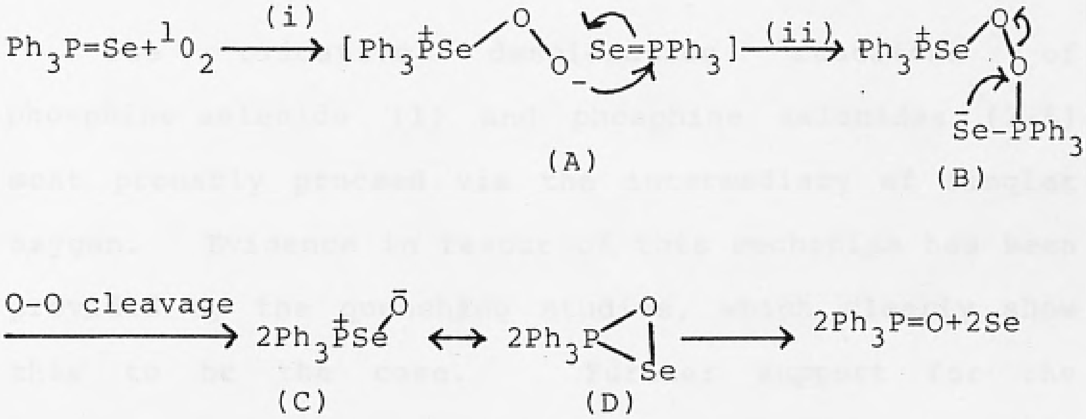
Fig.2.9



On the other hand, in the reaction of alkoxysulphuranes with hydrogen peroxide, both persulphoxide (A) and dioxathiirane (C) have been proposed.[39, 53] In brief the true nature of the intermediate (A), (B) or (C) has yet to be decided, although the zwitterionic persulphoxide (A) is considered thus far to be the most likely candidate for the oxidising intermediate.

The conclusions reached from these dye sensitised oxidiation reactions of dialkylsulphides can now be applied directly to the dye sensitised photooxidative deselenation reactions of triphenylphosphine selenide. Hence the following tentative mechanism for these deselenation reactions is proposed:

Scheme 2.9



It can be seen that the addition of triphenylphosphine selenide to singlet oxygen (reaction (i)) to produce the peroxidic intermediate (A), is analogous to that proposed for the singlet oxygenation of dialkylsulphides. This intermediate then acts as a nucleophile (reaction (ii)) and attacks a second molecule of triphenylphosphine selenide to produce intermediate (B) which rapidly undergoes O-O bond cleavage to generate species (C) and/or (D). Species (D) is an extremely strained structure and rapidly undergoes elimination to generate the triphenylphosphine oxide and elemental selenium which is observed to be precipitated at the end of each reaction. Although structures (C) and (D) are shown to exist in resonance with each other there is no evidence to suggest this is so.

2.3 Summary

The oxidative deselenation reactions of triphenylphosphine selenide (1) and phosphine selenides (2-5) most probably proceed via the intermediacy of singlet oxygen. Evidence in favour of this mechanism has been provided by the quenching studies, which clearly show this to be the case. Further support for the involvement of singlet oxygen has been given by the kinetic solvent isotope effect, which has been described as a diagnostic test.[37,38] In addition the structure of the intermediate, which is produced as a result of the action of singlet oxygen on the triphenylphosphine selenide (1), has been tentatively proposed to be a zwitterionic species and not a cyclic or biradical species. These intermediate species are discussed in detail in chapter 3.

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CHAPTER 3

OXIDATION OF PHOSPHINE SELENIDES AND SULPHIDES BY SPECIES GENERATED BY PHOTOOXIDATION OF SULPHIDES AND DIAZOCOMPOUNDS

3.1 INTRODUCTION

Currently there is much interest in reactive transient intermediate species, generated by dye sensitised photochemical oxidation reactions of both dialkylsulphides[1-3] (persulphoxides) and diazoalkanes[4-6] (carbonyl oxides). Although these intermediates are used as oxygen transfer reagents,[7-13] the mechanisms of their oxidation reactions are somewhat uncertain. The precise nature of these intermediates is as yet unclear, although several probable structures have been postulated. In order to explain the mechanisms involved in the photooxidative deselenation and desulphurisation reactions described in this chapter a survey of the chemistry of persulphoxides and carbonyl oxide intermediates is given.

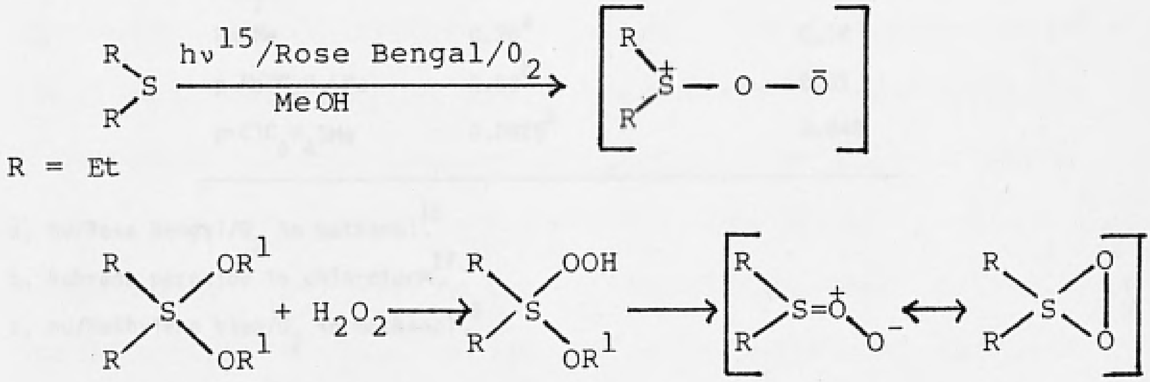
This chapter describes how these highly reactive intermediates have been successfully employed as rich sources of oxygen for the oxidation reactions of a series of phosphine selenides and phosphine sulphides.

This has been achieved by co-photooxidation of a particular phosphine selenide or phosphine sulphide with a suitable dialkylsulphide, namely di-n-hexylsulphide with Rose Bengal dye in chloroform:methanol (1:1 v/v), or diphenyldiazomethane with Rose Bengal dye in chloroform:methanol (1:1 v/v).

3.1a Persulphoxide intermediates

These intermediate species have not only been generated in situ by dye sensitised photooxidation of dialkylsulphides but also, recently, by the action of hydrogen peroxide on alkoxysulphurane[14] type compounds.

Scheme 3.1



R = Et

R = Ph, R^1 = $C(CF_3)_2Ph$

It has been suggested[16] that the singlet oxygen generated in dye sensitised photooxidation reactions behaves as an electrophile. Evidence for this electrophilic character has been provided by comparing the experimental rate constant results, measured for the reaction of singlet oxygen with a variety of dialkylsulphides in chloroform solution. Additional support, regarding the electrophilic nature of the singlet oxygen, has been provided by further rate constant[17] studies in methanol solution (table 3.1).

Table 3.1 Rate constants for selected reactions of disulphides with singlet oxygen

Sulphide	$K[M^{-1}S^{-1}] \times 10^{+7}$	Relative rate
Et_2S	$1.71^{a,c}$	1.00
Ph_2S	$\sim 0.01^{a}$	0.006
$^{t}Bu_2S$	0.013^{b}	0.0076
PhSMe	0.20^{a}	0.12
p-$MeOC_6H_4SMe$	0.53^{b}	0.31
p-ClC_6H_4SMe	0.0825^{b}	0.048

a, hν/Rose Bengal/O_2 in methanol.[16]

b, Rubrene peroxide in chloroform.[17]

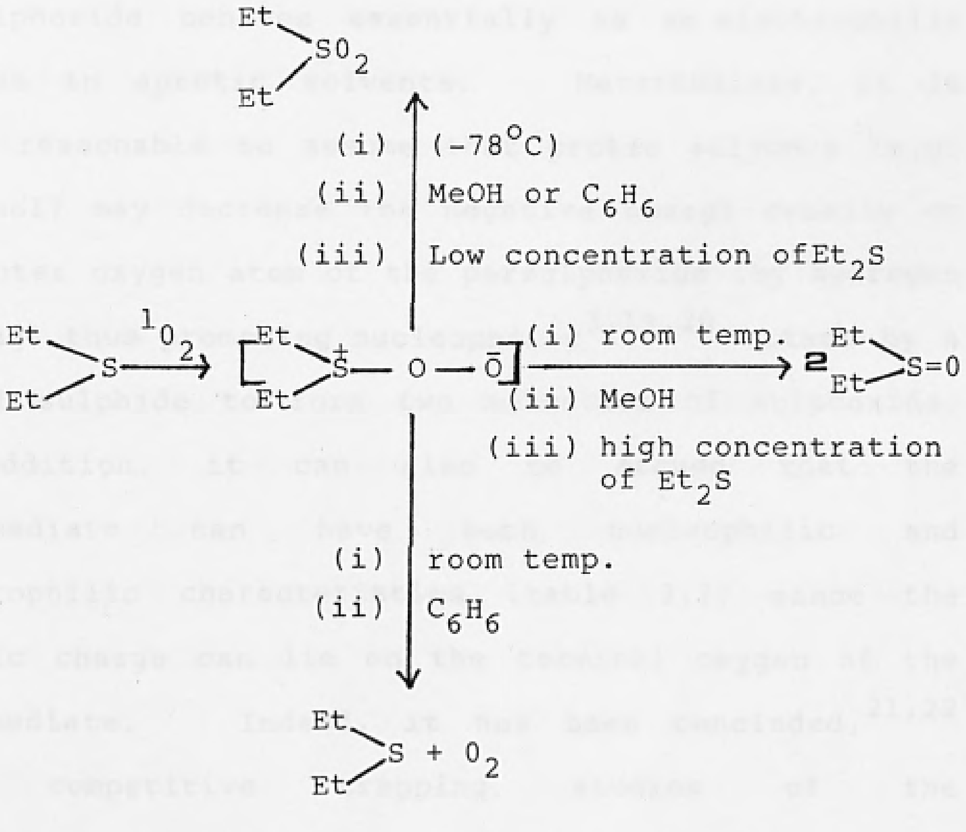
c, hν/Methylene blue/O_2 in methanol.[16]

It can be observed from table 3.1 that the rate constant for diethylsulphide is $1.71 \times 10^{7} M^{-1} S^{-1}$ whilst for the *di-tert*-butylsulphide and diphenylsulphide it is drastically reduced, to $0.013 \times 10^{7} M^{-1} S^{-1}$ and $\sim 0.01 \times 10^{7} M^{-1} S^{-1}$ respectively. This clearly shows that the reaction rate is significantly sensitive to steric effects. In addition it can be seen that the rate constant for methyl-(p-methoxyphenyl) sulphide has increased by 2.5 times, as compared with the parent compound methylphenylsulphide while it is decreased by 2.5 times for methyl-(p-chlorophenyl) sulphide.

This observation can be attributed to the electronic effects of the para-substituents of the benzene ring. The para-methoxy group further activates the reactive sulphur atom by donating its lone pairs of electrons, while the para-chloro group has the effect of deactivating the existing "reactive" sulphur atom. The effect of the former action is to increase the nucleophilicity of the sulphur atom towards singlet oxygen while the latter effect leads to a decrease in the nucleophilicity of the sulphur atom, hence the observed reduction in the rate constant. Furthermore, it was observed that the most suitable dialkylsulphide i.e. sulphide with relative rate of reaction of unity, is diethylsulphide. Hence it is not surprising that this is the most widely used sulphide for the production of persulphoxide intermediates.[3] It is particularly useful in co-photooxidation reactions, where the second dialkylsulphide or other compounds are usually less reactive towards singlet oxygen than is diethylsulphide. However, in these co-photooxidation reactions these less reactive compounds have been oxidised readily by the persulphoxide intermediate, to their corresponding oxides.

Currently, the photooxidation of diethylsulphide has been studied[1,3,18] in some depth to elucidate the precise nature of the reactive intermediate species. It was observed that using Et_2S in methanol at room temperature leads to a high yield of diethylsulphoxide (Et_2SO), while in dry benzene there was hardly any reaction at all.[1,3,18] It was also observed that the formation of the Et_2SO is not only solvent dependent but also dependent on the concentration of diethylsulphide. As the concentration of the sulphide was decreased (10^{-1} to 10^{-3}M), in protic and aprotic solvents, the major product formed was the diethylsulphone[3,18] (Et_2SO_2). This sulphone formation was thought to occur as a result of direct rearrangement of the persulphoxide intermediate. However, in general when the formation of the sulphoxide is high, traces of sulphone may also be formed via the oxidation of sulphoxide formed during the reaction. Furthermore, at low temperatures (-78°C), where the persulphoxide intermediate is stable regardless of the solvent polarity, the sulphone was the major product of reaction.[3,18] These observations are summarised in scheme 3.2

Scheme 3.2

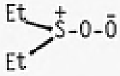
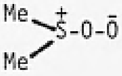
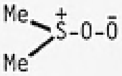
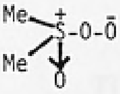
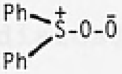


In conclusion, high concentration and protic solvents favour the sulphoxide formation whilst low concentration and aprotic solvent favour sulphone formation. In scheme 3.2 above, the persulphoxide intermediate is depicted by a zwitterionic species although the exact nature of the intermediate is still unclear. However, from a consideration of the electronic effects in the competitive dye sensitised oxidations of a variety of p-monosubstituted diphenylsulphides[15] with the persulphoxide intermediate of diethylsulphide, it was concluded that the persulphoxide behaves essentially as an electrophilic species in aprotic solvents. Nevertheless, it is quite reasonable to assume that protic solvents (e.g. Methanol) may decrease the negative charge density on the outer oxygen atom of the persulphoxide (by hydrogen bonding) thus promoting nucleophilic[3,19,20] attack by a second sulphide to form two molecules of sulphoxide. In addition, it can also be argued that the intermediate can have both nucleophilic and electrophilic characteristics (table 3.2) since the anionic charge can lie on the terminal oxygen of the intermediate. Indeed, it has been concluded,[21,22] from competitive trapping studies of the diethylpersulphoxide intermediate by sulphides in both protic and aprotic solvents, that two intermediates (A) and (B) exist.

Structure (A) is that of a zwitterionic species while structure (B) is a cyclic dioxathiirane species as illustrated in chapter 2, fig.2.9. This zwitterionic persulphoxide species is presumed to react as a nucleophile,[24] while the dioxathiirane behaves as an electrophile in their oxidation reactions. The cyclic structure has also been postulated previously,[23] in the oxidation of sulphoxide by the persulphoxide intermediate formed during the chrysene sensitised photooxidation of di-n-butylsulphide (nBu_2S) to di-n-butylsulphoxide (nBu_2SO). Furthermore, as reported in chapter 2, a third biradical structure of the intermediate has also been proposed.

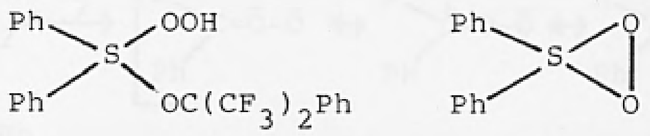
Although it is clear that there are three equally probable intermediates involved in these photooxidation reactions, the importance of each structure is not certain. However, it is generally accepted that the most probable candidate is the zwitterionic intermediate structure.

Table 3.2 Electrophilic and nucleophilic reactions of persulphoxide species with monosubstituted (A), disubstituted diphenylsulphides (B) and disubstituted diphenylsulphoxide (C).

Intermediate	Substrate	Conditions	ρ-values
 (in MeOH)[15]	A	Sulphide/hν/RB/O_2 room temp.	-0.61
 (in C_6H_6)[27]	C	Sulphide/hν/TPP/O_2 20°C	+0.252
 (C_6H_6:MeOH v/v)[27]	C	Sulphide/hν/TPP/O_2 20°C	-0.05
 (in C_6H_6)[27]	C	Sulphoxide/hν/TPP/O_2 20°C	+0.232
 (in CH_2Cl_2)[28]	B	Sulphurane-H_2O_2 -78°C	-0.43

Where RB is Rose Bengal, TPP is meso-tetraphenylporphyrin (metal free). Negative ρ-values indicate electrophilicity whilst positive ρ-values indicate nucleophilicity, of the sulphoxide intermediate. Also the latter intermediate may have both sulphurane type and dioxathiirane type structures.

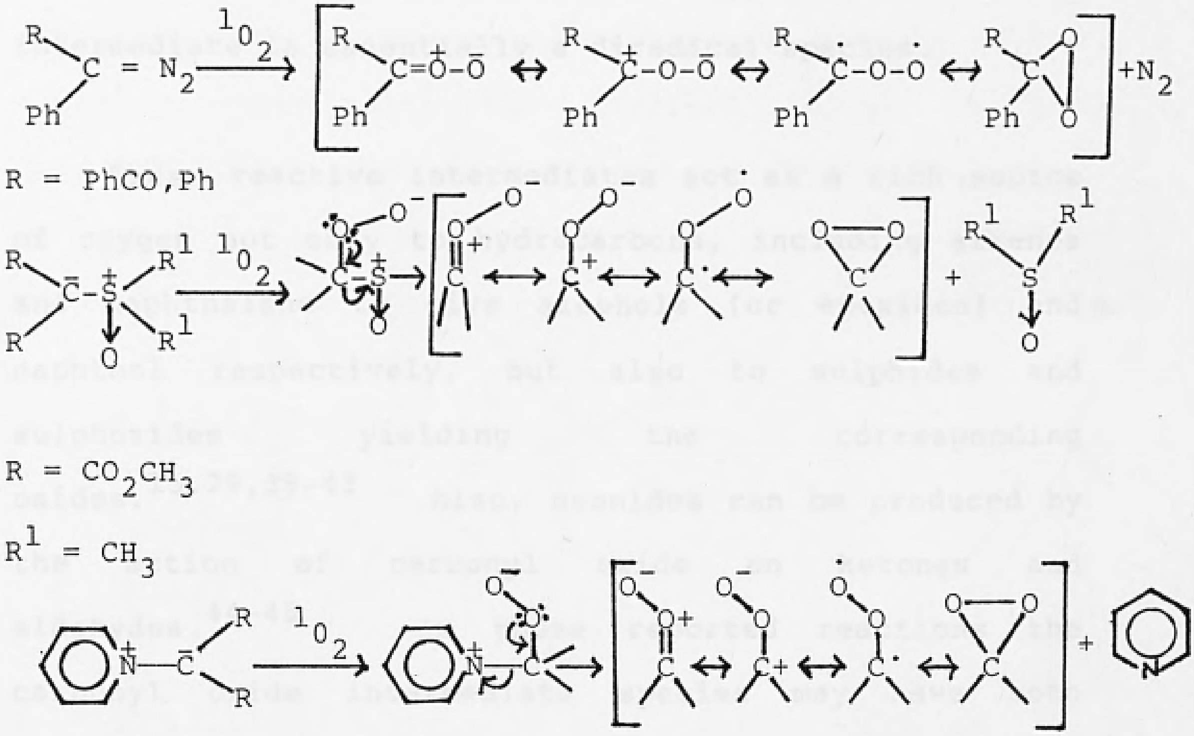
Fig.3.1



3.1b Carbonyl oxide intermediates

These highly reactive transient species have been generated in situ by dye sensitised photooxidations of diazoalkanes[26-28] and recently by dye sensitised photooxygenations[29] of sulphur and pyridinium ylids (scheme 3.3).

Scheme 3.3



R = PhCO,Ph

R = CO_2CH_3

R^1 = CH_3

Although the precise nature of the intermediates is not yet clear several probable structures have been proposed as shown in scheme 3.3. For example in the ozonolysis studies of alkenes, which have been well documented,[30-33] the carbonyl oxide has been proposed to be a zwitterionic species. However, quite recently, in the ozonolysis reactions of ethylene,[13,34,35] a cyclised carbonyl oxide species similar to that initially proposed for persulphoxide was suggested as being formed. Evidence for this cyclic structure has been provided by theoretical calculations.[36-38]

Furthermore, in the dye sensitised photooxidation of naphthalene to give α naphthol,[6] the nature of the intermediate is essentially a diradical species.

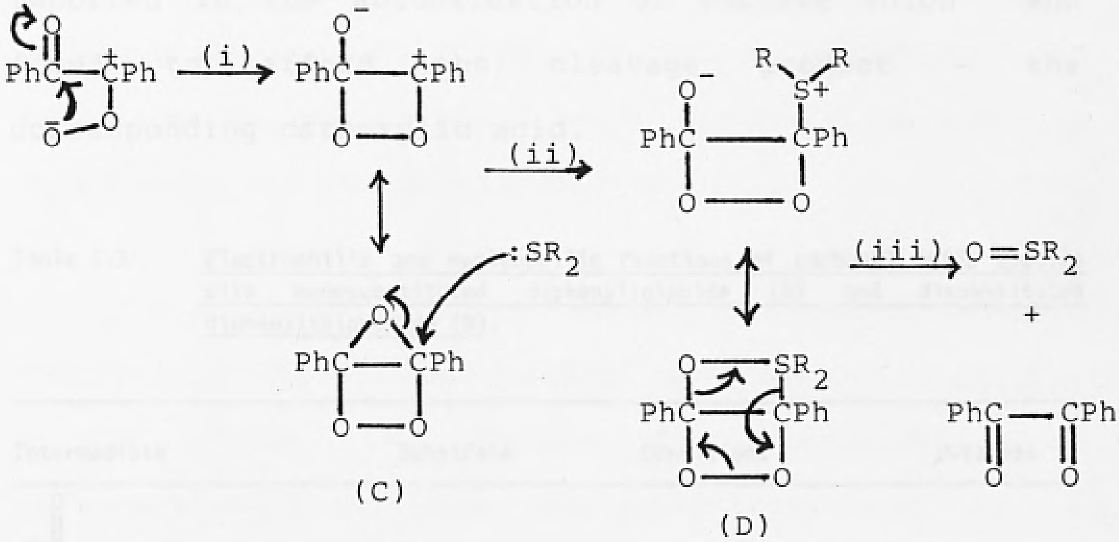
These reactive intermediates act as a rich source of oxygen not only to hydrocarbons, including alkenes and naphthalene to give alcohols (or epoxides) and α naphthol respectively, but also to sulphides and sulphoxides yielding the corresponding oxides.[15,29,39-43] Also, ozonides can be produced by the action of carbonyl oxide on ketones and aldehydes.[44-45] In these reported reactions the carbonyl oxide intermediate species may have both nucleophilic and electrophilic characteristics. Ando and co-workers[15] studied the oxidation of p-substituted di-phenylsulphoxide with carbonyl oxides, generated in situ from phenylbenzoyl - and diphenyldiazomethanes in benzene (table 3.3), and suggested that the behaviour of the intermediates was largely electrophilic. In addition, the electrophilic character of the carbonyl oxide of phenylbenzoyldiazomethane was greater than for that of the diphenyldiazomethane. The electrophilic nature of these two carbonyl oxides can be explained by proposing that the negative charge density on the terminal oxygen atom of the carbonyl oxides is lowered in protic solvents such as methanol, thus inducing electrophilic character into the intermediates while reducing their nucleophilicity. This lowering of the charge density is attributed to hydrogen bonding of the alcohol proton with the terminal oxygen of the intermediate as shown in structure (A) in fig.3.2.

Fig.3.2

(A) (B)

Another possibility is that methanol actually adds to the intermediate to produce structure (B). This is similar to the structures suggested by Martin and Martin.[25] For the second observation, it may be concluded that the negative charge density on the oxygen atom is further reduced by the α-carbonyl group thus increasing the electrophilicity[46] of the intermediate at the expense of its nucleophilicity. This has been shown in scheme 3.4 to occur through the formation of two intermediates (C) and (D).

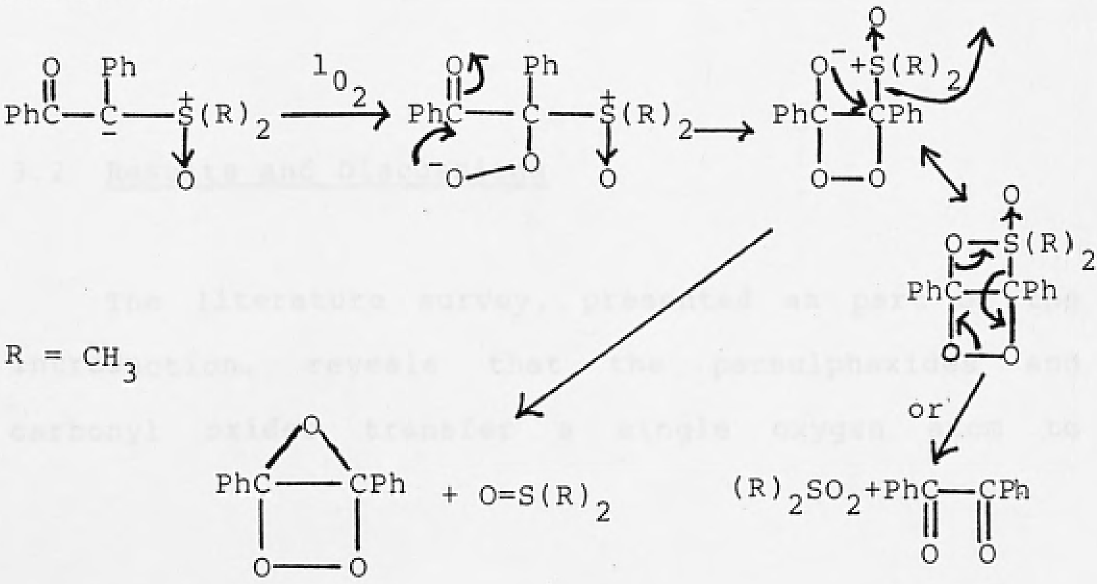
Scheme 3.4



R = monosubstituted phenyl

Evidence for the intermediates (C) and (D) has been reported for the photosensitised oxygenation of dimethyl-oxosulphonium-phenyl-phenacylid[29] with Methylene blue dye in methanol.

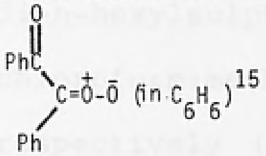
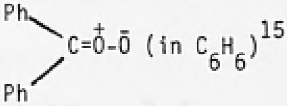
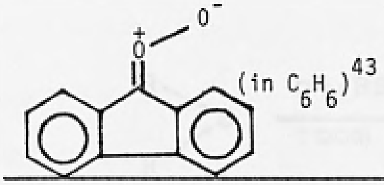
Scheme 3.5



R = CH$_3$

Furthermore, these types of intermediates were also reported in the autooxidation of enolate anion[47] and found to afford the cleavage product - the corresponding carboxylic acid.

Table 3.3 Electrophilic and nucleophilic reactions of carbonyl oxide species with monosubstituted diphenylsulphide (A) and disubstituted diphenylsulphoxide (B).

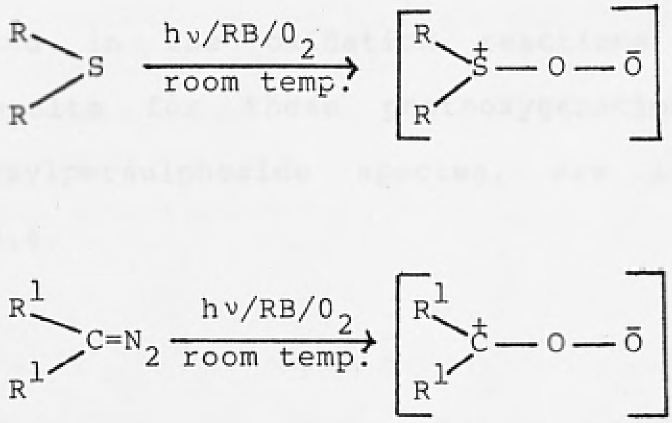
Intermediate	Substrate	Conditions	ρ-values
	A	Diazo.compd. hν/TPP/O_2 r.t.	-0.32
	A	Diazo.compd. hν/TPP/O_2 r.t.	-0.68
	B	Diazo.cmpd. hν/TPP/O_2 r.t.	+0.26

3.2 Results and Discussions

The literature survey, presented as part of the introduction, reveals that the persulphoxides and carbonyl oxides transfer a single oxygen atom to compounds that are usually less reactive or show low reactivity towards attack by singlet oxygen. Subsequently as a result of these oxidations the persulphoxide and carbonyl oxide species also generate sulphoxides and ketones respectively.

The persulphoxide and carbonyl oxide intermediates employed in the present studies, were generated in situ by Rose Bengal (RB) sensitised photooxygenation of di-n-hexylsulphide and diphenyldiazomethane in a chloroform:methanol (1:1 v/v) solvent system respectively (scheme 3.6). For details please refer to experimental section.

Scheme 3.6



where R = $CH_3(CH_2)_5$

R^1 = Ph

It is not unreasonable to presume that the types of intermediate species illustrated in scheme 3.6 are responsible for the observed photooxygenations or photooxidative deselenation and desulphurisation of the organophosphorus compounds (1-10). The deselenation and desulphurisation reactions have been investigated through trapping studies i.e. each organophosphorus compound, in turn, was co-photooxidised with di-n-hexylsulphide or diphenyldiazomethane in the presence of Rose Bengal dye.

As the di-n-hexylpersulphoxide or diphenylcarbonyl oxide intermediates were formed they reacted with the phosphorus compound at the diffusional rate to produce the observed phosphine oxide. Subsequently di-n-hexylsulphoxide and benzophenone were also generated in the oxidation reactions respectively. The results for these photooxygenations, with the di-n-hexylpersulphoxide species, are illustrated in table 3.4.

Table 3.4 Photooxidation of phosphine selenides and phosphine sulphides with di-n-hexylsulphide in the presence of Rose Bengal dye.

Compound	% oxidised phosphorus compound	% unchanged phosphorus compound
(1) $Ph_3PSe^{b,c,d}$	100	0
(2) $Ph_2P(Se)OEt^{b,d}$	96	4
(3) $PhP(Se)(OEt)_2{}^{b,d}$	64	36
(4) $(EtO)_3PSe^{b,d}$	51	49
(5) $(MeO)_3PSe^{b,d}$	41	59
(6) $Ph_3PS^{d,e}$	22,37^f	78,63^g
(7) $Ph_2P(S)OEt^{d,e}$	11,29^f	89,71^g
(8) $PhP(S)(OEt)_2{}^{d,e}$	4, 6^f	96,94^g
(9) $(EtO)_3PS^{d,e}$	2, 3^f	98,97^g
(10) $(MeO)_3PS^{d,e}$	3, 3^f	97,97^g

a, Rose Bengal 2×10^{-4}M, di-n-hexylsulphide 1.0×10^{-2}M, $CHCl_3$:MeOH (1:1 v/v).

b, 30min irradiation period.

c, In the absence of sulphide, only 3% phosphine oxide obtained.

d, Organophosphorus compound 2.5×10^{-3}M.

e, 60min irradiation period.

f, di-n-hexylsulphide 5.0×10^{-2}M.

g, % unchanged starting material from reaction with f.

In the control experiments, i.e. the dyesensitised photooxidation of each organophosphorus compound dissolved in chloroform:methanol (1:1 v/v)(2.5×10^{-3}M) in the absence of di-n-hexylsulphide, it was observed that no appreciable photooxygenation occurred. In the case of the most reactive phosphorus compound, i.e. triphenylphosphine selenide (1), only 3% of the corresponding phosphine oxide was formed. This implies that the phosphorus compounds (1-10), under these reaction conditions, do not react with singlet oxygen to produce their corresponding phosphine oxides. Hence it may be concluded that the observed photooxygenations of these phosphorus compounds in the presence of persulphoxide are likely to involve a different mechanism.

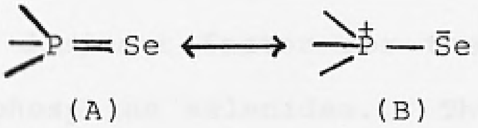
The phosphine selenides were observed to be more reactive than the analogous phosphine sulphides. Phosphine selenides (1) and (2) were completely oxidised to their corresponding phosphine oxides, 100 and 96% yields respectively while phosphine selenides (3-5) were oxidised to 64, 51 and 41% yields respectively to their corresponding phosphoryl analogues. These oxidation results reveal a reactivity order amongst the phosphine selenides (fig.3.3), i.e. phosphine selenide (1) is the most reactive while phosphine selenide (4) is the least reactive towards the persulphoxide species.

$Ph_3PSe>Ph_2P(Se)OEt>PhP(Se)(OEt)_2>(EtO)_3PSe><(MeO)_3PSe$

Fig.3.3 <u>Decreasing order of reactivity from left to right</u>.

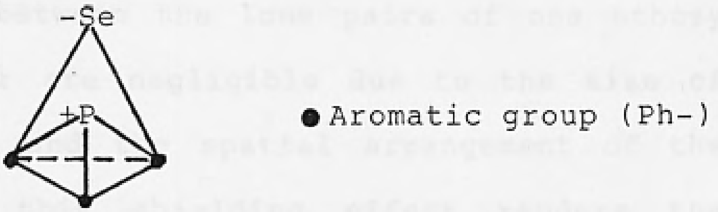
This order of reactivity can be explained by considering the delicate nature of the P=Se bond with the electronic effects of the groups attached to the phosphorus atom. The P=Se bond can be represented as shown in fig.3.4. The structure (B) is an ionic species with the electron density around the selenium.

Fig.3.4



However, the above reactivity trend can be most readily explained by considering the behaviour of structure (B). For the phosphine selenide (1) the three bulky aromatic groups are arranged below the phosphorus atom in a triangular array (fig.3.5).

Fig.3.5



This spatial array of the phenyl groups around the phosphorus atom stabilises the positive charge on the phosphorus somewhat through delocalisation of the

π - electron cloud. However, since the groups are bulky the 6 π - electrons, of each ring, will repel each other and reduce the delocalisation of the electrons around the phosphorus atom. This effect leads to a destabilisation of the positive charge on the phosphorus, leaving it open to attack by incoming nucleophiles.

Thus, the extent of stabilisation is presumed to be the dominant factor for the observed reactivity of these phosphine selenides. The phosphine selenide (2) has one aromatic group replaced by an ethoxy group. The oxygen atom on the ethoxy group has two lone pairs of electrons which stabilise the positive charge on the phosphorus even further, hence we would expect this selenide (2) to be less reactive, towards nucleophiles, than selenide (1). Phosphine selenide (4) has all the aromatic groups replaced by ethoxy groups, a total of six lone pairs of electrons arranged in a trigonal bipyramidal array around the phosphorus. The repulsion forces between the lone pairs of one ethoxy group with another are negligible due to the size of the ethoxy groups and the spatial arrangement of the atoms. Hence this shielding effect renders the phosphorus atom somewhat unreactive towards nucleophilic reagents. In addition the ethoxy groups can also withdraw electrons from the environment of the P=Se bond thus exposing the phosphorus atom to attack. However, this effect is generally regarded as negligible. Furthermore, it can be quantitatively observed that as the number of ethoxy groups increases, and the aromatics decrease, the phosphine selenides will show less and less reactivity. Indeed this has been observed in the photooxidations with both the persulphoxide species and the carbonyl oxide intermediate. From this observation it is reasonable to conclude that both intermediate species have a high probability of being nucleophilic in character.

The phosphine sulphides were found to be far less reactive than their analogous phosphine selenides, although a similar trend in the reactivity order was observed. The phosphine sulphide (6) being the most reactive whilst phosphine sulphide (9) is the least reactive, towards persulphoxide intermediate. The phosphine sulphide (6) showed approximately half the reactivity (i.e. 22%) of the least reactive phosphine selenide (4), while the phosphine sulphide (7) showed approximately a quarter of the reactivity (i.e. 11%) of the phosphine selenide (4). Furthermore the phosphine sulphides (8-10) hardly showed any reaction with the persulphoxide intermediate, i.e. 4, 2 and 3%

respectively. In addition it was noted that as the concentration of the di-n-hexylsulphide was increased from 1 x 10^{-2} to 5 x 10^{-2}M an increase in the reaction product yield for phosphines (6) and (7) was obtained i.e. 37 and 39% respectively, while the other phosphine sulphides were unaffected.

In all these photooxidations, in the presence of persulphoxide intermediates, the di-n-hexylsulphide was completely consumed during the reaction period and di-n-hexylsulphoxide was found to be the major product, with traces of di-n-hexylsulphone. The sulphone formation was assumed to occur from the photooxidation of the sulphoxide, already formed in the reaction.

The dye sensitised photooxygenation reactions of phosphorus compounds (1-10) in the presence of diphenyldiazomethane have also been studied in detail and the results are illustrated in table 3.5.

Table 3.5 Photooxidation of phosphine selenides and phosphine sulphides with diphenyldiazomethane in the presence of Rose Bengal^a dye.

Compound	Yield of oxidised organophosphorus compound (%)
Ph_3PSe(1)	98
$Ph_2P(Se)OEt$(2)	89
$PhP(Se)(OEt)_2$(3)	53
$(EtO)_3PSe$(4)	46
$(MeO)_3PSe$ (5)	37
Ph_3PS (6)	15,31^b
$Ph_2P(S)OEt$ (7)	6,10^b
$PhP(S)(OEt)_2$ (8)	0, 0^b
$(EtO)_3PS$ (9)	0, 0^b
$(MeO)_3PS$ (10)	0, 0^b

a, Rose Bengal 2×10^{-4}M, diphenyldiazomethane 1×10^{-2}M, organophosphorus compound 2.5×10^{-3}M, $CHCl_3$:MeOH (1:1 v/v), irradiation time 90mins.
b, Diphenyldiazomethane 5×10^{-2}M.

As observed with the persulphoxide reactions, the phosphine selenides are the most reactive compounds towards carbonyl oxide species in comparison with their analogous phosphine sulphides. The phosphine selenide (1) has been oxidised almost completely to its corresponding phosphine oxide, i.e. 98%, while the phosphine selenide (2) has been oxidised to 89%. The remaining phosphine selenides (3-5) have been oxidised, to their corresponding phosphine oxides, to a lesser extent i.e. 53, 46, and 37% respectively.

The reactivities of the phosphine sulphides towards peroxy species derived from diphenyldiazomethane, were observed to be lower than those for the phosphine selenides. However, the phosphine sulphide (6) showed approximately half the reactivity (15%) of the least reactive phosphine selenide (5), while the phosphine sulphide (7) showed only 6% oxidation product. The other remaining phosphine sulphides (8-10) showed no reactivity at all. Furthermore, as the concentration of the diphenyldiazomethane was increased from 1.0×10^{-2} to 5.0×10^{-2}M an increase in the product yield for phosphine sulphides (6) and (7) was observed i.e. 31 and 10% respectively, while the other phosphine sulphides remained unaffected.

These observations are consistent with those reported for the reactions with persulphoxide species in table 3.4. This seems reasonable since both di-n-hexylsulphide and diphenyldiazomethane generate analogous intermediates for these deselenation and desulphurisation reactions. Furthermore, it was observed that in the presence of diphenyldiazomethane and the absence of Rose Bengal dye, photooxidative deselenation and desulphurisation still occurred. These results are presented in table 3.6.

Table 3.6 Direct photooxidation[a] of phosphine selenides and phosphine sulphides in the presence of diphenyldiazomethane.

Compound	Yield of oxidised organophosphorus compound (%)
Ph_3PSe (1)	94
$Ph_2P(Se)OEt$ (2)	19
$PhP(Se)(OEt)_2$ (3)	14
$(EtO)_3PSe$ (4)	13
$(MeO)_3PSe$ (5)	10
Ph_3PS (6)	8
$Ph_2P(S)OEt$ (7)	0
$PhP(S)(OEt)_2$ (8)	0
$(EtO)_3PS$ (9)	0
$(MeO)_3PS$ (10)	0

a, diphenyldiazomethane 1×10^{-2}M, organophosphorus compound 2.5×10^{-3}M, $CHCl_3$:MeOH (1:1 v/v), irradiation time 24 hours.

As discussed earlier, the phosphine selenides generally tend to be more reactive towards diphenylcarbonyl oxide than their analogous phosphine sulphides. However, it was found that only the triphenylphosphine selenide (1) showed any great reactivity towards the carbonyl oxide species i.e. 94%. The remaining phosphine selenides (2-5) produced much reduced yields of oxidation products, as compared with the previous case, i.e. 19, 14, 13, and 10% respectively.

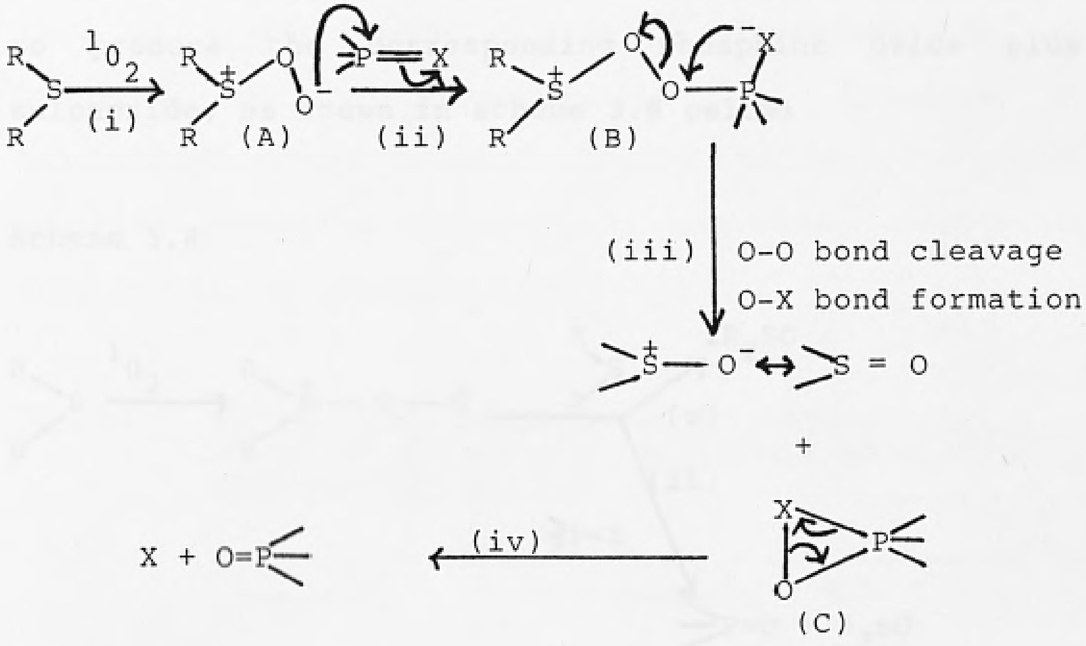
Furthermore, for the phosphine sulphides it was observed that only the triphenylphosphine sulphide (6) showed any reactivity at all i.e. 8% oxidation product was formed. The remaining phosphine sulphides (7-10) produced no oxidation products. In addition, it was noted that in these photooxygenation reactions the oxidation product of diphenyldiazomethane (benzophenone) was formed after the irradiation period. This implies, as in previous studies with diphenyldiazomethane, that carbonyl oxide intermediate species had also been formed in these reactions.

Conclusion

From the control experiments, i.e. the dye sensitised photooxidation of each phosphorus compound (1-10) dissolved in chloroform:methanol (1:1 v/v) in the absence of di-n-hexylsulphide and diphenyldiazomethane, it was observed that no appreciable deselenation or desulphurisation was achieved. This suggests that the observed photooxygenations of the phosphine selenides and phosphine sulphides with the di-n-hexylsulphide or diphenyldiazomethane are not the result of the direct action of the singlet oxygen on the phosphorus selenides or phosphorus sulphides, as described in chapter 2. A different oxidative mechanism must be involved.

From the literature survey presented on dialkylsulphides and diazoalkanes, it can be concluded that these compounds show a great affinity for reacting with singlet oxygen to generate highly reactive transient species <u>in situ</u>. These transients have been utilised to effect oxidations of compounds which are usually extremely unreactive towards singlet oxygen. For example, it has previously been mentioned that diphenylsulphide shows very little reactivity with singlet oxygen. However, diphenylsulphide has been found to be easily oxidised by diethylpersulphoxide species ($Et_2\overset{+}{S}OO^-$) to produce the corresponding diphenylsulphoxide (Ph_2SO).[1,3,18] Similarly, it can be concluded that the phosphine selenides and phosphine sulphides are most probably oxidised by analogous intermediates. Hence the following mechanism scheme 3.7 is proposed for the reactions of persulphoxide species with phosphine sulphides and selenides.

Scheme 3.7

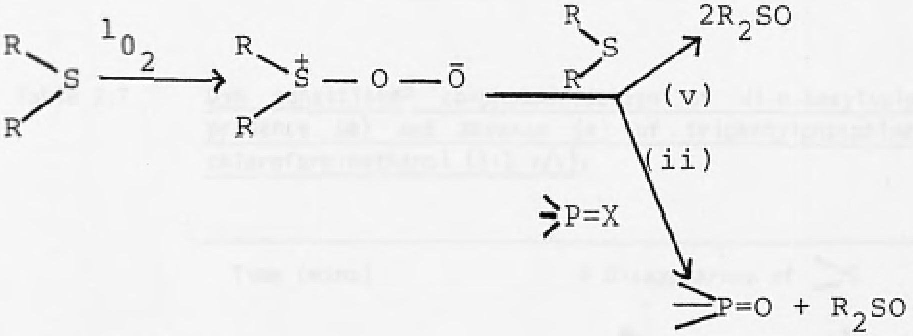


R = $CH_3(CH_2)_5$-

X = Se,S

The mechanism outlined in scheme 3.7 implies that as the persulphoxide intermediate species (A) is generated it is rapidly quenched by a molecule of organophosphorus compound, reaction (ii), to form intermediate (B) which undergoes O-O bond cleavage and O-X bond formation to generate sulphoxide and a cyclic dioxathiirane species (C). This cyclic structure also undergoes rearrangement to produce the phosphine oxide and elemental selenium or sulphur. Furthermore, according to reaction (ii) the organophosphorus compound functions as an intermolecular trap for the persulphoxide species and competes with a second molecule of the sulphide for the terminal oxygen atom to produce the corresponding phosphine oxide plus sulphoxide, as shown in scheme 3.8 below:

Scheme 3.8



$R = CH_3(CH_2)_5-$

X = Se,S

As a result of this competition, between reaction (ii) and (v), the rate of reaction for the formation of sulphoxide from di-n-hexylsulphide is likely to be reduced or conversely the rate of disappearance of the di-n-hexylsulphide is likely to be reduced. In order to test this point a mixture of di-n-hexylsulphide and Rose Bengal dye in chloroform:methanol (1:1 v/v) in the presence and absence of triphenylphosphine selenide (1) was irradiated. Readings were taken at regular intervals and the disappearance of the sulphide monitored by glc. These results are reported in table 3.7 and shown graphically in fig.3.5. Indeed, the rate of disappearance of the di-n-hexylsulphide was observed to be reduced, in the presence of triphenylphosphine selenide (refer to fig.3.5). In addition phosphine selenide (1) was almost completely consumed in the reaction (96%).

Table 3.7 Dye sensitised[a] co-photooxidation of di-n-hexylsulphide in the presence (●) and absence (+) of triphenylphosphine selenide in chloroform:methanol (1:1 v/v).

Time (mins)	% Disappearcne of >S	
	●	+
4	16	11.5
8	15	22
12	26	34
16	33	45
20	42	52
24	48	66.4
28	60	74.3
32	65	86
40	82	96

a, sulphide 1.0 x 10^{-2}M, Rose Bengal 2 x 10^{-4}M, Ph_3PSe 2.5x 10^{-3}M.

Similarly, for the dye sensitised reactions of diphenyldiazomethane with phosphine selenides and phosphine sulphides, the following mechanism is proposed (scheme 3.9).

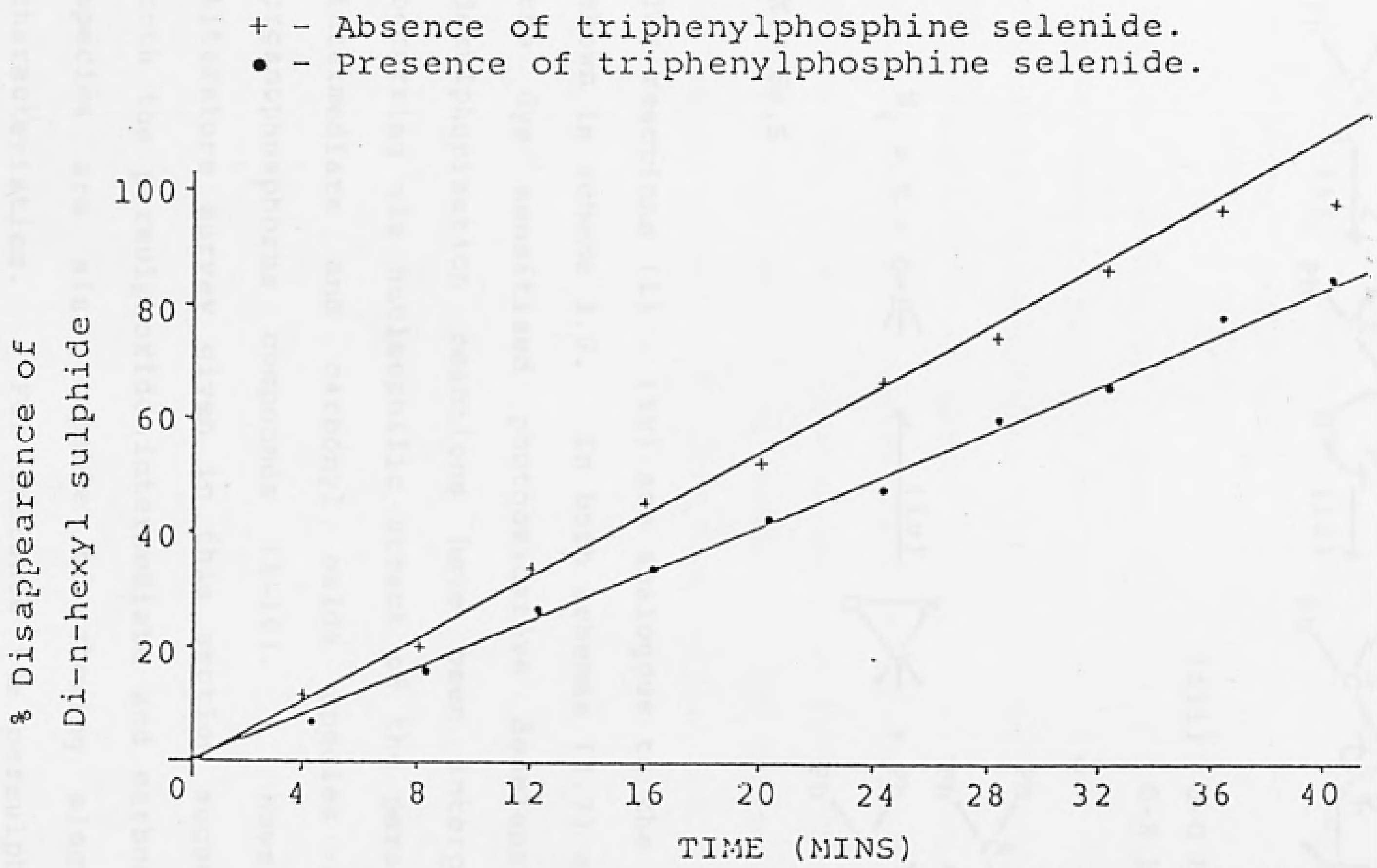
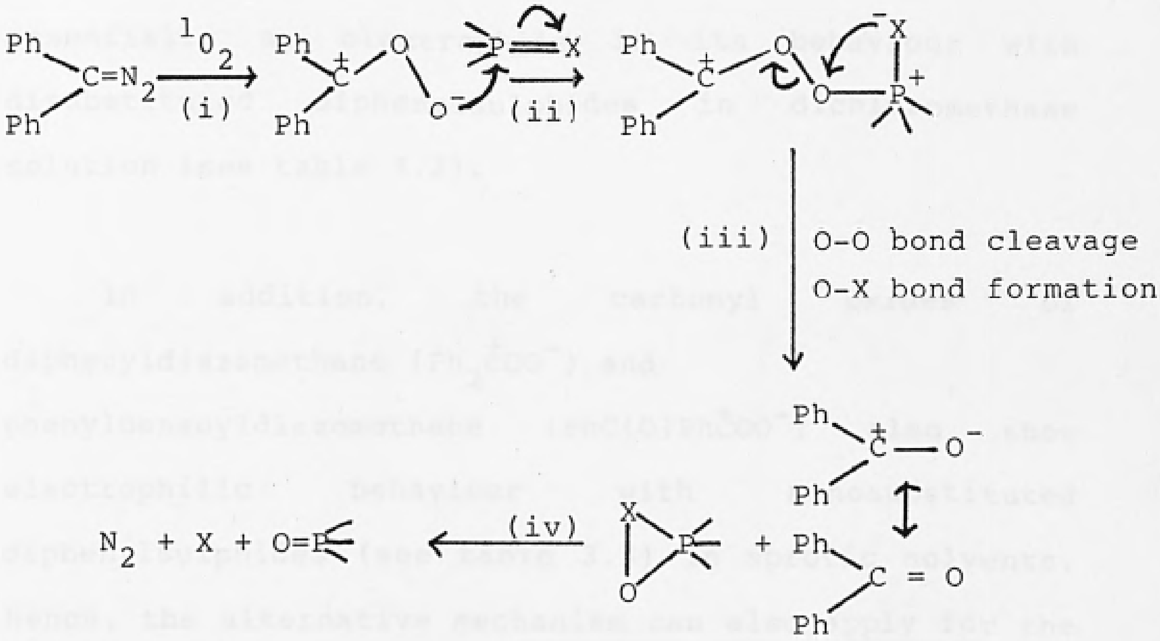


Fig 3.5 % Disappearance of Di-n-hexylsulphide with time and absence of triphenylphosphine selenide.

Scheme 3.9

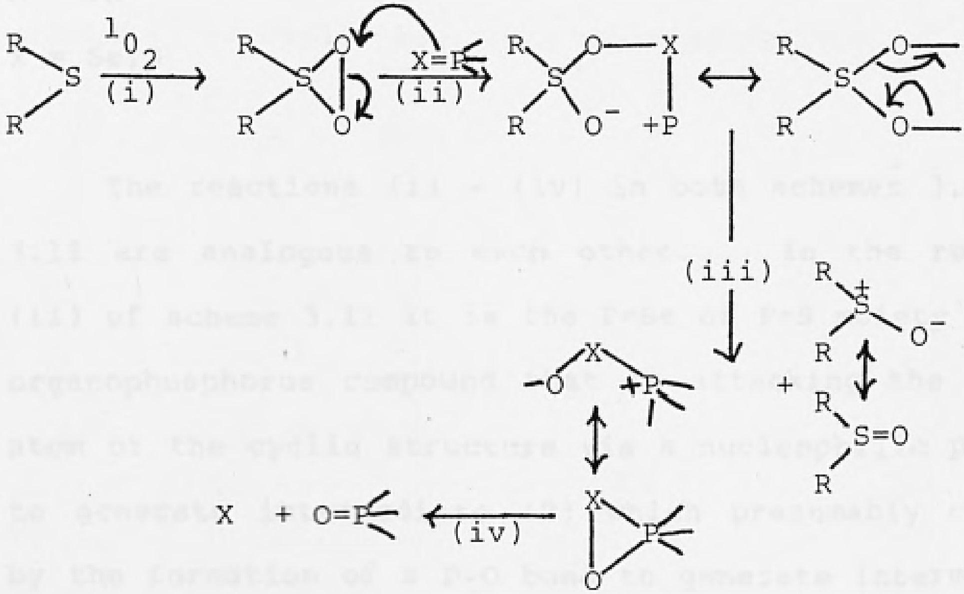


X = Se,S

The reactions (i) - (iv) are analogous to the reactions shown in scheme 3.7. In both schemes (3.7) and (3.9), the dye sensitised photooxidative deselenation and desulphurisation reactions have been interpreted as occurring via nucleophilic attack of the persulphoxide intermediate and carbonyl oxide species upon the organophosphorus compounds (1-10). However, the literature survey given in this section suggests that both the persulphoxide intermediate and carbonyl oxide species are also capable of showing electrophilic characteristics. For instance the persulphoxide of diethylsulphide ($Et_2\overset{+}{S}OO^-$) is reported to be an electrophile in its reactions with monosubstituted diphenylsulphides in methanol. Also, the persulphoxide of diphenylsulphide ($Ph_2\overset{+}{S}OO^-$) is reported to be essentially an electrophile in its behaviour with disubstituted diphenylsulphides in dichloromethane solution (see table 3.2).

In addition, the carbonyl oxides of diphenyldiazomethane ($Ph_2\overset{+}{C}OO^-$) and phenylbenzoyldiazomethane ($PhC(O)Ph\overset{+}{C}OO^-$) also show electrophilic behaviour with monosubstituted diphenylsulphides (see table 3.3) in aprotic solvents. Hence, the alternative mechanism can also apply for the observed dye sensitised photooxidative deselenation and desulphurisation reactions (schemes 3.10 and 3.11).

Scheme 3.10

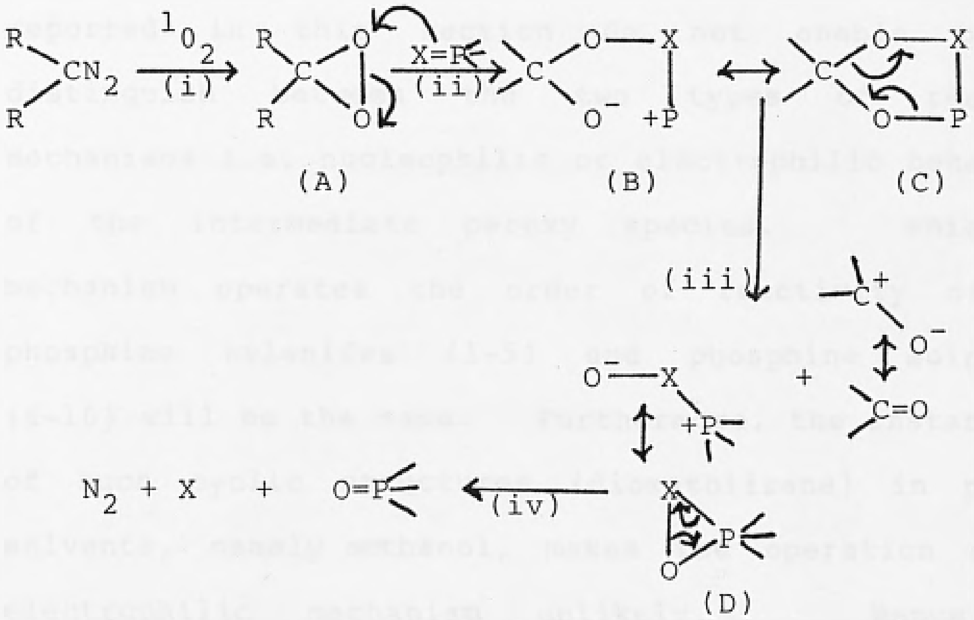


R = $CH_3(CH_2)_5$

X = Se,S

Similarly for carbonyl oxide species:

Scheme 3.11



R = Ph

X = Se,S

The reactions (i) - (iv) in both schemes 3.10 and 3.11 are analogous to each other. In the reaction (ii) of scheme 3.11 it is the P=Se or P=S moiety of the organophosphorus compound that is attacking the oxygen atom of the cyclic structure via a nucleophilic process to generate intermediate (B) which presumably cyclises by the formation of a P-O bond to generate intermediate (C). Subsequent rearrangement of this intermediate then produces carbonyl oxide and a strained cyclic structure (D) which rapidly rearranges to produce the desired phosphine oxide.

However, the dye sensitised photooxidation results reported in this section do not enable us to distinguish between the two types of reaction mechanisms i.e. nucleophilic or electrophilic behaviour of the intermediate peroxy species. Whichever mechanism operates the order of reactivity of the phosphine selenides (1-5) and phosphine sulphides (6-10) will be the same. Furthermore, the instability of such cyclic structures (dioxathiirane) in protic solvents, namely methanol, makes the operation of an electrophilic mechanism unlikely. Hence the nucleophilic mechanism predominates, in protic solvents, in these observed photooxygenations.

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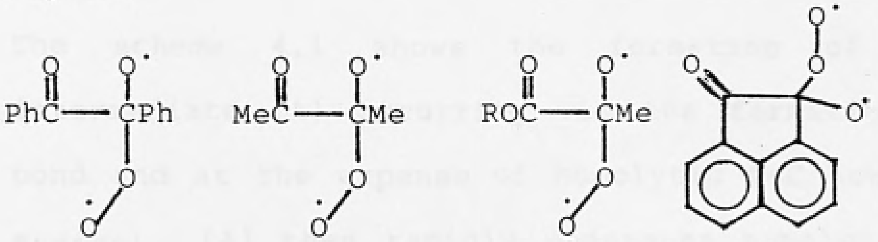
CHAPTER 4

OXIDATIVE DESELENATION REACTIONS OF PHOSPHINE SELENIDES WITH 1,2-DICARBONYL BASED PHOTOINITIATORS

4.1 INTRODUCTION

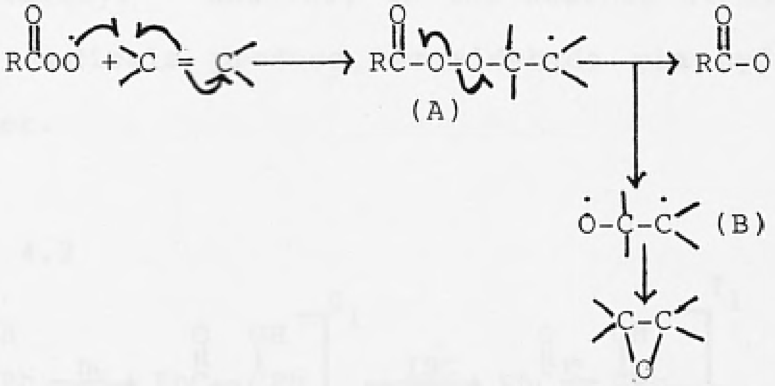
1,2-dicarbonyl compounds e.g. benzil, biacetyl, pyruvic acid, pyruvate esters and acenaphthanquinone are known[2,4-6,9,13,21] to produce 1,4-diradical species when their triplet states are quenched by ground state oxygen (fig.1.4).

Fig.1.4



These diradical intermediates may have sufficiently long lifetimes to participate directly in photooxidation reactions. For instance benzoin,[1] benzil,[2,4] and biacetyl[3] photoinitiate the transfer of an oxygen atom to alkenes to produce epoxides[6] (or oxiranes) and to sulphides to generate sulphoxides and sulphones.[3,5] It has been suggested that the intermediate species responsible for the epoxidations are the benzoylperoxy (generated from benzoin and benzil) and acetylperoxy (generated from biacetyl) radicals. The proposed radical mechanism is shown below:

Scheme 4.1

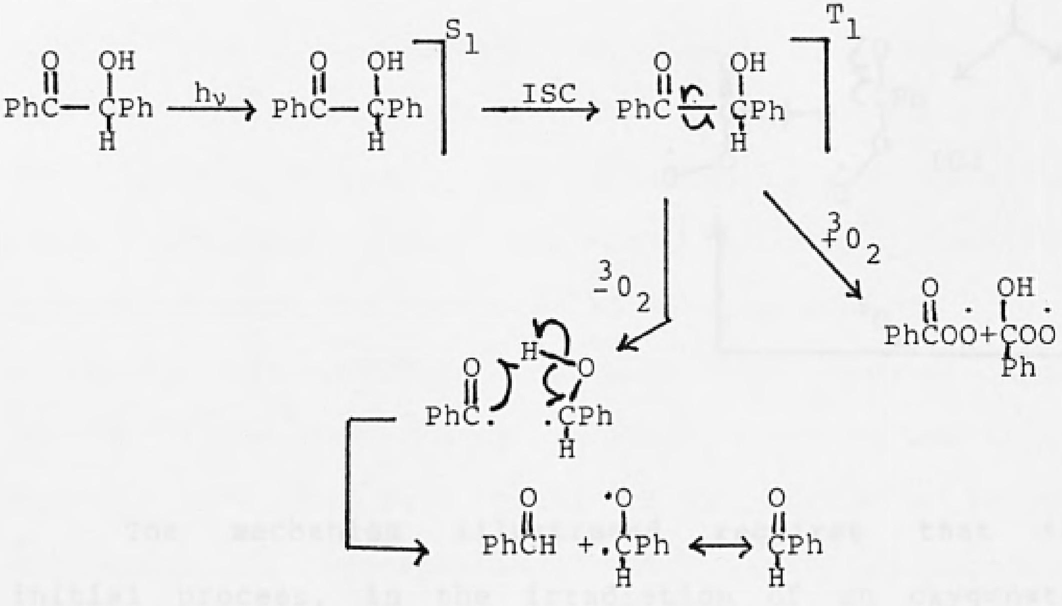


The scheme 4.1 shows the formation of a radical intermediate (A) occurring via the formation of a C-O bond and at the expense of homolytic C=C bond cleavage. Radical (A) then rapidly undergoes homolytic O-O bond cleavage to generate a diradical species (B) which undergoes rotation around the C-C bond, followed by intramolecular cyclisation to produce predominantly trans epoxides.

The formation of the benzoyl and acetylperoxy radicals may be understood from the photolyses studies of benzoin, benzil and biacetyl respectively.[1-4,7,8]

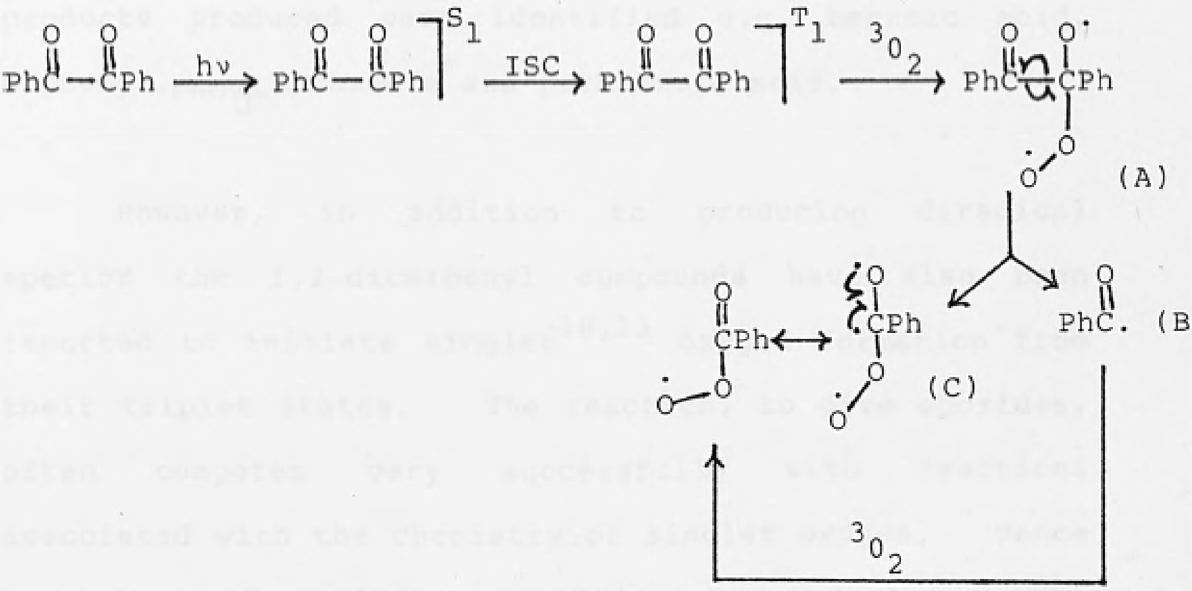
The photolysis of benzoin, in oxygenated solutions, is thought to occur through the homolytic cleavage of the C-C bond[7,8] with the initial formation of benzoyl and hydroxybenzyl radicals. Further reaction of the radicals, with molecular oxygen, occurs to generate benzoylperoxy and hydroxybenzylperoxy radicals respectively. However, in the absence of oxygen these former radicals produce benzaldehyde via hydrogen atom transfer:

Scheme 4.2



As previously mentioned, benzil has also been reported to photoinitiate the transfer of a single oxygen atom to alkenes to produce epoxides.[2,4] It was suggested that the intermediate species responsible for the epoxidation was analogous to that in the benzoin initiated photoepoxidation of alkenes, i.e. benzoylperoxy radical. The reaction of the intermediate with an alkene is shown in scheme 4.1, whilst its formation is shown in scheme 4.3:

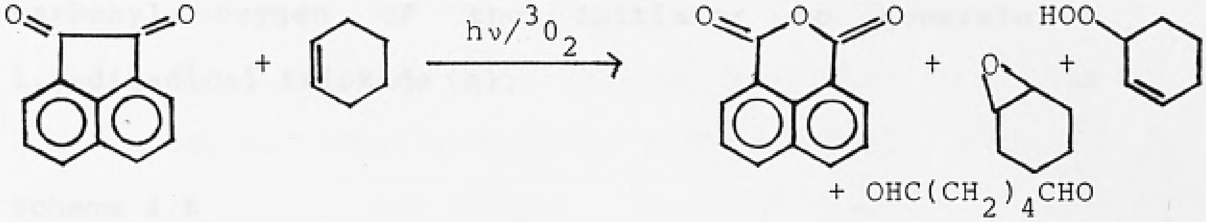
Scheme 4.3



The mechanism illustrated requires that the initial process, in the irradiation of an oxygenated benzil solution, involves the direct action of the initiator's triplet state with molecular oxygen. This quenching effect generates the 1,4-diradical intermediate species (A) which then undergoes rapid homolytic C-C bond cleavage to produce benzoyl (B) and benzoylperoxy (C) radicals. The benzoyl radical reacts with molecular oxygen to produce a benzoylperoxy radical. In addition the authors failed to detect any benzoyl radical formation during irradiation of benzil under nitrogen. This observation was reported to be consistent with previous studies with the benzil initiator.[7] Furthermore, benzil was reported to be completely consumed and several of the decomposition products produced were identified e.g. benzoic acid, biphenyl, phenyl benzoate and perbenzoic acid.

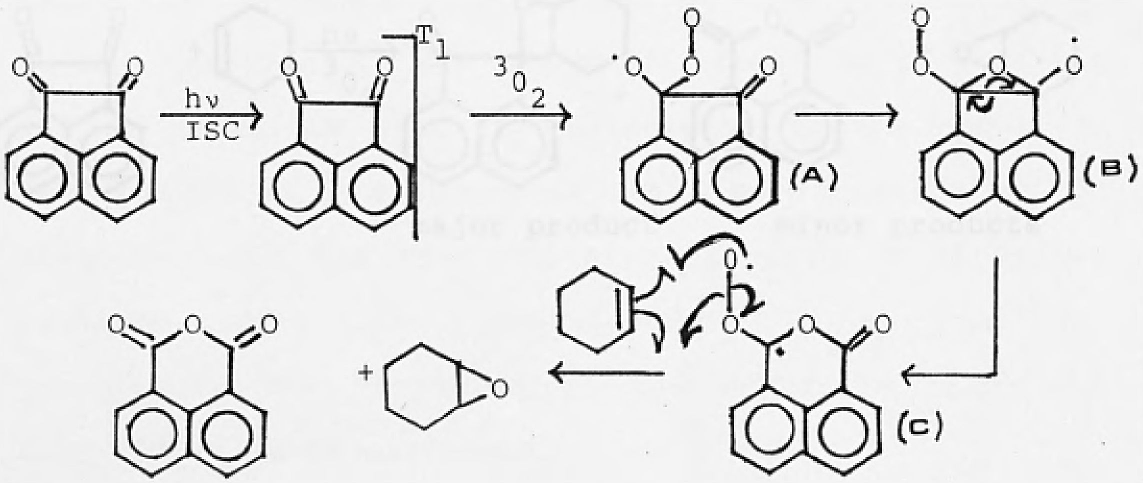
However, in addition to producing diradical species the 1,2-dicarbonyl compounds have also been reported to initiate singlet[10,13] oxygen formation from their triplet states. The reaction, to give epoxides, often competes very successfully with reactions associated with the chemistry of singlet oxygen. Hence a mixture of products, resulting from singlet oxygen photooxidation and peroxy radicals, may be obtained. Indeed, this has been found to be the case in the photolysis of acenaphthanquinone[25] with cyclohexene. The singlet oxygen derived photooxidation products were 3-hydroperoxy cyclohexene and adipaldehyde while the peroxy radical photooxidation products were the cyclohexene oxide and 1,8-naphthalic anhydride:

Scheme 4.4



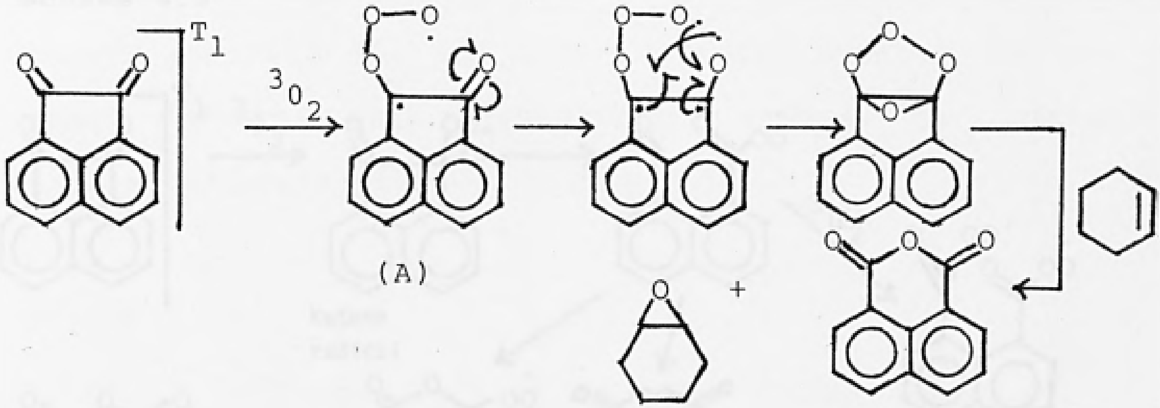
The formation of the peroxy photooxidation product, cyclohexene oxide, may be visualised as occurring via two separate mechanisms. Scheme 4.5 involves the molecular oxygen bonding to the carbonyl carbon of the initiator to produce 1,4-diradical species (A) which cyclises to generate an epoxide 1,5-diradical (B) followed by rapid homolytic C-C bond cleavage to produce 1,3-diradical (C), which is presumed to react with the alkene to produce the cyclohexene oxide and 1,8-naphthalic anhydride.

Scheme 4.5



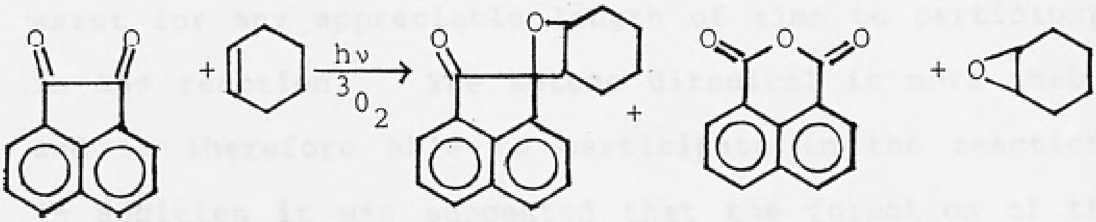
Alternatively a second mechanism may be equally probable and involves the molecular oxygen bonding to the carbonyl oxygen of the initiator to generate a 1,4-diradical trioxide (A).

Scheme 4.6



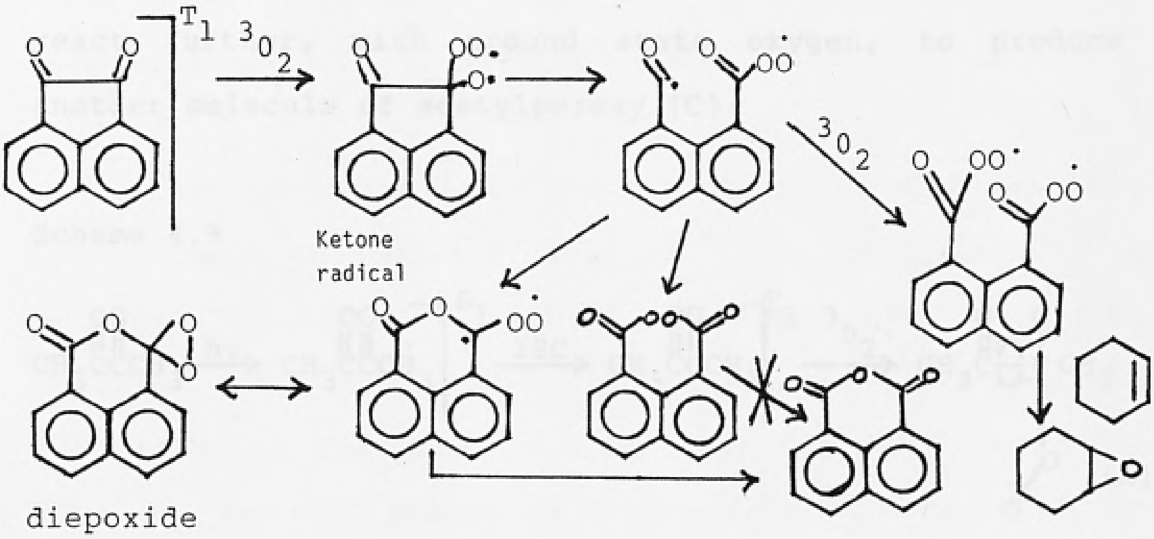
In a recent study[13] the photooxidation of cyclohexene with acenaphthanquinone was shown to produce 1:1 cyclohexene:quinone adduct as the major product.

Scheme 4.7



This large difference in the product formation has been attributed to the higher concentration of the cyclohexene used in the photolyses reactions. The authors have proposed the reaction mechanism in scheme 4.8, to explain the formation of minor products.

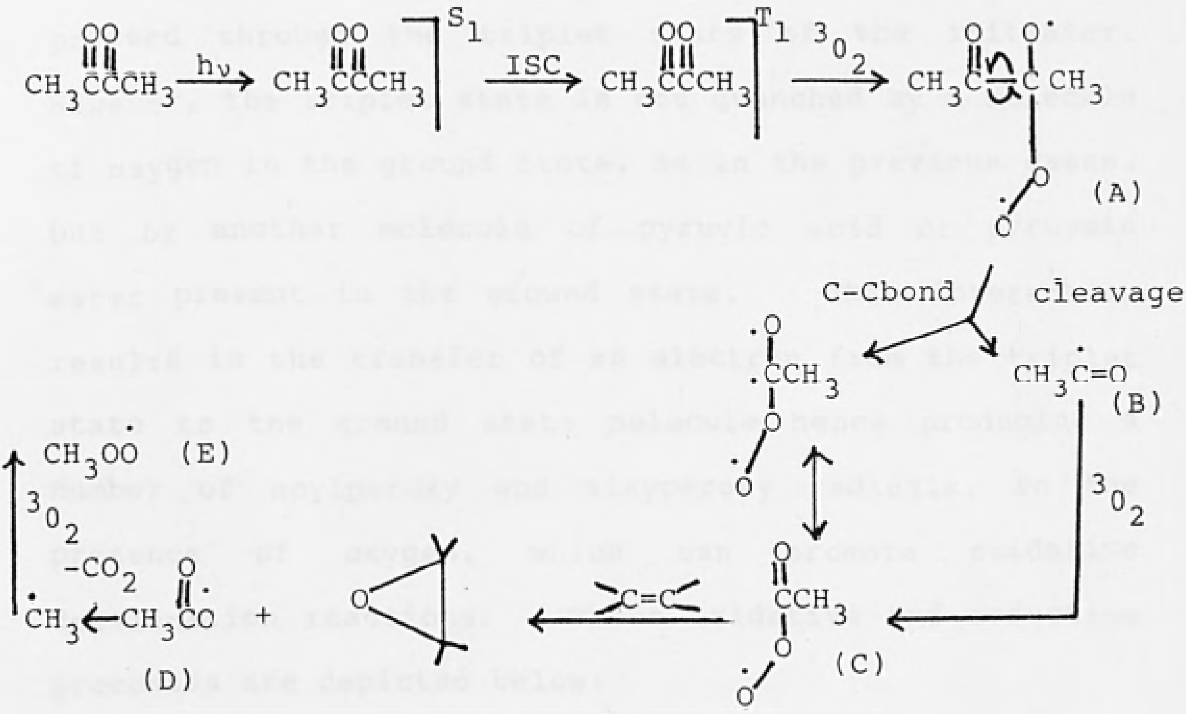
Scheme 4.8



The report suggested, in contrast to scheme 4.5, that the formation of the epoxide diradical was highly improbable since it is unstable and thus unlikely to exist for any appreciable length of time to participate in the reaction. The ketone diradical is more stable and is therefore able to participate in the reaction. In addition it was suggested that the formation of the diacylperoxide was also unlikely since no peroxide was isolated from the photolysis[25,13] solution and furthermore the formation of the anhydride, from the diacylperoxide is difficult.

Similarly, the photolysis of biacetyl has been presumed to proceed through the triplet state.[11] The mechanism is believed to be analogous to that of the initiator benzil i.e. involving the initial generation of the 1,4-diradical species (A) by the action of ground state oxygen on the triplet state of the initiator, followed by rapid homolytic C-C bond cleavage to produce acetyl radicals (B) and (C). Acetyl radical (B) may react further, with ground state oxygen, to produce another molecule of acetylperoxy (C)·:

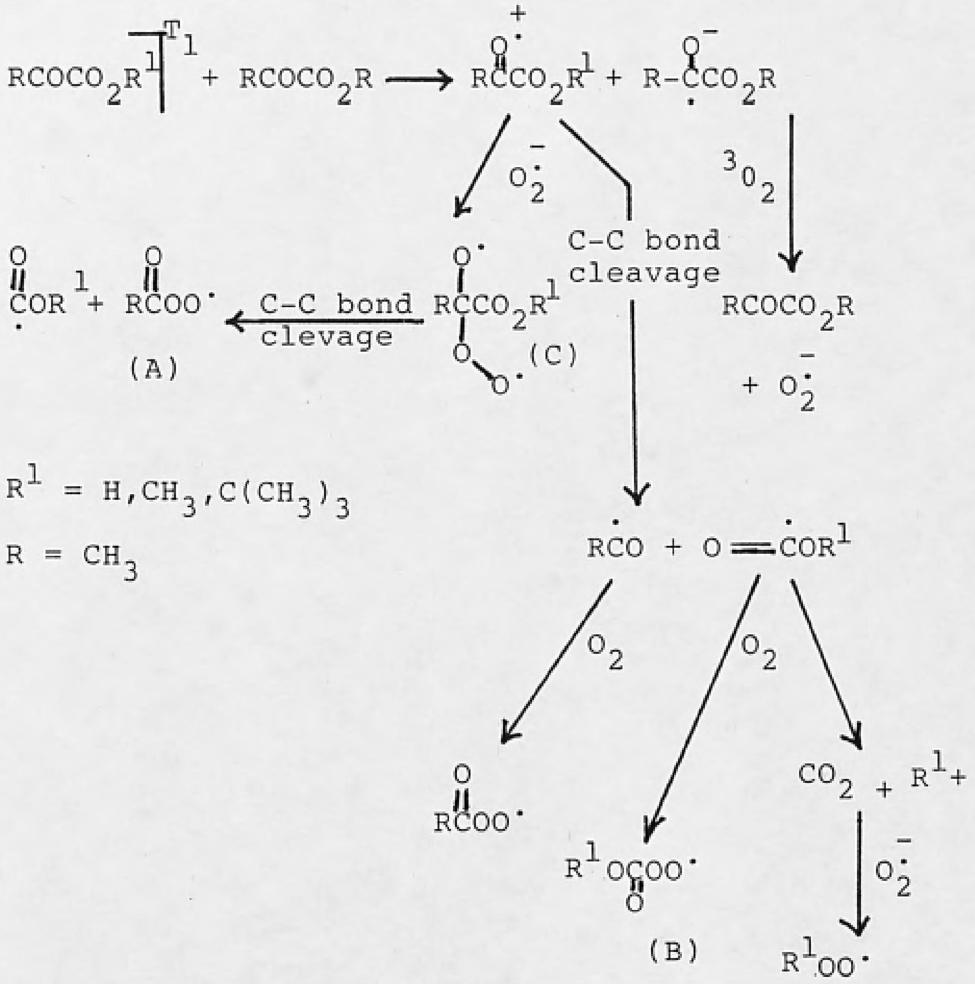
Scheme 4.9



It is generally accepted that the intermediate species (C) is responsible for the epoxidation reactions of the alkenes.[6] The acetyloxy radical (D), formed upon epoxidation, rapidly decarboxylates to give the methyl radical[12] which may add a molecule of oxygen to form the methylperoxy radical (E). It is this radical which is believed to be responsible for the formation of C-C bond cleavage products in biacetyl initiated photoepoxidations of alkenes[4] (refer to scheme 4.1).

The photolyses of pyruvic acid and pyruvate esters have been extensively studied[14-17] and presumed to proceed through the triplet state of the initiator. However, the triplet state is not quenched by a molecule of oxygen in the ground state, as in the previous cases, but by another molecule of pyruvic acid or pyruvate ester present in the ground state. This interaction results in the transfer of an electron from the triplet state to the ground state molecule hence producing a number of acylperoxy and alkyperoxy radicals, in the presence of oxygen, which can promote oxidative deselenation reactions. These oxidative and reductive processes are depicted below:

Scheme 4.10



4.2 Results and Discussion

On the basis of the known chemistry of 1,2-dicarbonyl compounds it is proposed that they could be used as initiators for the oxygenation of phosphine selenides. The remainder of this chapter is concerned with the investigation into the ability of, and mechanisms by which, a range of 1,2-dicarbonyl compounds initiate the photooxidative deselenation of a variety of phosphine selenides.

The photooxidative deselenation of phosphine selenides has been achieved by irradiating a mixture of the organophosphorus compound and a 1,2-dicarbonyl compound, e.g. benzoin, benzil and ethyl pyruvate, in the presence of oxygen. The results obtained are illustrated in table 4.1. All the selenides (1-5) were completely oxidised to their corresponding phosphine oxides. In all the oxygenation reactions the photoinitiators were found to be consumed during the reaction.

In consideration of the reported formation of peroxy radicals during the irradiation of 1,2-dicarbonyl compounds, it is not unreasonable to presume that these radicals could be responsible for the photooxidative deselenation of phosphine selenides. However, as indicated earlier the triplet state of the initiators benzil, biacetyl and acenaphthanquinone, react with a ground state oxygen molecule not only to generate 1,4-diradical species[2,4-6,9,20-22] but also undergo energy transfer to produce singlet oxygen.[10,13,25] Thus the photooxygenation reactions observed with the

1,2-dicarbonyl compounds could also be due to singlet oxygen reactions. In order to test this point the phosphine selenides were iradiated in the presence of Rose Bengal, Methylene blue or meso-tetraphenylporphyrin, which are efficient producers of singlet oxygen. These studies revealed that of the five phosphine selenides employed in the dye sensitised reactions, only the triphenylphosphine selenide (1) produced any appreciable reactivity with the singlet oxygen (table 4.2). The remaining phosphine selenides showed hardly any reactivity towards singlet oxygen. This implies that the observed reactivity of the triphenylphosphine selenide, in the 1,2-dicarbonyl initiated reactions, may be due to singlet oxygen reactions as well as the 1,4-diradical reactions. However, since the remaining phosphine selenides showed negligible reactivity towards singlet oxygen, it can be concluded that the observed photooxygenation reactions of the phosphine selenides with the 1,2-dicarbonyl initiators are more likely to involve the formation of 1,4-diradical intermediate species rather than singlet oxygen.

Table 4.1 Photooxidative deselenation[a] reactions of phosphine selenides (1-5) with 1,2-dicarbonyl based compounds

Compound	Initiator	Initiator mol. equivalent	% oxidise product
Ph_3PSe (1)	benzoin	4	100
	"	2	98
	benzil	4	100
	"	2	99
	biacetyl	4	99
	"	2	98
	acenaphthanquinone	2	96
	ethyl pyruvate	4	100
	"	2	97
	methyl pyruvate	4	100
	"	2	97
	pyruvic acid	4	98
	"	2	93
$Ph_2P(Se)OEt$(2)	benzoin	4	98
	"	2	98
	benzil	4	97
	"	2	98
	biacetyl	4	99
	"	2	95
	acenaphthanquinone	2	98
	ethyl pyruvate	4	96
	"	2	97
	methyl pyruvate	4	98
	"	2	96
	pyruvic acid	4	98
	"	2	94
$PhPSe(OEt)_2$(3)	benzoin	4	98
	"	2	99
	benzil	4	99
	"	2	100
	biacetyl	4	96
	"	2	97
	acenaphthanquinone	2	95
	ethyl pyruvate	4	100
	"	2	98
	methyl pyruvate	4	99
	"	2	100
	pyruvic acid	4	97

Table 4.1 contd.

$(EtO)_3PSe$ (4)	benzoin	4	97
	"	2	100
	benzil	4	98
	"	2	96
	biacetyl	4	98
	"	2	99
	acenaphthanquinone	2	96
	ethyl pyruvate	4	97
	"	2	95
	methyl pyruvate	4	92
	"	2	97
	pyruvic acid	4	99
$(MeO)_3PSe$(5)	benzoin	4	100
	"	2	96
	benzil	4	99
	"	2	95
	biacetyl	4	97
	"	2	99
	acenaphthanquinone	2	95
	ethyl pyruvate	4	93
	"	2	96
	methyl pyruvate	4	94
	"	2	97
	pyruvic acid	4	98

a, phosphine selenide 1.5×10^{-2}M, irradiation time 24 hours, under oxygen atmosphere, in $CHCl_3$(dry), at 350nm.

Table 4.2 Product yields (%) for dye sensitised reactions of phosphine selenides (1-5).

Dye[a]	% oxidation of phosphine selenides[b]				
	Ph_3PSe (1)	$Ph_2PSe(OEt)$ (2)	$PhPSe(OEt)_2$ (3)	$(EtO)_3PSe$ (4)	$(MeO)_3PSe$ (5)
Rose Bengal[d]	97	23	6	1	0
Meso-tetraphenylporphyrin[c]	75	4	2	< 1	1
Methylene blue[c]	80	9	3	< 1	2

a, dye concentration 2.0×10^{-4} Mdm^{-3}.

b, phosphine selenide (1-5) concentration 3.0×10^{-2} Mdm^{-3}, irradiated under oxygen for 5 hours through 2% $K_2Cr_2O_7$ solution with day light fluorescent lamps.

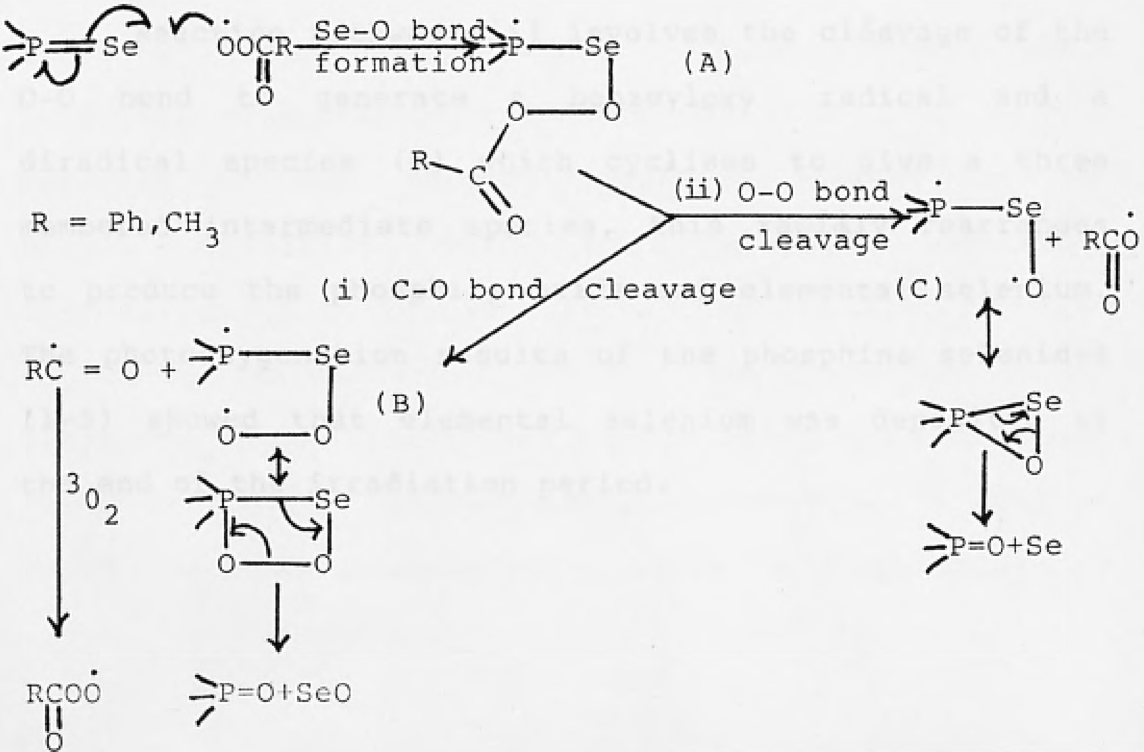
c, chloroform as solvent.

d, chloroform:methanol (1:1 v/v).

The results in table 4.1 show that all the phosphine selenides (1-5) have been completely oxidised to their corresponding phosphine oxides. This suggests that the action of peroxy radicals upon these phosphine selenides is a very efficient process.

In the case of the benzoin initiator, it has been proposed that the photoepoxidation reactions involve the benzoylperoxy radicals as intermediates.[1] Similarly it can be concluded that the benzyoylperoxy radical, generated by irradiating benzoin in chloroform, can also be responsible for the observed oxygenation reactions of the phosphine selenides. Hence the following mechanism scheme 4.11 is proposed.

Scheme 4.11



The benzoylperoxy radical reacts with the phosphine selenide to generate an intermediate species (A), via the formation of an Se-O bond. Species (A) may then decompose, via two reaction pathways, to produce the desired phosphine oxide product.

Reaction pathway (i) involves the homolytic cleavage of a C-O bond to generate a benzoyl radical and a diradical species (B) which rapidly cyclises to generate a four membered intermediate which in turn undergoes rearrangement to eventually produce the phosphine oxide and selenium oxide products. In addition, the benzoyl radical regenerates the benzoylperoxy radical, which in turn attacks another molecule of phosphine selenide to regenerate intermediate (A).

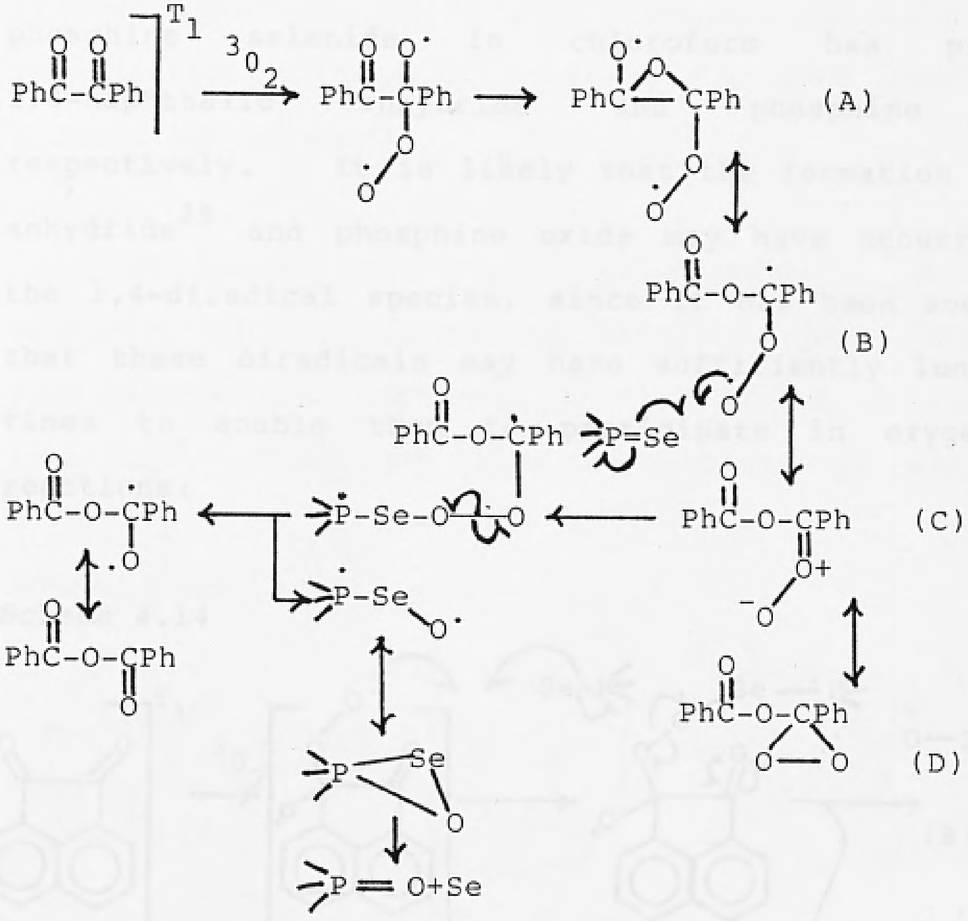
Reaction pathway (ii) involves the cleavage of the O-O bond to generate a benzoyloxy radical and a diradical species (C) which cyclises to give a three membered intermediate species, this rapidly rearranges to produce the phosphine oxide and elemental selenium. The photooxygenation results of the phosphine selenides (1-5) showed that elemental selenium was deposited at the end of the irradiation period.

This suggests that for the photooxidative deselenation reactions the mechanism proceeds via the reaction pathway (ii) only and not via reaction pathway (i). Analogous S-oxide intermediates to that shown by intermediate species (C) have been suggested currently, in the peracid oxidation of phosphinothioates[18] and in the enzymic metabolism of parathion.[19] Similarly, the hydroxybenzylperoxy radical, generated in situ by irradiation of benzoin, may also lead to the oxidation of phosphine selenides via reaction pathway (ii).

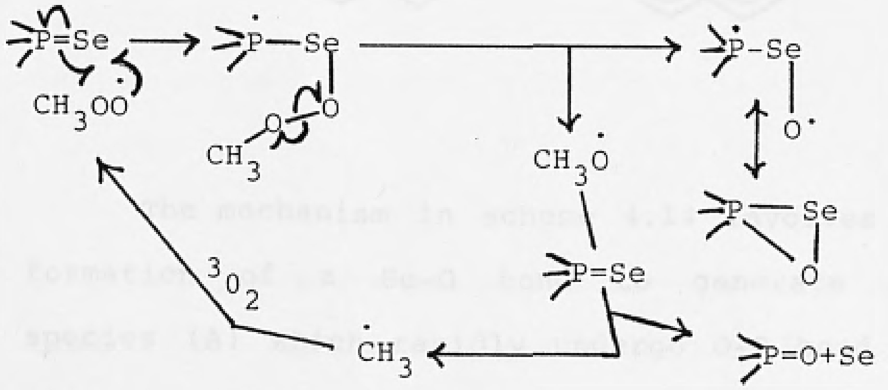
For benzil as initiator, it is likely that the benzoylperoxy radical, generated in situ by irradiating benzil in chloroform, is again responsible for the observed photooxidative deselenation reactions and the reaction proceeds via the reaction pathway (ii) i.e. involving the formation of a three membered ring as shown in scheme 4.11 (R=Ph). Alternatively, these oxidative deselenation reactions may also occur by the reaction of some photodecomposition product of the benzil initiator with the phosphine selenide. Irradiation of benzil in acetonitrile has been reported to produce benzoic anhydride.[20] The formation of the anhydride may be visualised as occurring via a carbonyl oxide or epoxide intermediates, scheme 4.12. Each of these resonance intermediates could be responsible for the photooxygenation reactions of the phosphine selenides. However, it has been suggested[13] that the diradical epoxide intermediate (A) is energetically less favourable than its corresponding intermediates (B), (C) or (D). The intermediate species, epoxide (D), is unlikely to have an appreciable lifetime in protic solvents, namely chloroform, due to its reaction with the solvent.[23-24] Furthermore, the carbonyl oxides have been shown (chapter 3) to be very efficient oxygen transfer reagents towards the phosphine sulphides and phosphine selenides to produce the corresponding phosphine oxides.

The biacetyl initiator generates acetylperoxy radical, on irradiation, which subsequently reacts with the phosphine selenides according to the reaction pathway (ii) in scheme 4.11, where R=CH_3. However, it may also be possible that the observed oxygenation reactions of the phosphine selenides could be due to the interaction of a methylperoxy radical, formed from methyl radical after decarboxylation of the acetyloxy radical, with the phosphine selenides (scheme 4.13). In addition the resulting methoxy radical may also react with another molecule of phosphine selenide to produce the corresponding phosphine oxide and a methyl radical, which may subsequently be scavenged by ground state oxygen to regenerate the methylperoxy radical.

Scheme 4.12

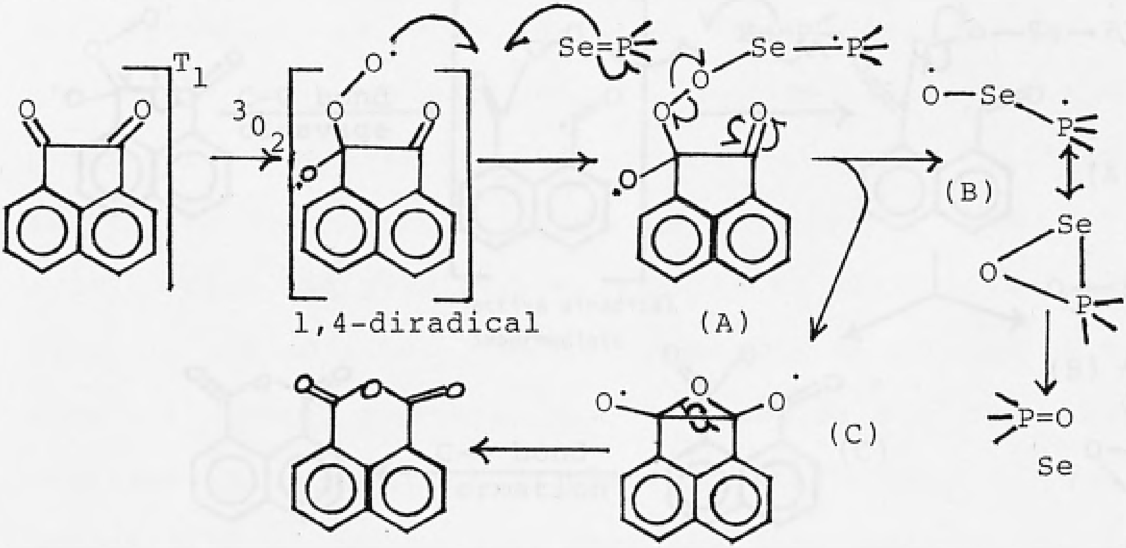


Scheme 4.13



Irradiating a mixture of acenaphthanquinone and phosphine selenide in chloroform has produced 1,8-naphthalic anhydride and phosphine oxide respectively. It is likely that the formation of the anhydride[25] and phosphine oxide may have occurred via the 1,4-diradical species, since it has been suggested that these diradicals may have sufficiently long life times to enable them to participate in oxygenation reactions:

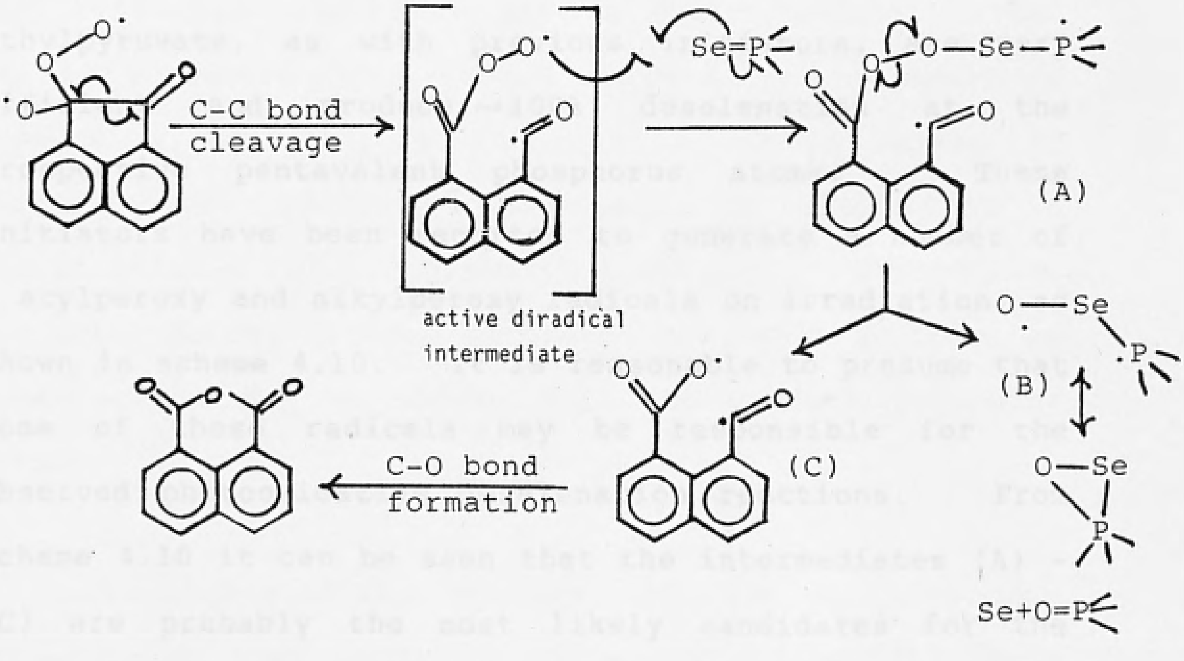
Scheme 4.14



The mechanism in scheme 4.14 involves the initial formation of a Se-O bond to generate intermediate species (A) which rapidly undergo O-O bond cleavage to give diradical intermediates (B) and (C). The intermediate species (B) cyclises and rearranges to produce phosphine oxide and elemental selenium, while intermediate species (C) undergo C-C bond cleavage to produce the anhydride.

In addition, these 1,4-diradicals may also generate sibling acylperoxy radicals, which may have facilitated the observed photooxidative deselenation reactions. Hence the following mechanism is proposed:

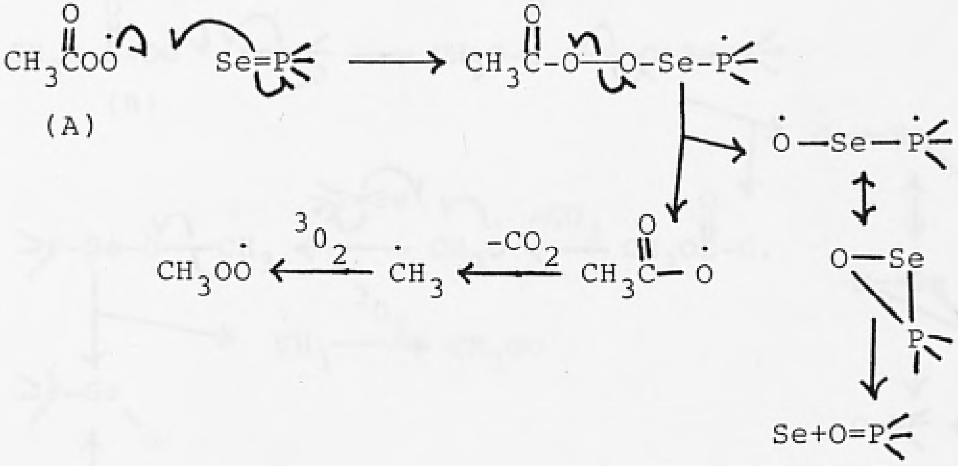
Scheme 4.15



In the above mechanism (scheme 4.15) it is implied that the active diradical intermediate species, generated from the 1,4-diradical species via C-C bond cleavage, reacts with a molecule of phosphine selenide to give an intermediate species (A) which is analogous to species (A) in scheme 4.14. As in the earlier scheme, this intermediate decomposes to produce two further reaction intermediates (B) and (C). Species (B) cyclises and eventually produces phosphine oxide and elemental selenium, while species (C) rapidly undergo C-O bond formation to generate the anhydride.

The photooxygenation reactions of phosphine selenides with pyruvic acid, methylpyruvate and ethylpyruvate, as with previous initiators, are very efficient and produce ~100% deselenation at the prospective pentavalent phosphorus atoms. These initiators have been reported to generate a number of acylperoxy and alkylperoxy radicals on irradiation, as shown in scheme 4.10. It is reasonable to presume that some of these radicals may be responsible for the observed photooxidative deselenation reactions. From scheme 4.10 it can be seen that the intermediates (A) - (C) are probably the most likely candidates for the photooxygenation reactions of the phosphine selenides. Intermediate species (A) is an acetylperoxy radical, which can react with a phosphine selenide molecule as shown below:

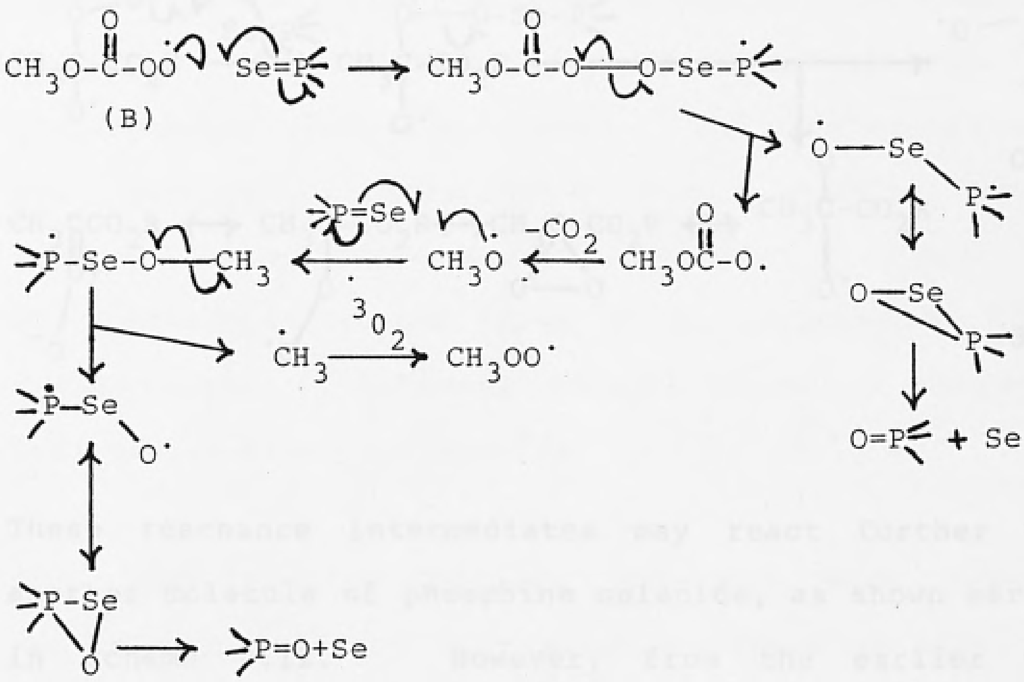
Scheme 4.17



The acetyloxy radical generated in the reaction rapidly decarboxylates to give a methyl radical, which may be scavenged by a ground state oxygen molecule to produce a methylperoxy radical. These series of reactions are similar to that shown in scheme 4.9, in the irradiation of the biacetyl initiator. Furthermore the methylperoxy radical generated may react further, as shown previously in scheme 4.13, to produce phosphine oxide.

The intermediate species (B) has an analogous structure to that of the acetylperoxy radical (A) hence a similar reaction mechanism is proposed:

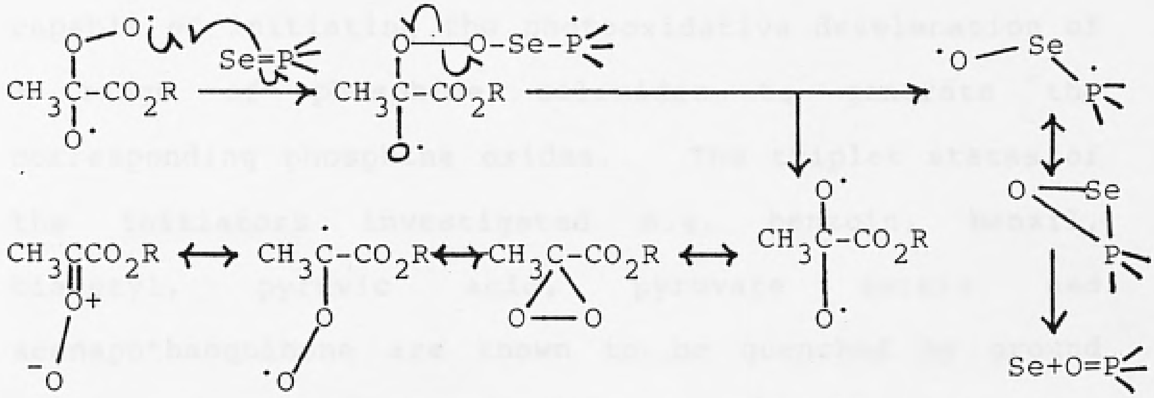
Scheme 4.18



The methoxy radical may react with another molecule of phosphine selenide to produce phosphine oxide, elemental selenium and a methyl radical. This radical may then be scavenged by another ground state molecule, as earlier, to generate a methylperoxy radical.

The intermediate (C) is a 1,4-diradical species which may react with a molecule of phosphine selenide as shown in scheme 4.19

Scheme 4.19



These resonance intermediates may react further with another molecule of phosphine selenide, as shown earlier in scheme 4.12. However, from the earlier work reported in chapter 3, it can be concluded that the carbonyl oxides are efficient oxygen donors towards the phosphine selenides and hence produce phosphine oxides quite readily. Furthermore, the epoxide intermediate species has been proposed to have insufficient lifetime, in protic solvents, to produce any appreciable oxidation.

4.3 Summary

The nature of the intermediate oxidising species in the photooxidative deselenation reactions is unclear.

It has been shown that, 1,2-dicarbonyl compounds are capable of initiating the photooxidative deselenation of a range of phosphine selenides to generate the corresponding phosphine oxides. The triplet states of the initiators investigated e.g. benzoin, benzil, biacetyl, pyruvic acid, pyruvate esters and acenaphthanquinone are known to be quenched by ground state oxygen to generate singlet molecular oxygen as well as 1,4-diradical species.

However, the results obtained using dyes as sensitisers indicate that singlet oxygen is relatively unreactive towards the phosphine selenides tested with the exception of triphenylphosphine selenide. Therefore, the ability of the 1,2-dicarbonyl compounds to act as initiators for photooxidative deselenation reactions is attributed to their ability to generate 1,4-diradical species. In order to explain the observed results a number of mechanisms are proposed.

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CHAPTER 5

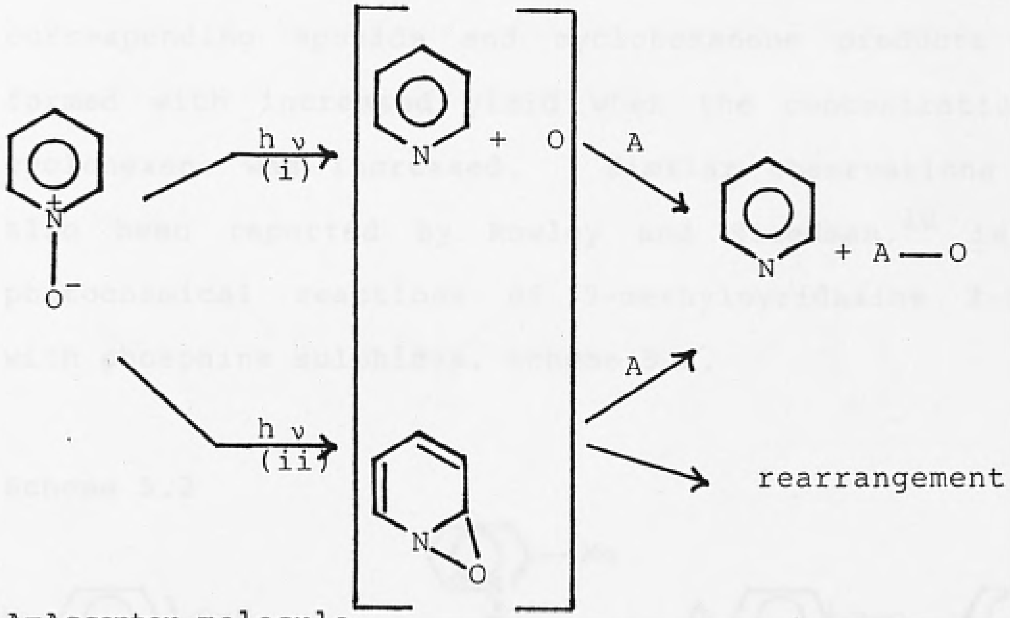
OXYGENATION REACTIONS OF PHOSPHINE SELENIDES AND PHOSPHINE SULPHIDES WITH HETEROCYCLIC N-OXIDES

5.1 INTRODUCTION

There has been considerable interest shown in the literature regarding the nature and reactivity of the "active intermediate species", generated *in situ* by heteroaromatic N-oxides upon irradiation. However, in order to have some insight into the mechanism of oxygen transfer, from N-oxides to the phosphine selenides or phosphine sulphides, it is necessary to discuss the background literature concerning the photoreactions of heteroaromatic N-oxides.

Heteroaromatic N-oxides have been extensively used as efficient photochemical oxidisers for alkanes,[1] alkenes,[2-5,8] epoxides[6] and currently sulphides[5,7] to produce alcohols, epoxides (or in some cases ketones), ketones and sulphoxides respectively. The mechanisms for oxygen transfer from N-oxides to the above mentioned substrates have not been fully elucidated as yet, although two probable reaction mechanisms have been proposed:[3,10-12]

Scheme 5.1

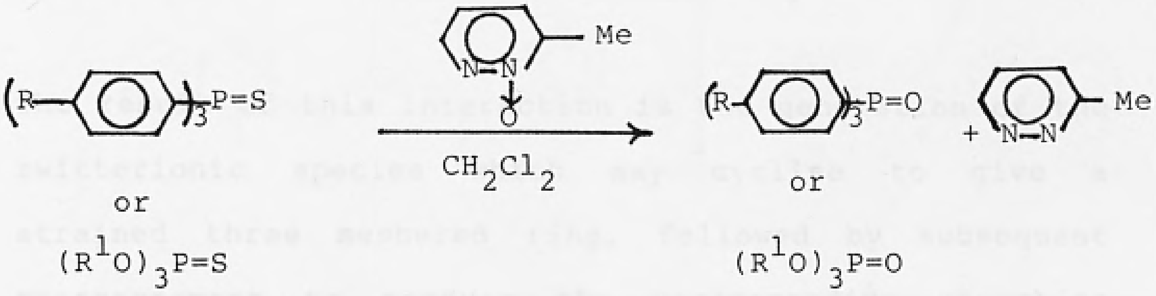


A=Acceptor molecule

The reaction pathway (i) involves the elimination of the oxygen atom from the photoexcited N-oxide to generate an electron deficient "oxene" (atomic oxygen), followed by its reaction with the acceptor molecule. Alternatively, the oxidation reactions may proceed via the interaction of the photoexcited N-oxide or its rearrangement product (oxaziridine) with the acceptor molecule followed by oxygen transfer, pathway (ii).

Involvement of an oxene has been inferred by Iwasaki and co-workers,[3] based on their observations that in the conversion of 3-methylpyridazine 2-oxide in the presence of cyclohexene no marked effect upon the consumption of the N-oxide was seen. In addition the corresponding epoxide and cyclohexanone products were formed with increased yield when the concentration of cyclohexene was increased. Similar observations have also been reported by Rowley and Steedman,[10] in the photochemical reactions of 3-methylpyridazine 2-oxide with phosphine sulphides, scheme 5.2.

Scheme 5.2

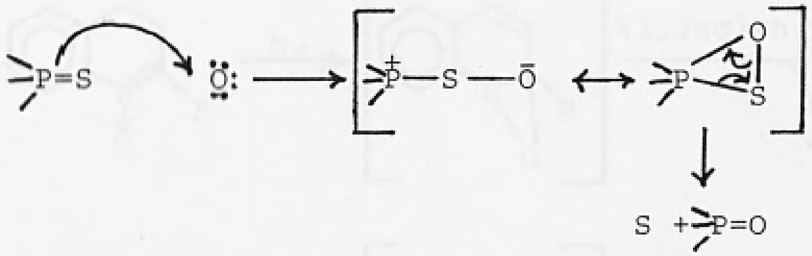


$R=Me,OMe,H,Cl,CO_2Me$

$R^1=Me,Et,Ph$

These reactions showed that the product yield of 3-methylpyridazine was independent of the nature of the substrate or its concentration. In addition the rate of formation of the amine, both in the presence and absence of these phosphine sulphides, was remarkably unaffected. Thus, these observations provided the circumstantial evidence for the involvement of the intermediacy of oxene as the active oxygenating species in these oxidative desulphurisation reactions. Oxene, which is of course electron deficient, could easily fit the role of a highly reactive electrophile and react with phosphine sulphides as shown:

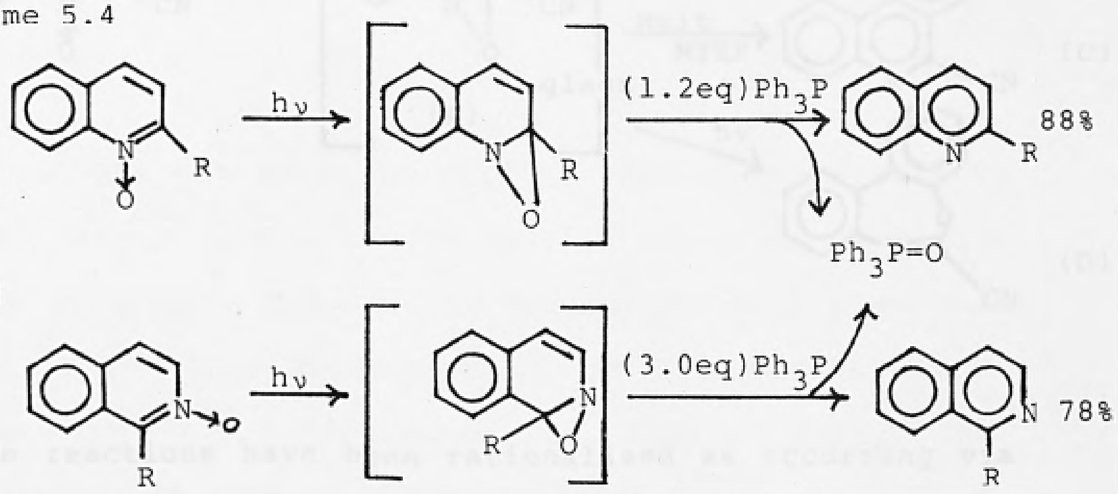
Scheme 5.3



The result of this interaction is the generation of the zwitterionic species which may cyclise to give a strained three membered ring, followed by subsequent rearrangement to produce the corresponding phosphine oxides and elemental sulphur. Although the scheme shows an equilibrium between these two intermediate species there is no evidence to suggest this is so.

The involvement of an oxaziridine intermediate, generated initially by the rearrangement of N-oxides during irradiation, has been proposed by Kaneko and co-workers,[11] based on their observations that the ratio of deoxygenation versus rearrangement depended on the concentration of the acceptor molecule for several N-oxides. In the specific case, 1.2 molar equivalents of triphenylphosphine has been found to be sufficient to cause quantitative deoxygenation in some phenanthridine N-oxides, while higher concentrations of the substrate were required in other cases:

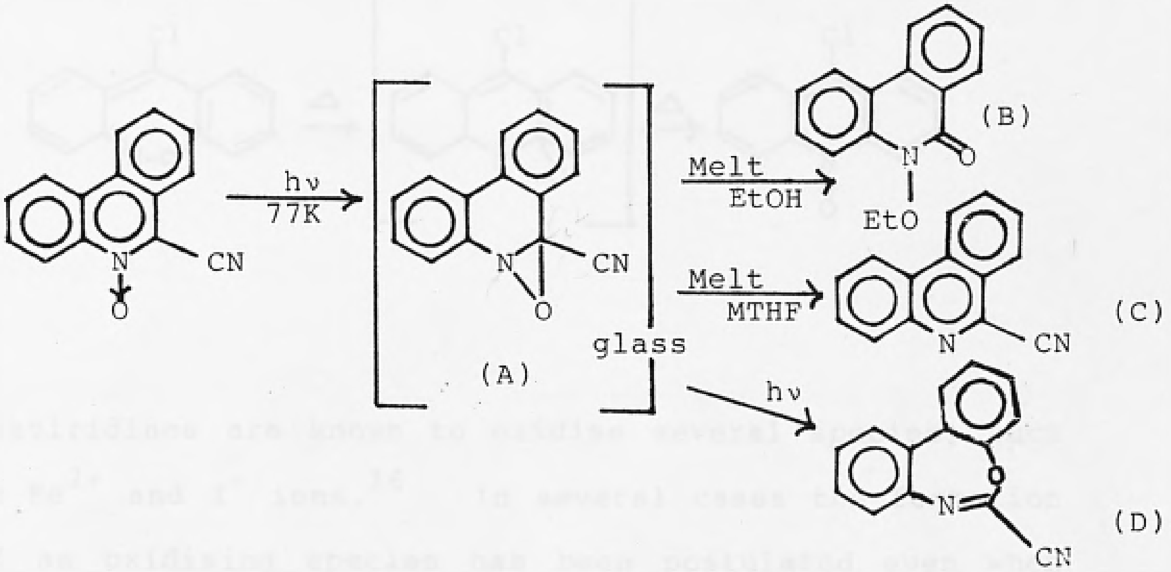
Scheme 5.4



R=CN

However, direct evidence in favour of the intermediacy of an oxaziridine has been currently provided by the isolation, in a matrix, of an oxaziridine species (A), generated by the photolysis of 6-cyanophenanthridine N-oxide i.e. scheme 5.5. The scheme shows that on melting the glass matrix, in the presence of ethanol or 2-methyltetrahydrofuran (MTHF),[12] products (B) and (C) were formed respectively. In addition the irradiation of the oxaziridine intermediate, in the matrix, produces the product (D) which can also be obtained directly by irradiation at room temperature.

Scheme 5.5

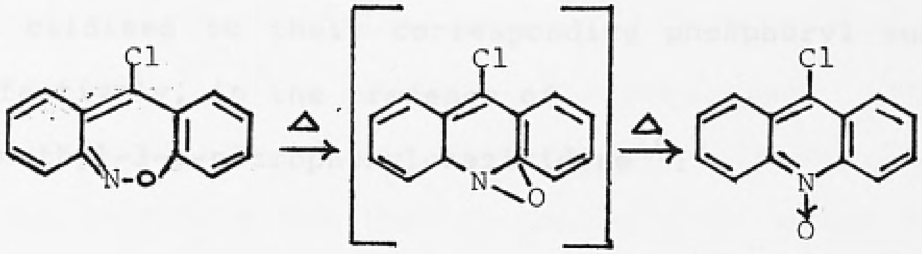


These reactions have been rationalised as occurring via the common oxaziridine intermediate species (A).

In several cases, however, indirect evidence for the oxaziridine being an intermediate has been presented. Part of this evidence comes from a study of the thermal reactions of 1,2-oxazepines.[14,15] These compounds are valence tautomers of oxaziridines and under suitable conditions thermally rearrange to the starting N-oxide; a process that can be rationalised as occurring via the oxaziridine, scheme 5.6.

The second body of evidence involves chemical trappings of oxaziridines with nucleophiles and oxygen acceptors.

Scheme 5.6

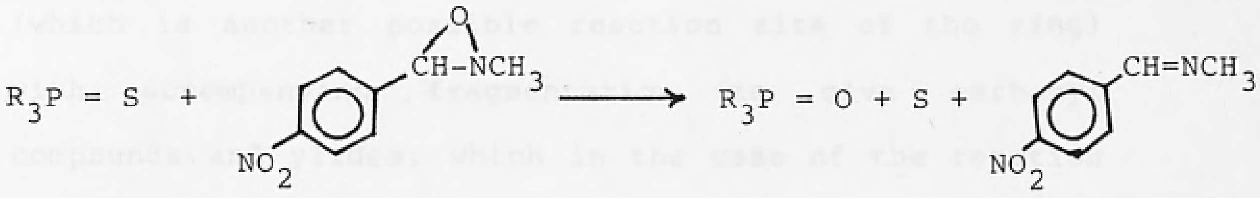


Oxaziridines are known to oxidise several species, such as Fe^{2+} and I^- ions.[16] In several cases the formation of an oxidising species has been postulated even when there is no other indication of the intermediacy of an oxaziridine e.g. liberation of iodine during the irradiation of some quinoline N-oxides.[17,18]

Whether or not oxaziridines are involved in the photochemical transfer of oxygen (to various substrates) is difficult to assess, due to the difficulty in establishing how much the invoked benzoxaziridines would differ from the natural oxaziridines in their chemical properties.[19-22] Oxaziridines have been found to transfer oxygen to various substrates. In particular, sulphonyloxaziridines have been studied in this respect, and found to transfer oxygen to organic sulphur compounds,[19,20] and alkenes.[22] However, with other substrates this reaction is not observed.[21]

Currently, triarylphosphine sulphides have been shown to be oxidised to their corresponding phosphoryl analogues effectively, in the presence of 3-methyl-3-p-nitrophenyloxaziridine[10]:

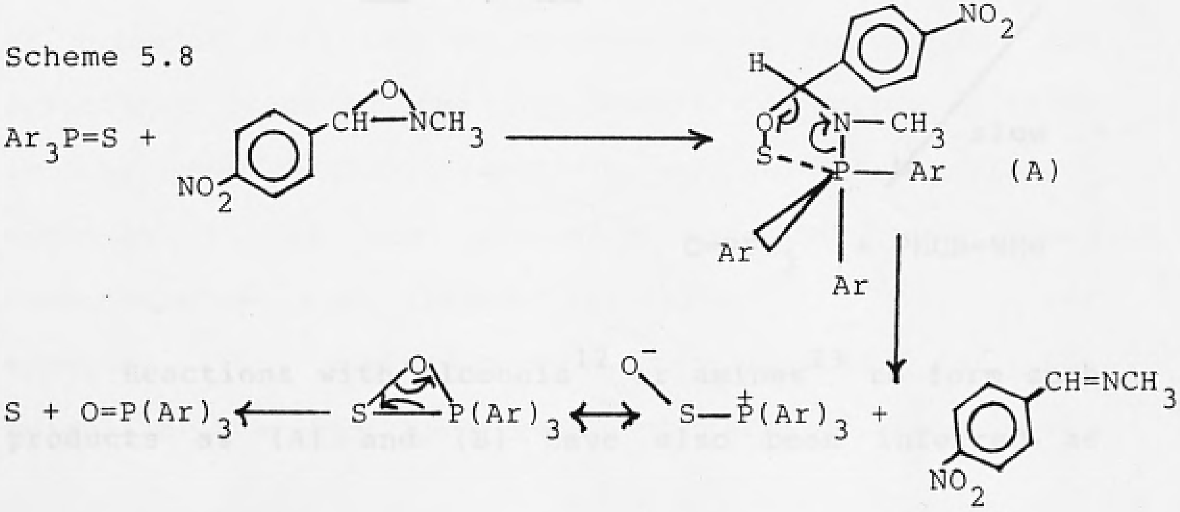
Scheme 5.7



$R=C_6H_5, 4\text{-}CH_3OC_6H_4,$
$4\text{-}CH_3C_6H_4, 4\text{-}ClC_6H_4$

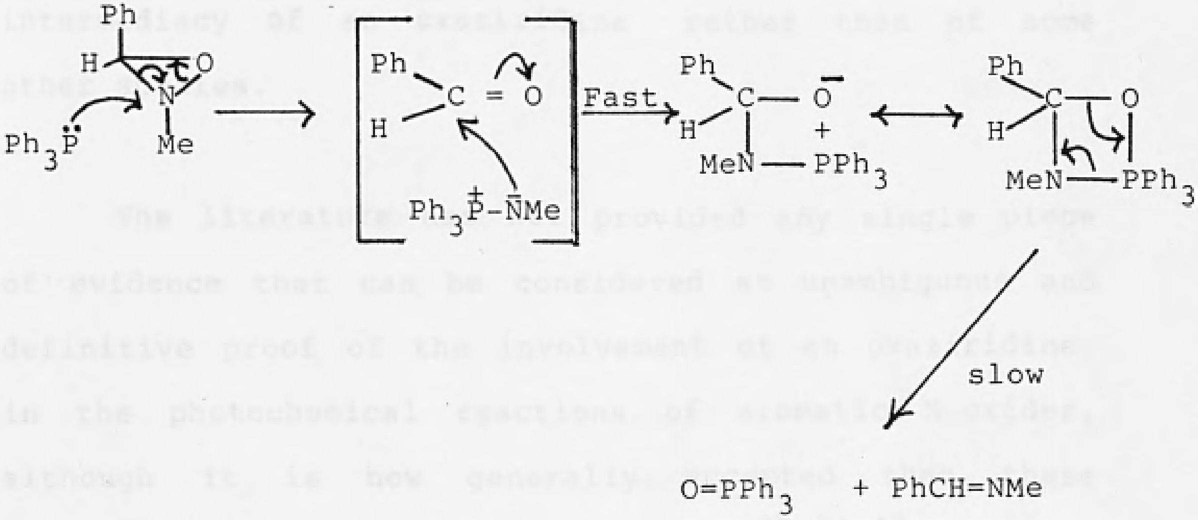
The mechanism proposed involved the direct nucleophilic attack of the thiophosphoryl sulphur on the oxaziridine oxygen to generate intermediate species (A) which rearranges to give a zwitterionic species, which may cyclise and eventually generate phosphine oxides:

Scheme 5.8



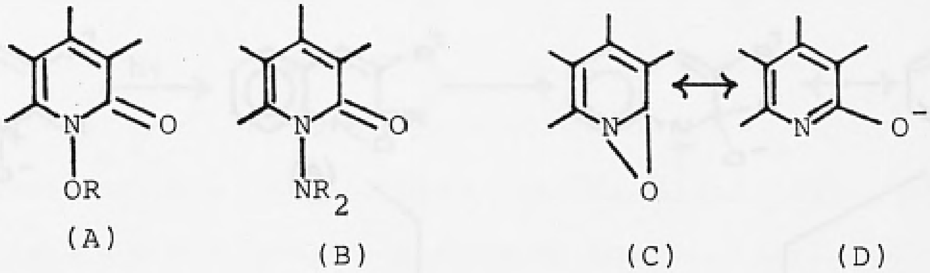
Alternatively, the oxaziridines have been found to react with nucleophiles, amines,[25,26] sulphides[27,28] and phosphines,[27,28] through fragmentation of the oxaziridine ring rather than nucleophilic opening. In these reactions the initial nucleophilic attack has been proposed to occur exclusively at the nitrogen atom (which is another possible reaction site of the ring) with accompanying fragmentation to give carbonyl compounds and ylides, which in the case of the reaction of triphenylphosphine with cis-2-methyl-3-phenyloxaziridine gradually disappears to generate triphenylphosphine oxide and N-(benzylidene)-methylamine:

Scheme 5.9



Reactions with alcohols[12] or amines[23] to form such products as (A) and (B) have also been inferred as evidence for the oxaziridine intermediate (C), although these products could equally well involve an open zwitterionic species[24] (D) as shown below:

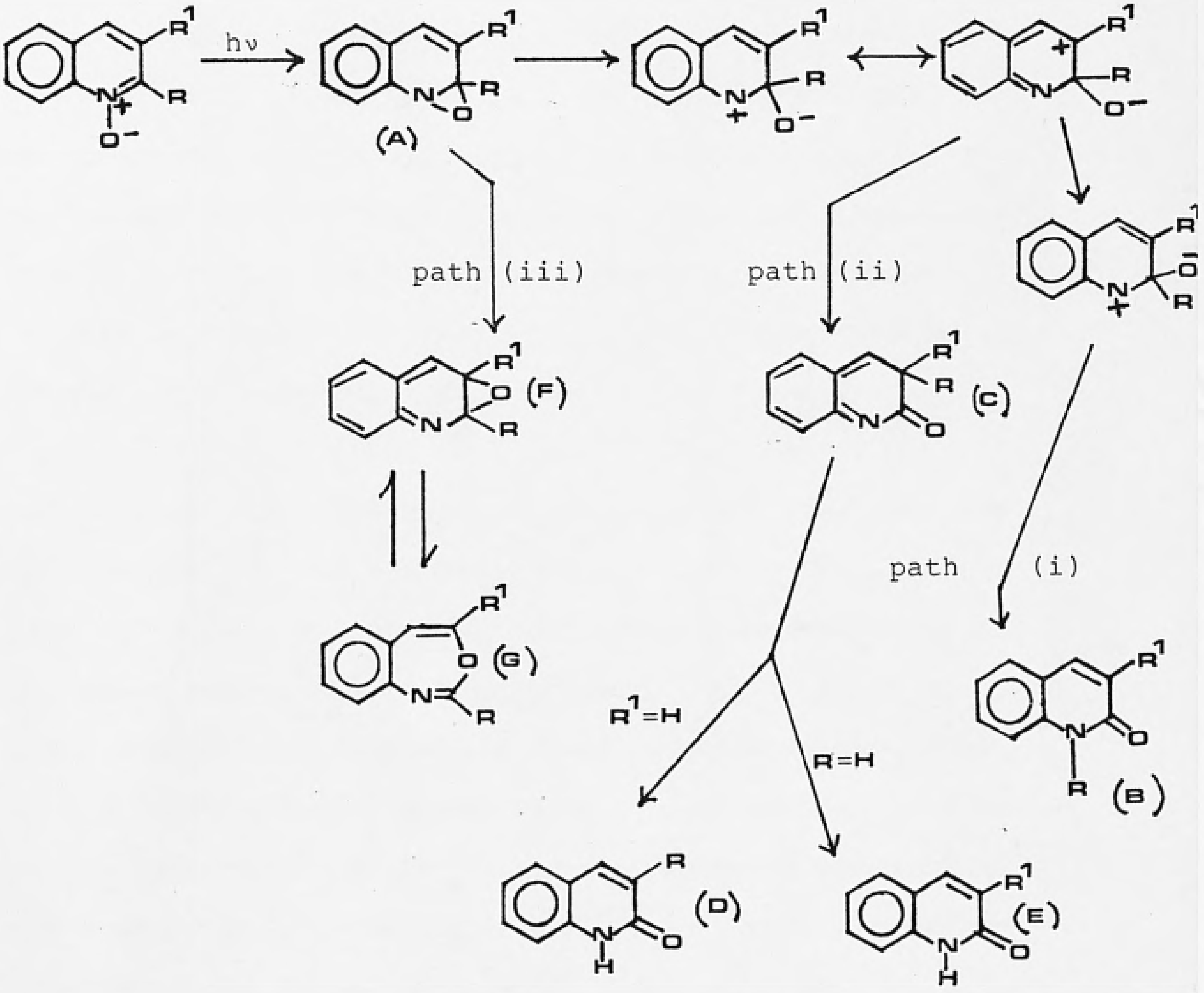
Fig.5.1



Thus, it appears that caution is needed in rationalising the N-oxide reaction as an indication of the intermediacy of an oxaziridine rather than of some other species.

The literature has not provided any single piece of evidence that can be considered as unambiguous and definitive proof of the involvement of an oxaziridine in the photochemical reactions of aromatic N-oxides, although it is now generally accepted that these intermediates are formed initially.[29,34-43] For example, the photochemical rearrangements of the quinoline N-oxides have been extensively investigated and reported to occur via the formation of an oxaziridine.[44-47] Thus the large majority of these rearrangement products have been explained by invoking various pathways from the oxaziridine,[48] as shown in scheme 5.10. Similar pathways are also proposed for other aromatic N-oxides.

Scheme 5.10



Paths (i)-(ii) are believed to involve the formation of the zwitterions, which may rearrange by the indicated 1,2 or 2,3 shifts to generate the observed products (B) and (C) respectively. Similarly, in the series with R^1=R =H analogous 1,3 shifts occur to give products (D) and (E).

Reaction pathway (iii) involves the symmetry-allowed thermal [1,5]-sigmatrophic shift[49,50] to generate the oxaziridine intermediate (F) which rearranges to the observed species (G). Analogies for the (A) to (F) rearrangements have been discussed in related systems,[51] while the thermal rearrangement of (F) to (G) has many precedents.[52]

There is, however, some evidence against the involvement of oxaziridine intermediates. Thus, in the case of some isoquinoline and phthalazine N-oxides it has been shown that the primary photoproduct (i.e. isocarbostyril or a diazo derivative, respectively) was formed within a few nanoseconds of excitation. This observation excluded the existence of an intermediate of any stability at room temperature.[53] Also during the irradiation of pyridine N-oxide, in matrix at 10K,[50] no intermediate has been detected. Furthermore, no oxaziridines have been observed from 2-cyanoquinoline

N-oxide and 1-cyanoisoquinoline N-oxide.[13] Hence, these examples put severe limits on the general concept that all photoreactions of N-oxides involve oxaziridines.

5.2 Results and Discussion

The literature survey presented above implies that a large majority of the aromatic N-oxides can be used successfully to effect oxygenation reactions with a wide variety of substrates by the transfer of a single oxygen atom. Thereby generating the respective parent amines and/or rearrangement products, in addition to oxidised products of the various substrates.

In this investigation a number of aromatic N-oxides have been employed to study the oxidative deselenation and desulphurisation reactions of a series of trisubstituted phosphine selenides (1-5) and phosphine sulphides (6-10). These oxidation reactions have been achieved by co-photooxidation of phosphine selenides or phosphine sulphides with each N-oxide in turn. The results of these studies are illustrated in tables 5.1 and 5.2. In addition the organophosphorus compounds (1-10) were also treated with 2-phenylsulphonyl-3-(p-nitrophenyl) oxaziridine. The reactions were stirred at room temperature in the absence of light to initiate oxidative deselenation and desulphurisation reactions.

Table 5.1 Photosensitised oxidation of phosphine selenides (1-5) by N-oxide in nitrogen purged dichloromethane.

N-oxide	% oxidation of organophosphorus selenides				
	Ph_3PSe	$Ph_2PSe(OEt)$	$PhPSe(OEt)_2$	$(EtO)_3PSe$	$(MeO)_3PSe$
	(1)	(2)	(3)	(4)	(5)
Pyridine[a]	96	96	91	86	89
2-Picoline[a]	96	96	92	88	89
Quinoline[b]	100	89	88	83	80
7-Hydroxy-3H-phenoxazine-3-one[c]	100	100	97	12	15
p-Cyano-N,N-dimethylaniline[a]	100	100	98	99	99
3-Methylpyridazine[b]	99	99	100	98	100

a, Phosphine selenide 2×10^{-3}M, N-oxide 5×10^{-3}M, solutions irradiated at 254nm for 24 hours.

b, Phosphine selenide 2×10^{-3}M, N-oxide 5×10^{-3}M, solutions irradiated by medium pressure mercury lamp (M.P.Hg) for 24 hours.

c, Phosphine selenide 1×10^{-3}M, N-oxide 2.5×10^{-3}M, irradiated by high pressure mercury lamp (H.P.Hg) for 24 hours in $CHCl_3$:MeOH (1:1 v/v).

Table 5.2 Photosensitised oxidation of phosphine sulphides (6-10) by N-oxides in nitrogen purged dichloromethane.

N-oxide	% oxidation of organophosphorus sulphides				
	Ph_3PS (6)	$Ph_2PS(OEt)$ (7)	$PhPS(OEt)_2$ (8)	$(EtO)_3PS$ (9)	$(MeO)_3PS$ (10)
Pyridine[a]	93	90	88	83	87
2-Picoline[a]	41	30	26	22	18
Quinoline[b]	29	18	14	3	3
7-Hydroxy-3H-phenoxazine-3-one[c]	16	14	14	8	9
p-Cyano-N,N-dimethylaniline[a]	24	16	11	8	9
3-Methylpyridazine[b]	75	61	60	58	53

a, Phosphine sulphide 2 x 10^{-3}M, N-oxide 5 x 10^{-3}M, solutions irradiated at 254nm for 24 hours.

b, Phosphine sulphide 2 x 10^{-3}M, N-oxide 5 x 10^{-3}M, solutions irradiated by M.P.Hg lamp for 24 hours.

c, Phosphine sulphide 1 x 10^{-3}M, N-oxide 2.5 x 10^{-3}M, irradiated by H.P.Hg lamp for 24 hours in $CHCl_3$:MeOH (1:1 v/v).

The data presented in tables 5.1 and 5.2 clearly shows that the phosphine selenides (1-5) exhibit greater reactivity towards the oxidising intermediate species, generated <u>in situ</u> by the irradiation of the respective N-oxides, than their analogous phosphine sulphides. This has been invoked from the consideration of the percentage product yields of the corresponding phosphine oxides. However, the photochemical reaction between the phosphine selenides (1-5) or phosphine sulphides (6-10) and pyridine N-oxide resulted in the oxidative deselenation and desulphurisation, at the respective pentacovalent phosphorus centre, in good yields. In the case of the selenides (1-5) 86-96% oxidations were observed, while the sulphides (6-10) gave 83-93% oxidation yields.

The reaction between 2-picoline N-oxide and phosphine selenides (1-5) gave almost complete oxidation of all the selenides, similar to above, while the sulphides (6-10) produced oxidation yields in much lesser amounts i.e. 18-41%. Similarly phosphine selenides (1-5), in the presence of quinoline N-oxide, resulted in the formation of the corresponding phosphine oxides in high yields i.e. between 80-100%, while its analogous sulphides (6-10) gave the much reduced oxidations i.e. 3-29%. Furthermore, the phosphine selenides (1-3), in the presence of 7-hydroxy-3H-phenoxazine-3-one, showed greater reactivity than the phosphine sulphides (6-8) although selenides (4,5) showed the much less characteristic yields of the sulphides i.e. 12 and 15% respectively. Also phosphine sulphides (6-10) gave the expected oxidation products in low yield i.e. 8-16%.

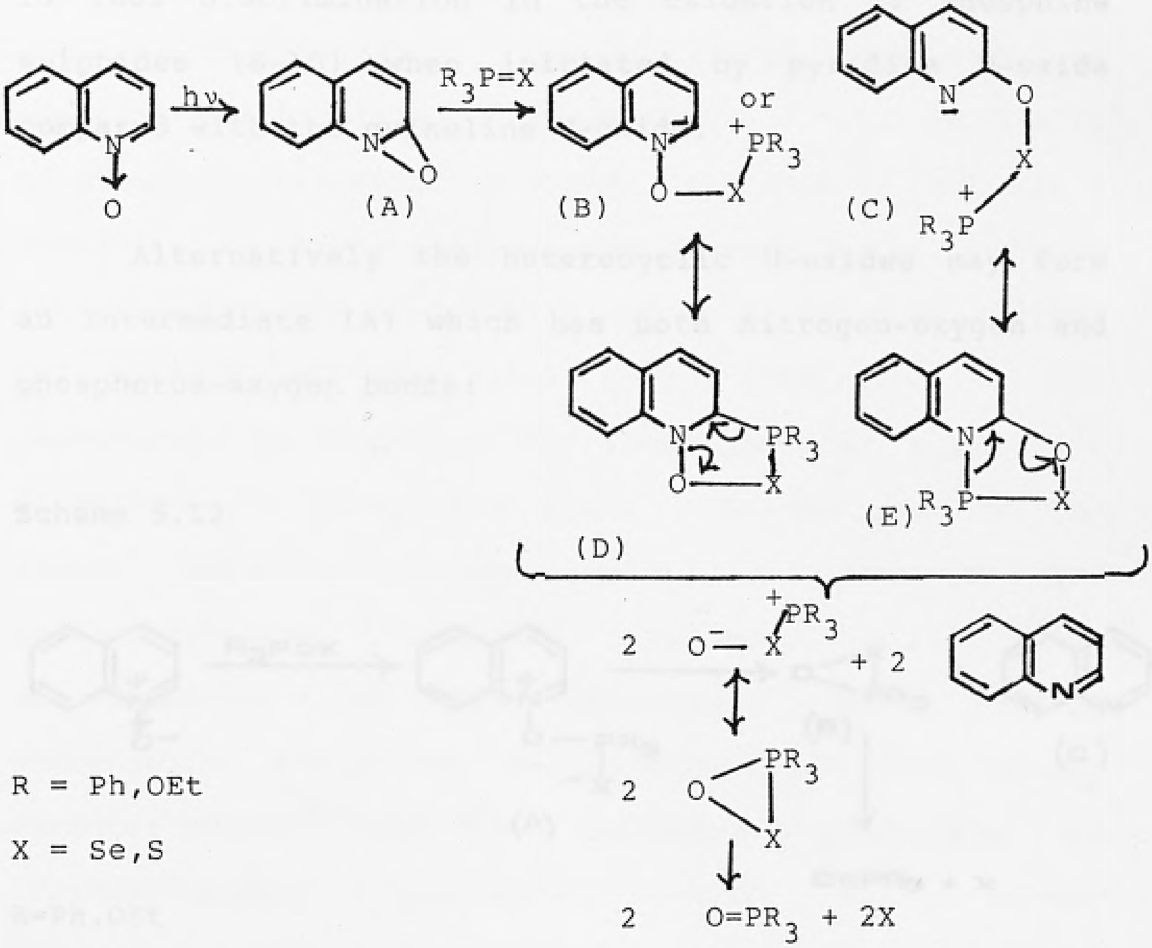
Phosphine selenides (1-5), in the presence of p-cyano-N,N-dimethylaniline N-oxide, were observed to be completely converted to their corresponding phosphoryl analogues i.e. 99-100% yields while the analogous sulphides (6-10) gave the normally reduced oxidation product yields in the range of 9-24%. Similar product yields were also observed in the reaction of phosphine selenides with 3-methylpyridazine 2-oxide. In these oxygenation reactions almost complete oxidative deselenation occurred to form the corresponding phosphine oxides in 98-100% yields. However, the oxygenation reactions of the phosphine sulphides were observed to be lower than the selenides i.e. between 53-75%.

In the presence of 2.5 times molar excess of 2-phenylsulphonyl-3-(p-nitrophenyl) oxaziridine, dissolved in dichloromethane, organophosphorus compounds (1-10) of concentration 2 x 10^{-3}M have been observed to undergo oxidative deselenation or desulphurisation to produce the corresponding oxidation products in 100% yields within 5-8 minutes at room temperature, in the absence of ultra-violet radiation. In the case of the phosphine selenides elemental selenium was observed to be precipitated in the reaction vessels, while elemental sulphur was difficult to see in the sulphide reactions since the experimental solutions were yellow.

However, since selenium deposition was observed in the selenide reactions it is not unreasonable to presume that sulphur may also be precipitated during the sulphide oxidations. Thus we can conclude that a similar mechanism may be operating in both of these reactions.

The nature of the active oxygenating species generated on irradiation of heteroaromatic N-oxides is not definitely established, although it is now generally assumed that the first stage in the reaction is the formation of an oxaziridine.[15,24,30] Recently Boyed and co-workers[5] have presented convincing evidence that it is this oxaziridine itself which reacts directly with sulphides. Hence it is entirely possible that the oxaziridine intermediate may be generated in the photolysis reactions of phosphine selenides and phosphine sulphides with the N-oxides of pyridine, 2-picoline, quinoline and 7-hydroxy-3H-phenoxazine-3-one. Since the reactions of the oxaziridines have been thoroughly investigated[10,28,31] and inferred to proceed by direct nucleophilic attack at the ring oxygen (although some reaction at the nitrogen also occurs) the following reaction mechanism scheme 5.11 is postulated. The specific reaction of the phosphine selenides and phosphine sulphides with quinoline N-oxide is depicted below:

Scheme 5.11



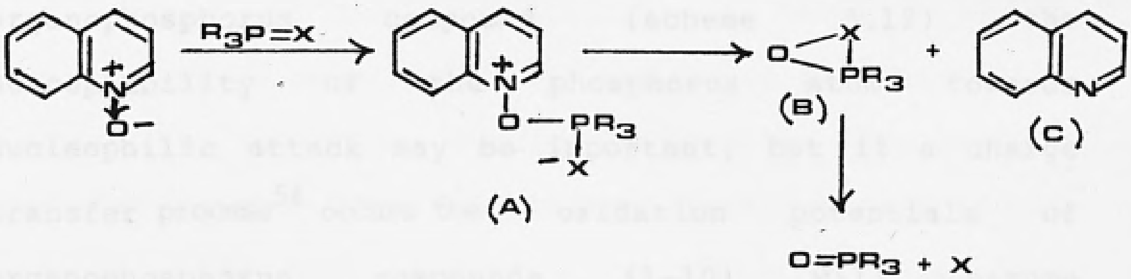
R = Ph,OEt

X = Se,S

The scheme 5.11 involves the nucleophilic attack of an organophosphorus compound on the ring oxygen of intermediate species (A) to generate intermediates (B,C), which can cyclise via the formation of P-C and P-N bonds to give two new five membered rings (D,E) which readily undergo rearrangement to produce the phosphine oxides, elemental selenium (or sulphur) and also the parent amines. The driving force of this reaction will be the formation of the aromatic heterocycle. Thus it may not be fortuitous that there is less discrimination in the oxidation of phosphine sulphides (6-10) when initiated by pyridine N-oxide compared with the quinoline N-oxide.

Alternatively the heterocyclic N-oxides may form an intermediate (A) which has both nitrogen-oxygen and phosphorus-oxygen bonds:

Scheme 5.12



R=Ph,OEt

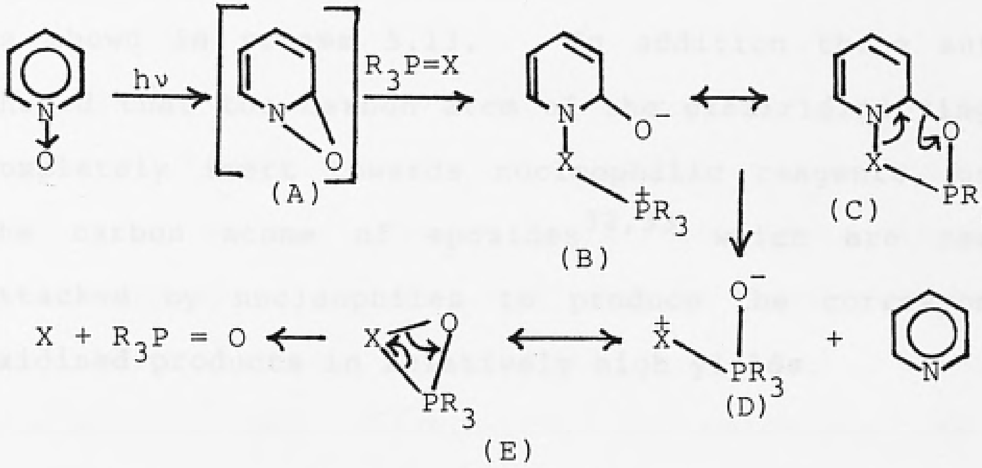
X=Se,S

The nitrogen-oxygen bond cleavage may then proceed to produce the parent amine and a three membered ring which subsequently undergo rearrangement to generate the respective oxidation products and elemental selenium (or sulphur).

Presumably this latter mechanism competes with the oxaziridine mechanism (scheme 5.11). However, a similar mechanism may be appropriate for explaining the reactions of the N-oxides of p-cyano-N,N-dimethylaniline and 3-methylpyridazine, which cannot rearrange to generate the oxaziridine intermediate. The reactivity of phosphine selenides (1-5) and sulphides (6-10), via a mechanism involving oxaziridines (scheme 5.11), will be determined by the nucleophilicity of selenium or sulphur and ability of the alkyl groups (attached to the phosphorus) to stabilise the development of a positive charge on the phosphorus atom. In the case of the direct reaction of the excited N-oxide with the organophosphorus compound (scheme 5.12) the susceptibility of the phosphorus atom towards nucleophilic attack may be important, but if a charge transfer process[54] occurs the oxidation potentials of organophosphorus compounds (1-10) will assume importance.

However, the ring nitrogens of the oxaziridines of pyridine, 2-picoline, quinoline and 7-hydroxy-3H-phenoxazine-3-one could have been attacked by the organophosphorus compounds (1-10) to produce the observed oxidation products:

Scheme 5.13



X=Se,S

R=Ph,OEt

Attack of the organophosphorus compound on the nitrogen of the oxaziridine (A) generates an intermediate species (B) which may cyclise to give a strained five membered species (C). Subsequent rearrangement of this species would then produce a zwitterionic intermediate (D) and the parent amine. Species (D) may then undergo cyclisation (E) or direct conversion to give the desired products.

Several authors have investigated the reactions of oxaziridines with a variety of nucleophiles, such as sulphides[27-28] and phosphines.[27,28] They proposed that the initial attack occurs exclusively at the ring nitrogen followed by subsequent fragmentation of the oxaziridine ring rather than the nucleophilic opening, as shown in scheme 5.13. In addition these authors showed that the carbon atom of the oxaziridine ring was completely inert towards nucleophilic reagents, unlike the carbon atoms of epoxides[32,33] which are readily attacked by nucleophiles to produce the corresponding oxidised products in relatively high yields.

However, the experimental results presented in this chapter cannot distinguish between the mechanism of fragmentation and the mechanism of nucleophilic opening of the oxaziridine ring.

Recently, the photochemical reactions of 3-methylpyridazine 2-oxide with tri-p-substituted triarylphosphine sulphides have been investigated and reported to proceed via the intermediacy of an "oxene" species.[10] Evidence in favour of this intermediate was provided by the observation that the decomposition of the N-oxide was independent of the nature and concentration of the phosphine sulphides. Furthermore, the photochemical decomposition of the N-oxide was unperturbed by the presence or absence of an oxygen acceptor. An oxene species has also been proposed by Iwasaki and co-workers[3] in the photochemical reaction of 3-methylpyridazine 2-oxide with cyclohexene, based on the grounds that the presence or absence of cyclohexene had no effect on the decomposition of the N-oxide.

These reports[3,10] and a current publication[55] suggest that the photochemical reactions of 3-methylpyridazine proceed via the intermediacy of oxene species. Thus it is not unreasonable to initially assume that the observed oxidative deselenation and desulphurisation reactions occurred involving the oxene intermediate. However, if this was the case the highly reactive oxene intermediate would not have discriminated between the phosphine selenides (1-5) and phosphine sulphides (6-10), hence similar orders of reactivity would have been observed. Since the results presented in tables 5.1 and 5.2 clearly indicate differing order of reactivity between the phosphine selenides (1-5) and sulphides (6-10) it can be concluded that the involvement of an oxene intermediate in these oxygenation reactions is highly unlikely.

5.3 Summary

Oxidative deselenation and desulphurisation reactions have been successfully carried out by co-photooxidation of phosphine selenides (1-5) and phosphine sulphides (6-10) with a variety of heterocyclic N-oxides and 2-phenylsulphonyl-3-(p-nitrophenyl) oxaziridine in either dry dichloromethane or dry chloroform:methanol (1:1 v/v) solvent. However, from the results obtained it is not possible to distinguish the precise nature of the "active oxygenating species", although it could be presumed that the reactions involving heterocyclic N-oxides have oxaziridines as intermediates which cause deselenation or desulphurisation reactions.

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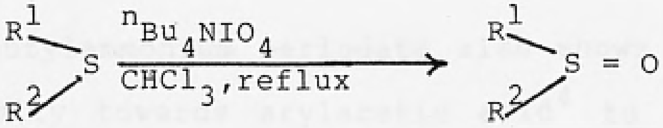
CHAPTER 6

OXYGENATION OF PHOSPHINE SELENIDES AND RELATED COMPOUNDS WITH TETRABUTYLAMMONIUM PERIODATE ($^{n}Bu_4NIO_4$) CATALYSED BY MANGANESE III MESOTETRAPHENYLPORPHYRIN CHLORIDE

6.1 INTRODUCTION

Currently, the interest in quaternary ammonium salts as phase transfer catalysts has led to the development of a number of tetraalkylammonium periodate compounds as selective oxidising agents towards a variety of organic substrates. Thus, tetra butylammonium periodate has been shown to oxidise sulphides[1] to sulphoxides in good yields:

Scheme 6.1



R^1=R^2=C_6H_5; R^1=CH_3-C_6H_5, R^2=n-C_4H_9;

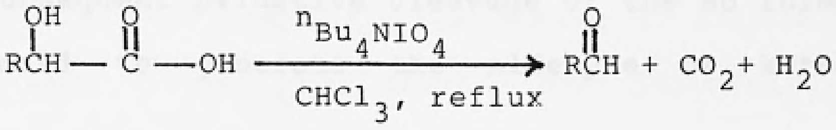
R^1=CH_3-C_6H_5, R^2=CH_3; R^1=R^2=CH_3-C_6H_5

R^1=R^2= -$(CH_2)_4$ -

Analogous oxidation reactions of sulphides have been achieved by the use of aqueous sodium metaperiodate[2] and recently[3] with sodium metaperiodate adsorbed on acidic alumina and an excess of oxidant in protic solvents.

While tetrabutylammonium periodate shows no reactivity towards 2-oxoglutaric acid, α-hydroxycarboxylic acids are readily decarboxylated to their corresponding aldehydes, scheme 6.2. This suggests that these decarboxylation reactions are selective for α-hydroxycarboxylic acids.

Scheme 6.2

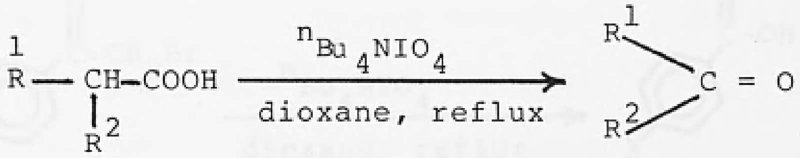


$$\mathrm{R\overset{OH}{C}H-\overset{O}{\overset{\|}{C}}-OH} \xrightarrow[\mathrm{CHCl_3,\ reflux}]{{}^{n}\mathrm{Bu_4NIO_4}} \mathrm{R\overset{O}{\overset{\|}{C}}H} + \mathrm{CO_2} + \mathrm{H_2O}$$

$R=n-C_3H_7$, $n-C_4H_9$, $n-C_6H_5$, $n-C_{14}H_{29}$

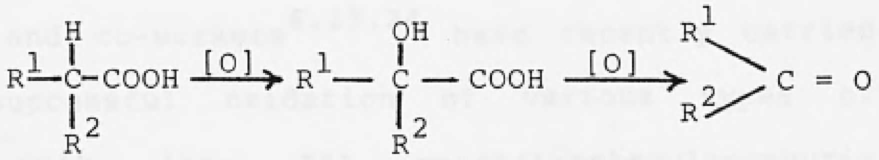
Tetrabutylammonium periodate also shows relatively high reactivity towards arylacetic acid[4] to afford the corresponding ketones or aldehyde products, scheme 6.3. For instance, diphenylacetic acid ($R^1=R^2=C_6H_5$) produces benzophenone in 85% yield, while p-chlorophenylacetic acid (R^1=p-Cl.C_6H_4,R^2=H) and p-methoxyphenylacetic acid (R^1=p-MeO.C_6H_4,R^2=H) react with tetrabutylammonium periodate to afford the corresponding benzaldehydes in 65 and 70% yields respectively.

Scheme 6.3



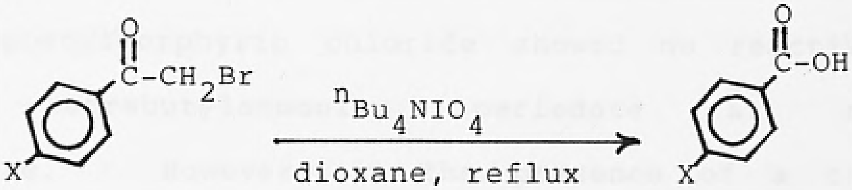
Alkaline solutions of sodiumhypochlorite[5] have also been shown to oxidise the arylacetic acids to afford, in this case, two oxidation products i.e. nor-aldehydes and acids. The oxidation reactions of arylacetic acids by tetrabutylammonium periodate may be rationalised by hydroxylation of the relatively activated methylene group and subsequent oxidative cleavage of the so formed 2-hydroxy acid to generate the aldehyde or ketone products:

Scheme 6.4



α-Bromoketones,[1] like sulphides, α-hydroxycarboxylic acids and arylacetic acids, are readily oxidised by tetrabutylammonium periodate to produce benzoic acid in good yields:

Scheme 6.5

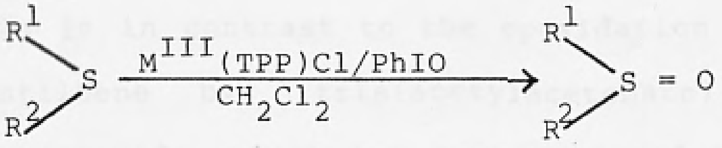


X=H,Br

Single oxygen donors such as tetrabutylammonium periodate,[6] iodosobenzene[7-11] (PhIO), alkylhydroperoxides[12-14] (ROOH), hydrogen peroxide[14] (H_2O_2), sodiumhypochlorite[15-18] (NaOCl) and activated N-oxides[19-22] are currently employed in conjunction with metalloporphyrins to mimic the oxidation reactions of cytochrome P-450. They thus provide some understanding of the mechanisms involved in the action of cytochrome P-450 monoxygenase or monoxygenases in general.

Ando and co-workers[6,23,24] have recently carried out the successful oxidation of various types of sulphides with iron III mesotetraphenylporphyrin chloride/tetrabutylammonium periodate, iron III mesotetraphenylporphyrin chloride/iodosobenzene and manganese III mesotetraphenylporphyrin chloride/iodosobenzene systems, in good yields. These studies showed that sulphides which are normally difficult to oxidise are easily converted to the corresponding sulphoxides. In a particular case, diphenylsulphide in the absence of iron III mesotetraphenylporphyrin chloride showed no reactivity towards tetrabutylammonium periodate at room temperature. However, in the presence of a trace amount of iron III mesotetraphenylporphyrin chloride it yielded 95% diphenylsulphoxide. This clearly illustrates the importance of these porphyrin oxidations. In addition it was suggested that the "active oxidising intermediates", responsible for the observed sulphide oxidations, were most likely to be porphyrin bound $M^{V}=O$ or $M^{iv}=O$, scheme 6.6. Furthermore, while the formation of the oxo-metal is faster with more electron rich p-MeO.C_6H_4IO, the reactivity of the sulphides is quite complex for the oxo-metal intermediate.

Scheme 6.6



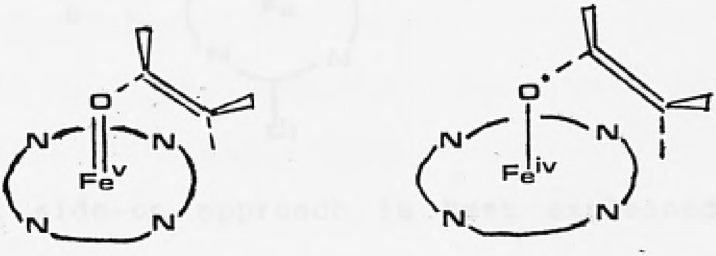
R^1, R^2 = alkyl, aryl

M = Fe, Mn

This efficiency of the catalyst is presumed to be a function of the central metal atom, and is in favour of iron III mesotetraphenylporphyrin chloride. Groves and co-workers[7] have extended the use of this system to epoxidise alkenes. The cis alkenes were found to be more reactive than the trans alkenes. In a particular case, cis-stilbene was epoxidised by iron III mesotetraphenylporphyrin chloride/iodosobenzene in 77% yield, while the trans-stilbene was found to be relatively unreactive under these conditions. This selectivity was suggested to result from non-bonded interactions between the phenyl groups of trans-stilbene and the meso-phenyl groups of the porphyrin. Thus, with the chlorodimethylferriprotoporphyrin [Fe(TMPCl)], where the interactions between the porphyrin meso-groups and phenyl groups of trans-stilbene are dramatically reduced, in the presence of iodosobenzene both cis- and trans-stilbene gave the corresponding stilbene oxides. However, this is in contrast to the epoxidation of cis- and trans-stilbene by tris(acetylacetonato) iron III/hydrogen peroxide, which has been reported to yield the trans epoxide from both starting materials.[25]

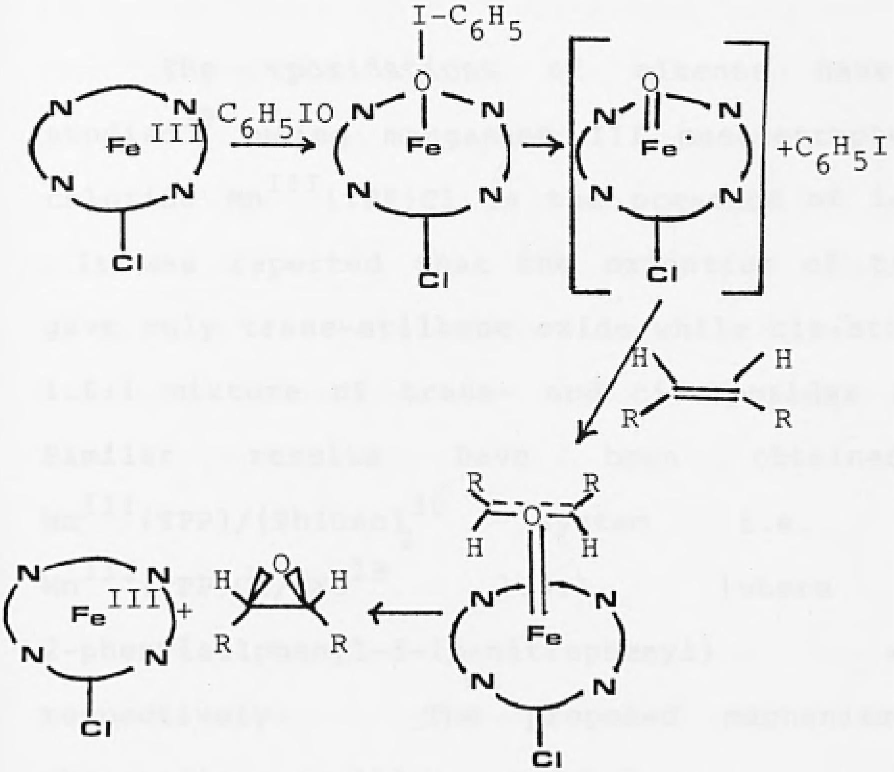
Such dramatic variations in selectivity with changes in the substitution pattern of the porphyrin suggest that oxygen transfer must take place at or very close to the porphyrin. From these observations it has been proposed that the approach of the double bond of cis-stilbene to the iron-oxo intermediate is relatively unhindered by phenyl-phenyl interactions between the iron-oxo intermediate and the substrate. However, for the trans-stilbene significant phenyl non-bonded interactions apparently develop between the porphyrin and trans-stilbene for any geometry except side-on parallel approach to the porphyrin plane directly from above (fig.6.1):

Fig.6.1



The nature of the active iron-oxo intermediate has been suggested to be either $\mathrm{Fe^{V}{=}O}$ or $\overset{+}{\mathrm{P}}\cdot\!-\!\mathrm{Fe^{iv}{=}O}$ once the iodosobenzene has transferred its oxygen to the iron of the porphyrin. These two intermediates have received a great deal of attention in the past, particularly as they relate to the putative oxidised intermediates of peroxidase[26] and cytochrome P-450.[27] In addition the iron IV-porphyrin cation radical has been reported[28] to afford analogous epoxidation reactions effectively. Hence, a mechanism for alkene epoxidation was proposed:

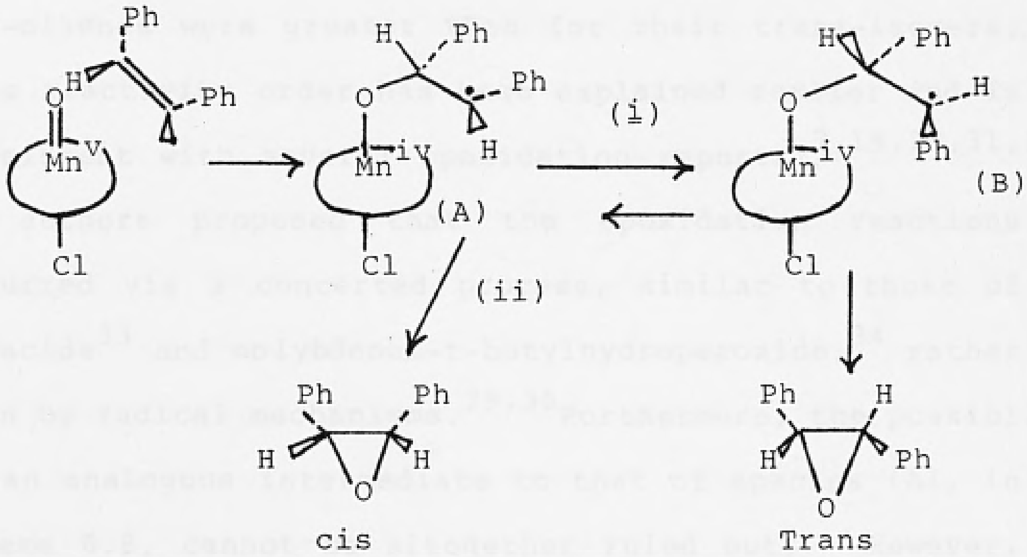
Scheme 6.7



The apparent side-on approach is best explained as the result of a stereoelectronic effect. The electronic structure expected for iron IV or iron V in an oxo-porphyrin complex will have two singly occupied dxz and dyz orbitals which overlap with the Px, and Py orbitals of the oxygen to produce the resulting Fe-O π -antibonding orbitals. The maximum overlap between these π-antibonding orbitals and the π-orbitals of the approaching alkene will be most likely to occur when the angle of the alkene with the plane of the porphyrin ring is small. Hence, through this interaction the oxygen atom may be transferred to the alkene, although the precise mechanism for this transfer is unclear.

The epoxidations of alkenes have also been studied[29] using manganese III mesotetraphenylporphyrin chloride $Mn^{III}(TPP)Cl$ in the presence of iodosobenzene. It was reported that the oxidation of trans-stilbene gave only trans-stilbene oxide while cis-stilbene gave a 1.6:1 mixture of trans- and cis-epoxides respectively. Similar results have been obtained with a $Mn^{III}(TPP)/(PhIOAc)_2$[30] system i.e. 1.7:1 and $Mn^{III}(TPP)Cl/OXO$[19] 1.3:1, [where oxo is 2-phenylsulphonyl-3-(p-nitrophenyl) oxaziridine], respectively. The proposed mechanism for these observations is illustrated below:

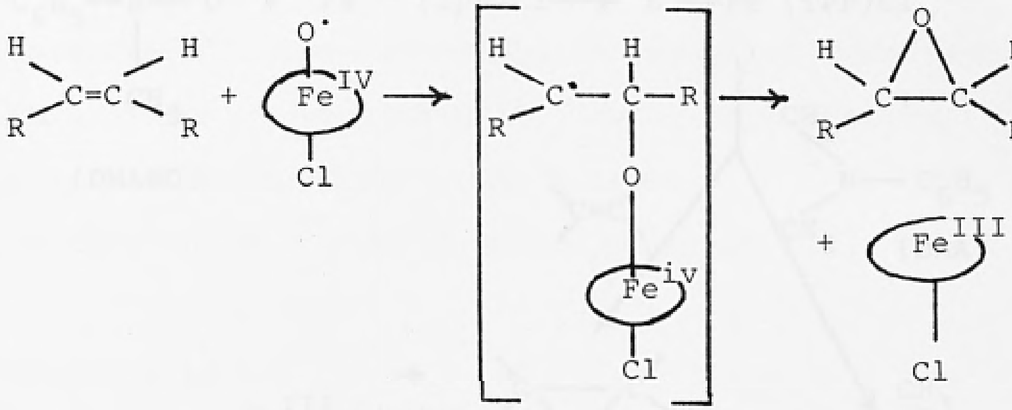
Scheme 6.8



Cis-stilbene reacts faster[19] than trans-stilbene since there are little or no non-bonded interactions between the meso-phenyl groups of the porphyrin and the cis-phenyl groups, to generate intermediate species (A). This intermediate for oxirane formation changes its stereochemistry by rotation about the central C-C bond to produce the more stable trans-conformer (B). This partially isomerises to regenerate species (A) before ring closure occurs to give the stable trans-stilbene oxide.

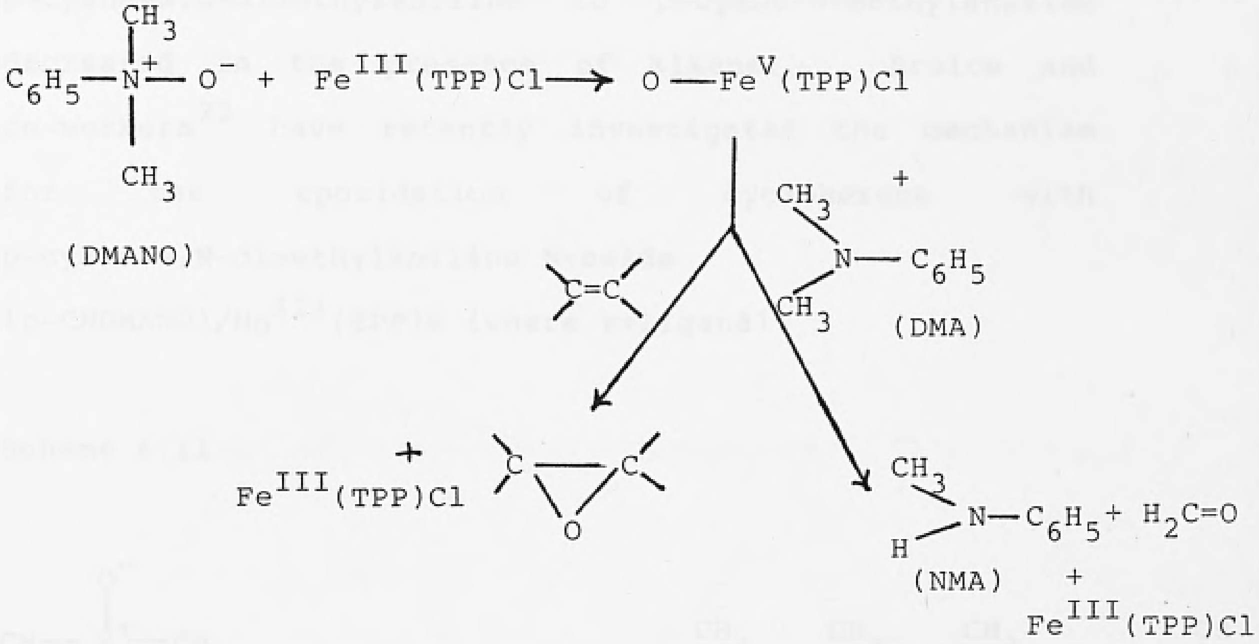
The expoxidation of alkenes has also been reported by Smith and co-workers[8] with the system iron III mesotetraphenylporphyrin chloride/iodosobenzene. It was shown that the oxidations exhibited syn stereospecificity and the reactivities of the cis-alkenes were greater than for their trans-isomers. This reactivity order has been explained earlier and is consistent with several epoxidation reports.[7,19,29,31,32] The authors proposed that the epoxidation reactions occurred via a concerted process, similar to those of peracids[33] and molybdenum-t-butylhydroperoxide,[34] rather than by radical mechanisms.[29,35] Furthermore, the possibility of an analogous intermediate to that of species (A), in scheme 6.8, cannot be altogether ruled out. However, it has been presumed that if such a species does exist it is highly probable that it is short-lived and thus unable to undergo C-C rotation prior to ring closure:

Scheme 6.9



The epoxidation reactions, with iodosoaromatics are not practical because of their polymeric nature,[36] insolubility in organic solvents and the oxidative destruction of the porphyrin ring which occurs in the absence of saturated hydrocarbons.[21] Recently[20] detailed kinetic investigations have been reported using N-oxides since they are soluble in most organic solvents and appear to leave the porphyrin intact in the absence of added alkenes. N,N-dimethylaniline N-oxide (DMANO)[37] has been shown to epoxidise 2,3-dimethyl-2-butene in the presence of iron III mesotetraphenylporphyrin chloride, although the yield of epoxide is low. This was probably due to a result of N,N-dimethylaniline (DMA) competing with the alkene for the active oxygen species, scheme 6.10, to generate N-methylaniline (NMA).

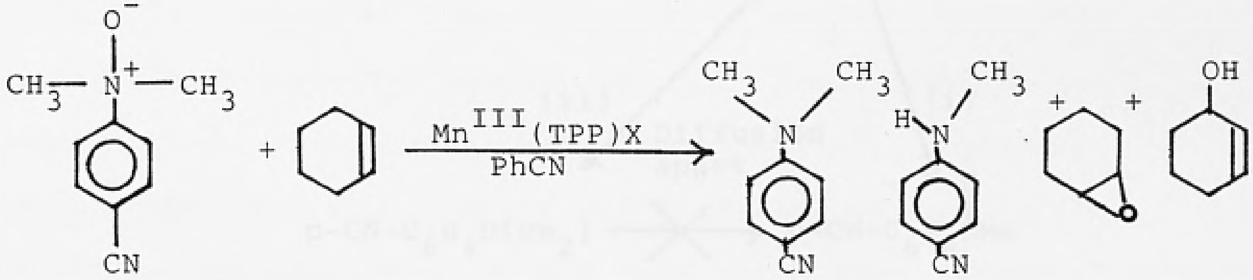
Scheme 6.10



The above reaction scheme 6.10 implies that the yield of epoxidation may be increased by reducing the reactivity of N,N-dimethylaniline N-oxide, while increasing the rate of monoxygen transfer from the N,N-dimethylaniline N-oxide, towards the Fe^V-O moiety. It has been suggested[20] that this could be achieved by substitution of an electron withdrawing group (p-CN) on the phenyl ring of N,N-dimethylaniline N-oxide. Thus the results showed that in the presence of p-cyano-N,N-dimethylaniline N-oxide/iron III mesotetraphenylporphyrin chloride and 2,3-dimethyl-2-butene the epoxide was produced in 90%

yield. In addition it was also observed, as expected, that the yield dealkylation of p-cyano-N,N-dimethylaniline to p-cyano-N-methylaniline decreased in the presence of alkene. Bruice and co-workers[22] have recently investigated the mechanism for the epoxidation of cyclohexene with p-cyano-N,N-dimethylaniline N-oxide (p-CNDMANO)/Mn^{III}(TPP)X (where x=ligand):

Scheme 6.11

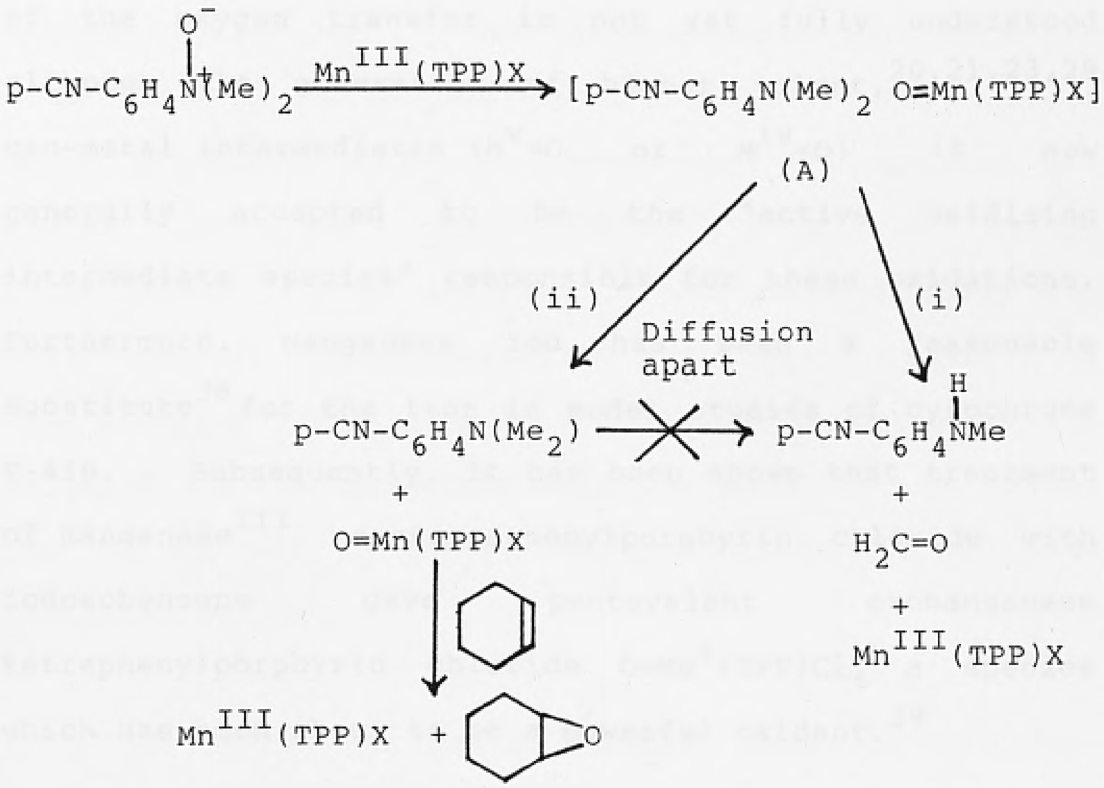


(p-CNDMANO) (p-CNDMA) (p-CNNMA)

X=F$^-$,Cl$^-$,Br$^-$,I$^-$,OCN$^-$

It was observed that three major products were produced; p-cyano-N,N-dimethylaniline (p-CNDMA), p-cyano-N-methylaniline (p-CNNMA) and cyclohexene epoxide with the addition of cyclohexene-3-ol as the minor product. Furthermore, no p-cyanoaniline was produced. Reaction kinetics suggested that the demethylation of p-cyano-N,N-dimethylaniline N-oxide occurs within the complex (A), in scheme 6.12 reaction (i), and not in a bimolecular reaction of the separate entities p-CNDMA and O=Mn(TPP)X formed after oxygen transfer and diffusion apart, rection (ii).

Scheme 6.12



6.2 Results and Discussion

The above literature survey indicates that compounds which are usually difficult to oxidise e.g. p-substituted diphenylsulphides and in particular terminal alkenes, have been easily converted to their oxidised forms in the presence of a variety of monoxygen donors and a metallo-porphyrin. The detailed mechanism of the oxygen transfer is not yet fully understood although the generation of higher valent,[20,21,23,29,39] oxo-metal intermediates ($M^{V}=O$ or $M^{iv}=O$) is now generally accepted to be the "active oxidising intermediate species" responsible for these oxidations. Furthermore, manganese ion has been a reasonable substitute[38] for the iron in model studies of cytochrome P-450. Subsequently, it has been shown that treatment of manganese^{III} mesotetraphenylporphyrin chloride with iodosobenzene gave pentavalent oxomanganese tetraphenylporphyrin chloride $O=Mn^{V}(TPP)Cl$, a species which has been shown to be a powerful oxidant.[29]

In the present study manganese III mesotetraphenylporphyrin chloride [$Mn^{III}(TPP)Cl$] and manganese III mesotetra(2,6-dichlorophenylporphyrin) chloride [$Mn^{III}(TDClPP)Cl$] were used in the presence of tetrabutylammonium periodate ($^{n}Bu_4NIO_4$) to afford the oxygenation reactions of the least reactive phosphine selenides. These results are presented in table 6.1.

The data shown in table 6.1 indicate that diethyl phenylphosphonoselenoic acid (1) is more reactive towards oxidative deselenation than its analogous triethyl phosphoroselenoic acid (2) and trimethyl phosphoroselenoic acid (3), which both showed similar reactivity. Tetrabutylammonium periodate has been found to be an efficient oxidising agent towards these phosphine selenides producing 75, 40 and 43% yields of the corresponding phosphine oxides respectively. In addition it was observed that the efficiency of the deselenation reactions increased, on the addition of manganese III mesotetraphenylporphyrin chloride to the periodate reaction mixtures, to afford 92, 59 and 64% yields of the corresponding respective phosphine oxides.

Similarly Ando and co-workers[6] have reported that sulphides which are normally inactive towards oxidising agents have been easily converted to their sulphoxides by the addition of a catalytic amount of iron III mesotetraphenylporphyrin chloride. In particular diphenylsulphide, as mentioned earlier, showed hardly any reactivity towards the tetrabutylammonium periodate at room temperature.

Table 6.1 Oxidative[a] deselenation at phosphorus, induced by nBu_4NIO_4/Mn(TPP)Cl or Mn(TDClPP)Cl catalyst.

Reagent[b]	Compound	Yield of oxidation (%)
$^nBu_4NIO_4$	$PhPSe(OEt)_2$ (1)	75
$^nBu_4NIO_4$ + Mn(TPP)Cl	"	92
$^nBu_4NIO_4$ + Mn(TPP)Cl + imidazole	"	100
$^nBu_4NIO_4$	$(EtO)_3PSe$ (29)	40
$^nBu_4NIO_4$ + Mn(TPP)Cl	"	59
$^nBu_4NIO_4$ + Mn(TPP)Cl + imidazole	"	100
$^nBu_4NIO_4$ + Mn(TDClPP)Cl	"	43
$^nBu_4NIO_4$ + Mn(TDClPP)Cl + imidazole	"	16

Table 6.1 contd.

$^{n}Bu_4NIO_4$	$(MeO)_3PSe$ (3)	37
$^{n}Bu_4NIO_4$ + Mn(TPP)Cl	"	64
$^{n}Bu_4NIO_4$ + Mn(TPP)Cl + imidazole	"	100
$^{n}Bu_4NIO_4$ + Mn(TDClPP)Cl	"	35
$^{n}Bu_4NIO_4$ + Mn(TDClPP)Cl + imidazole	"	12

a, Phosphine selenides 1.5×10^{-2}M, stirred for 24 hours at 25°C in $CHCl_3$.

b, $^{n}Bu_4NIO_4$(2eq), Mn(TPP)Cl(0.02eq), Mn(TDClPP)Cl(0.02eq) and imidazole (1eq).

However, the addition of iron III mesotetraphenylporphyrin chloride to this periodate reaction mixture resulted in the formation of the corresponding sulphoxide in 95% yield.

Several authors[7-11] have currently exploited this important catalytic property of the porphyrins, to induce reactivity into the generally inert compounds such as alkanes[29] and terminal alkenes.[13,18,19,38-41] Cyclohexane[29] has been oxidised with manganese III mesotetraphenylporphyrin chloride/iodosobenzene, in dichloromethane, to give 2.5:1 mixture of cyclohexanol and cyclohexyl chloride in a combined yield of 70%, based on iodosobenzene. Similarly cyclohexene[22] has been converted into cyclohexene oxide plus trace quantities of cyclohex-2-enol and 2-enone with manganese III mesotetraphenylporphyrin chloride catalyst using p-cyano-N,N-dimethylaniline N-oxide as an oxygen source.

The addition of imidazole to the phosphine selenides (1-3)/periodate/manganese III mesotetraphenylporphyrin chloride mixture resulted in the complete oxidation of the three phosphine selenides. Recently[13] in the oxidation reactions of various alkenes similar behaviour of imidazole was encountered. For example, 2-methylhept-2-ene with cumylhydroperoxide

($PhCMe_2OOH$) catalysed by manganese III mesotetraphenylporphyrin chloride/imidazole gave 2-methylhept-2-ene oxide in 41% yield. However in the absence of imidazole, but presence of manganese III mesotetraphenylporphyrin chloride, <1% of the oxidised product was produced. Also the oxidation of cyclohexene with cumylhydroperoxide/manganese III mesotetraphenylporphyrin chloride/imidazole produced cyclohexene oxide as a major product, in 27% yield. In the absence of imidazole <1% of oxide was produced. These results suggest that the imidazole most probably ligates or binds to the central manganese ion, which has been shown to be present in the higher oxidation state of $\underline{\bar{v}}$ thus improving the oxygen transfer from the oxo-Mn moiety to the substrates.

The addition of hindered mesotetra(2,6-dichlorophenyl)porphyrin [Mn^{III}(TDClPP)Cl] to the phosphine selenides (2,3)/periodate reaction mixture, in contrast to mesotetraphenylporphyrin [Mn^{III}(TPP)Cl], showed no further increase in the oxidative product yields of the selenides. This is presumably because the periodate molecule's approach to the central manganese ion may be hindered and thus the "active OXO-Mn intermediate" species, which is responsible for oxidative deselenations, may not be formed. The hindrance can be visualised as occurring through non-bonding interactions which apparently develop between one of the bulky chlorine atoms, protruding out of the horizontal surface plane and away from the axial ligated chlorine atom, and the periodate molecule as it approaches closer to the central manganese ion. Hence as a result of these steric effects the periodate and the central manganese ion are not in close proximity for the oxygen transfer mechanism to occur. Thus no O=Mn^{V}(TPP)Cl is formed. The "free" periodate, as anticipated, would then react with the phosphine selenides as if the porphyrin was absent from the reaction mixture. Indeed, this seems to be the case in the deselenation reactions. Alternatively, these results may be rationalised by postulating that the periodate, with some difficulty, has been able to generate the active intermediate Mn^{V}=O. However, the approach of the phosphine selenide molecule to this activated species is somewhat inhibited by similar steric factors to those discussed above. Nevertheless, partial oxygen transfer may occur to produce the phosphine oxides in low yields.

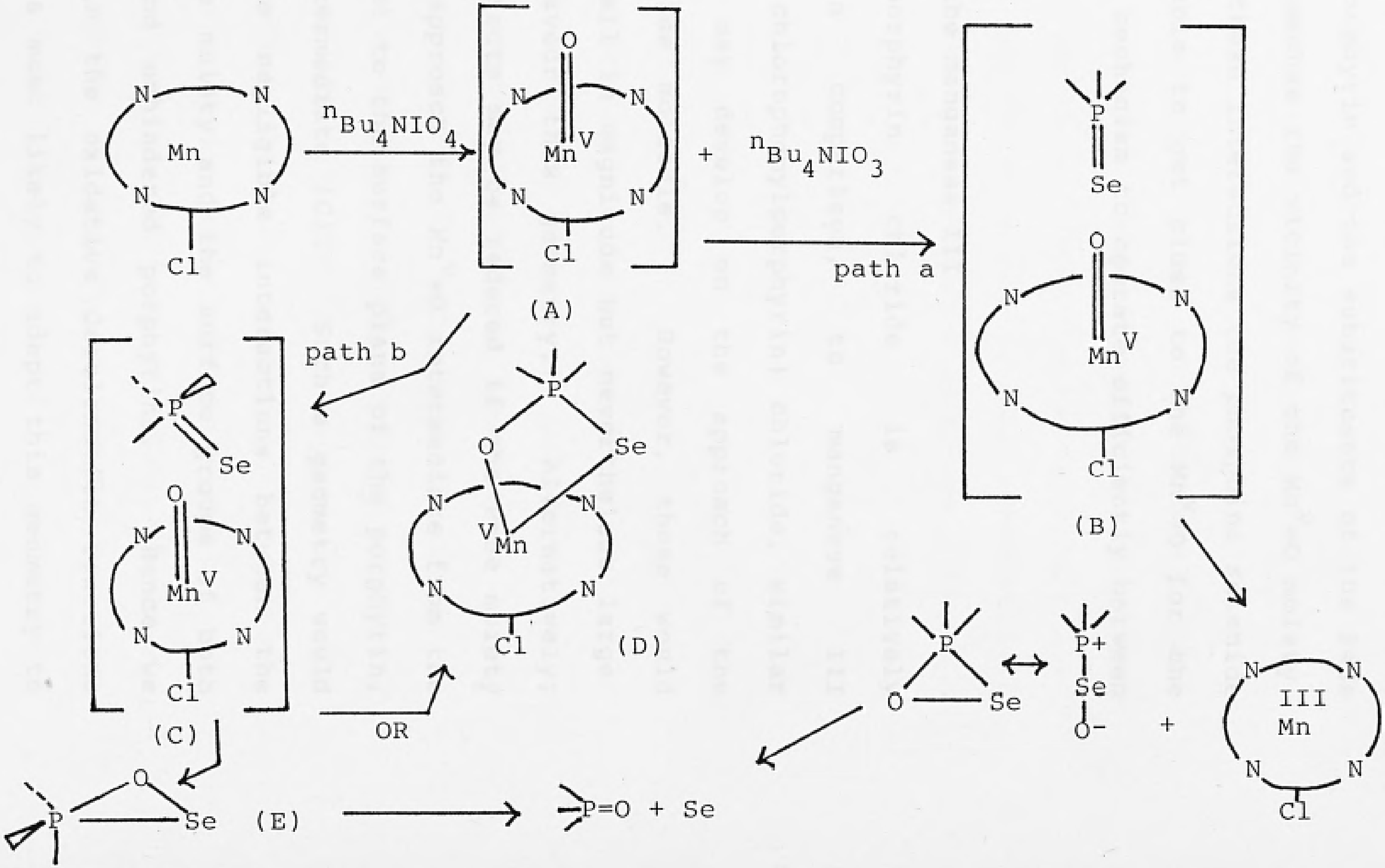
The addition of imidazole to phosphine selenides (2,3) / periodate / manganese III mesotetra

(2,6-dichlorophenylporphyrin) chloride mixture, unexpectedly, resulted in a dramatic reduction in the efficiency of the oxidative deselenation reactions. Oxidation products of 16 and 12% yields were produced from phosphine selenides (2) and (3) respectively. These observations suggest that the imidazole has the effect of reducing the reactivity of the periodate in these reactions, most likely by acting as a substrate towards the periodate and in so doing being itself oxidised.

The precise mechanism of oxygen transfer from the manganese ion to the P=Se double bond, in these oxidative deselenation reactions, is not clear although two reasonable geometries for the approach of a P=Se bond to the Mn-OXO group are depicted in scheme 6.13.

The inconclusion of intermediate (B) implies that the phosphine selenide molecule may approach the $Mn^{V}=O$ moiety, of the activated intermediate species (A), at an angle of 90^{o} to the horizontal plane of the porphyrin. However, in the case of the hindered mesotetra(2,6-dichlorophenyl)porphyrin, where the two chlorines are attached at ortho-positions to one of the four phenyl groups present at the surface plane, it is highly probable that such a geometry will develop large

Scheme 6.13



non-bonding interactions between the bulky surface groups of the porphyrin and the substituents of the P=Se bond as it approaches the vicinity of the Mn^V=O moiety. As a result of these interactions the phosphine selenide molecule is unable to get close to the Mn^V=O for the oxygen transfer mechanism to operate efficiently between these entities.

Although the manganese III mesotetraphenylporphyrin chloride is relatively unhindered, in comparison, to manganese III mesotetra(2,6-dichlorophenylporphyrin) chloride, similar steric effects may develop on the approach of the phosphine selenide molecule. However, these would obviously be small in magnitude but nevertheless large enough to disfavour this geometry. Alternatively, these steric effects may be reduced if the P=Se moiety is presumed to approach the Mn^V=O intermediate from the side and parallel to the surface plane of the porphyrin, as shown by intermediate (C). Such a geometry would probably produce negligible interactions between the approaching P=Se moiety and the surface groups of both the hindered and unhindered porphyrins. Hence we conclude that in the oxidative deselenation reactions the P=Se bond is most likely to adopt this geometry to eventually produce the phosphine oxides either via intermediate (D), regenerating the original porphyrin or via the strained tricyclic intermediate (E) which readily rearranges to produce the desired products.

The results obtained in the oxidative deselenation reactions do not allow us to distinguish between these two mechanistic routes. However, it is likely that these reactions may be occurring by the reaction path (b) rather than path (a) as depicted in scheme 6.13.

6.3 Summary

Chemical oxidation of phosphine selenides (1-3) has been achieved by the use of a potent monoxygen transfer agent, tetrabutylammonium periodate. In addition tetrabutylammonium periodate employed in conjunction with manganese III mesotetraphenylporphyrin chloride has been found to lead to an increase in yield of the corresponding phosphine oxides. Furthermore, the efficiency of these deselenation reactions has been further increased by the addition of imidazole to the reaction mixtures. However, tetrabutylammonium periodate in the presence of a hindered mesotetra(2,6-dichlorophenyl) porphyrin

[Mn^{III}(TDClPP)Cl] showed no increase in the percentage product yields. Also the addition of imidazole to these reaction mixtures had the effect of dramatically reducing the product yields.

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CHAPTER 7

CHEMICAL OXIDATIVE DESELENATION OF SELENOPHOSPHORUS COMPOUNDS

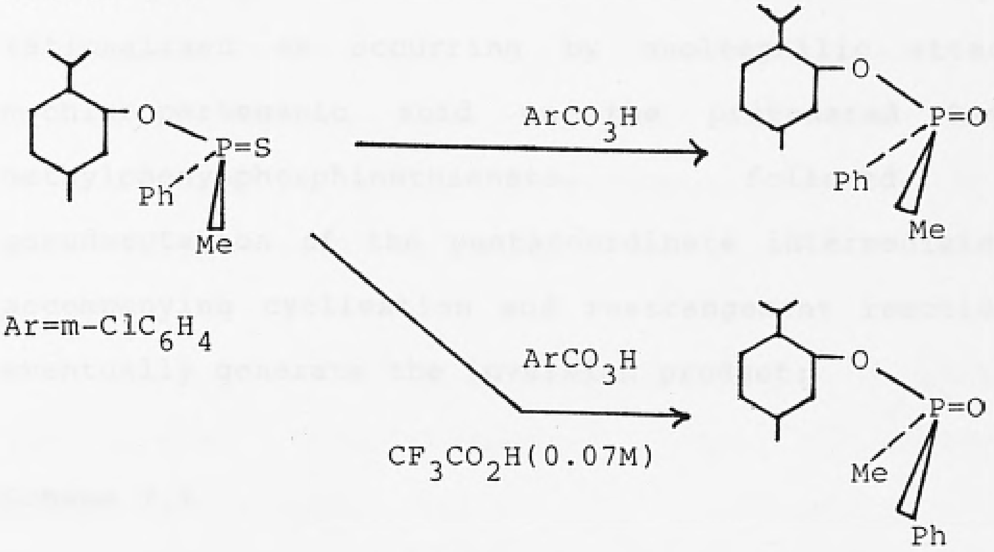
7.1 INTRODUCTION

There are a number of readily available conventional oxidising reagents which have the potential to bring about oxidative deselenation of selenophosphorus compounds. Details of their reactions with other substrates and the mechanisms involved are mentioned below.

7.1a m-Chloroperbenzoic acid (m-$ClC_6H_4CO_3H$).

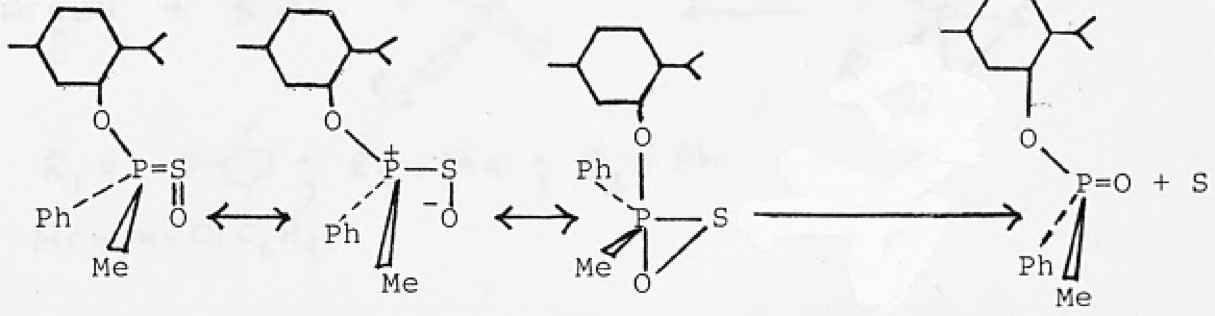
This has been successfully employed to effect oxidations of various substrates.[1-7] In particular, it has been shown to be an extremely efficient oxidising agent in the desulphurisation of the P=S moiety.[8] Furthermore, the reaction was observed to occur rapidly with almost complete retention of configuration. However, the addition of trifluoroacetic acid (CF_3CO_2H), a stronger acid than m-chloroperbenzoic acid, results in inversion of configuration at the phosphorus, scheme 7.1

Scheme 7.1



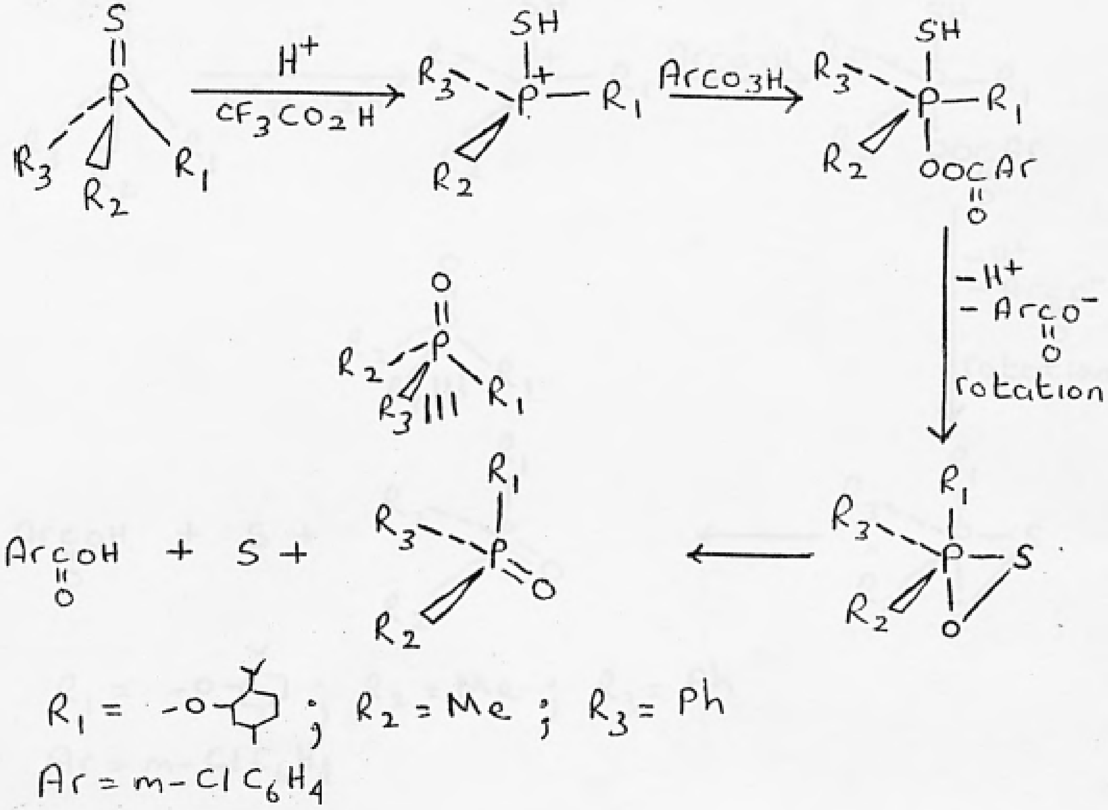
The retention of stereochemistry may be visualised by analogy with the oxidation of thiocarbonyl groups to sulphines.[9] The analogous S-oxide zwitterion, a plausible intermediate species, closes to generate a three-membered ring which subsequently undergoes rearrangement to lose elemental sulphur and thus retain the configuration at the phosphorus;

Scheme 7.2



Alternatively, the inversion reaction may be rationalised as occurring by nucleophilic attack of m-chloroperbenzoic acid on the protonated O-menthyl methylphenylphosphinothionate, followed by pseudorotation of the pentacoordinate intermediate with accompanying cyclisation and rearrangement reactions to eventually generate the inversion product;

Scheme 7.3



Oxidation of the analogous O-methyl t-butylphenylphosphinothionate,[10] to its corresponding phosphoryl oxide, has also been investigated using m-chloroperbenzoic acid. The reaction showed retention of configuration, thus implying that the oxidative desulphurisation occurs in a manner similar to that reported previously in scheme 7.2.

Recently,[11,12] m-chloroperbenzoic acid oxidations have also been reported for a number of phosphorothiolates;

Scheme 7.4

$$R_1R_2P(O)SR_3 \xrightarrow{m\text{-}ClC_6H_4CO_3H} R_1R_2P(O)OS(O_2)R_3 + R_1R_2P(O)OP(O)R_1R_2$$

$$+ R_1R_2P(O)OC(O)C_6H_4Cl\text{-}m + R_1R_2P(O)OH$$

$$+ HOS(O_2)R_3$$

$R_1=R_2=OCH_3$, $R_3=CH_3$

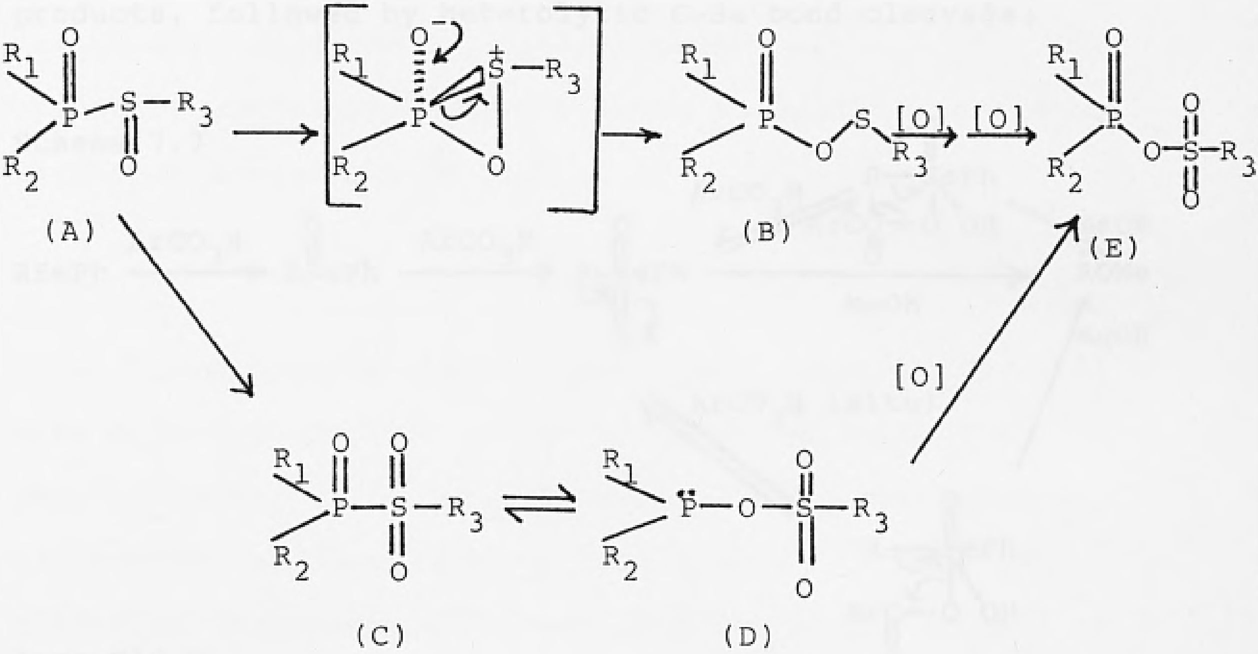
$R_1=R_2=OEt$, $R_3=CH(CH_3)_2$

$R_1=R_2=OEt$, $R_3=CH_2C(Cl)=CH_2$

$R_1=OCH_3$, $R_2=NH_2$, $R_3=CH_3$

The formation of phosphinyloxysulphonates, the major product, has been reported[11,12] to occur by rearrangement of the initially formed phosphinyloxysulphonate (A) followed by subsequent oxidations. Alternatively,[13,14] the compound (A) may oxidise to generate phosphinylsulphinate (C) and then insertion of oxygen into the P-S bond or oxidation of the PIII anhydride (D), which is believed to exist in equilibrium with the sulphinate, produces the desired product (E);

Scheme 7.5



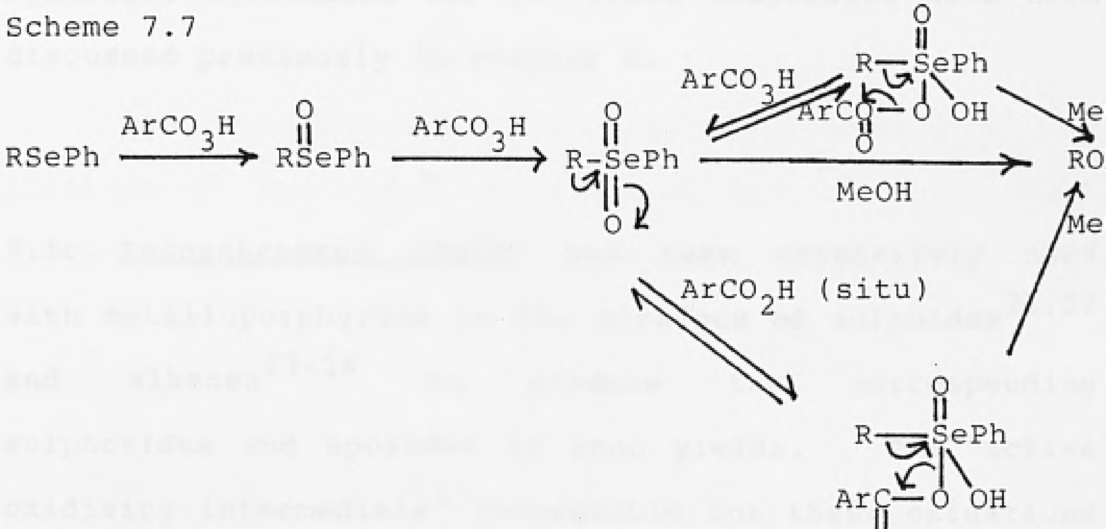
m-Chloroperbenzoic acid has been successfully employed as a specific oxidising agent in the oxidation reactions of various alkyl phenyl selenides,[15] to yield their corresponding alkyl ethers, aldehydes or ketones;

Scheme 7.6

$$\mathrm{R{-}Se{-}Ph} \xrightarrow[\mathrm{m\text{-}ClC_6H_4CO_3H}]{\mathrm{MeOH}} \mathrm{ROMe}$$

Product formation has been rationalised as occurring via nucleophilic attack of methanol on the active alkyl phenyl selenone or its m-chloroperbenzoic acid addition products, followed by heterolytic C-Se bond cleavage;

Scheme 7.7



$Ar=m\text{-}ClC_6H_4$

Evidence for the formation of the selenone has been provided by Sharpless and co-workers[16] in the oxidation of dodecylphenyl selenide with hydrogen peroxide/trifluroacetic acid, and by Kuwajima and co-workers[17] in the oxidation of a vinylic selenide with m-chloroperbenzoic acid.

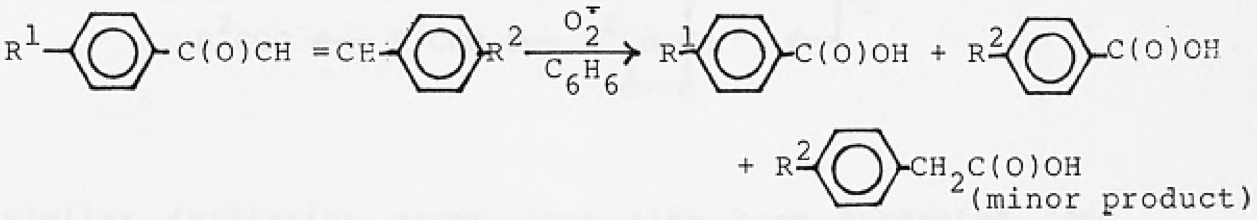
7.1b <u>Tetrabutylammonium periodate ($^nBu_4NIO_4$)</u> has been reported to be a mild selective monoxygen donor, similar to m-chloroperbenzoic acid, towards a variety of sulphides,[18] α-hydroxycarboxylic acid,[18] arylacetic acids[19] and α-bromoketones.[18] In addition tetrabutylammonium periodate has recently been used in conjunction with metalloporphyrins, under neutral and homogenous conditions, to effect the oxidation of relatively unreactive dialkylsulphides.[20] The oxidative mechanisms for the above substrates have been discussed previously in chapter 6.

7.1c. <u>Iodosobenzene (PhIO)</u> has been extensively used with metalloporphyrins in the presence of sulphides[21,22] and alkenes[23-26] to produce the corresponding sulphoxides and epoxides in good yields. The "active oxidising intermediate" responsible for these oxidations was proposed[23-26] to be a porphyrin bound metal^V-OXO or metal^{IV}-OXO moiety, which readily transfers its oxygen to the sulphides or alkenes as they approach its vicinity. The steric factors involved in these reactions, particularly with the alkenes have been discussed in detail in chapter 6.

7.1d. Potassium superoxide (KO_2): since the discovery of the enzyme superoxide dismutase,[27] considerable attention has been paid to the chemistry of potassium superoxide. A major effort has been directed to "*in situ*" generation and reactions of this species in aqueous media.[28] The observation by Valentine and Curtis[29] that potassium superoxide can be dissolved appreciably in aprotic solvents by complexation with crown ethers, has further promoted the use of this reagent.[30-33]

The reaction of potassium superoxide in the presence of 18-crown-6 ether, with chalcones[34] has been shown to produce carboxylic acids efficiently;

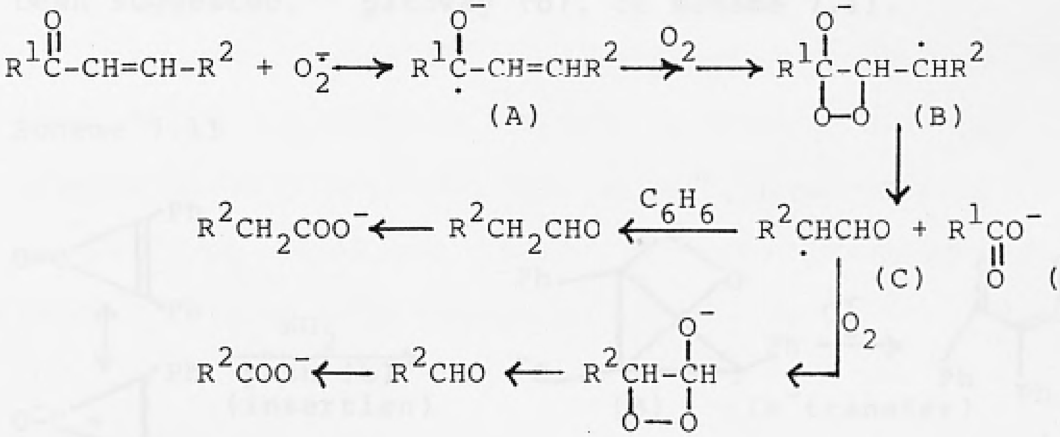
Scheme 7.8



$R^1=CH_3$, $R^2=H$; $R^1=OCH_3$, $R^2=H$; $R^1=Cl$, $R^2=H$
$R^1=Br$, $R^2=CH_3$; $R^1=H$, $R^2=Cl$

The authors suggested that oxygen was not incorporated into the products by direct nucleophilic attack of a superoxide anion ($O_2^{\cdot -}$), but probably the reaction proceeded by initial electron transfer from superoxide anion to the enone system of the substrate. The resulting radical anion (A) reacts in turn with the surrounding molecular oxygen to generate intermediate (B) which undergoes bond cleavage to generate two species (C,D) which eventually produce the appropriate carboxylic acids via the steps illustrated in scheme 7.9.

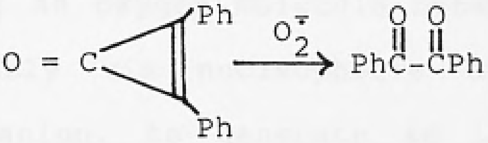
Scheme 7.9



Similar initiation steps have also been suggested for the oxidation of 3,5-di-t-butylcatechol with potassium superoxide.[3,5]

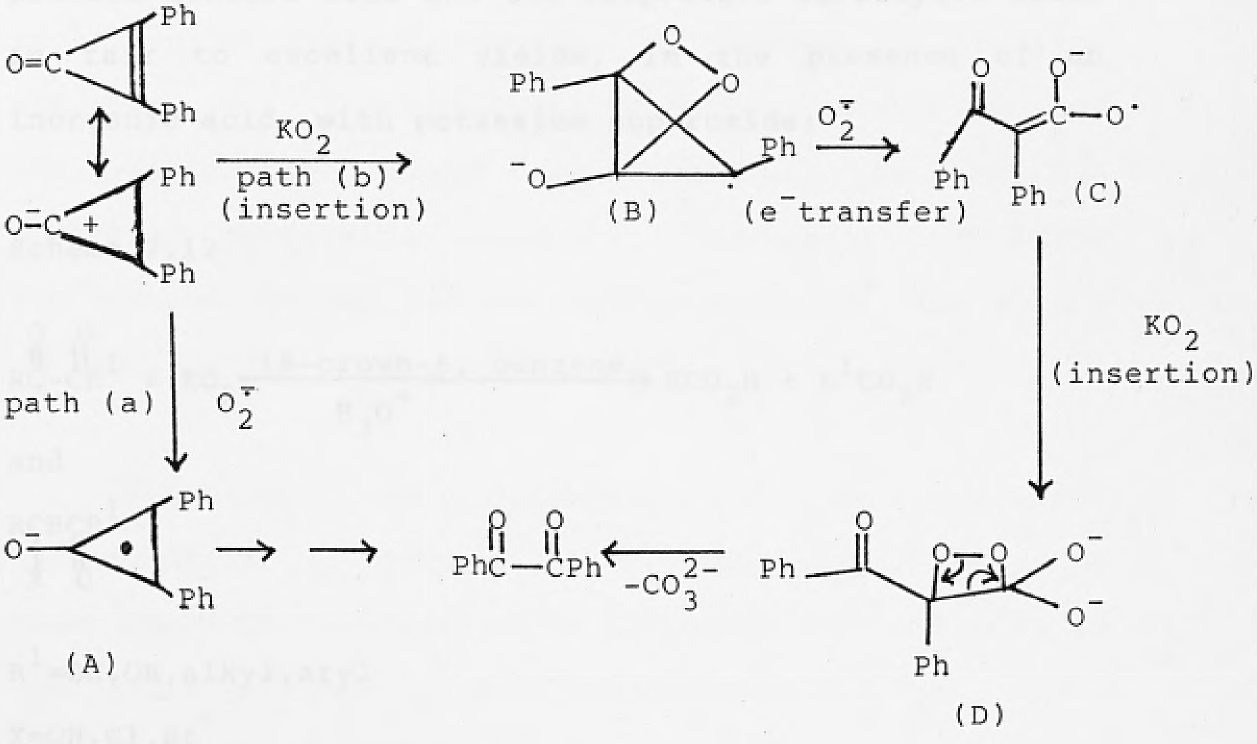
Oxidation of diphenylcyclopropenone[36] with potassium superoxide, in the presence of 18-crown-6 ether, has recently been shown to produce benzil;

Scheme 7.10



The product formation has been proposed to occur via initial electron transfer from potassium superoxide anion to the substrate thus generating the radical anion (A), pathway (a), which is known to form benzil in the presence of oxygen.[37] Alternatively, a mechanism which does not involve electron transfer as the first step has been suggested,[36] pathway (b), of scheme 7.11.

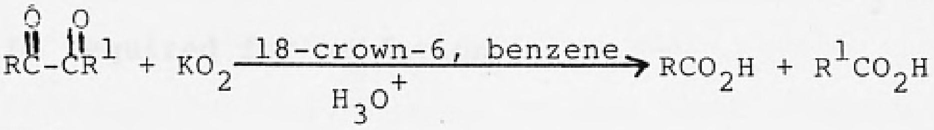
Scheme 7.11



The preliminary step involved in this mechanism is the insertion of an oxygen molecule between the C(1) - C(2) bond, probably via nucleophilic attack of potassium superoxide anion, to generate an intermediate radical species (B). Electron transfer from the superoxide anion species occurs readily to produce intermediate radical (C) which behaves in an analogous manner to that of diphenylcyclopropenone towards potassium superoxide. Thus incorporation of oxygen at the double bond occurs to give intermediate (D) which subsequently decarboxylates to yield the desired product.

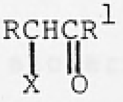
However, benzil[41] and analogous compounds have been shown to undergo facile oxidative cleavage to produce benzoic acid and the respective carboxylic acids in fair to excellent yields, in the presence of an inorganic acid, with potassium superoxide;

Scheme 7.12



$$R\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}R^1 + KO_2 \xrightarrow[H_3O^+]{\text{18-crown-6, benzene}} RCO_2H + R^1CO_2H$$

and



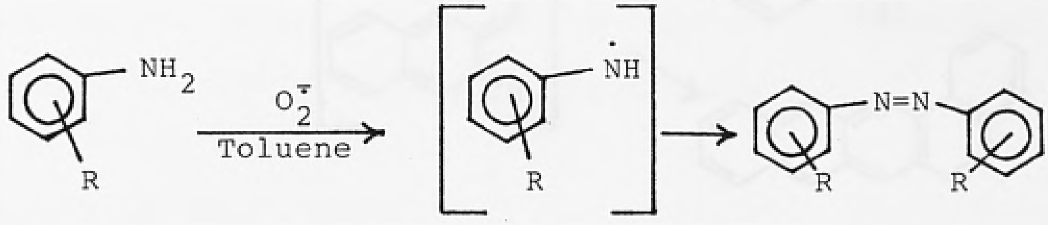
$$R\underset{X}{\underset{|}{C}}H\underset{O}{\underset{\|}{C}}R^1$$

R^1=OH,OR,alkyl,aryl

X=OH,Cl,Br

The reactions of ortho- and para-phenylenediamines[38] with potassium superoxide have been reported to yield azo derivates;

Scheme 7.13

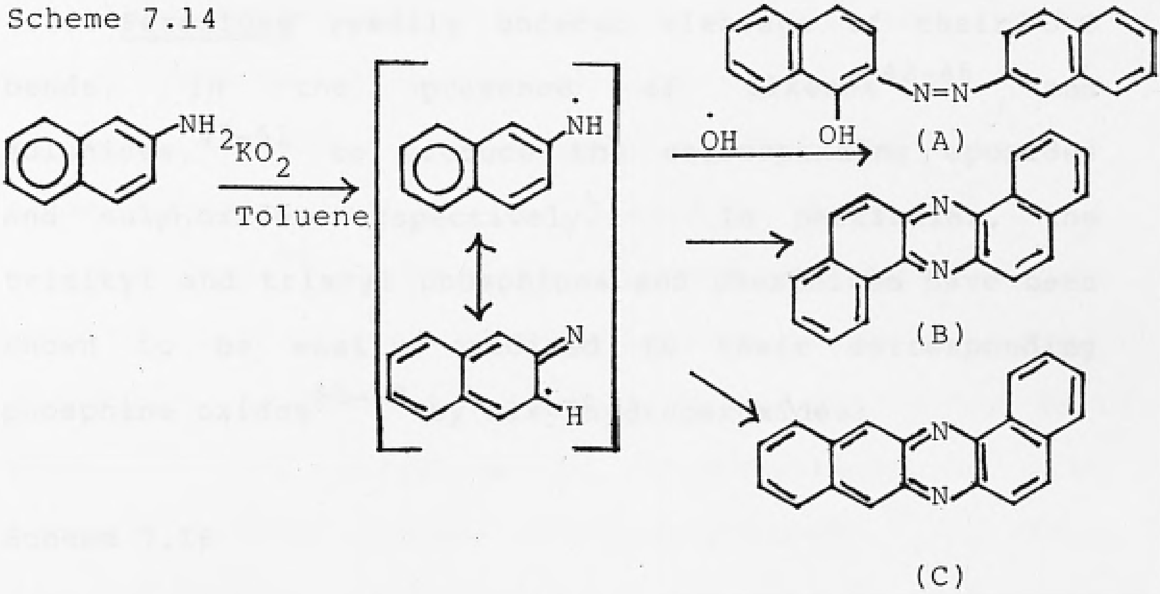


R=NH_2 or OH

These reactions have been interpreted in terms of initial hydrogen abstraction by potassium superoxide anion from the substrate to generate a radical intermediate which subsequently reacts further, by a mechanism at present unknown, to produce the observed products. In addition meta-phenylenediamine and meta-aminophenol showed no reactivity towards the potassium superoxide agent. Presumably significant conjugation between the two substituents (NH_2 and R) may be required for oxidation.

Recently, the formation of an analogous azoderivative (1-hydroxy-2,2'-azonaphthalene (A)) has been observed in addition to compounds (B) and (C), in the oxidation reaction of β-naphthylamine;[39]

Scheme 7.14



Product formation, as outlined earlier, may be visualised as occurring by initial abstraction of a hydrogen atom to generate an intermediate with two resonance structures which undergo radical C-N or N-N coupling to yield the observed products. However, the formation of the azoderivative (A) strongly indicates the participation of the hydroxyl radical [$\dot{O}H$] in the superoxide reaction. Although it is not certain how hydroxyl radical arises in the reaction, a concerted two hydrogen abstraction from the amine could produce the hydroxyl radical moiety, as has been claimed by Nanni and Sawyer;[40]

Scheme 7.15

$$AH_2 \xrightarrow{O_2^{\bar{}}} \bar{O}H + \dot{O}H + A$$

7.1e. Peroxides readily undergo cleavage of their O-O bonds, in the presence of alkenes[42-46] and sulphides,[47-51] to produce the corresponding epoxides and sulphoxides respectively. In particular, the trialkyl and triaryl phosphines and phosphites have been shown to be easily oxidised to their corresponding phosphine oxides[52-59] by alkylhydroperoxides;

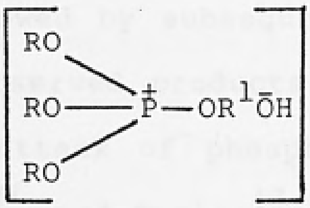
Scheme 7.16

$$R_3P + HOOR^1 \longrightarrow R_3P{=}O + R^1OH$$

R=Ar,OAr,R,OR

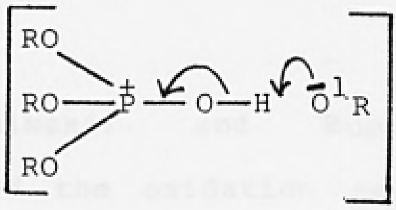
These oxidation reactions were initially presumed to occur by nucleophilic attack of the phosphorus on the oxygen attached to the R^1-group, thereby generating an ion pair intermediate,[52] fig.7.1, which subsequently collapses to give the observed products.

Fig.7.1



For this mechanism to be valid the ion pair should easily undergo exchange with the hydroxyl ion in an aqueous solvent. However, the oxidation of triphenylphosphine by cumenehydroperoxide[53] in methanol/water[18] produced no oxygen-18 enrichment in the reaction products (triphenylphosphine oxide and cumyl alcohol). Complete retention of configuration has been shown in the oxidation of triphenylphosphine with optically active 1-phenylethylhydroperoxide.[60] These results suggest that a different ion pair to that shown in fig.7.1 must be involved, and the structure shown in fig.72 was proposed.

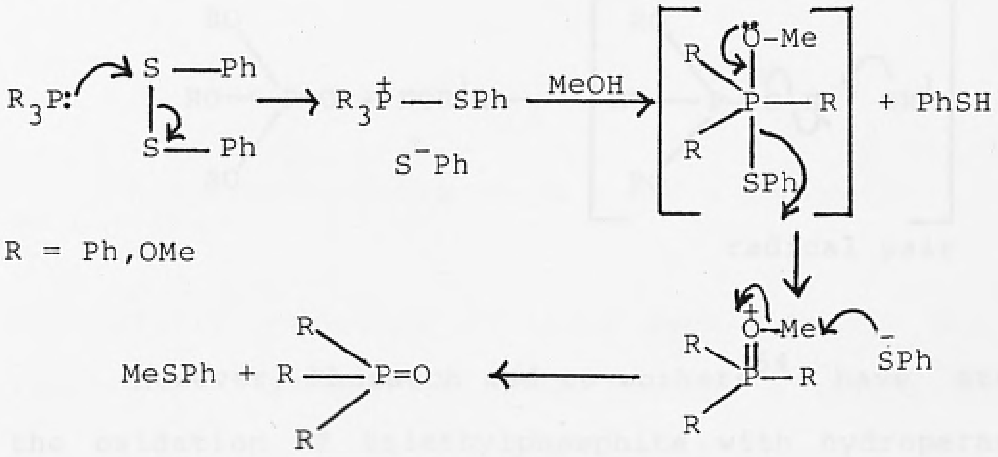
Fig.7.2



Ion pair formation can be visualised as occurring by nucleophilic attack at the hydroxyl oxygen atom of the peroxides, followed by subsequent splitting of a proton to yield the observed products. It is not altogether clear why the attack of phosphorus is at this oxygen, although Bunton[61] and Davies[47] ascribe this to its lower electron density, while Edwards[61] attributes it to less steric hindrance.

Alternatively the formation of phosphine oxides has also been interpreted as occurring via involvement of a penta co-ordinate phosphorus[62a] intermediate, in the oxidation reactions of a trisubstituted phosphine or phosphite with diphenyl disulphide in methanol;

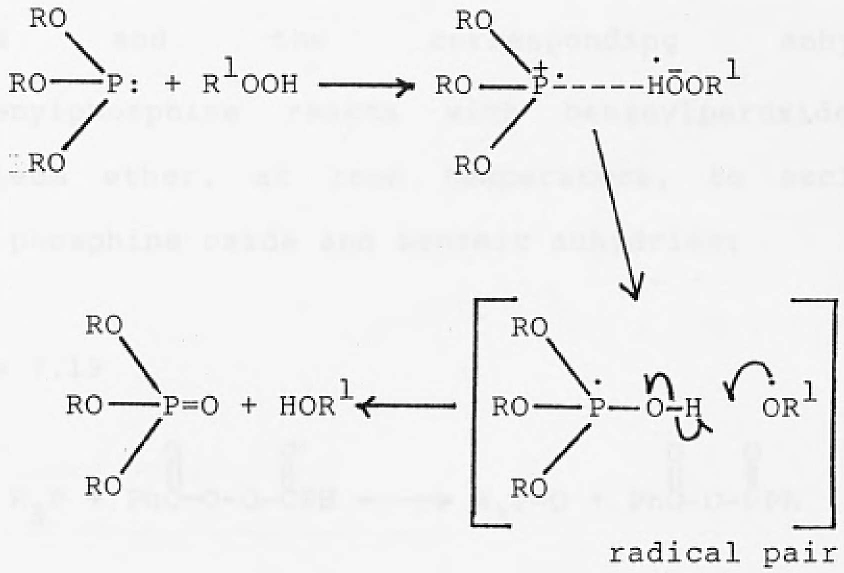
Scheme 7.17



R = Ph,OMe

Pobedimskii and Buchachenko[62b] have also investigated the oxidation reactions of trisubstituted phosphines and phosphites, by hydroperoxides. They suggested that a radical mechanism was operating in these reactions, probably with the transfer of an electron from the phosphite to hydroperoxide to form an ion-radical complex which may be converted readily into a radical pair, in neutral media. This is followed largely by disproportionation as illustrated in scheme 7.18.

Scheme 7.18



However, Kharasch and co-workers[54] have studied the oxidation of triethylphosphite with hydroperoxides and reported that the oxidation of the phosphite was unaffected by the addition of trinitrobenzene,[52] inhibitor of homolytic reactions, to the reaction mixtures. This provided strong evidence in favour of an ionic mechanism. Also, an extensive kinetic study of the reaction of triphenylphosphine with butylhydroperoxides[63] has now shown this reaction to be almost certainly non-radical. Moreover, it has been shown by Denny and Jones[64] that certain phosphites reduce non-tertiary dialkylperoxides to ethers cleanly, in what appears to be a non-radical reaction.

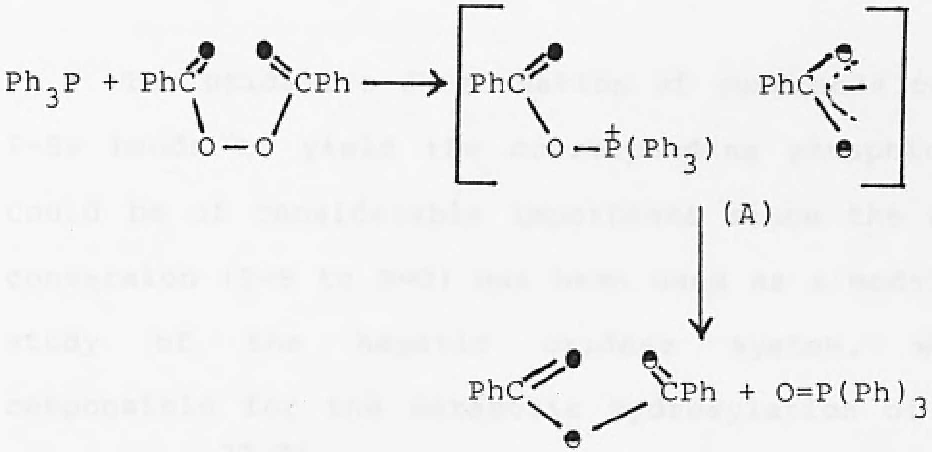
Acylperoxides react with phosphines, in an analogous manner to hydroperoxides, to produce phosphine oxides and the corresponding anhydrides. Triphenylphosphine reacts with benzoylperoxide,[65] in petroleum ether, at room temperature, to exclusively yield phosphine oxide and benzoic anhydride;

Scheme 7.19

$$R_3P + Ph\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}PH \longrightarrow R_3P{=}O + Ph\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}Ph$$

The authors suggested an ionic mechanism for the above reaction. Phosphines which possess a strong affinity for oxygen and have a large dipole moment, react with benzoylperoxide bimolecularly to form a primary intermediate (A). The O-O bond is then polarised by the unshared pair of electrons in the phosphine. A tetrasubstituted phosphonium salt, existing in all probability as an ion pair, is formed. The benzoate ion presumably attacks the carbonyl carbon of the salt to yield the observed products. The evidence for this mechanism has been provided by the reaction of triphenylphosphine with benzoylperoxide, labelled with ^{18}O in the carbonyl groups;[66,67]

Scheme 7.20



● ^{18}labelled oxygen

◐ half of the original label

All of the ^{18}O was found in the anhydride, and none in the triphenylphosphine oxide. Furthermore, close examination of the oxygens in the anhydride showed that only one oxygen atom was always labelled; the others had a 50% chance of being substituted by ^{18}O oxygen from the starting material. These results confirm the formation of the ion pair intermediates, proposed by Walling and Rabinowitz.[52]

7.2 Results and Discussion

The oxidative deselenation of compounds containing P=Se bonds to yield the corresponding phosphine oxides could be of considerable importance since the analogous conversion (P=S to P=O) has been used as a model for the study of the hepatic oxidase system, which is responsible for the metabolic hydroxylation of aromatic substrates,[73-75] and for the metabolic activation of phosphine sulphides.[76]

The oxygen source used for the deselenation reactions has been provided by a number of conventional oxidising reagents, which are surveyed in the literature. Their ease of availability and solubility have enabled successful usage. Furthermore, in the absence of these oxidising reagents, the phosphine selenides showed susceptibility towards oxidative deselenation reactions during ultrasonic excitation. These results are illustrated in table 7.1

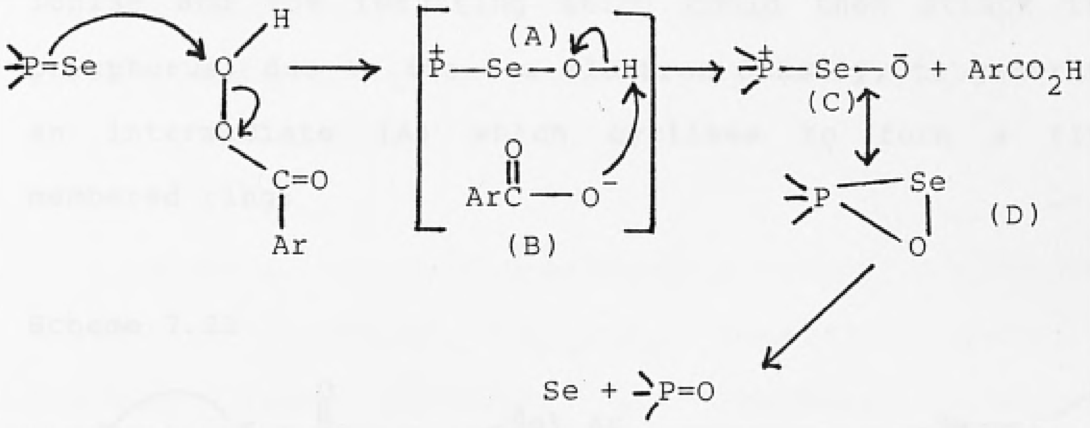
Table 7.1 Oxygenation reactions of phosphine selenides[a](1-5) in chloroform.

Oxidising agent	Mol.equ.	(%) oxidation of organophosphorus selenides				
		Ph_3PSe (1)	$Ph_2PSe(OEt)$ (2)	$PhPSe(OEt)_2$ (3)	$(EtO)_3PSe$ (4)	$(MeO)_3PSe$ (5)
$m\text{-}ClC_6H_4CO_3H$[b]	2	100	100	100	100	100
$^nBu_4NIO_4$	2	100	92	75	40	37
	4	-	100	96	66	64
C_6H_5IO[c]	2	100	100	99	98	100
KO_2/(18-C-6)[d]	2	65	54	48	36	29
	4	93	89	80	65	60
Sonication	-	18	10	10	8	7

a, Selenide 3.0×10^{-2}M, stirred at room temperature for 24 hrs, red selenium precipitated in solution after reaction time.
b, Reaction time 20mins, precipitation of red selenium seen.
c, Reaction time 10mins, almost immediate precipitation of red selenium.
d, 1,4,7,10,13,16-hexaoxacyclooctadecane.

The data presented in table 7.1 reveal that m-chloroperbenzoic acid is an extremely efficient oxidising agent towards oxidative deselenation reactions. All the phosphine selenides were observed to be completely oxidised to their corresponding phosphine oxides. These oxidations were accompanied by precipitation of selenium from the reaction mixtures. The proposed mechanism for these observed oxygenations is shown below;

Scheme 7.21



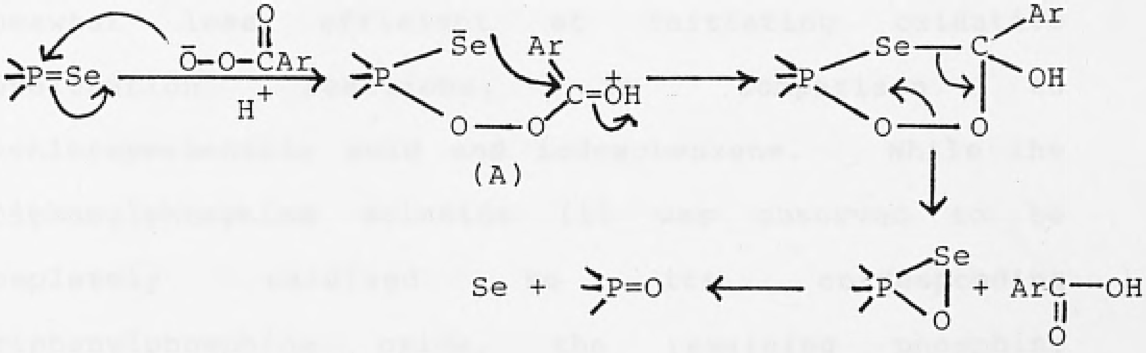
Ar=M-ClC$_6$H$_4$

The mechanism implies that nucleophilic attack by the P=Se moiety occurs at the hydroxyl oxygen atom of the peracid to generate initial intermediates (A) and (B), presumably in close proximity to each other. This spatial arrangement allows the proton abstraction to proceed and thus a zwitterionic species (C) and m-chlorobenzoic acid are formed. This zwitterionic species may cyclise to generate a three membered ring (D) which subsequently rearranges its bonding electrons to yield phosphine oxides and elemental selenium.

Analogous S-oxide zwitterion species have been proposed by Herriott,[8] in the desulphurisation of compounds containing P=S bonds with m-chloroperbenzoic acid.

Alternatively, the m-chloroperbenzoic acid may ionise and the resulting anion could then attack the phosphorus, due to its low electron density, to generate an intermediate (A) which cyclises to form a five membered ring;

Scheme 7.22



Ar=m-ClC$_6$H$_4$

Rapid bond cleavage of this ring occurs to generate the m-chlorobenzoic acid and a three membered ring, which consequently rearranges to yield the corresponding phosphoryl oxide and elemental selenium.

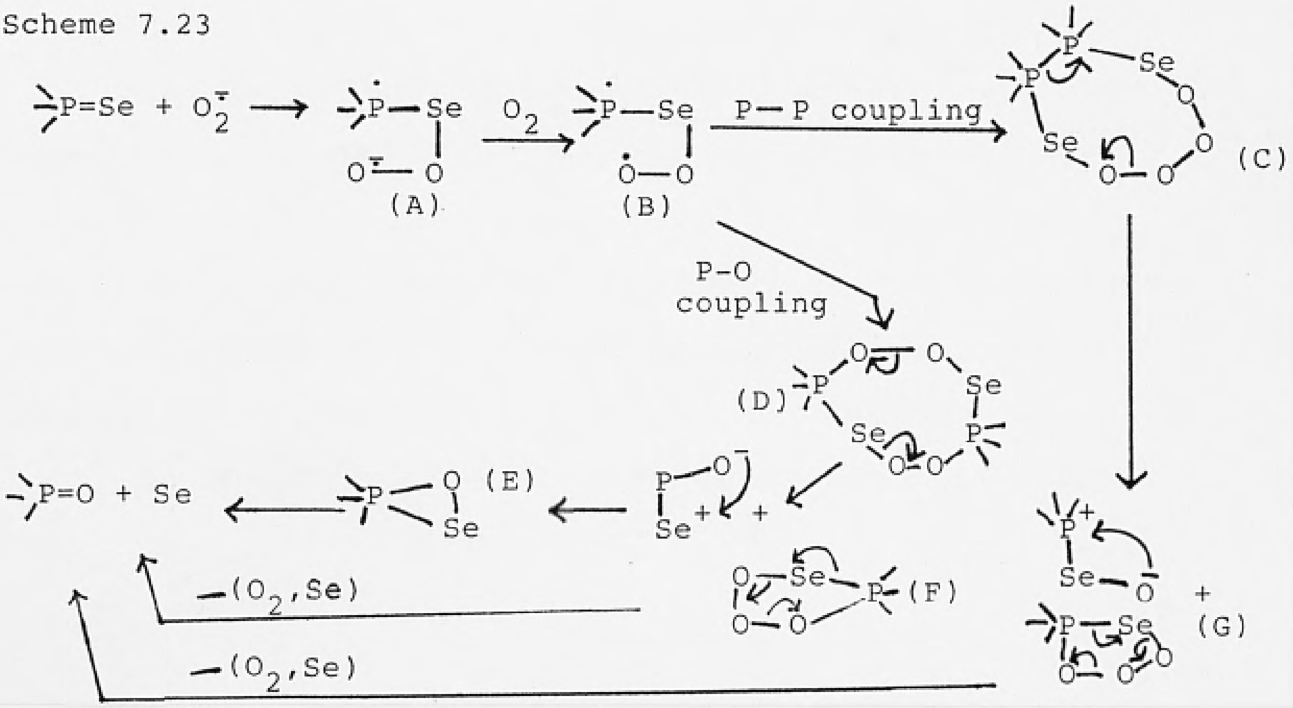
Iodosobenzene (PhIO) has also been found to be an effective oxidising agent, like m-chloroperbenzoic acid, towards compounds containing P=Se bonds. Oxidative deselenation occurs rapidly, with the immediate precipitation of elemental selenium, upon addition of 2 molar equivalents of iodosobenzene to the selenide reaction mixtures. All the selenides were oxidised to their corresponding phosphine oxides in 98-100% yields, within a few minutes.

However, the data presented in table 7.1 indicates that the periodate ($^{n}Bu_4NIO_4$) oxidising agent is somewhat less efficient at initiating oxidative deselenation reactions, in comparison to m-chloroperbenzoic acid and iodosobenzene. While the triphenylphosphine selenide (1) was observed to be completely oxidised to its corresponding triphenylphosphine oxide, the remaining phosphine selenides (2-5) showed 92, 75, 40 and 37% oxidations respectively, in the presence of 2 molar equivalents of periodate. Increasing the periodate concentration to 4 molar equivalents resulted in an increase in the phosphine oxide yields.

The oxidation mechanism for the oxygenation reactions of these phosphine selenides, with periodate and iodosobenzene, is proposed to be the same as that depicted for the m-chloroperbenzoic acid oxidation. These former oxidising reagents donate a single oxygen atom to compounds containing P=Se bonds to generate the intermediate zwitterionic species ($\overset{+}{P}$-Se-O^-), which is then converted to the appropriate phosphine oxide via cyclisation and rearrangement reactions, as shown in the earlier scheme 7.21. Also the mechanism shown in scheme 7.22 could also operate.

However, potassium superoxide oxidations have been observed to be much milder than the periodate (table 7.1). The most reactive phosphine selenide (1) showed only 65% oxidative deselenation at pentacovalent phosphorus, while the remaining phosphine selenides (2-5) produced 54, 48, 36 and 29% respectively, with 2 molar equivalents of potassium superoxide and 0.2 molar equivalents of 18-crown-6 ether. In addition, as for the periodate case, doubling the concentration of the superoxide produced higher yields of oxidation products (table 7.1). The mechanism proposed for these observed oxidations is given in scheme 7.23.

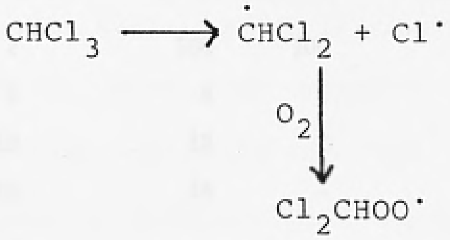
Scheme 7.23



Scheme 7.23 suggests that the primary step in these oxidative deselenation reactions may involve the addition of superoxide anion at the selenium atom, probably by nucleophilic attack, to generate the initial intermediate (A). In the presence of oxygen intermediate (A) is converted to a diradical species (B) and superoxide anion. The intermediate (B) then spontaneously dimerises either via P-P coupling, to generate intermediate (C), or via P-O coupling, to produce intermediate (D) or even a mixture of both derivatives. Subsequent rearrangement of bonding electrons, within the dimeric species, generates the three membered ring species (E) and also two other similar five membered ring species (F and G), which readily lose molecular oxygen and selenium to produce the desired products.

The sonication of chloroform solutions of phosphine selenides (1-5), using an ultrasound bath, in the absence of any added oxidising reagent promoted 'cleaner' oxidative deselenation reactions but in lower yields over a given time period. The phosphine selenides (1-5) yielded 18, 10, 10, 8 and 7% oxidation products respectively. These oxygenation reactions may have arisen through the formation of radicals and in turn peroxy radicals, which may donate a single oxygen atom to the phosphine selenides and thus induce oxygenation reactions;

Scheme 7.24



Apart from the chemical oxidative deselenation reactions with conventional oxidising reagents, tertbutylhydroperoxide (^{t}BuOOH), di-tert-butylperoxide (^{t}BuOO^{t}Bu) and tert-butylperbenzoate (PhC(O)OO^{t}Bu) have also been found to effectively facilitate the formation of the phosphine oxides, via cleavage of the O-O bond at room temperature. However, the di-tert-butylperoxide under these milder conditions showed lower reactivity towards the P=Se compounds (1-5). These observations are presented below.

Table 7.2 Oxidative deselenation reactions of phosphine selenides (1-5)[a] with compounds undergoing O-O bond cleavages in chloroform.

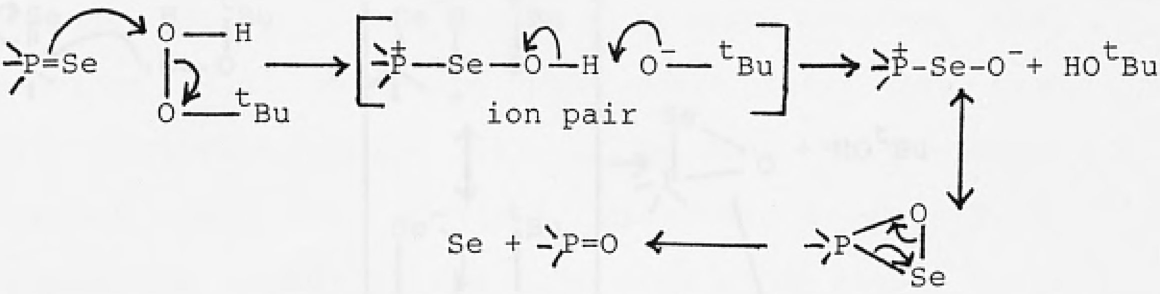
Oxidising agent	mol.equ.	% oxidation of organophosphine selenides				
		Ph_3PSe (1)	$Ph_2PSe(OEt)$ (2)	$PhPSe(OEt)_2$ (3)	$(EtO)_3PSe$ (4)	$(MeO)_3PSe$ (5)
$^tBuOOH^b$	2	100	100	100	100	100
$^tBuOO^tBu$	2	8	1	<1	0	0
$^tBuOO^tBu$	10	12	2	0	0	0
$^tBuOO^tBu/H_2O^c$	10	14	-	-	-	-
$PhCO_2O^tBu$	2	25	18	12	2	<1
$PhCO_2O^tBu$	10	100	95	87	12	14

a, Selenide 3.0×10^{-2}M, stirred at room temperature for 24hrs, red selenium precipitated in solution after reaction time.
b, Reaction time 20mins, precipitation of red selenium seen.
c, 20 molar equivalents of H_2O.

The results shown in table 7.2 indicate that t-butylhydroperoxide is a far better oxidising agent, towards oxidative deselenation reactions, than its analogues. Addition of 2 molar equivalents of tert-butylhydroperoxide to each of the phosphine selenide reaction mixtures (1-5) produced, after 20 minutes, the corresponding phosphine oxides in 100% yields, accompanied by precipitation of selenium from each mixture.

Similarly, trisubstituted phosphines have been readily converted into their corresponding phosphine oxides in high yields.[52-59] The results of these reactions suggested the formation of an ion pair,[53,61] presumably formed by the nucleophilic attack of phosphorus on the hydroxyl oxygen atom, which is deprotonated to give the phosphine oxides. However, since the charge density in the vicinity of the P=Se bond is generally concentrated around the selenium it is not unreasonable to presume that the selenium attacks the hydroxyl oxygen atom rather than the electron deficient phosphorus atom. Hence an analogous reaction scheme operates for the observed oxidative deselenation reactions;

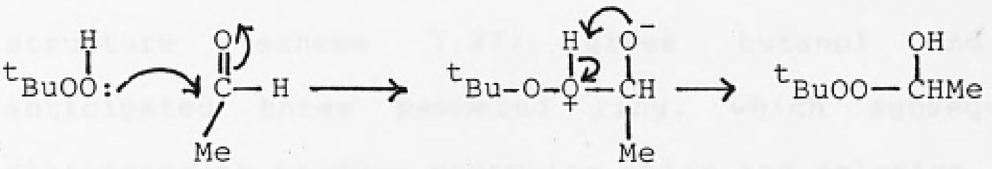
Scheme 7.25



Abstraction of a proton in the ion pair by the butoxy anion produces butanol and a zwitterionic species which cyclises and then rearranges to yield the phosphine oxides.

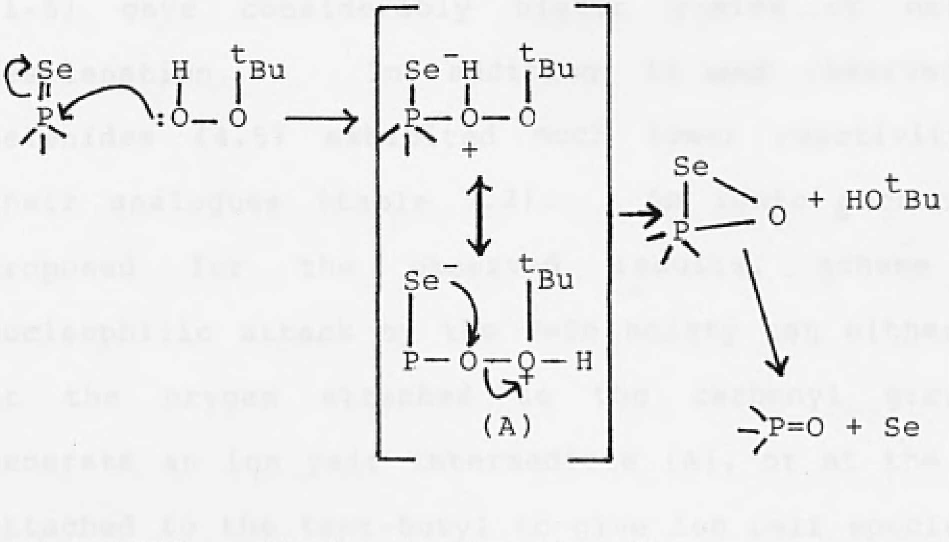
The tert-butylhydroperoxide has also been shown to behave as a nucleophile towards the carbonyl groups of aldehydes under neutral conditions;[68,69]

Scheme 7.26



Hence, the proposed nucleophilic mechanism for these deselenation reactions as given in scheme 7.27 could also operate.

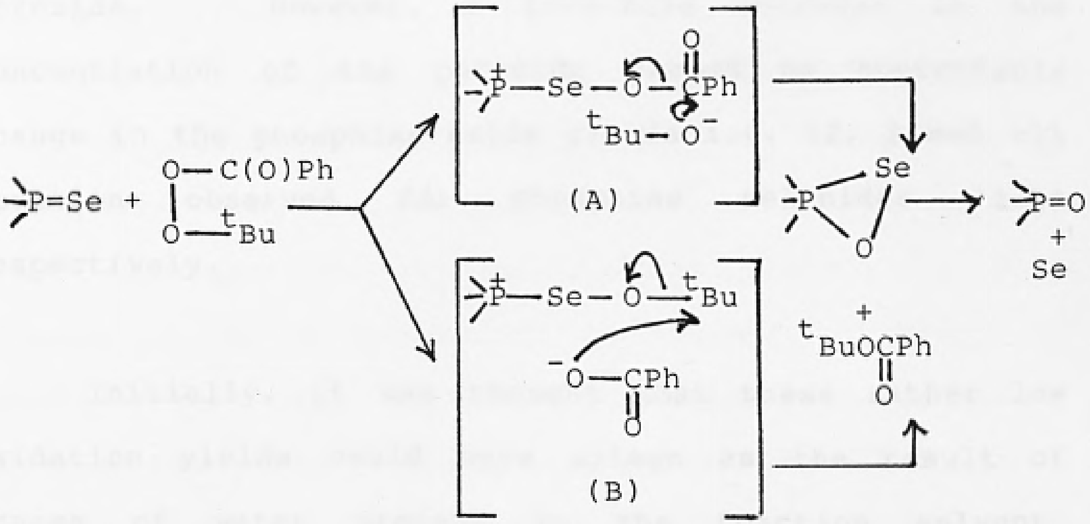
Scheme 7.27



Nucleophilic attack at the phosphorus occurs, probably due to its low electron density, to generate intermediate (A) which probably undergoes a proton shift and thereby exists as one of two equally probable structures. Such proton shifts have been suggested to occur readily by Denney and co-workers[53] for similar compounds. Cyclisation of the lower resonance structure (scheme 7.27) gives butanol and the anticipated three membered ring, which subsequently rearranges to produce phosphine oxide and selenium.

Phosphine selenides (1-5) in the presence of 2 molar equivalents of tert-butylperbenzoate gave lower yields of the corresponding phosphine oxides than the oxidation reactions with the tert-butylhydroperoxide (table 7.2). However, on increasing the concentration of the perbenzoate by five times, phosphine selenides (1-5) gave considerably higher yields of oxidative deselenation. In addition it was observed that selenides (4,5) exhibited much lower reactivity than their analogues (table 7.2). An ionic mechanism is proposed for the observed results, scheme 7.28. Nucleophilic attack by the P=Se moiety can either occur at the oxygen attached to the carbonyl group, to generate an ion pair intermediate (A), or at the oxygen attached to the tert-butyl to give ion pair species (B). These two intermediates may react in the manner shown below to produce the observed phosphine oxide products.

Scheme 7.28



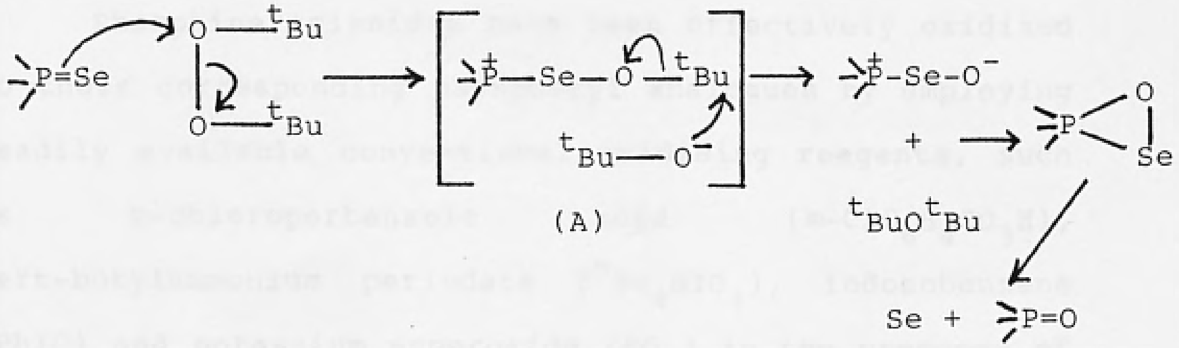
However, from the results obtained for the oxidative deselenation reactions (table 7.2) it is not possible to distinguish between these two mechanisms. Although, from consideration of steric effects it is highly probable that nucleophilic attack occurs presumably at the oxygen attached to the carbonyl group.

Di-tert-butylperoxide (^{t}BuOO^{t}Bu) is found to be the least reactive peroxide towards the oxidative deselenation reactions of phosphine selenides (1-5), under the mild experimental conditions employed for these investigations. Although triphenylphosphine selenide (1) was the only substrate which exhibited any reactivity towards the peroxide, the overall oxidation product yield was only 8%. Phosphine selenides (2-5) produced <1% oxidation with 2 molar equivalents of peroxide. However, a five-fold increase in the concentration of the peroxide caused no appreciable change in the phosphine oxide yields i.e. 12, 2 and <1% reaction observed for phosphine selenides (1-5) respectively.

Initially, it was thought that these rather low oxidation yields could have arisen as the result of traces of water present in the reaction solvent. However, the addition of 20 molar equivalents of water to the reaction mixture of triphenylphosphine selenide (1) plus 10 molar equivalents of di-tert-butylperoxide, produced no change in the percentage product yield of the triphenylphosphine oxide, table 7.2. This suggests that these observed oxygenation reactions genuinely arise from the interaction of peroxide with the respective phosphine selenides.

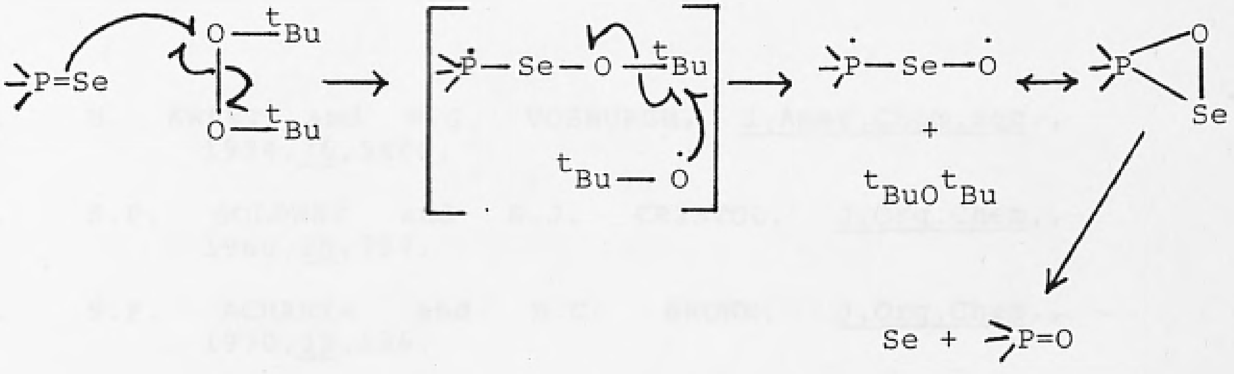
The reactions of dialkylperoxides usually occur only at elevated temperatures or under photoillumination and may proceed by either homolytic or heterolytic cleavage.[70-72] Thus, in the reaction of trialkylphosphines with diethylperoxide in benzene (80°C,24hrs) formation of ethyl-ether was detected and in the reaction of triphenylphosphine with di-tert-butylperoxide (110-120°C,30hrs) the formation of tert-butyl ether was observed From these observations the authors[57] proposed an ionic mechanism, analogous to that of phosphines with acylperoxides. Furthermore, Denney and Jones[64] have reported that certain phosphites reduce non-tertiary dialkylperoxides cleanly by what appears to be a non-radical reaction. Hence we conclude that the oxidative deselenation reactions, reported here, are probably also proceeding via an ionic pathway, scheme 7.29. Partial heterolytic cleavage of the peroxide bond, under the experimental conditions employed, occurs to produce an ion pair (A) of relatively low concentration which collapses to give the phosphine oxide and t-butyl ether.

Scheme 7.29



Alternatively, the partial cleavage of the peroxide bond could have occurred by the action of the fluorescent light upon the peroxide, thus a radical mechanism is proposed:

Scheme 7.30



However, the results presented here do not enable us to distinguish between these two reaction pathways.

7.3 Summary

Phosphine selenides have been effectively oxidised to their corresponding phosphoryl analogues by employing readily available conventional oxidising reagents, such as m-chloroperbenzoic acid ($m\text{-}ClC_6H_4CO_3H$), tert-butylammonium periodate ($^nBu_4NIO_4$), iodosobenzene (PhIO) and potassium superoxide (KO_2) in the presence of 18-crown-6 ether. In addition oxidative deselenation reactions have been achieved by the use of peroxides i.e. tert-butylhydroperoxide (^tBuOOH), di-tert-butylperoxide ($^tBuOO^tBu$) and tert-butylperbenzoate ($^tBuO_2(O)CPh$).

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CHAPTER 8

EXPERIMENTAL

8.1 Preparation of compounds containing P=Se and P=S bonds.

Compounds containing P=Se and P=S moieties were prepared according to reported literature[1-8] methods. In general, the selenides or sulphides were prepared from the appropriate tervalent organophosphorus compound which was treated with excess selenium or sulphur (1.5 molar equivalent), in dry benzene (100ml). The mixture was stirred at room temperature under nitrogen atmosphere for 24 hours. The excess selenium or sulphur was filtered and the solvent removed to give the desired product. The selenides or sulphides, if solids were purified by recrystallisation from ethanol or if liquids by fractional distillation under vacuum.

8.1.1 Triphenylphosphine selenide, Ph_3PSe

White solid, yield 88%.

Melting point 180-182°C (Lit.[2] 184-185°C).

Microanalysis for $C_{18}H_{15}PSe$;

% Theory C, 63.34; H, 4.39; P, 9.09.

% Found C, 63.49; H,4.50; P, 9.02.

^{1}H n.m.r. ($CDCl_3$) δ;

7.3 (m, 9H, aromatic meta and para),

7.7 (ddd, 6H, $^3J_{HCCP}$ 11.5Hz, $^3J_{HCCH}$ 7Hz, $^4J_{HCCCH}$ 2Hz, H-ortho).

IR (KBr disc) cm^{-1};

3052(w), 1822(w) 1584(w), 1478(m), 1432(s), 1331(w), 1305(m), 1180(w), 1158(w), 1096(s), 1068(m), 1026(m), 997(m), 853(w), 745(s), 711(s), 689(s), 618(w), 561(s), 505(s), 451(w), 428(w).

8.1.2 Ethyl diphenylphosphinoselenoic acid, $Ph_2PSe(OEt)$

Pale yellow solid, yield 93%.

Melting point 46-48°C.

Microanalysis for $C_{14}H_{15}OPSe$;

% Theory C, 54.33; H, 4.85; P, 10.02.

% Found C, 54.63; H, 5.00; P, 10.18.

^{1}H n.m.r. ($CDCl_3$) δ;

7.4 (m, 6H, aromatic meta and para),

7.8 (ddd, 4H, $^3J_{HCCP}$ 14Hz, $^3J_{HCCH}$ 9Hz, $^4J_{HCCCH}$ 2Hz, H-ortho),

3.9 (dq, 2H, $^3J_{HCOP}$ 9.5Hz, $^3J_{HCCH}$ 8.5Hz, $-OCH_2-$),

1.3 (t, 3H, $^3J_{HCCH}$ 7Hz, $-CH_3$).

IR(nujol mull) cm^{-1};

1380(m), 1310(w), 1150(m), 1130(w), 1110(s), 1025(s), 1070(w), 945(s), 770(s), 745(s), 715(s), 700(s), 685(s).

8.1.3 Diethyl phenylphosphonoselenoic acid, $PhPSe(OEt)_2$

Colourless liquid, yield 91%.

Boiling point 125-128°C/15mmHg.

Microanalysis for $C_{10}H_{15}O_2PSe$;

% Theory C, 43.29; H,5.41; P, 11.18.

% Found C, 43.31; H, 5.53; P, 11.21.

^1H n.m.r. ($CDCl_3$) δ;

7.3 (m, 3H, aromatic meta and para),

7.6 (ddd, 2H, $^3J_{HCCP}$13Hz, $^3J_{HCCH}$8.5Hz, $^4J_{HCCCH}$2Hz, H-ortho),

3.9 (ddq, 4H, $^3J_{HCOP}$9Hz, $^3J_{HCCH}$8.5Hz, $-OCH_2-$),

1.3 (t, 6H, $^3J_{HCCH}$6.5Hz, $-CH_3$).

IR (neat film) cm^{-1};

3060(w), 2980(m), 2930(w), 2900(w), 1475(w), 1440(s), 1390(m), 1310(w), 1280(w), 1160(m), 1120(s), 1100(w), 1035(s), 965(s), 740(s), 720(s), 690(s).

8.1.4 Triethyl phosphoroselenoic acid, $(EtO)_3PSe$

Colourless liquid, yield 92%.

Boiling point 93-95°C/12mmHg (Lit.[3] 85°C/9mmHg).

Microanalysis for $C_6H_{15}O_3PSe$;

% Theory c, 29.37; H, 6.12; P, 12.65.

% Found C, 29.59; H, 6.14; P, 12.69.

^{1}H n.m.r. ($CDCl_3$) δ;

3.9 (dq, 6H, $^3J_{HCOP}$9Hz, $^3J_{HCCH}$8Hz, $-OCH_2-$),

1.3 (t, 9H, $^3J_{HCCH}$7.5Hz, $-CH_3$).

IR (neat film) cm^{-1};

2980(m), 2930(w), 2900(w), 1470(w), 1440(w), 1390(m), 1290(w), 1160(m), 1100(w), 1020(s), 965(s), 770(s).

8.1.5 Trimethyl phosphoroselenoic acid, $(MeO)_3PSe$

Colourless liquid, yield 90%.

Boiling point 85-88°C/15mmHg (Lit.^{3}73-74°C/11mmHg).

Microanalysis for $C_3H_9O_3PSe$;

% Theory C, 17.73; H, 4.43; P, 15.26.

% Found C, 18.00; H, 4.47; P, 15.30.

^{1}H n.m.r. ($CDCl_3$) δ;

3.7 (d, 9H, $^3J_{HCOP}$14Hz, $-CH_3$).

IR (neat film)cm^{-1} ;

2900(w), 2955(m), 2840(w), 1460(w), 1440(w), 1180(s), 1025(s), 825(s), 780(s).

8.1.6 Triphenylphosphine sulphide, Ph_3PS

White solid, yield 83%.

Melting point 154-157°C (Lit.^{4}158-162°C).

Microanalysis for $C_{18}H_{15}PS$;

% Theory C, 73.39; H, 5.09.

% Found C, 73.25; H, 5.27.

^1H n.m.r. ($CDCl_3$) δ;

7.3 (m, 9H, aromatic meta and para),

7.8 (ddd, 6H, $^3H_{HCCP}$11Hz, $^3J_{HCCH}$8Hz, $^4J_{HCCCH}$2Hz, H-ortho).

IR(KBr disc) cm^{-1};

3054(w), 1827(w), 1584(w), 1478(m9, 1432(s), 1307(m), 1182(w), 1104(s), 1068(m), 1025(m), 998(m), 855(w), 754(s), 747(s), 714(s), 690(s), 638(s), 613(s), 511(s), 479(m), 456(m), 428(w).

8.1.7 Ethyl diphenylphosphinothionic acid, $Ph_2PS(OEt)$

Yellow solid, yield 85%.

Melting point 38-40°C (Lit.[5] 42-43°C).

Microanalysis for $C_{14}H_{15}OPS$;

% Theory C, 64.12; H, 5.70.

% Found C, 63.22; H, 5.88.

^1H n.m.r. ($CDCl_3$) δ;

7.3 (m, 6H, aromatic meta and para),

7.8 (ddd, 4H, $^3J_{HCCP}$12Hz, $^3J_{HCCH}$8Hz, $^4J_{HCCCH}$2Hz, H-ortho),

4.1 (dq, 2H, $^3J_{HCOP}$9Hz, $^3J_{HCCH}$7.5Hz, $-OCH_2-$).

1.3 (t, 3H, $^3J_{HCCH}$7Hz, $-CH_3$).

IR (neat film) cm^{-1};

3060(m), 2980(m), 2930(w), 2900(w), 1480(m), 1440(s), 1390(m), 1310(w), 1180(w), 1160(m), 1115(s), 1030(s), 995(w), 955(s), 790(s), 745(s), 720(s), 690(s), 635(s), 615(s).

8.1.8 Diethyl phenylphosphonothionic acid, $PhPS(OEt)_2$

Colourless liquid, yield 79%.

Boiling point 130-132°C/16mmHg

(Lit.[6] 72-73°C/0.02mmHg).

Microanalysis for $C_{10}H_{15}O_2PS$;

% Theory C, 52.17; H, 6.52.

% Found C, 52.39; H, 6.78.

^{1}H n.m.r. ($CDCl_3$) δ;

7.3 (m, 3H, aromatic meta and para),

7.7 (ddd, 2H, $^3J_{HCCP}$13Hz, $^3J_{HCCH}$7Hz, $^4J_{HCCCH}$2Hz, H-ortho),

4.1 (ddq, 4H, $^3J_{HCOP}$8Hz, $^3J_{HCCH}$7.5Hz, $-OCH_2-$),

1.3 (t, 6H, $^3J_{HCCH}$7Hz, $-CH_3$).

IR (neat film) cm^{-1};

3060(w), 2980(m), 2930(w), 2900(w), 1475(w), 1440(s), 1390(m), 1310(w), 1285(w), 1160(m), 1120(s), 1100(w), 1030(s), 960(s), 790(s), 745(s), 730(s), 690(s), 625(s).

8.1.9 Triethyl phosphorothionic acid, $(EtO)_3PS$

Colourless liquid, yield 82%.

Boiling point 105-108°C/18mmHg (Lit.[7] 95.5°C/12mmHg)

Microanalysis for $C_6H_{15}O_3PS$;

% Theory C, 36.33; H, 7.57.

% Found C, 36.45; H, 7.84.

^1H n.m.r. ($CDCl_3$) δ;

4.2 (dq, 6H, $^3J_{HCOP}$9.5Hz, $^3J_{HCCH}$8Hz, $-OCH_2-$),

1.4 (t, 9H, $^3J_{HCCH}$7Hz, CH_3-).

IR (neat film) cm^{-1};

2980(m), 2930(w), 2900(w), 1475(w), 1440(w), 1390(m), 1290(w), 1160(m), 1100(w), 1025(s), 965(s), 820(s).

8.1.10 Trimethyl phosphorothionic acid, $(MeO)_3PS$

Colourless liquid, yield 77%.

Boiling point 90-93°C/16mmHg (Lit.[8] 75°C/3mmHg).

Microanalysis for $C_3H_9O_3PS$;

% Theory C, 23.06; H, 5.76.

% Found C, 22.81; H, 5.80.

^1H n.m.r. ($CDCl_3$) δ;

3.7 (d, 9H, $^3J_{HCOP}$13Hz, CH_3-).

IR (neat film) cm^{-1};

3000(w), 2955(m), 2840(w), 1460(w), 1440(w), 1180(m), 1025(s), 825(s).

8.2.1 Preparation of benzophenone hydrazone, $Ph_2C{=}NNH_2$

Hydrazine hydrate (4.68g, 46.8mMol) was added to benzophenone (10g, 27.5mMol) in absolute ethanol (60ml) and a few drops of glacial acetic acid were added. The mixture was heated under reflux overnight, and solution cooled at room temperature to give white crystals of benzophenone hydrazone. Crystals were filtered and washed with cold ether.

Yield 72%.

Melting point 89-92°C (Lit.[9] 95-98°C),

Microanalysis for $C_{13}H_{12}N_2$;

% Theory C, 79.56; H, 6.16; N, 14.27.

% Found C, 79.41; H, 6.24; N, 14.32

^1H n.m.r. ($CDCl_3$) δ;

7.4-7.5 (m,10H), 5.5 (s,2H).

8.2.2 Preparation of diphenyldiazomethane, Ph_2CN_2

Anhydrous sodium sulphate (2.31g) and saturated solution of potassium hydroxide (0.8ml) were added to benzophenone hydrazone (2.0g, 10mMol) in dry ether (30ml). The solution was stirred vigorously and mercuric oxide (5.39g, 24.8mMol, red grade) was then added slowly. Stirring was continued for 20 hours and the solution filtered and ether removed under vacuum. The residue was taken up in 40-60° petroleum ether, filtered and evaporated to dryness to leave dark red crystals.

Yield 91%.

Melting point 27-29°C (Lit.[9] 29-32°C).

Microanalysis for $C_{13}H_{10}N_2$;

% Theory C, 80.38; H, 5.18; N, 14.42.

% Found C, 80.55; H, 5.21; N, 14.40.

^{1}H n.m.r. ($CDCl_3$) δ; 7.1-7.4 (m,10H).
IR (nujol film) cm^{-1}; νPh_2CN_2 2038.

8.3.1 Preparation of 3-methylpyridazine 2-oxide

3-methylpyridazine (2.4g) was added to glacial acetic acid (15ml), and 30% hydrogen peroxide (7ml) and mixture heated at 70°C for 3 hours. Further 30% H_2O_2 (7ml) was added and again mixture heated for another 3 hours at 70°C. To this solution water (15ml) was added and the reaction mixture reduced under vacuum, and procedure repeated twice. After neutralisation with sodium carbonate, the solution was extracted with chloroform, the chloroform layer was dried over anhydrous sodium sulphate, and evaporated under vacuum. The residue was dissolved in benzene and chromatographed on alumina (27g) and the column was eluted with benzene. The residue from the fraction eluted with benzene was recrystallised from benzene to colourless crystals.

Yield 26%.

Melting point 76-79°C (Lit.[10] 83-84°C).

Microanalysis for $C_5H_6N_2O$;

% Theory C, 54.52; H, 5.49; N, 25.44.

% Found C, 54.27; H, 5.52; N, 25.23.

^{1}H n.m.r. ($CDCl_3$) δ; 6.8-8.1 (m, 3H), 2.5 (s,3H).
IR (nujol film) cm^{-1}; νN-O 1375.

8.4.1 Preparation of p-Cyanodimethylaniline N-oxide (P-CNDMANO[11])

A solution of m-chloroperbenzoic acid (2.5g, 15ml/$CHCl_3$,1M) was added slowly at 0-5°C to an ice-cold, stirred solution of p-cyanodimethylaniline (2.5g, 17ml/$CHCl_3$,1M). Stirring was continued for a total of 3 hours, during which time the mixture was allowed to reach room temperature. The solution was passed through a column of alkaline alumina (100g) and traces of unreacted amine removed by washing with chloroform. The column was then eluted with methanol:chloroform (1:3), solvent removed under vacuum and the crude white product recrystallised from methanol-ether (1:1).

Yield 80%.

Microanalysis for $C_9H_{10}N_2O$;

% Theory C, 66.64; H, 6.21; N, 17.27.

% Found C, 66.46; H, 6.52; N, 16.95.

^{1}H n.m.r. ($CDCl_3$) δ;

7.7-8.3 (4H, $^3J_{HCCH}$ 9Hz, $^4J_{HCCCH}$ 2Hz, aromatics),

3.6 (s, 6H, CH_3-).

8.5.1 Preparation of di-n-hexylsulphoxide $[CH_3(CH_2)_5]_2SO$

The sulphoxide was prepared from the corresponding sulphide using the procedure reported by Leonard and Johnson.[12] Sodium metaperiodate in methanol/water (1:1

v/v) at $0^{\circ}C$ was added to di-n-hexylsulphide (1 equivalent) and stirred for 24 hours on an ice-bath. The precipitate of sodium iodate was filtered off and the filtrate extracted with chloroform. The chloroform layer was dried over anhydrous magnesium sulphate and the solvent removed under vacuum to yield the sulphoxide which was recrystallised from ethanol.

Yellowish solid, yield 88%.

Melting point 56-58°C (Lit.[13] 58-59°C).

^{1}H n.m.r. ($CDCl_3$) δ;

2.8-2.4 (t, 2H); 1.9-1.6 (m, 2H); 1.6-1.1 (m, 6H); 1.0-0.7 (m, 3H).

8.5.2 Preparation of di-n-hexylsulphone $[CH_3(CH_2)_5]_2SO_2$

Hydrogen peroxide (1.5mls, 30% aqueous solution) in acetic acid (1.5mls) was added dropwise to an ice-cooled solution of the di-n-hexylsulphide (1g) in glacial acetic acid (20mls). The mixture was stirred at room temperature for 24 hours before removal of the volatile components by rotary evaporation. The resultant product was recrystallised from ethanol.

White-yellowish solid, yield 92%.

Melting point 70-72°C (Lit.[14] 72.6-73°C).

^{1}H n.m.r. ($CDCl_3$) δ;

3.5-3.2 (m, 2H); 2.3-2.1 (m,2H); 1.9-1.6 (m, 5H); 1.3-1.2 (t,3H).

8.6 Photooxidation of compounds containing P=Se bonds with, benzoin, 1,2-dicarbonyl, pyruvate esters and pyruvic acid initiators.

Compounds containing P=Se bonds have been oxidised using a wide range of initiators, both photochemical and chemical. However, in this section the oxidation procedures employed with the above initiators will be discussed.

Parent stock solutions for each of the five phosphine selenides were prepared to a known concentration (1.5×10^{-2}M). To 10ml portions of each stock solution, a known quantity of the initiator (i.e. 2,4 molar equivalents) was added. The resulting 5 solutions were then irradiated, in pyrex photolysis tubes for 24 hours, with black-light fluorescent lamps (max. emission 350nm). All the solutions were purged with oxygen throughout the irradiation period. At the end of the irradiation, all the solutions were analysed, in turn, for any unreacted starting material and their corresponding phosphoryl analogues. The stock solutions prepared were as follows:

Ph_3PSe	0.2560g	in 50ml of dry chloroform
$Ph_2PSe(OEt)$	0.2320g	"
$PhPSe(OEt)_2$	0.2078g	" "
$(EtO)_3PSe$	0.1838g	" "
$(MeO)_3PSe$	0.1525g	" "

8.7 Dye sensitised photooxidation of compounds containing P=Se bonds

Three types of dyes were employed for studies with these P=Se compounds, namely Rose Bengal (RB), Methylene blue (Mb), and meso-tetraphenylporphyrin (metal-free, TPP).

As previously, parent stock solutions of the five phosphine selenides were prepared to a known concentration (3×10^{-2}M). To 10ml portions of each stock solution, a known quantity of dye (2×10^{-4}M) was added. The resulting 5 solutions were then irradiated, in pyrex photolysis tubes for 5 hours through 2% potassium dichromate filter solution with chryselco daylight fluorescent lamps. The solutions were continually purged with oxygen throughout the period of irradiation. The phosphine selenides were then analysed, as before, for any unreacted starting material and their corresponding phosphoryl analogues. The results of these experiments are reported in table 2.1.

Stock solutions of the P=Se compounds prepared

Ph_3PSe	0.5120g	in 50ml of dry chloroform: methanol (1:1 v/v)
$Ph_2PSe(OEt)$	0.4640g	"
$PhPSe(OEt)_2$	0.4155g	"
$(EtO)_3PSe$	0.3675g	"
$(MeO)_3PSe$	0.3050g	"

Dyes:

Rose Bengal 2mg in 10ml portion of each of the above stocks
Methylene blue 0.75mg " "
Meso-tetraphenylporphyrin 1.23mg "

8.8 Quenching studies of compounds containing P=Se bonds with dyes

The quenchers employed for these studies were β-carotene, 1,4-diazabicyclo[2,2,2] octane (DABCO), and 6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid (Trolox), while dyes were Rose Bengal, Methylene blue and meso-tetraphenylporphyrin. The former three are known efficient quenchers for singlet oxygen at concentrations that are sufficiently low to ensure that competitive quenching of the sensitiser's excited state or triplet state does not occur. It is assumed that over the concentration ranges used, e.g. β-carotene 1.0×10^{-3} - 1.0×10^{-4}; DABCO 2.0×10^{-2} - 1.3×10^{-3}; Trolox 1.0×10^{-3} - 2.0×10^{-3}M, the triplet states of the dyes were not quenched. In addition Trolox is also a known efficient radical scavenger.

The general experimental procedures employed in this section are as follows. In the specific case, a stock solution of triphenylphosphine selenide (3×10^{-2}M) plus Rose Bengal dye (2×10^{-4}M) was prepared as;
Ph_3PSe (0.4g) + Rose Bengal (8mg) in 40ml chloroform:methanol (1:1 v/v).
3 x 10ml portions of this stock were removed and known quantities of β-carotene, DABCO and Trolox were added respectively. The remaining 10ml portion was used as a blank. The 4 solutions were then irradiated, as previously, for 5 hours under oxygen with (8/20W) circular array of chryselco daylight fluorescent lamps through a potassium dichromate filter solution. Samples were taken at regular intervals and analysed by glc. This process was repeated, using Methylene blue and meso-tetraphenylporphyrin dyes. Furthermore, these two sensitisers were studied in a single solvent system. The results from these studies are given in table 2.2. In addition the graphs extrapolated from these

experimental data are also given (figs.2.3-2.6).

Stock solutions prepared for these studies

Ph_3PSe 0.3072g + Methylene blue 2.25mg in 30ml chloroform:methanol (1:1 v/v)
" " + meso-tetraphenylporphyrin 3.69mg in 30ml chloroform:methanol (1:1 v/v)
" " + Methylene blue 2.25mg in 30ml chloroform
" " + meso-tetra phenylporphyrin 3.69mg in 30ml chloroform

NB: For quencher concentrations, in 10ml of above stocks please refer to table 2.2.

8.9 Dye sensitised reactions of compounds containing P=Se and P=S bonds with di-n-hexylsulphide and diphenyldiazomethane

Stock solutions of compounds P=Se (2.5×10^{-3}M) and P=S (2.5×10^{-3}M) with Rose Bengal dye (2×10^{-4}M) were prepared as in previous sections. In the specific case, a stock solution of triphenylphosphine sulphide (2.5×10^{-3}M) and Rose Bengal (2×10^{-4}M) was prepared as;
Ph_3PSe (22.20mg) + Rose Bengal (6mg) in 30ml chloroform:methanol (1:1 v/v).
2 x 10ml portions of this stock were removed and

di-n-hexylsulphide (20.2mg, 10 x 10^{-3}M) and diphenyldiazomethane (19.4mg, 10 x 10^{-3}M) added respectively. The remaining 10ml portion was used as a blank or control. The three solutions were irradiated under the same conditions as dye sensitised reactions (pyrex tubes, dichromate filter, oxygen and chryselco daylight fluorescent lamps). Each sample was concentrated before analysis by glc, at the end of the irradiation period.

This procedure was repeated for the remaining P=Se compounds and also for the compounds containing P=S bonds.

<u>The following stock solutions were also prepared</u>

Ph_2PSOEt	(19.80mg)	+ Rose Bengal	(6mg)	in 30ml chloroform:methanol (1:1 v/v)
$PhPS(OEt)_2$	(17.40mg)	"	"	"
$(EtO)_3PS$	(15.00mg)	"	"	"
$(MeO)_3PS$	(11.70mg)	"	"	"

Ph_3PSe	(24.90mg)	"	"	"
$Ph_2PSe(OEt)$	(23.40mg)	"	"	"
$PhPSe(OEt)_2$	(20.70mg)	"	"	"
$(EtO)_3PS$	(18.60mg)	"	"	"
$(MeO)_3PS$	(15.30mg)	"	"	"

8.10 Chemical oxidation of compounds containing P=Se bonds by a wide range of oxidising reagents

As mentioned already, stock solutions of the P=Se compounds were prepared to known concentrations in dry chloroform solvent. In general, several 10ml portions of a stock solution of a particular selenide, were taken and a known quantity of the oxidising reagent was added to each portion, in a 25ml round bottom flask. All the flasks were then stoppered and the solutions were stirred at room temperature for 24 hours. The reaction mixture was then analysed by glc as before. In the case of the potassium superoxide reagent (2 and 4 molar equivalents), the granules were ground to a fine powder in solution to give a larger surface area for reaction, and unnecessary exposure to the atmosphere was prevented. Furthermore, 18-crown-6 ether (15.9mg, 0.2 molar equivalent), acting as a phase transfer catalyst was added to all the superoxide reactions.

With the tetrabutylammonium periodate, reactions were carried out using similar molar equivalents as above, i.e. 2 and 4 of the reagent. However, for the diethyl phenylphosphonoselenoic acid [PhPSe (OEt)$_2$], triethyl phosphoroselenoic acid (EtO)$_3$PSe and trimethyl phosphoroselenoic acid (MeO)$_3$PSe, in addition to tetrabutylammonium periodate (2 molar equivalents), manganese III mesotetraphenylporphyrin chloride (0.02molar equivalent) or manganese III mesotetra(2,6-dichlorophenylporphyrin) chloride (0.02 molar equivalent) plus imidazole were added. The results for these reactions are presented in table 6.1.

Oxidation reactions with m-chloroperbenzoic (2 molar equivalents), iodosobenzene (2 molar equivalents), tert-butylhydroperoxide (2 molar equivalents), di-tert-butylperoxide (2,10 molar equivalents) and tert-butylperoxybenzoate (2,10 molar equivalents) were carried out as described earlier. The concentration of the P=Se compounds were prepared to 3 x 10^{-2}M in chloroform. The following quantities of the latter three reagents, tert-butylhydroperoxide (0.2ml, 1ml/2,10 molar equivalents), di-tert-butylperoxide (0.11ml, 0.55ml/2,10 molar equivalents) and tert-butylperoxybenzoate (0.12ml, 0.60ml/2,10 molar equivalents) were added to each 10ml portion of each P=Se compound stock solution.

8.11 Oxidation of compounds containing P=Se and P=S bonds with heterocyclic N-oxides

The following procedure was adopted for these reactions. In general, a stock solution of the N-oxide was prepared to a known concentration of 5×10^{-3}M in 50ml of dichloromethane. 5 x 10ml portions of the stock solution were taken and known quantities of the five P=Se compounds, present in pyrex or quartz photolysis tubes, were added to each 10ml portion and all the solutions were purged with nitrogen for 10 minutes before irradiation for 24 hours with an applied source of light. The solutions after irradiation were concentrated and analysed by glc for unreacted starting materials and their corresponding phosphoryl analogues. This method was repeated, with the same N-oxide stock solution, for the P=S compounds also.

The stock solutions prepared for each of the N-oxides were as follows:

1. Pyridine N-oxide 23.78mg in 50ml dichloromethane
2. 2-picoline N-oxide 27.28mg "
3. Quinoline N-oxide 36.29mg "
4. P-cyanodimethylaniline N-oxide 40.5mg "
5. 3-methylpyridazine 2-oxide 27.50mg "
6. 2-phenylsulphonyl-3(P-nitrophenyl)oxaziridine 76.50mg "
7. 7-hydroxy-3H-phenoxazine-3-one 31.39mg(2.5×10^{-3}M) in 50ml chloroform:methanol (1:1 v/v)

The following amounts of P=Se compounds were added to the N-oxides 1-6;
Ph_3PSe (6.8mg); $Ph_2PSe(OEt)$ 6.2mg); $PhPSe(OEt)_2$ (5.5mg); $(EtO)_3PSe$ (4.9mg) and $(MeO)_3PS$ (4.1mg). The concentrations of all the selenides and sulphides, in 10ml, were 2×10^{-3}M. For the
7-hydroxy-3H-phenoxazine-3-one N-oxide (7), which had a concentration of 2.5×10^{-3}M, all the above quantities of P=Se and P=S compounds were halved. The results for these experiments are reported in tables 5.1 and 5.2. Furthermore, the irradiation source for each N-oxide is also given.

8.12 Instrumentation

Melting points, which are uncorrected, were determined in capillary tubes, while all the liquid compounds were distilled under reduced pressure using a Büchi Kugel oven. Boiling points are also uncorrected.

^{1}H n.m.r. spectra were measured on a JEOL 60mHz spectrometer, using tetramethylsilane (TMS) as the internal standard and deuterochloroform ($CDCl_3$) as the solvent. The following abbreviations are used to

interpret the spectra:-
singlet s, doublet d, triplet t, quartet q, and multiplet m.

IR spectra were measured as neat films or as nujol mulls on a Perkin-Elmer 157G spectrophotometer. The following three abbreviations are used to interpret the i.r spectra:-
strong s, medium m, weak w.

8.12.1 Gas liquid chromatography(glc)

All glc analyses were carried out using a Shimadzu GC-mini2 gas chromatograph (FID detector) in conjunction with a Shimadzu chromatopac C-R1B integrator, and a copper capillary column: 50 metres x 0.031cm SE54 0.2JDF, unless stated otherwise. The gas pressure or flow of the carrier gas was reduced for the phosphine sulphides while the temperatures of the capillary column and detector were unchanged. This enabled a good separation between the phosphine sulphides and their corresponding phosphoryl analogues. The glc conditions for each compound analysed by this method are given in table 8.1. No internal standard was used since calibration curves were found to give a linear relationship between P=X (where X=Se,S) and the oxidised P=O products, over the concentration range used. Each sample was analysed twice in non-chronological order.

Peak areas were obtained directly from the integrator, from which the percentage yields for the corresponding phosphine oxides were obtained.

Table 8.1 Showing glc conditions for $\geqslant$P=X (where X=Se,S and O) compounds and others

Compound	Temperature (^{o}C)		N_2 pressure Kg/cm^2	Retention time (mins.)
	Oven	Detector		
Ph_3PSe	300	350	1.1	6.21 (5.59)
$Ph_2PSe(OEt)$	235	260	"	5.86 (4.92)
$PhPSe(OEt)_2$	180	220	"	5.23 (4.27)
$(EtO)_3PSe$	130	200	"	4.96 (3.81)
$(MeO)_3PSe$	100	160	"	4.48 (3.40)
Ph_3PS	300	350	0.9	7.50 (6.80)
$Ph_2PS(OEt)$	235	260	"	7.33 (6.36)
$PhPS(OEt)_2$	180	220	"	7.03 (6.04)
$(EtO)_3PS$	130	200	"	5.37 (4.88)
$(MeO)_3PS$	100	160	"	5.10 (4.34)
$[CH_3(CH_2)_5]_2S$	180	240	1.2	4.87
$[CH_3(CH_2)_5]_2SO$	"	"	"	11.26
$[CH_3(CH_2)_5]_2SO_2$	"	"	"	12.84
Ph_2SO_2	"	"	"	14.62
Ph_2CO	235	260	"	3.98
1,8-naphthalic anhydride *	190	250	-	2.0

(   ) denotes the corresponding phosphoryl analogue.

* column 20", 10% UCW 982 (80-100WAW DCMS B-8), N_2 flow 40ml Min^{-1}.

8.13 Photochemical reactors and mercury lamps

8.13.1 Daylight reactor; consisted of a total of eight 20W circular array of chryselco daylight fluorescent lamps, which are kept cooled by a fan fitted to the base of the reactor.

8.13.2 350nm reactor; consisted of a total of sixteen 8W, F8T5/BLB sylvania black-light fluorescent lamps (having a maximum emission at 350nm) which were kept cool by means of a fan, similar to that of the daylight reactor.

8.13.3 254nm reactor; the 350nm reactor was adapted to give a maximum emission at 254nm, by replacing the sixteen 8W sylvania black-light fluorescent lamps with sixteen sylvania Gl 5T8 lamps. In all other respects this reactor was similar to the 350nm reactor.

8.13.4 Medium pressure mercury arc lamps; the mercury arc or 1 litre photochemical reactor operates in the region of approximately 1 atmosphere with high currents (50Hz). This gives rise to a multiplicity of pressure-broadened lines between 240-580nm, characteristic of this type of arc. The arc, contained inside a water-cooled jacket, was connected to a Hanovia power source of 125 watts, serial no.37451.

8.13.5 High pressure mercury arc lamps; these types of arcs operate at very high pressures in the region of 100-400 atmospheres and hence the emission obtained from these lamps is almost a continuum. The photochemical reactor was contained inside a water-cooled jacket and connected to an applied photophysics source of 400 watts.

8.14 Source of chemicals

Aldrich Chemical Co.Ltd: Triphenyl phosphine, triphenyl phosphonate, diphenyl ethoxy phosphine, diethoxy phenyl phosphine, triethoxy phosphine, triethoxy phosphonate, trimethoxy phosphine, trimethoxy phosphonate, selenium metal, methylene blue (metal free), di-n-hexylsulphide, hydrazine hydrate, benzophenone, m-chloroperbenzoic acid, β-carotene, 1,4-diazabicyclo[2,2,2] octane, 6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid, imidazole, pyridine, quinoline N-oxide, 7-hydroxy-3H-phenoxazin-3-one (85% dye content), 3-methylpyridazine, p-cyanodimethylaniline, deuterochloroform (gold label), 18-C-6 ether, tetrabutylammonium periodate, calcium hydride (anhydrous), tert-butylhydroperoxide, di-tert-butylperoxide, tert-butylperoxybenzoate, benzoin, benzil, methylpyruvate, ethylpyruvate, pyruvic acid, biacetyl, acenaphthanquinone.

Fisons Chemical Co. Ltd: Chloroform, benzene, acetic acid, methanol, dichloromethane (analar grade), potassium dichromate.

May & Baker Co. Ltd: Diethyl ether, ethanol, petroleum ether (40-60° and 60-80°).

BDH Chemical Ltd: Hydrogen peroxide, potassium hydroxide (pellets), sodium sulphate (anhydrous), sodium carbonate, alkaline alumina.

Lancaster Chemical Co. Ltd: Pyridine N-oxide, 2-picoline N-oxide.

Eastman Kodak Co. Ltd: Rose Bengal.

Koch-Light Chemical Ltd: Phosphorus pentoxide.

Hopkins and Williams: Mercuric oxide (red grade).

The City University Laboratory: Manganese III mesotetraphenylporphyrin chloride, manganese III mesotetra(2,6-dichlorophenylporphyrin) chloride, 2-phenylsulphonyl-3(p-nitrophenyl) oxaziridine.

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