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PHOTOCHEMICAL STUDIES IN ORGANOPHOSPHORUS CHEMISTRY

A thesis submitted in fulfilment
of the conditions for the
Degree of Doctor of Philosophy

by

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The City University, London

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Cariad a diolch i Nhad a Mam am ei
cyfraniad mawr im llwythiant.

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Statement

The work reported in this thesis was carried out by the author in the Department of Chemistry, The City University, London between October 1981 and September 1984. The work has not been presented, and is not being presented for any other degree.

January 1985.

SIMON JOHN BUCKLAND.

Some of this work has been presented in the following publication:-

S.J. Buckland and R.S. Davidson,

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University of Nice, France, September 1983

European Postgraduate Symposium on Photochemistry,
The City University, London, April 1984

Abstract

An introduction to photochemistry with a review on organophosphorus photochemistry is given in chapters one and two respectively.

In chapter three the chemistry of singlet oxygen and its reaction with anthracenyl compounds is discussed. The photooxidation of a variety of anthracenyl phosphorus compounds has been studied, and found to occur via a Type II process. All products observed can be accounted for by involving a 9,10-endoperoxide which may subsequently fragment, resulting in cleavage of the phosphorus moiety from the anthracene nucleus. The participation of singlet oxygen has been shown by solvent isotope studies, and by the isolation and subsequent thermolysis of a 9,10-endoperoxide. Where fragmentation of an endoperoxide occurs, the phosphorus moiety may be lost as a phosphorus ylid. The influence of phosphorus on anthracenyl photooxidation chemistry and the synthetic potential of this work is mentioned.

The principal methods for oxidative desulphurisation at pentavalent phosphorus are reviewed in chapter four. The photochemistry of 1,2-dicarbonyl based compounds is discussed in the light of their ability to epoxidize olefins. It has been found that the oxidation of phosphorus thionate and thiolate compounds may be achieved by the photochemical generation of peroxy radicals from 1,2-dicarbonyl compounds. The reaction of such peroxy radicals with a number of thiophosphoryl compounds is shown to result in the formation of the phosphoryl analogue, while thiolate compounds are transformed into their corresponding phosphorus acid. The significance of this work towards the activation and detoxication of thiophosphorus pesticides is mentioned, and illustrated by the oxidative desulphurisation of parathion and chlormephos. Finally a number of novel chemical

methods which may carry out a similar thiophosphoryl-phosphoryl interconversion are given.

Contents

Chapter 1 Introduction to Photochemistry.

Chapter 2 A Review on Organophosphorus Photochemistry.

Chapter 3 The Photooxidation of some Anthracenyl Phosphorus Compounds.

Chapter 4 Photooxidative Desulphurisation at Pentavalent Phosphorus.

Preface.

Numerous textbooks have been written on the science of photochemistry. The publications by,

Barltrop and Coyle - 'Excited States in Organic Chemistry', John Wiley & Sons,

Calvert and Pitts - 'Photochemistry', John Wiley & Sons,

Cowan and Drisco - 'Elements of Organic Photochemistry', Plenum Press,

and Turro - 'Modern Molecular Photochemistry', Benjamin/Cummings Publishing Co.,

all provide excellent reviews in this area. The brief coverage on photochemistry given in chapter one is therefore intended as a simple introduction to the subject, illuminating only those topics of concern to the work presented in this thesis.

ONE

INTRODUCTION TO PHOTOCHEMISTRY

General Aspects of Photochemistry.

Photochemistry is the science dealing with chemical changes brought about by the action of light.

The importance of photochemistry is clearly illustrated by the light dependent biological processes of photosynthesis, vision and phototropism[1]. Photographic processes have been in use for well over a century, and these two are based on the ability of visible radiation to produce a chemical change in a system[2].

Because photochemistry is concerned with the interaction of electromagnetic radiation with matter, it is at the crossroads of chemistry and physics. In discussing a photochemical process, one must therefore consider all the related physical processes (such as the absorption and emission of radiation) which in themselves do not strictly involve any 'chemical'change.

The Absorption of Electromagnetic Radiation.

It was first suggested by de Broglie[3], that both light and matter have simultaneous wave and particle properties. Thus light can be thought of as a quantised source of energy absorbed, transmitted and emitted in discrete units known as photons, whose energy is related to the frequency of the radiation ν, by the Equation,

$$E = h\nu = hc/_{\lambda} \qquad (1\text{-}1)$$

where h = Plank's constant,

c = velocity of light,

ν = frequency of the radiation

and λ = wavelength of the radiation.

When a photon passes close to a molecule, an interaction occurs between the electric field associated with the molecule and that associated with the radiation. This interaction may result in the absorption of the photon by the molecule. In such cases, the photon will cease to exist and its energy will be transferred to the molecule. Since the total energy, E_t, of a molecule in its electronic ground state can be expressed in terms of the sum of its electronic, E_{el}, vibrational, E_{vib}, and rotational, E_{rot}, energies, the effect of an interaction with a photon will be to perturb these energies with a resultant change in electronic structure. Transitions affecting only E_{rot} can be brought about by far-infrared radiation, those involving E_{rot} and E_{vib} by radiation in the near-ir and finally transitions involving E_{vib} and E_{el} by radiation in the visible and ultraviolet region of the electromagnetic spectrum.

For a simple diatomic molecule, the relative positions of these energy levels and the possible transitions between them are best represented using Morse curves, Figure 1.1. The curves for the electronic ground state S_0, and excited state, S_1, are shown, each point on

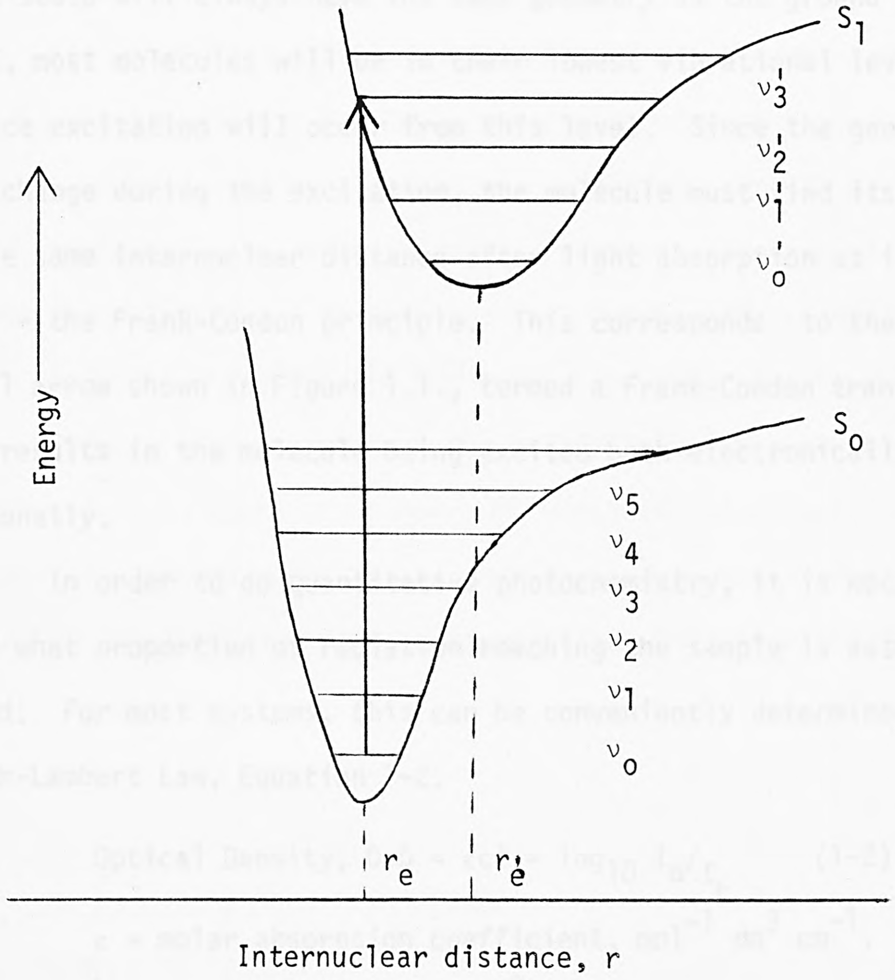


Figure 1.1. Morse potential energy curve for a simple diatomic molecule.

the curve representing the net energy of nuclear-nuclear, nuclear-electronic and electronic-electronic interactions at a particular bond distance, r. It can be seen that at a certain internuclear distance (r_e, r'_e), the energy is at a minimum. This corresponds to the equilibrium internuclear distance for each state. The horizontal lines in the wells of these potential curves represents the vibrational levels of the states.

Since a transition from the ground state to the excited state is essentially instantaneous (ca. 10^{-15} - 10^{-16} sec) in comparison with the time for internuclear motion (ca. 10^{-13}sec), the initially formed excited state will always have the same geometry as the ground state. At 25°C, most molecules will be in their lowest vibrational level, ν_o, and hence excitation will occur from this level. Since the geometry cannot change during the excitation, the molecule must find itself, with the same internuclear distance after light absorption as it had before, - the Frank-Condon principle. This corresponds to the vertical arrow shown in Figure 1.1., termed a Frank-Condon transition, and it results in the molecule being excited both electronically and vibrationally.

In order to do quantitative photochemistry, it is necessary to know what proportion of radiation reaching the sample is actually absorbed. For most systems, this can be conveniently determined using the Beer-Lambert Law, Equation 1-2.

$$\text{Optical Density, O.D} = \varepsilon c l = \log_{10} I_o/I_t \qquad (1\text{-}2)$$

where ε = molar absorption coefficient, $\text{mol}^{-1}\ \text{dm}^3\ \text{cm}^{-1}$.

c = concentration, mol dm^{-3},

l = path length, cm,

I_o= intensity of incident radiation,

and I_t= intensity of transmitted radiation.

If the incident intensity is known, the absorbed intensity, Ia, can be calculated since,

$$I_a = I_o - I_t \qquad (1\text{-}3)$$

and thus,

$$I_a = I_o\,(1 - e^{-2.3\varepsilon c l}) \qquad (1\text{-}4)$$

Energy Distribution in the Excited Molecule.

The various intramolecular processes initiated by light absorption are illustrated schematically in Figure 1.2. Such a representation of the energy levels and photophysical processes which can occur in the excited molecule is known as a Jablonski diagram.[4,5]

The electronic states are represented by the heavy horizontal lines; the symbols S_0, S_1 and S_2 represent the ground state and first and second excited singlet states (electron spins 'antiparallel' or 'paired') respectively, while T_1 and T_2 represent the triplet states (electron spins 'parallel' or 'unpaired'). These energy levels are known as the singlet and triplet manifolds, and refer to the multiplicity of the electronic state. The multiplicity is given by the expression, $2n + 1$, where n = number of 'unpaired' electrons. In accordance with Hund's rule, any excited triplet state, T_i (where i = 1, 2, 3...m), is always of lower energy than the corresponding excited singlet state, S_i.

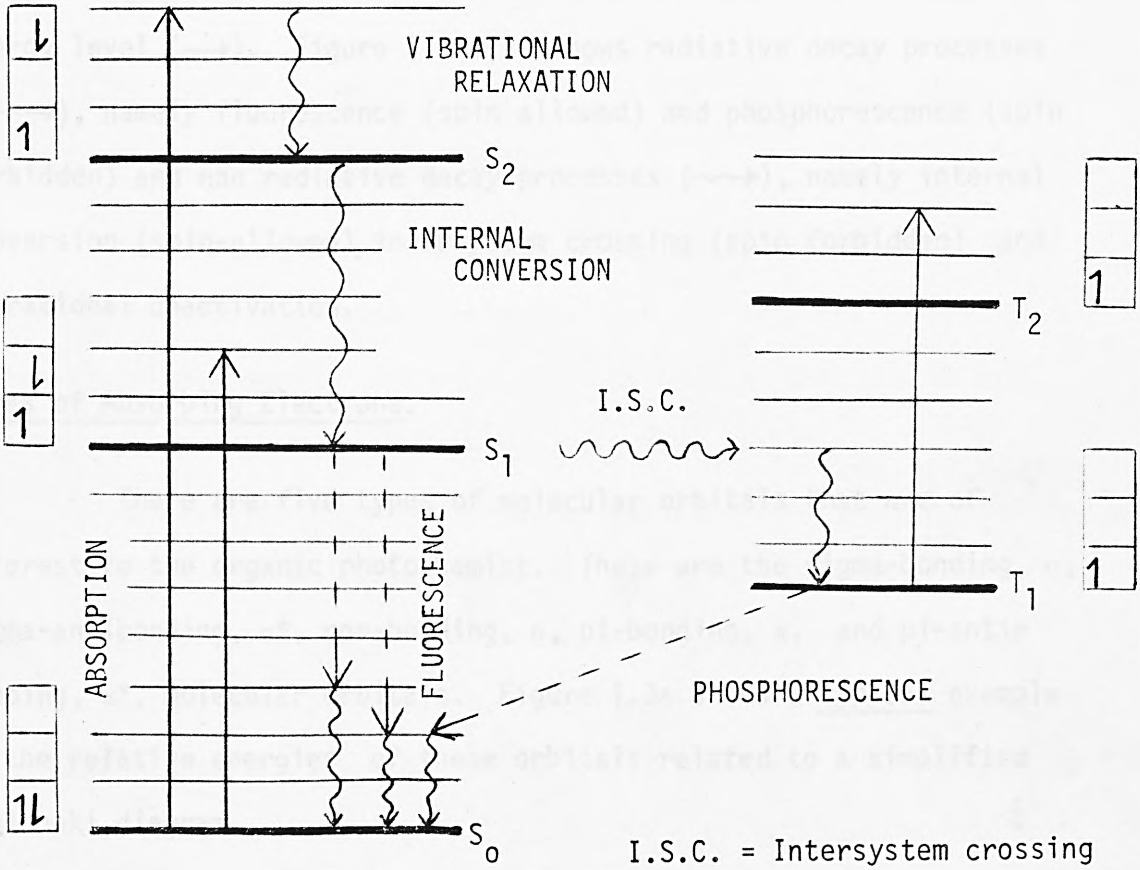


Figure 1.2. A Jablonski diagram.

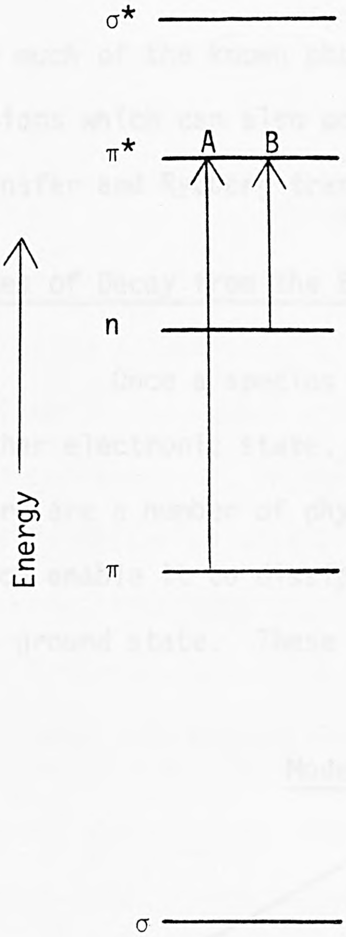
For the vast majority of organic molecules, the outer electrons will have all their spins paired in accordance with the Pauli Exclusion Principle, and so the ground state energy level must be a singlet state, S_0. Since selection rules determine that transitions in which there is a change in the electronic spin quantum number are spin forbidden, the absorption of radiation can only excite an electron from the ground singlet state to another singlet state, S_i (where $i = 1, 2, 3...n$).

However, if during excitation the electron spin were to invert, the excited state of the molecule would now be a triplet, T_i (where $i = 1, 2, 3...n$). Because this type of absorption is spin-forbidden and can only occur when the system is perturbed, Singlet - Triplet absorption bands are in general very much weaker than the corresponding Singlet - Singlet absorption bands.

Apart from the absorption of a photon by the ground state energy level (⟶), Figure 1.2 also shows radiative decay processes (- - - →), namely fluorescence (spin allowed) and phosphorescence (spin forbidden) and non radiative decay processes (⇝), namely internal conversion (spin-allowed), intersystem crossing (spin forbidden) and vibrational deactivation.

Types of Absorbing Electrons.

There are five types of molecular orbitals that are of interest to the organic photochemist. These are the sigma-bonding, σ, sigma-antibonding, σ^*, non-bonding, n, pi-bonding, π, and pi-antibonding, π^*, molecular orbitals. Figure 1.3a shows a typical example of the relative energies of these orbitals related to a simplified Jablonski diagram.



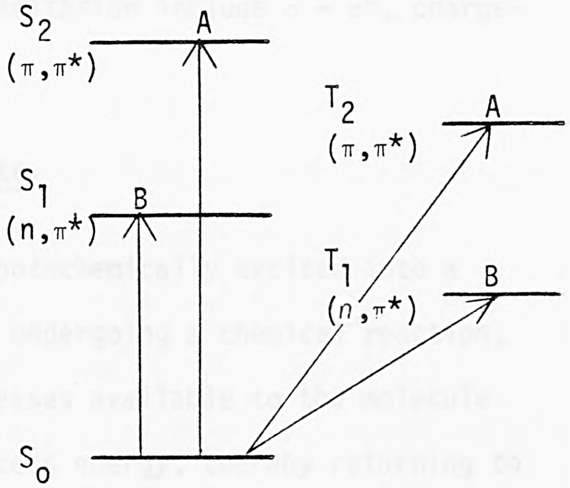


Figure 1.3a Typical example of the relative orbital energies.

Figure 1.3b Simplified Jablonski diagram.

The absorption of radiation in the ultra violet or visible region of the spectrum causes the transition of electrons present in either the sigma-bonding, non-bonding or pi-bonding orbitals of the chromophore involved to higher energy molecular orbitals.

The most common transitions encountered in organic molecules are: n → π*, π → π* and less frequently n → σ* transitions. For example the excitation of an electron from a non-bonding orbital, n, into a pi-antibonding orbital, π*, is called an n → π* transition, and the resulting excited state an n, π* state. Similarly, the movement of an electron from a pi-bonding orbital, π, to a pi-antibonding orbital, π*, is called a π → π* transition, and the resulting excited state a π, π* state. These two transitions and the resulting four states account for much of the known photochemistry of organic molecules. Other transitions which can also occur upon excitation include $\sigma \rightarrow \sigma^*$, charge-transfer and Rydberg transitions.

Modes of Decay from the Excited State.

Once a species has been photochemically excited into a higher electronic state, apart from undergoing a chemical reaction, there are a number of physical processes available to the molecule which enable it to dissipate its excess energy, thereby returning to the ground state. These are summarised in Figure 1.4.

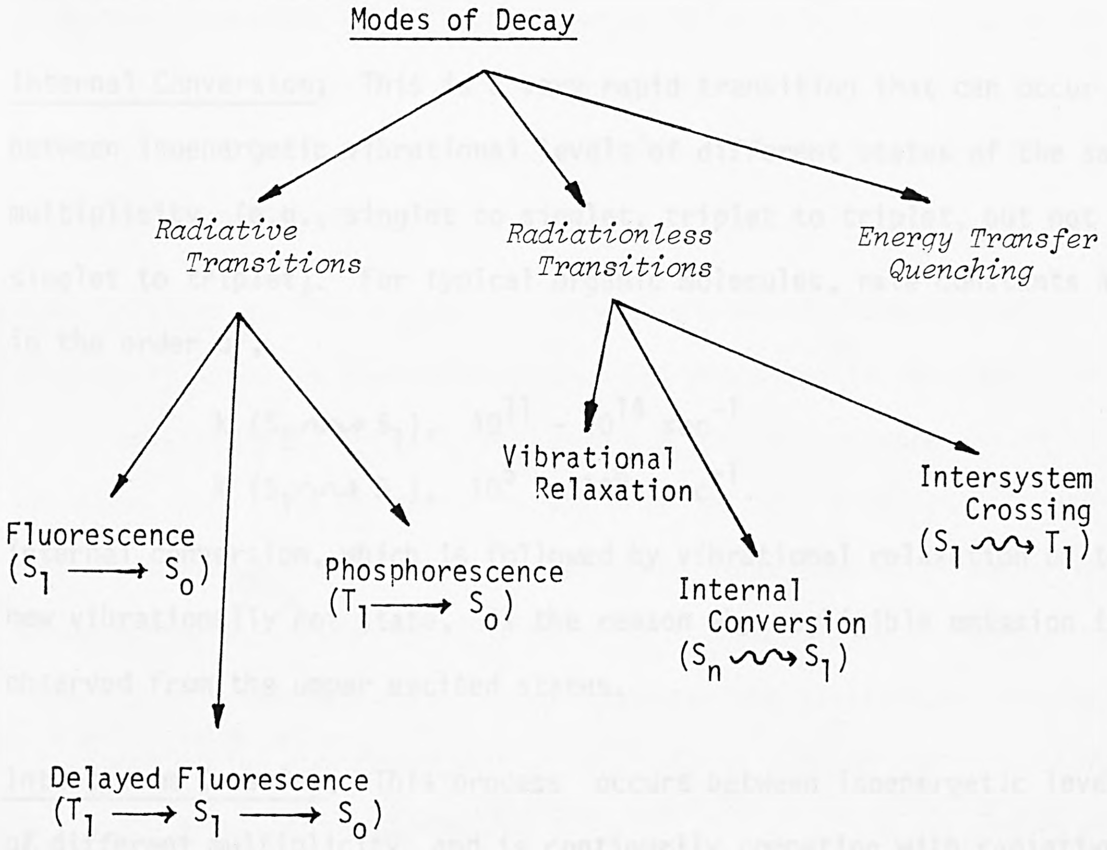


Figure 1.4. Possible pathways for the decay of an excited state species.

Radiationless Transitions

There are three radiationless transitions that the excited species may undergo:

Vibrational Relaxation; This involves the loss of excess vibrational energy by molecular collisions to yield the electronically excited species in its lowest vibrational level of the excited state. With rate constants, k, in the order of 10^{13} sec^{-1}, this process is usually faster by several orders of magnitude than the intramolecular processes involving transitions between electronic states, and hence most processes involving a change in electronic state take place from the lowest vibrational level.

Internal Conversion; This is a very rapid transition that can occur between isoenergetic vibrational levels of different states of the same multiplicity (e.g., singlet to singlet, triplet to triplet, but not singlet to triplet). For typical organic molecules, rate constants are in the order of,

$$k\ (S_2 \rightsquigarrow S_1),\quad 10^{11} - 10^{14}\ sec^{-1}$$
$$k\ (S_1 \rightsquigarrow S_0),\quad 10^{5} - 10^{8}\ sec^{-1}.$$

Internal conversion, which is followed by vibrational relaxation of the new vibrationally hot state, is the reason why negligible emission is observed from the upper excited states.

Intersystem Crossing; This process occurs between isoenergetic levels of different multiplicity, and is continually competing with radiative transitions. Rate constants, $k\ (S_1 \rightsquigarrow T_1)$, are in the order of $10^7 - 10^8$ sec^{-1}. Intersystem crossing, although strictly forbidden due to non conservation of spin, is the normal route for the population of the triplet manifold. It is considerably enhanced by the presence of halogen atoms either within the excited species, or the solvent - the so-called heavy atom effect.[6,7].

Radiative Transitions

In radiative transitions, the excited species returns to the electronic ground state with the emission of a photon.

Fluorescence; The transition between states of the same multiplicity is known as fluorescence. Kasha's rule[8] states that the light-emitting level of a given multiplicity is the lowest excited level of that multiplicity. This is reflected in the relatively large rate constants for the non radiative process, $S_2 \rightsquigarrow S_1$ compared with those for fluorescence - $S_1 \dashrightarrow S_0$, ca 10^7 - 10^9 sec^{-1}. Several exceptions to this rule have been established in which $S_2 \dashrightarrow S_0$ fluorescence can be observed,[9,10] but they are very few in number. Fluorescence is affected by solvent interactions, solvent pH, temperature and the presence of quenching species.

Phosphorescence; The transition between states of different multiplicity is known as phosphorescence. The processes in spin-forbidden and consequently $T_1 \dashrightarrow S_0$ or $T_n \dashrightarrow S_0$ phosphorescence is very uncommon, with rate constants in the order of 10^{-2} - 10^4 sec^{-1}. The long radiative life times of triplet states make them very susceptible to quenching by impurities, and hence it is normally very difficult to detect phosphorescence in solution. However the utilization of lasers to generate high concentrations of the triplet species now facilitates the study of phosphorescence.

Quenching of Excited Species

Another method by which the energy of a molecule in an electronically excited state can be lost is by the interaction of the excited species with a ground state atom or molecule in a quenching process. The two most important photophysical quenching mechanisms are self-quenching (or concentration quenching), and impurity quenching.

The Photochemical Reaction.

From the excited state, a chemical reaction can take place ranging from anything between a simple concerted formation of products to a complex process involving one or more reactive intermediates.

A photochemical reaction may be chronologically divided into three stages;

1. *The absorptive act* which produces the electronically excited state.
2. *The primary photochemical processes* which involve the electronically excited state.

and 3. *The secondary or 'dark' (thermal) reactions* of the various chemical species produced by the primary processes.

Since a photochemical reaction requires activation by light, (the absorptive act), a useful parameter in quantitative photochemistry is the relationship between the number of molecules of product formed and the number of photons absorbed per unit time. This is known as the quantum yield of product formation, $\phi_{product}$, and is a measure of the efficiency of photon usage. It is commonly expressed as,

$$\phi_{product} = \frac{\text{Number of molecules of product formed}}{\text{Number of photons of radiation absorbed.}}$$

In the same way, one can define the quantum yield of the reactant loss as,

$$\phi_{reactant} = \frac{\text{Number of reactant molecules which disappear}}{\text{Number of photons of radiation absorbed}}$$

The wavelength of light required to initiate a photochemical reaction will be dependent upon not only the presence of a particular chromophore within the molecule, but also the nature of the molecule in question. In organophosphorus photochemistry, in addition to the latter consideration, the oxidation state of the phosphorous atom will determine the type of transitions that the phosphorus chromophore may undergo.

Phosphine, alkyl phosphines and phosphites, and phosphorus halides have intense absorption bands in the 180 - 200 nm region corresponding to an $n \rightarrow \sigma^*$ transition of the nonbonding electrons on the phosphorus atom. The same $n \rightarrow \sigma^*$ transition in aryl phosphines such as triphenylphosphine occurs between 200 - 300nm. For pentacovalent organophosphorus compounds with $d_\pi - p_\pi$ bonding, the primary photochemical process can be either an $n \rightarrow \pi^*$ or a $\pi \rightarrow \pi^*$ transition, which occurs above 200nm. Photochemical reactions that involve these transitions, that is $n \rightarrow \sigma^*$, $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions, will nearly always result in a change of bonding at phosphorus; for example, cleavage of P-H, P-Cl, P-O, P-C and P-P bonds. In addition, photochemical processes in which the integrity of the phosphorus bonds remain unchanged may also occur through similar $n \rightarrow \sigma^*$, $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions occurring in other chromophores present in the molecule but not directly associated with the phosphorus functionality.

Preparative Organic Photochemistry.

Energy Sources.

In essence there are two basic designs that are most frequently used for carrying out photochemical reactions. The first design utilizes an external light source, while the other has the light source immersed in the solution being irradiated, the so called immersion lamps.

For synthesis involving excitation with light of wavelengths in the visible region of the spectrum, an external light source is commonly employed. Convenient sources of visible radiation are the conventional tungsten-halogen filament lamps and fluorescent lamps. For wavelengths in the ultraviolet region, the light sources most commonly employed are low -, medium -, or high-pressure mercury discharge lamps. These lamps generate high intensity light by passing an electrical current through a mixture of inert gas and mercury vapour contained in a small arc tube.

Low Pressure Mercury Arc Lamps: Low pressure arcs in which the mercury vapour is at about 10^{-3} torr emit primarily two bonds of radiation, centered predominantly (95%) at 253.7nm and to a much lesser extent at 184.9nm. These are often referred to as Germicidal lamps.

Medium Pressure Mercury Arc Lamps: Medium pressure arcs operate with mercury pressures in the region of 1 atmosphere, and with much higher currents. This has the effect that the initially formed excited states which would otherwise give rise to the low pressure resonance lines are further excited to even higher energy levels. Emission from these other states now gives rise to a multiplicity of pressure-broadened lines between 240nm and 580nm which are characteristic of this type of arc. Because of the high total radiant power, and the near line character of the emission spectra, these lamps are particularly suited for photochemical work when used in conjunction with monochromators and filters to select the desired wavelength.

High Pressure Mercury Arc Lamps: High pressure mercury arc lamps operate at very high pressures in the region of 100 - 400 atmospheres, and consequently the emission obtained from these lamps is almost a continuum. These lamps are often used when high intensity radiation is required.

Both the low-pressure and medium-pressure arcs may be obtained in the form of immersion lamps. The major advantage of immersion lamps is that the use of quartz reaction vessels is unecessary when carrying out photochemical work with radiation below 300nm.

Fluorescent Lamps: A fluorescent lamp consists of a low pressure mercury lamp with a fluorescent phosphor coated on the inside of the arc tube. In essence the lamp operates in the usual manner to a standard mercury arc, except that the 253.7nm radiation which is emitted is immediatly absorbed by the fluorescent phosphor, and reemitted as a continuous band of either ultraviolet or visible radiation depending upon the composition of the phosphor. Fluorescent lamps which reemit the 253.7nm radiation as a broad band between 320 and 380nm, with a λ_{max} at ca. 350nm are commonly known as 'black-light' fluorescent lamps.

Other metals, such as sodium, zinc or cadmium which have appreciable vapour pressure at relatively low temperatures may also be used in place of mercury in discharge lamps, with concomitant changes in the spectral output.

Apart from discharge lamps, electronically excited organic molecules can also be obtained by the use of ionizing radiation. Here the species on exposure to α-, β- or γ- radiation becomes ionized, and the ensuing recombination reactions generate excited states, often in high yields. Even more important is the ever increasing use of lasers to produce excited states. As lasers emit a powerful, high directional monochromatic and coherent beam of light, they are ideally suited for exciting a molecule from its ground state into a predetermined excited state, (ie. selective photochemical excitation). Consequently, lasers are extreemly useful in studying the photophysical properties and related chemical changes of excited molecules.

Sensitizers and Sensitization

Sensitizers enable the photochemical study of many compounds which contain either no chromophore, or a chromophore which is unsuitable for the absorption of radiation at a specific wavelength. Their function is to facilitate the input of energy into the system. They do this by absorbing the incoming radiation and subsequently via a molecular collision transfer this energy to a molecule in the system under investigation without themselves undergoing any permanent chemical change. This process in which the excited sensitizer collapses to its ground state and the acceptor molecule is promoted to an excited state is known as sensitization. The most commonly used sensitizers in photochemistry are the highly coloured dyes. These include the xanthenes (rose bengal, erythrosin, eosin, fluorescein), the thiazines (methylene blue), the porphyrins (chlorophyll, hematoporphyrin), and the porphines (tetraphenylporphine). Ideally the sensitizer should have a large molar absorption coefficient at the pertinent wavelength and a low tendency towards self-oxidation (reactions that cause dye bleaching). Further the energy of the relevant excited state of the sensitizer must be greater (usually be at least some 5 kcal mol^{-1}) than the relevant excited state of the acceptor molecule. As well as the choice of sensitizer, the importance of having the sensitizer present in a 'balanced concentration' is crucial to the success of a reaction. At low sensitizer concentrations, the dye cannot absorb all the useful light that is available while at high concentrations, it absorbs all the light at the parimeters of the reaction vessel, thereby filtering the bulk solution of the incoming radiation. In either case, a decrease in the efficiency of the reaction is observed.

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TWO

A REVIEW ON ORGANOPHOSPHORUS PHOTOCHEMISTRY

Introduction.

The photochemistry of organophosphorus compounds has received little attention in the literature. In 1967, Halmann[1] reviewed the photochemical and radiation reactions of phosphorus, while Cadogan,[2] Bentrude[3] and Roberts[4] have each reviewed the chemistry of phosphorus radicals, devoting some attention to photochemically induced phosphorus radicals. A review by Tomioka[5] on the photochemical reactions of organophosphorus compounds appeared in the Japanese literature in 1976. General photochemical reports relating to phosphorus compounds were summarised annually by Davidson[6] for the period 1970 to 1977. Two reviews have appeared on the synthesis of organophosphorus compounds by radiation.[7,8]

Phosphines, Halophosphines and Related Compounds.

The earliest studies on the photochemistry of phosphorus compounds concerned the investigation of compounds containing a phosphorus hydrogen or a phosphorus halogen bond.

The photochemical decomposition of phosphine has been shown to produce hydrogen gas and red phosphorus,[9,10] in which the primary process is believed to be the dissociation to the phosphino ($\cdot PH_2$) and hydrogen ($H\cdot$) radicals.[11] Cleavage of the P-H bond has been shown in comparative studies with deuterophosphine[12,13] to be a rate controlling step in the reaction. The presence of the phosphino radical, phosphinidene radical ($:\ddot{P}H$) and dimeric phosphorus species (P_2) were reported in the flash photolysis of phosphine,[10] these being transient intermediates in its stepwise conversion to hydrogen and red phosphorus. The possibility of the phosphinidene radical has also been noted by Sam and Yardley,[14] and DiStefano et. al.[15] reported its detection by interpretation of infrared transmission bands. Ferris and Benson[16,17] and Blazejowski[13] have all reported the formation of the dimeric product P_2H_4 on photolysis. The flash photolysis of phosphine has enabled the absorption spectra of the $\cdot PH_2$ radical to be obtained,[18] and more recently its fluoresence has been studied.[19] The tetrafluorosilane photosensitized decomposition of phosphine and phosphine-silane mixtures has been reported.[20]

The synthetic use of addition reactions of compounds containing P-H bonds is well recognised.[21] Many examples have been reported of the photoinduced cleavage of P-H bonds to give phosphorus radicals, and their addition to olefins. These are summarised in Table 2.1. The addition of the phosphino radical is believed to proceed via a radical chain mechanism. However the formation of cis-2-butene in the reaction with trans-2-butene indicates that the addition of the radical is reversible.[28] A similar isomerisation has been reported for the non-photochemical addition of phosphino radicals to olefins.[33] Several synthetic applications for the addition of dialkylphosphino radicals to olefins have been reported.[34,35]

Table 2.1. Addition of phosphino radicals to olefins

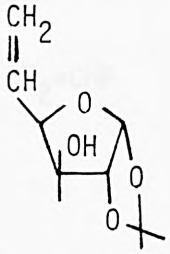
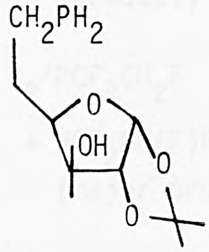
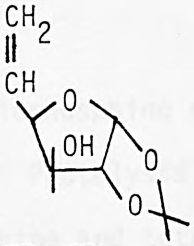
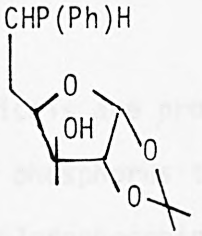
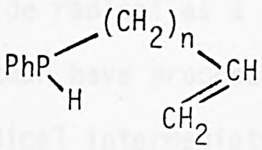
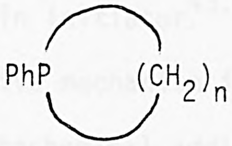
Phosphorus compound	Olefin	Product(s)	Reference
PH_3	$R_2C=CR_2$	$(R_2CHCR_2)_nPH_{3-n}$	22
			23
	$F_2C=CR_2$ (R=H,F)	$HF_2CCR_2PH_2$	24
	$F_2C=CHF$	$F_2C(PH_2)CH_2F$ + $HF_2CCH(F)PH_2$ (major product)	25
	$CF_3CF=CF_2$	$CF_3CHFCF_2PH_2$ (major product) + $CF_3CF(PH_2)CHF_2$	24,25
	$H_2C=C=CH_2$	$CH_3\text{-}C(PH_2)=CH_2$	26
$R'PH_2$	$RCH=CH_2$	$(RCH_2CH_2)_nPR'H_{2-n}$	22
$H_2PCH_2CH=CH_2$		$H_2P(CH_2)_3P(H)CH_2CH=CH_2$	27
$PhPH_2$			23
$R_2'PH$ ($R'=CH_3$, CF_3)	$CR_2=CR_2$ (R=H,F)	$R_2'PCR_2\text{-}CHR_2$	28

Table 2.1. continued.

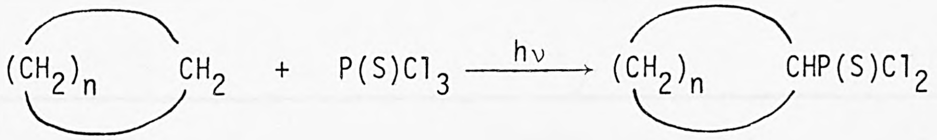
Phosphorus compound	Olefin	Product(s)	Reference
$R_2'PH$ ($R' = CH_3, CF_3$)	$FC(R)=CH_2$ (R=H,F)	$H_2C(R)CH_2PR_2'$ (only or major product)	29
	$CF_2=CHF$	$R_2'PCF_2CH_2F$ + $HCF_2CH(F)PR_2'$ (major product)	30
	$CH_3CH=CH_2$	$CH_3CH_2CH_2PR_2'$	28,29
$(CH_3)_2PH$	$CH_3CH\overset{t}{=}CHCH_3$	$CH_3CHP(CH_3)_2\dot{C}HCH_3$ $CH_3CH\overset{c}{=}CHCH_3$ $CH_3P(CH_3)_2CHCH_2CH_3$	28
 n = 2,3,4			31
$Ph_2P(S)H$	$CH_2=CHCN$	$Ph_2P(S)CH_2CH_2CN$	32
$EtP(CF_3)_2$	$H_2C=CH_2$	$Et(CF_3)_2PCH_2CH_2CF_3$	29

Similarly halophosphino radicals are produced when halophosphines are irradiated. Photolysis of phosphorus trichloride gives both the dichlorophosphine and tetrachlorophosphine radicals[36-38] which were examined by electron spin resonance (esr) spectroscopy, while the chlorophosphinidene radical ($\underset{\cdot\cdot}{\ddot{P}}Cl$) has also been identified.[39]

$$PCl_3 \xrightarrow{h\nu} Cl_2P\cdot + \cdot Cl$$

$$PCl_3 + \cdot Cl \longrightarrow Cl_4P\cdot$$

With dichloromethylphosphine, a four coordinate species of the type $(CH_3)_nPCl_{4-n}$ where n maybe 1 or 2 was observed.[36,37] The flash photolysis of phosphorus tribromide has been shown to produce the bromophosphinidene radical ($\ddot{\underset{\cdot\cdot}{P}}Br$).[40] Semi-stable phosphino radicals with half lives of upto one year have been produced from the photoysis of sterically crowded P(III) monochloro compounds {eg. $((Me_3Si)_2CH)_2PCl$ and $(Me_3Si)_2CHP(NMe_2)Cl$}, and studied by esr spectroscopy.[41] Unlike the $H_2P\cdot$ radical, the addition of halophosphino radicals to olefins produces the Anti-Markovnikoff type addition product as the major isomer isolated,[42-45] Table 2.2. This has been explained by proposing the halide radical as a competing chain initiator.[43,45,46] However Little and Hartman have proposed an alternative mechanism involving a bridged PCl_2 radical intermediate.[42] The photochemical addition of the dibromophosphino radical to other carbon carbon multiple bonds has also been reported.[46,47] The UV-initiated reaction of thiophosphoryl chloride with cycloalkanes to give cycloalkyldichlorophosphonothionates has been reported.[48]

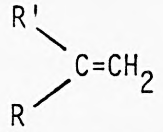


n = 4,5,7

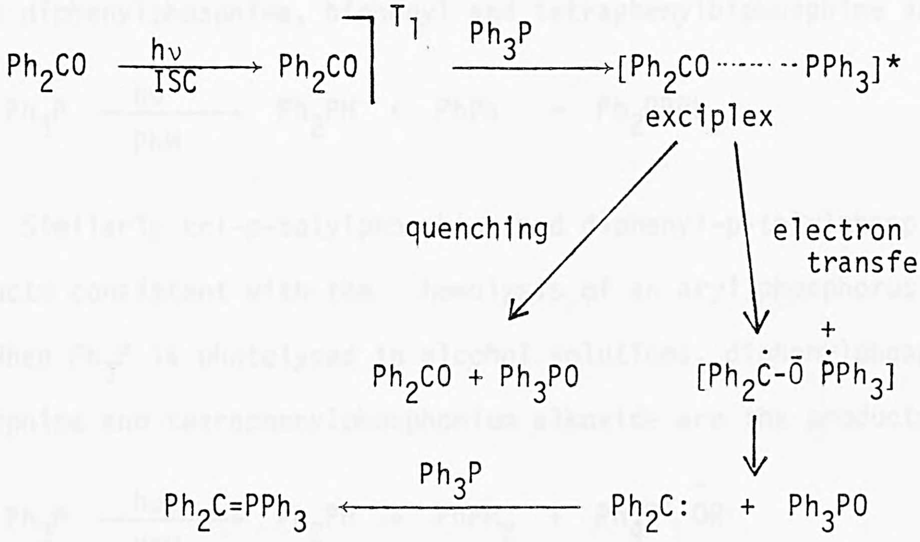
The photocleavage of the P-P bond in tetrafluorobiphosphine to give the difluorophosphinyl radical has been reported,[49] and the subsequent addition of such radicals to olefins[50,51] is summarised in Table 2.3.

Triphenylphosphine has been found to quench the excited

Table 2.2. Addition of halophosphino radicals to carbon carbon multiple bonds.

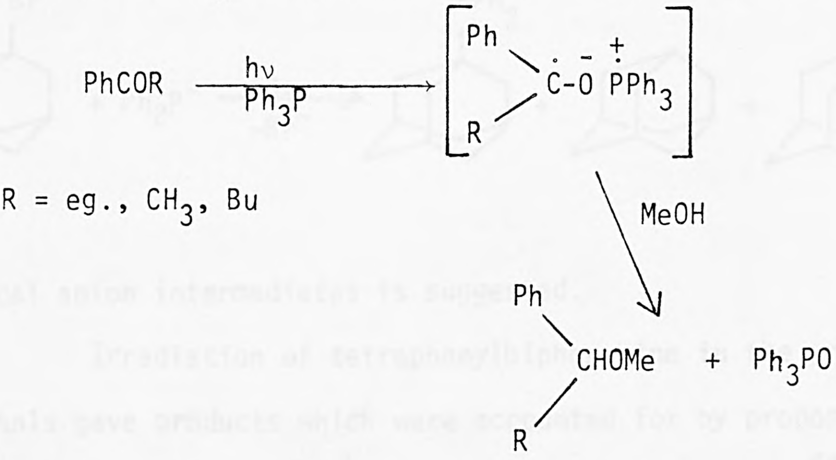
Phosphorus compound	Olefin	Product(s)	Reference
PCl_3	 $(R'=R=CH_3)$ $(R'=H, R=C_5H_{11}, C_6H_{13})$	$R(R')CClCH_2PCl_2$ $+ R(R')C(PCl_2)CH_2Cl$ (major product)	42,43
PBr_3	$RCH=CH_2$ $(R=CH_3, C_5H_{11})$	$RCHBrCH_2PBr_2$ + $RCH(PBr_2)CH_2Br$ (major product)	43
	$CH_2=CHCH_2X$ $(X=Cl, Br)$	$BrCH_2CH(PBr_2)CH_2X$	44
	$PhCH=CH_2$	$BrCH_2CH(PBr_2)Ph$	45
	$CH_2=C=CH_2$	$CH_2=C(Br)CH_2PBr_2$	46
$Br_2PCR=CHBr$	$R'C\equiv CH$	$BrCH=CHRP(Br)CR=CHBr$	47

singlet states of anthracene and its derivatives,[52-54] fluorenone and biacetyl.[52] The quenching action can be attributed to exciplex formation for which the participation of the lone pair of electrons on phosphorus is required. Similarly triphenylphosphine has been found to quench the excited triplet state of benzophenone.[52] By irradiating benzophenone in the presence of triphenylphosphine, deoxygenation of the carbonyl group occurs with formation of diphenylmethylene. This may then react with a second phosphine molecule to give a phosphorus ylid.[55,56] The formation of other phosphorus ylids



from the U.V. irradiation of diaryl and aryl alkyl ketones in the presence of Ph_3P has also been reported.[56]

The photolysis of phenyl alkyl ketones in methanol containing Ph_3P gives in addition to the expected Norrish Type II products, Ph_3PO and 1-phenyl-1-methoxyalkanes.[57] The triplet state of the ketones are quenched by Ph_3P to give the zwitter ion which forms the observed



R = eg., CH_3, Bu

products via solvent incorporation.

The photolysis of triphenylphosphine results in the initial dissociation to phenyl and diphenylphosphino radicals.[58-60] This

$$Ph_3P \xrightarrow{h\nu} Ph\cdot + Ph_2P\cdot$$

dissociation is believed to occur from the triplet state.[61] The $Ph_2P\cdot$ radical has been observed by e.s.r. from the photolysis of Ph_3P.[62] In benzene diphenylphosphine, biphenyl and tetraphenylbiphosphine are

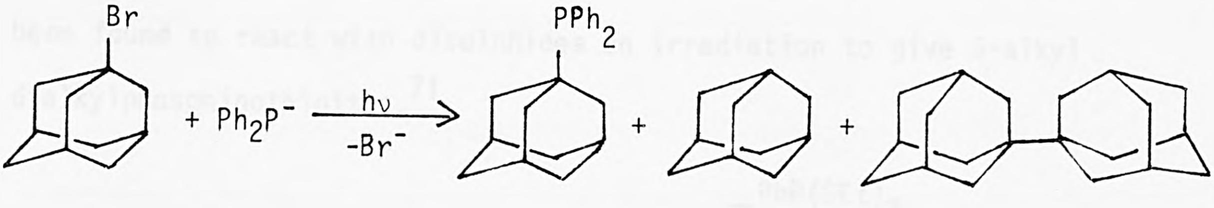
$$Ph_3P \xrightarrow[PhH]{h\nu} Ph_2PH + PhPh + Ph_2PPPh_2$$

formed.[60] Similarly tri-p-tolylphosphine and diphenyl-p-tolylphospine give products consistent with the homolysis of an aryl phosphorus bond.[60] When Ph_3P is photolysed in alcohol solutions, diphenylphosphine, phenylphosphine and tetraphenylphosphonium alkoxide are the products

$$Ph_3P \xrightarrow[ROH]{h\nu} Ph_2PH + PhPH_2 + Ph_4P^+ \bar{O}R$$

obtained.[58]

The photoreaction of 1-bromoadamantane with diphenylphosphide in liquid ammonia is reported to give good yields of the substitution product, together with small amounts of adamantane and 1,1'-biadamantyl.[63] A nucleophilic substitution mechanism involving radical and



radical anion intermediates is suggested.

Irradiation of tetraphenylbiphosphine in the presence of alcohols gave products which were accounted for by proposing the generation of the $Ph_2P\cdot$ radical from P-P bond homolysis.[64,65] Subsequently the $Ph_2P\cdot$ radical was observed by e.s.r from the photolysis

$$Ph_2PPPh_2 \xrightarrow[ROH]{h\nu} Ph_2PH + Ph_2POR$$

of the biphosphine in benzene.[66] Okazaki et. al. has examined the photoreaction of the biphosphine with benzophenone.[67] A mechanism

$$Ph_2PPPh_2 + Ph_2CO \xrightarrow[S_8]{h\nu} Ph_2C{=}CPh_2 + Ph_2C{=}S$$
$$+ Ph_2P(O)CHPh_2 + Ph_2P(O)OH$$

involving metathesis of the P-P bond by n-π* triplet benzophenone was suggested.

Irradiation of biphosphine disulphides and dioxides in the presence of oxygen gave products derived from initial cleavage of the P-P bond.[68] When tetraphenylbiphosphine disulphide is irradiated in

$$Ph_2P(S)P(S)Ph_2 \xrightarrow[MeOH]{h\nu} Ph_2P(S)H + Ph_2P(S)OMe$$

the presence of methanol, diphenylphosphine sulphide and O-methyl diphenylphosphinothioate are obtained.[68]

Similarly the photolysis of tetramethylbiphosphine and tetrakis(trifluoromethyl)biphosphine results in P-P bond cleavage.[30,69,70] In the presence of olefins, products arising from radical addition are obtained, Table 2.3. Tetraalkylbiphosphines have been found to react with disulphides on irradiation to give S-alkyl dialkylphosphinothioites.[71]

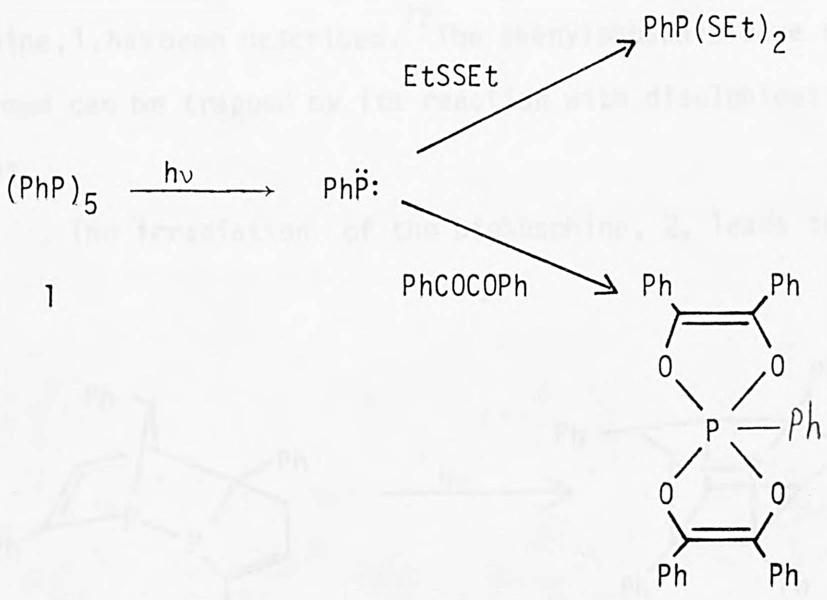
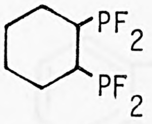
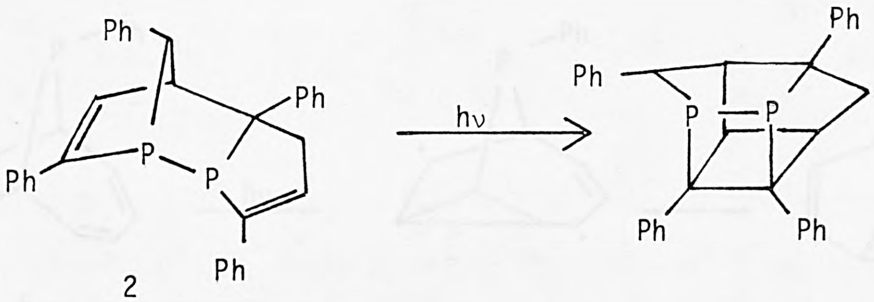


Table 2.3. Formation of phosphino radicals from biphosphines and their addition to olefins.

Phosphorus compounds	Olefin	Product	Reference
$F_2P\text{-}PF_2$	$CH_2{=}CH_2$	$F_2PCH_2CH_2PF_2$	50,51
	$CH_3CH{=}CHR$ $(R{=}H,CH_3)$	$CH_3CH(PF_2)CH(PF_2)R$	51
			51
$Me_2P\text{-}PMe_2$	$CF_2{=}CHF$	$Me_2PCF_2CHFPMe_2$	30
	$CH_2{=}CH_2$	$Me_2PCH_2CH_2PMe_2$	69
	$CF_2{=}CF_2$	$Me_2PCF_2CF_2PMe_2$	70
$(CF_3)_2P\text{-}P(CF_3)_2$	$CF_2{=}CF_2$	$(CF_3)_2PCF_2CF_2P(CF_3)_2$	69

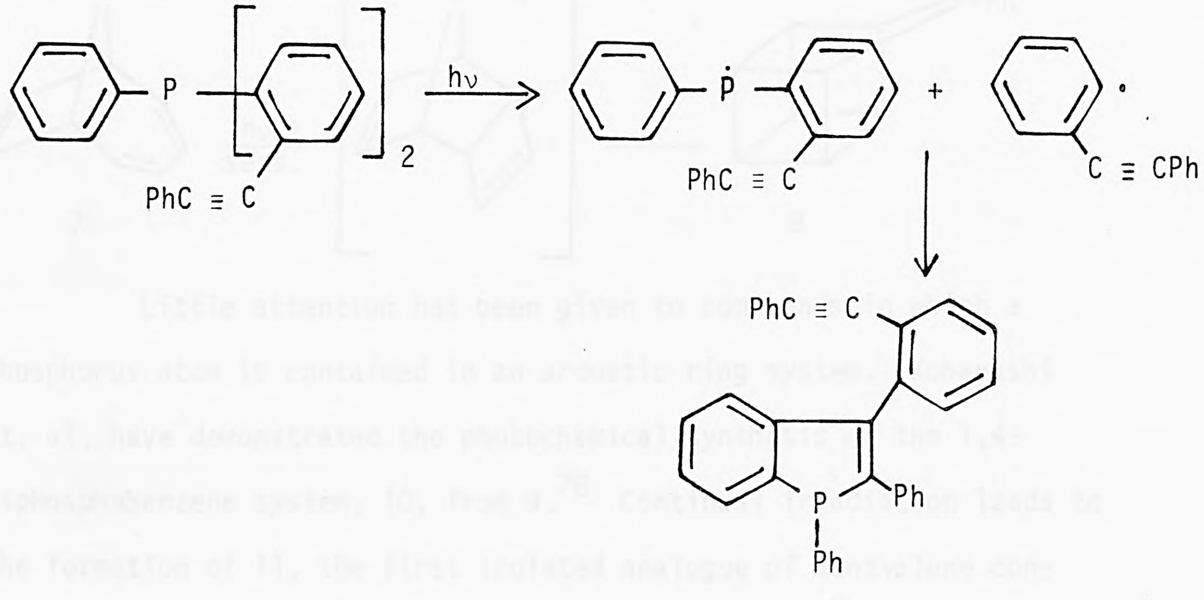
The photochemical decomposition of pentaphenylcyclopentaphosphine, 1, has been described.[72] The phenylphosphinidene radical that is formed can be trapped by its reaction with disulphides and α-diketones.

The irradiation of the biphosphine, 2, leads to cyclization.[73]



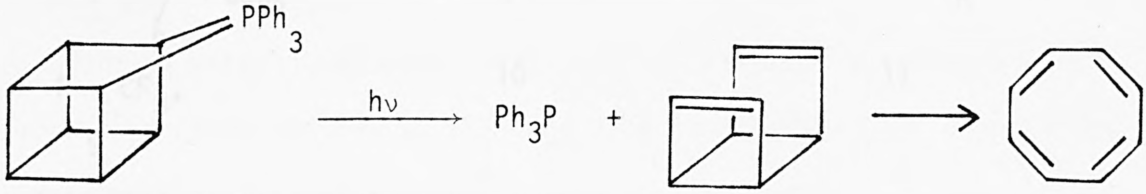
2

Winter has reported a photochemical cyclization of bis-{(O-phenylethynyl)phenyl}phenylphosphine to give 3, in which aryl phosphorus bond cleavage was proposed as the primary chemical process.[74]



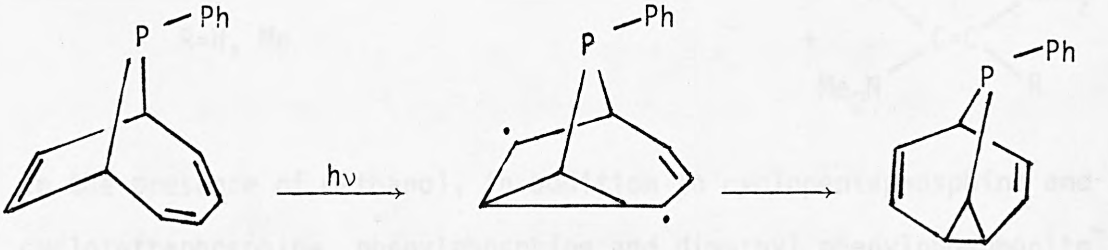
3

Irradiation of the quinquecovalent phosphine, 4, results in the elimination of triphenylphosphine.[75]



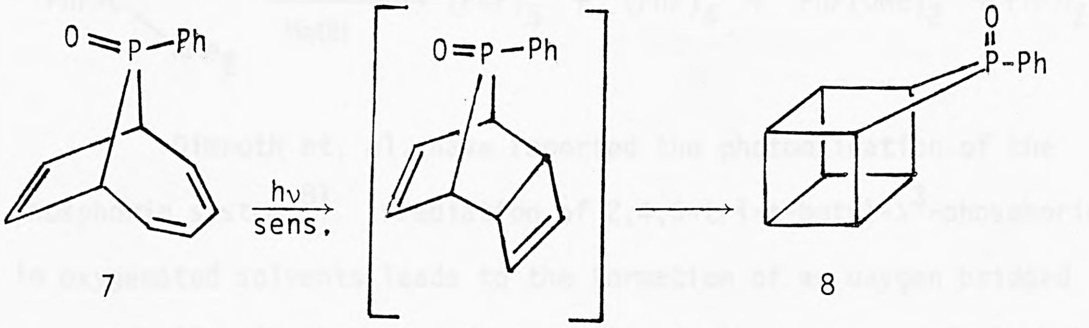
4

The direct irradiation of the phosphine 5 yields 6 via a di-π-methane rearrangement.[76]



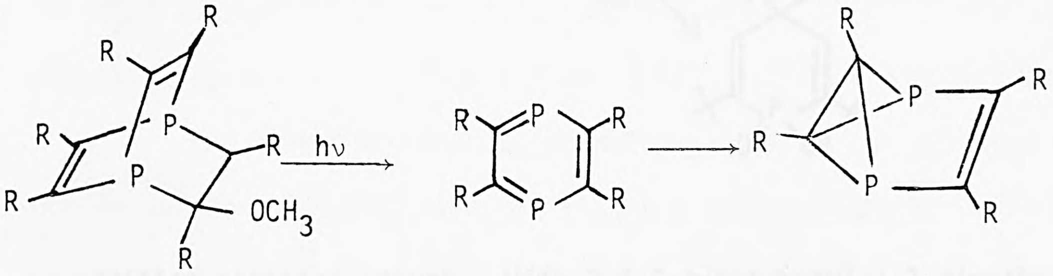
5 6

The triplet sensitized photolysis of 7 forms the phosphine oxide 8.[76,77]



7 8

Little attention has been given to compounds in which a phosphorus atom is contained in an aromatic ring system. Kobayashi et. al. have demonstrated the photochemical synthesis of the 1,4-diphosphabenzene system, 10, from 9.[78] Continual irradiation leads to the formation of 11, the first isolated analogue of benzvalene con-

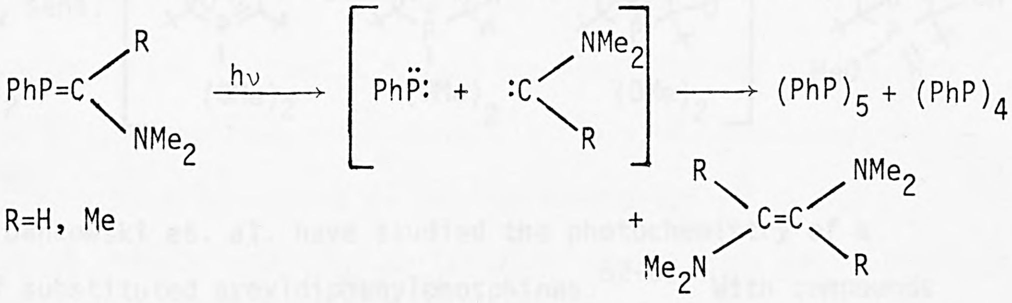


R = CF$_3$, 10 11

9

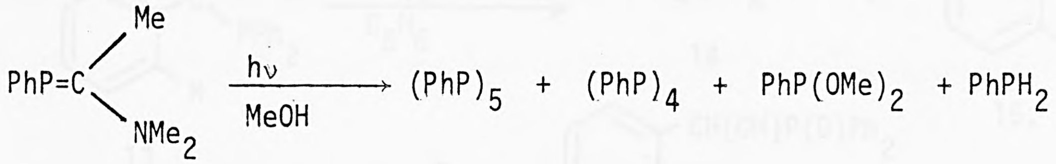
taining heteroatoms in its ring system.

The photolysis of phosphaalkenes has been studied and found to result in the formation of the phosphinidene and carbene species.[79,80]

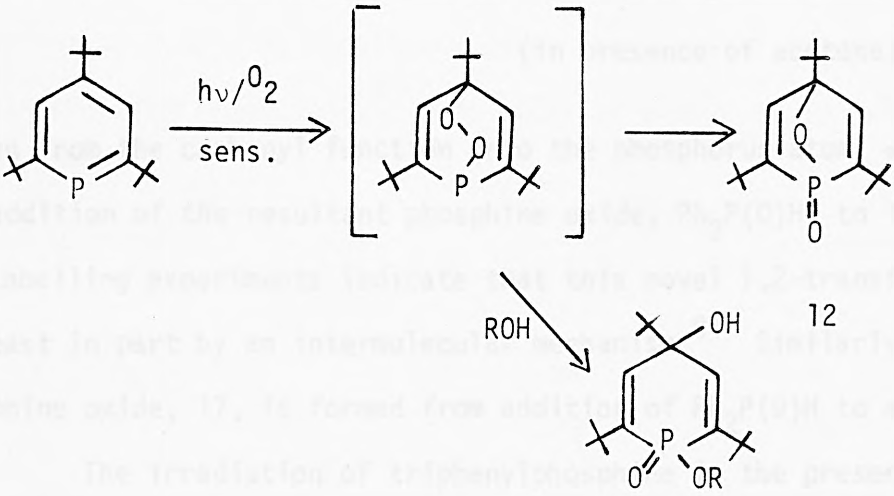


R=H, Me

In the presence of methanol, in addition to cyclopentaphosphine and cyclotetraphosphine, phenylphosphine and dimethyl phenylphosphonite are also obtained from the phenylphosphinidene radical.

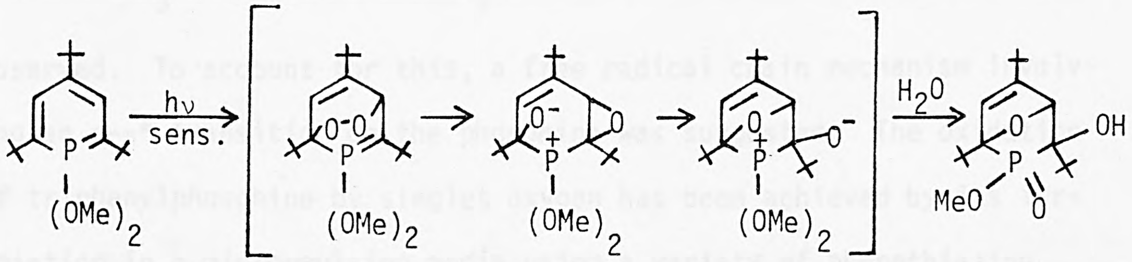

$$\mathrm{PhP{=}C(Me)(NMe_2)} \xrightarrow[\mathrm{MeOH}]{h\nu} (\mathrm{PhP})_5 + (\mathrm{PhP})_4 + \mathrm{PhP(OMe)_2} + \mathrm{PhPH_2}$$

Dimroth et. al. have reported the photooxidation of the phosphorin system.[81] Irradiation of 2,4,6-tri-t-butyl-λ^3-phosphorin in oxygenated solvents leads to the formation of an oxygen bridged compound, 12, via the 1,4-endoperoxide. In the presence of alcohols,

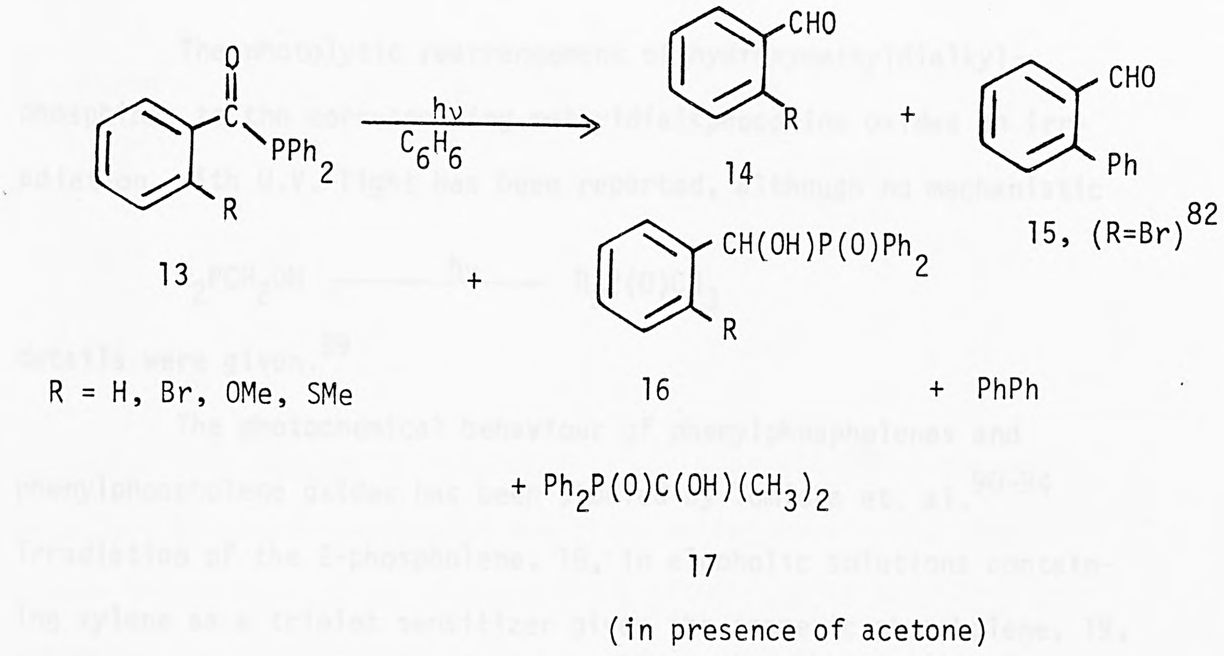


12

an addition reaction occurs. With 2,4,6-tri-t-butyl-1,1-dimethoxy-λ^5-phosphorin cycloaddition to the ring is also observed, but without the involvement of the heteroatom.[81]



Dankowski et. al. have studied the photochemistry of a variety of substituted aroyldiphenylphosphines.[82-85] With compounds of the type 13, α-cleavage and photosubstitution products are isolated. The formation of 16 is explained by the photoinduced 1,2-transfer of



oxygen from the carbonyl function onto the phosphorus atom, α-cleavage, and addition of the resultant phosphine oxide, $Ph_2P(O)H$, to 14. ^{18}O-Labelling experiments indicate that this novel 1,2-transfer occurs at least in part by an intermolecular mechanism.[84] Similarly the phosphine oxide, 17, is formed from addition of $Ph_2P(O)H$ to acetone.[83-85]

The irradiation of triphenylphosphine in the presence of oxygen has been briefly reported to yield triphenylphosphine oxide.[58,60] Geoffroy et. al.[86] have investigated the photooxidation of this and other phosphines. In all cases a quantum yield efficiency of >3 was

$$R_3P \xrightarrow{h\nu/O_2} R_3PO$$

observed. To account for this, a free radical chain mechanism involving an n-π* transition on the phosphine was suggested. The oxidation of triphenylphosphine by singlet oxygen has been achieved by its irradiation in a microemulsion media using a variety of phenothiazine catalysts.[87] Similarly singlet oxygen has been proposed as the oxidizing agent in the conversion of triphenylphosphine selenide to triphenylphosphine oxide.[88]

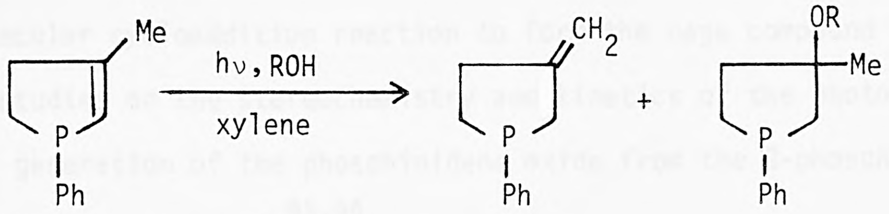
$$Ph_3PSe \xrightarrow[\text{sensitizer}]{h\nu/\ O_2} Ph_3PO + Se$$

The photolytic rearrangement of hydroxymethyldialkylphosphines to the corresponding methyldialkphosphine oxides on irradiation with U.V. light has been reported, although no mechanistic

$$R_2PCH_2OH \xrightarrow{h\nu} R_2P(O)CH_3$$

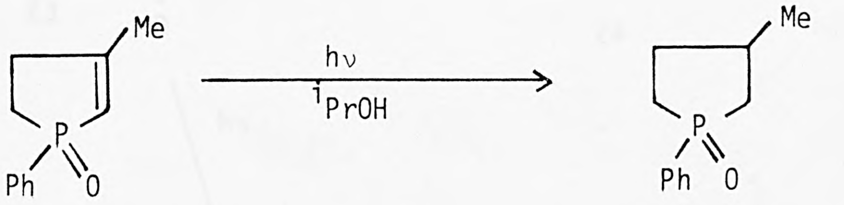
details were given.[89]

The photochemical behaviour of phenylphospholenes and phenylphospholene oxides has been studied by Tomioka et. al.[90-94] Irradiation of the 2-phospholene, 18, in alcoholic solutions containing xylene as a triplet sensitizer gives the isomeric phospholene, 19, and the addition product 20.[90] The relative yields of 19 and 20 are



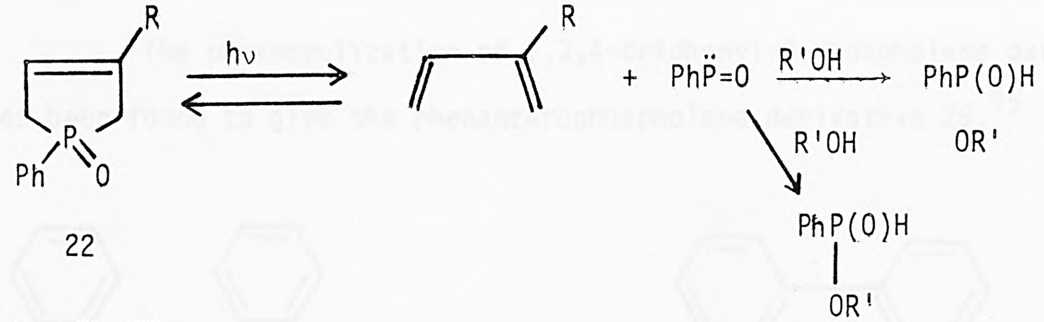
18 19 20

dependent upon the alcohol used. Thus t-butanol, by comparison with methanol favours 19. In contrast, irradiation of isomeric 1-phenyl-3-methyl-3-phospholene does not give rise to photoisomerization or photoaddition products. Photolysis of the analagous 2-phospholene oxide 21 gave only reduction products on irradiation in protic solvents.



21

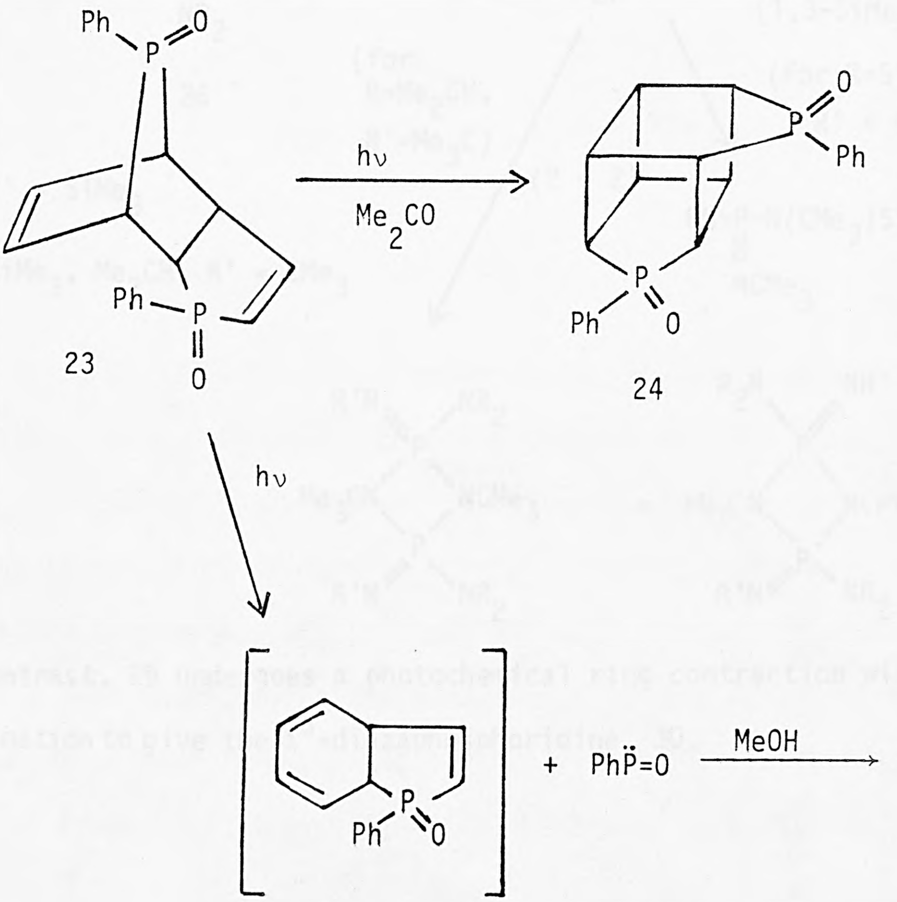
The 3-phospholene oxide 22 gives on irradiation the diene and phosphinidene oxide.[91] The latter species can be trapped with alcohols to give the corresponding phosphinate. From the observation that the reaction



22

R = H, CH_3

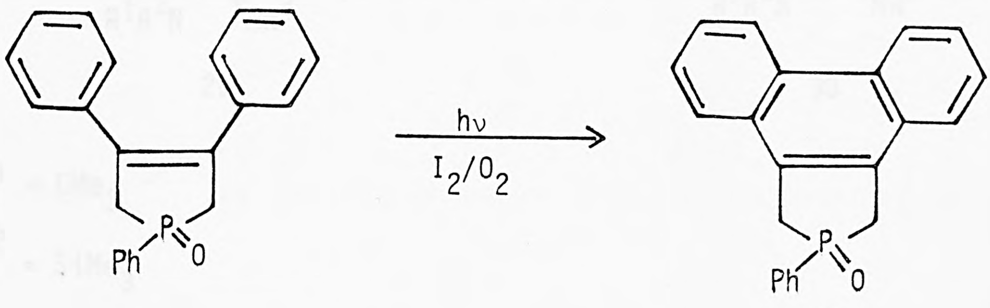
proceeded less readily in t-butanol it was suggested that the phosphinidene oxide can react with the diene to regenerate 22. The direct irradiation of the 3-phospholene oxide 23 also gives the phosphinidene oxide, which can again be trapped if methanol is used as the solvent.[92] On acetone sensitized irradiation, 23 undergoes an intramolecular cycloaddition reaction to form the cage compound 24. Further studies on the stereochemistry and kinetics of the photochemical generation of the phosphinidene oxide from the 3-phospholene system have been reported.[93,94]



23

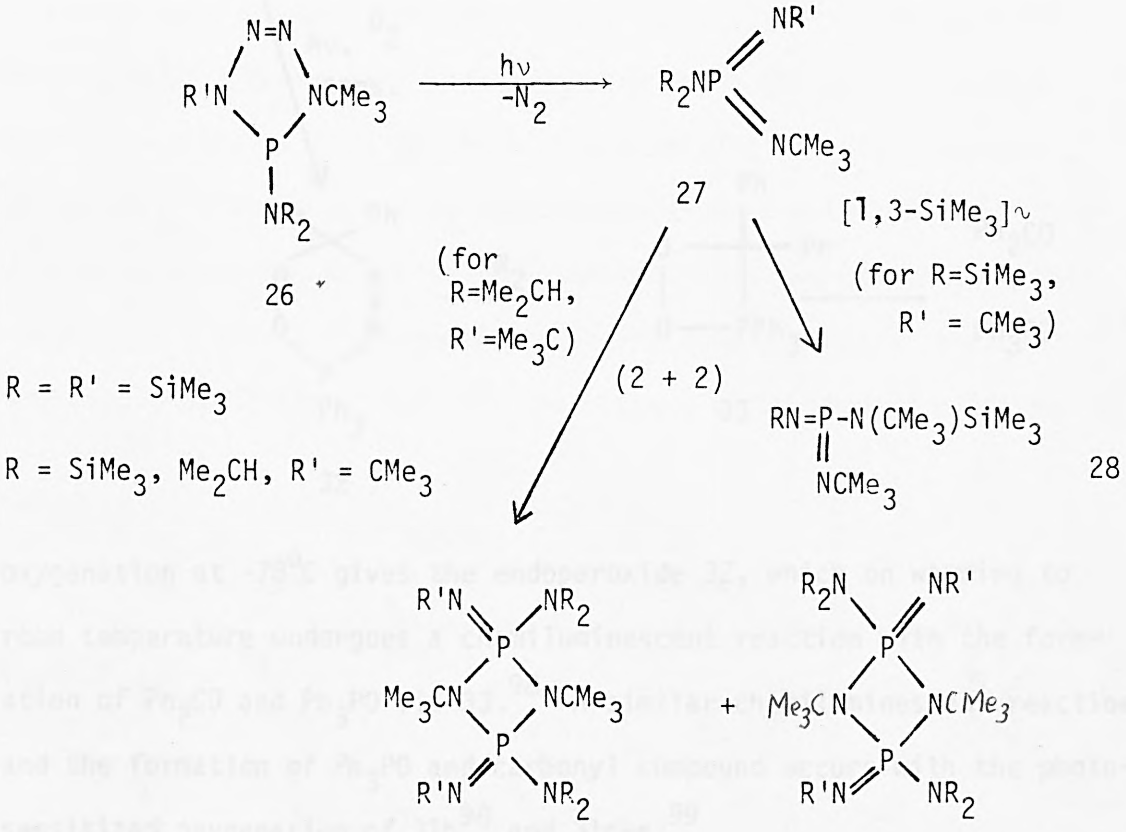
24

The photocyclization of 1,3,4-triphenyl-3-phospholene oxide has been found to give the phenanthrophospholene derivative 25.[95]

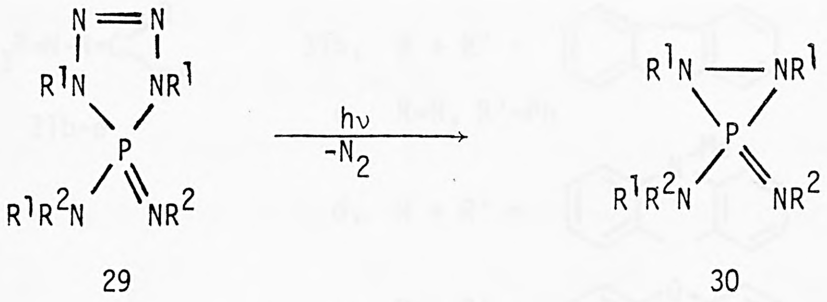


25

λ^3-Tetrazaphospholenes 26 decompose via nitrogen elimination to form the diaminophosphoranes 27 (and 28 for $R=SiMe_3$, $R'={}^tBu$ - from isomerisation by $SiMe_3$ migration in 27).[96] With 27 (for $R=Me_2CH$, $R'={}^tBu$), this can only be captured as its (2+2)-cyloaddition product.



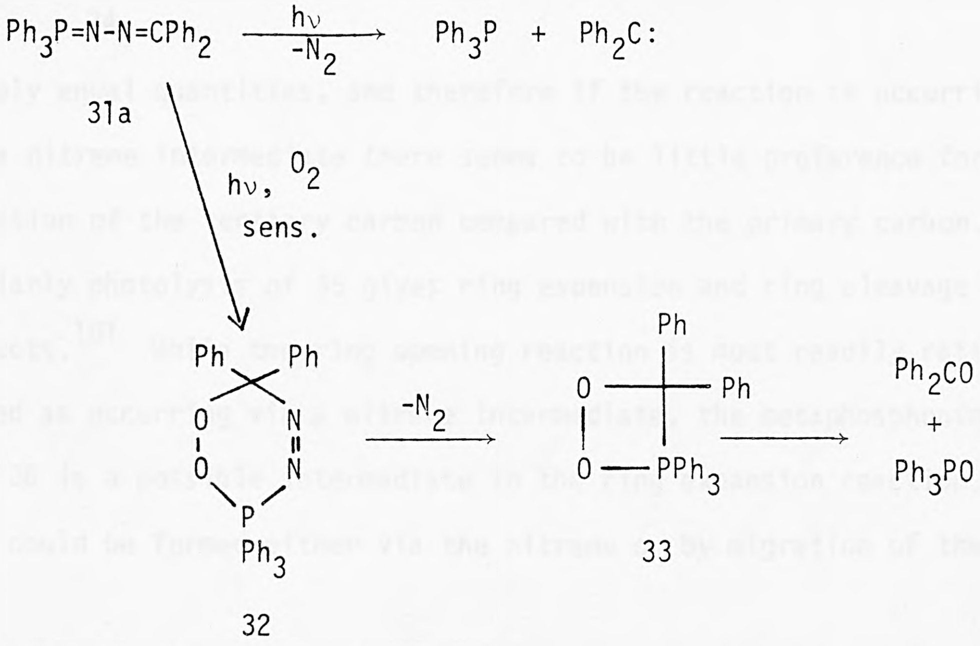
In contrast, 29 undergoes a photochemical ring contraction with nitrogen elimination to give the λ^5-diazaphosphoridine, 30.



R^1 = CMe_3

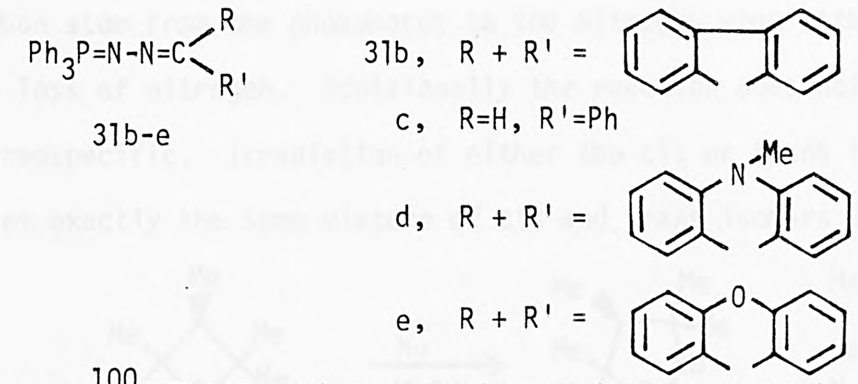
R^2 = $SiMe_3$

Irradiation of the phosphazine 31a leads to elimination of nitrogen with formation of diphenylmethylene.[97] Its photosensitized

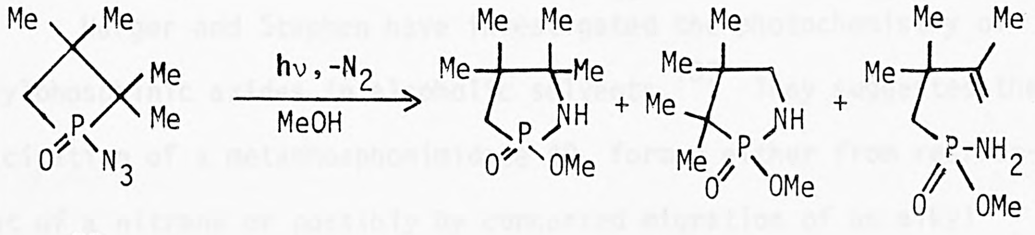


oxygenation at -78°C gives the endoperoxide 32, which on warming to room temperature undergoes a chemiluminescent reaction with the formation of Ph_2CO and Ph_3PO via 33.[98] A similar chemiluminescent reaction and the formation of Ph_3PO and carbonyl compound occurs with the photosensitized oxygenation of 31b[98] and 31c-e.[99]

The photochemical behaviour of a variety of azidophosphorus compounds has been investigated. Photolysis of the azidophosphetan oxide 34 gave products resulting from both ring expansion and ring

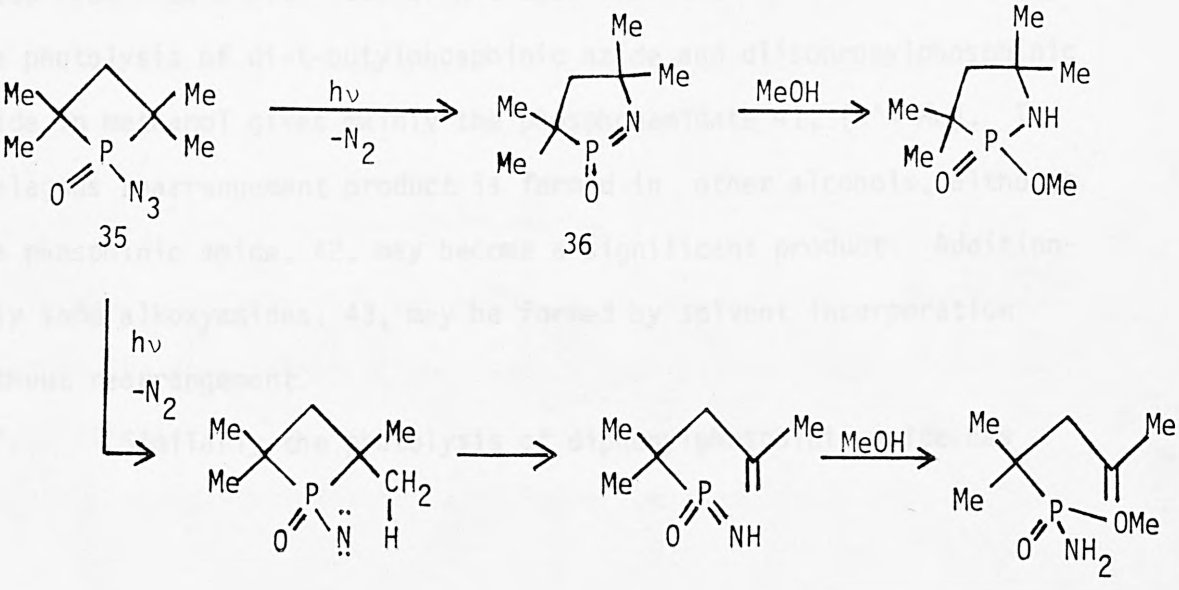


cleavage.[100] The two ring expansion products are obtained in approx-

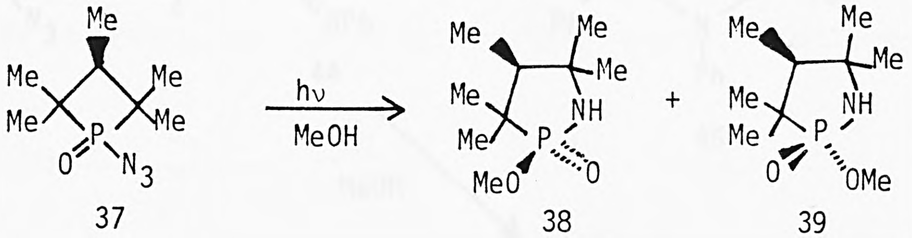


34

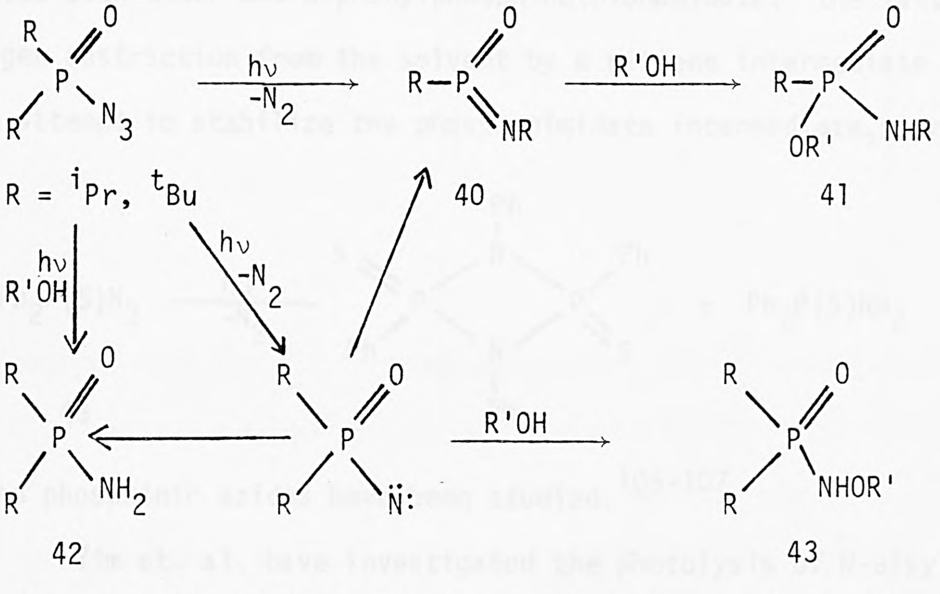
imately equal quantities, and therefore if the reaction is occurring via a nitrene intermediate there seems to be little preference for migration of the tertiary carbon compared with the primary carbon. Similarly photolysis of 35 gives ring expansion and ring cleavage products.[101] While the ring opening reaction is most readily rationalized as occurring via a nitrene intermediate, the metaphosphonimidate 36 is a possible intermediate in the ring expansion reaction. This could be formed either via the nitrene or by migration of the



carbon atom from the phosphorus to the nitrogen atom with simultaneous loss of nitrogen. Additionally the reaction does not appear to be stereospecific. Irradiation of either the cis or trans isomer of 37 gives exactly the same mixture of cis and trans isomers 38 and 39.[102]

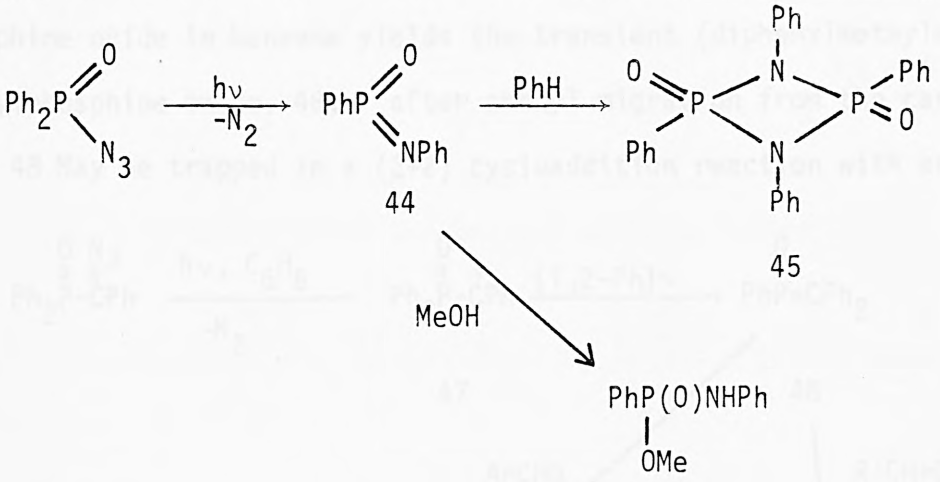


Harger and Stephen have investigated the photochemistry of dialkylphosphinic azides in alcoholic solvents.[103] They suggested the participation of a metaphosphonimidate 40, formed either from rearrangement of a nitrene or possibly by concerted migration of an alkyl

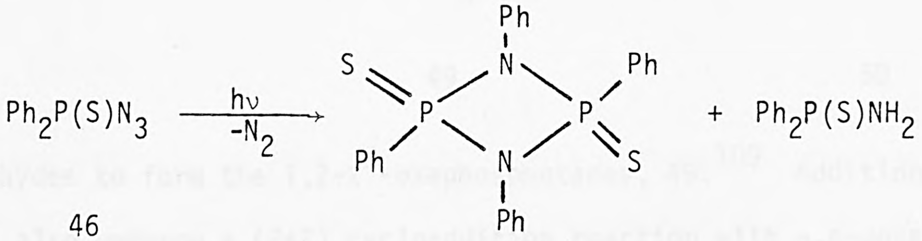


group from P to N with loss of nitrogen from the excited azide. Thus the photolysis of di-t-butylphosphinic azide and diisopropylphosphinic azide in methanol gives mainly the phosphonamidate 41, (R'= Me). The analagous rearrangement product is formed in other alcohols, although the phosphinic amide, 42, may become a significant product. Additionally some alkoxyamides, 43, may be formed by solvent incorporation without rearrangement.

Similarly the photolysis of diphenylphosphinic azide has been shown to form the phosphonimidate 44, which in aprotic solvents undergoes a head to tail dimerization to 45, while in methanol gives



methyl N,P-diphenylphosphonamidate.[104-107] The thiophosphoryl azide 46 gives both dimer and diphenylphosphinothionamidate, the latter via hydrogen abstraction from the solvent by a nitrene intermediate.[105] In an attempt to stabilize the phosphonimidate intermediate, sterically



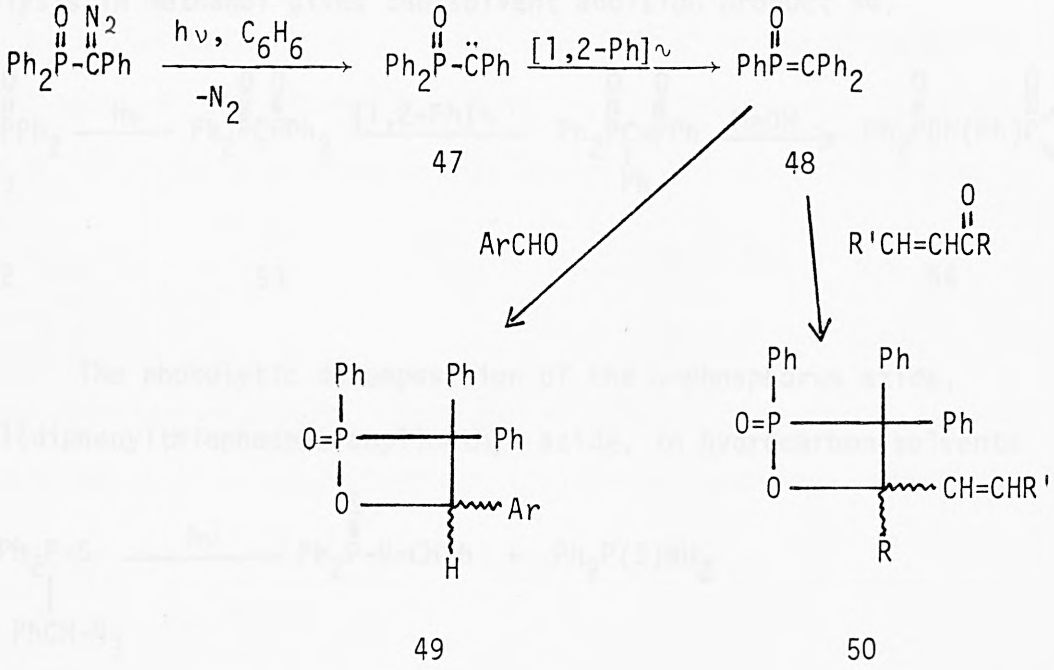
crowded phosphinic azides have been studied.[105-107]

Yim et. al. have investigated the photolysis of N-alkyl and N-aryl triphenyliminophosphoranes.[108] Irradiation of the N-aryl derivatives in inert solvents gave triphenylphosphine and diaryl azo compounds. Small amounts of the phosphine oxide and anilines were

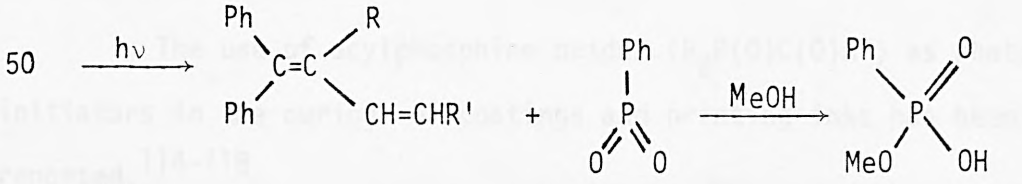
$$ArN{=}PPh_3 \xrightarrow{h\nu} ArN{=}NAr + Ph_3P$$

also formed. The reactions are believed to proceed via an ylid intermediate. The irradiation of the N-alkyl derivatives leads to rearrangement of the alkyl substituent, with formation of triphenylphosphine. No dialkyl azo compounds were isolated.

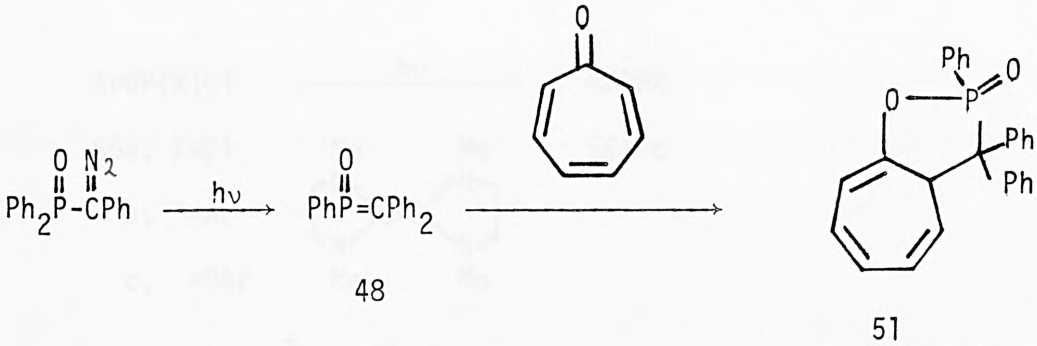
Regitz et. al. have investigated the photolysis of α-diazo phosphorus compounds.[109-112] Irradiation of (diazobenzyl)diphenylphosphine oxide in benzene yields the transient (diphenylmethylene) phenylphosphine oxide, 48, after phenyl migration from the carbene 47. 48 May be trapped in a (2+2) cycloaddition reaction with aromatic



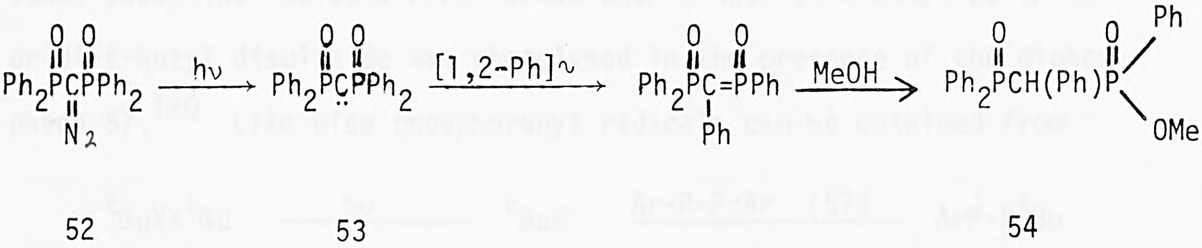
aldehydes to form the 1,2-λ^5-oxaphosphetanes, 49.[109] Additionally 48 will also undergo a (2+2) cycloaddition reaction with α,β-unsaturated aldehydes and ketones to yield the 1,2-λ^5-oxaphosphetanes 50.[109,110] These phosphetanes undergo some photofragmentation to yield a diene



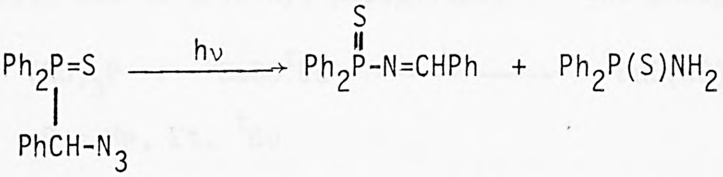
and phenyloxophosphine oxide.[110] In methanol $PhPO_2$ is intercepted by the solvent to give methyl hydrogen phenylphosphonate. Similarly photochemically generated 48 undergoes an (8+2) cycloaddition with tropone to give the cyclic phosphinate 51.[111] The bis(diphenylphosphoryl)carbene 53 has also been obtained from the diazo compound 52.[112]



Photolysis in methanol gives the solvent addition product 54.



The photolytic decomposition of the α-phosphorus azide, phenyl(diphenylthiophosphoranyl)methyl azide, in hydrocarbon solvents



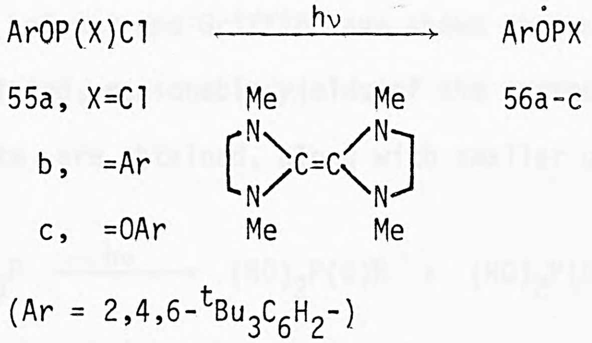
$$Ph_2\underset{PhCH-N_3}{P}=S \xrightarrow{h\nu} Ph_2\overset{S}{\overset{\parallel}{P}}-N=CHPh \;+\; Ph_2P(S)NH_2$$

has been reported to give benzylideneaminodiphenylthiophosphorane and aminodiphenylthiophosphorane.[113] This decomposition in the first thiophosphorus group migration observed. It is believed to occur more in a concerted fashion rather than by a mechanism involving a discrete nitrene intermediate.

The use of acylphosphine oxides {$R_2P(O)C(O)R'$} as photo-initiators in the curing of coatings and printing inks has been reported.[114-118]

Tervalent Phosphorus Acids and Related Compounds.

The formation of phosphino radicals from the irradiation of phosphines, alkyl and aryl phosphines, halophosphines and biphosphines has been mentioned. Similarly the alkoxyphosphino radicals 56a-c have been generated by the photolysis of the corresponding phosphorus chloride 55a-c in the presence of an electron rich olefin.[119-120]



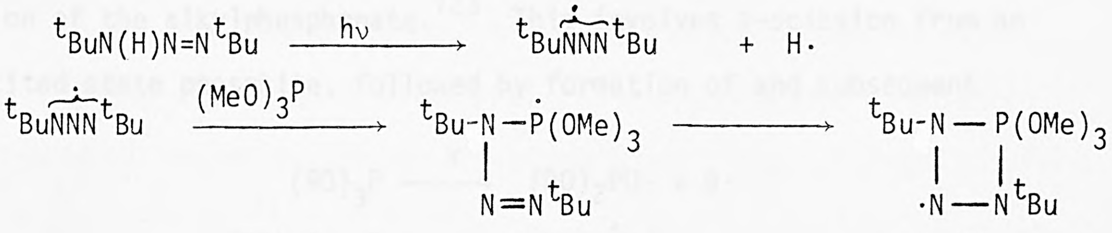
Other phosphino radicals were formed when either di-t-butyl peroxide or di-t-butyl disulphide was photolysed in the presence of the diphosphene 57.[120] Like wise phosphoranyl radicals can be obtained from radical addition reactions. Thus photochemically generated t-butoxy radicals add to trialkyl phosphites.[121] The phosphoranyl radical 58 is a proposed intermediate in the photoreaction of 1,3-di-t-butyltriazine with trimethyl phosphite to give the phosphorane 59.[122] The pseudorotation of 59 was studied by e.s.r. Finally the γ-irradiation of di- and trialkyl phosphites and some chlorophosphites have been shown to give phosphino and phosphoranyl radicals.[123-125]

$$ {}^t\mathrm{BuXX}{}^t\mathrm{Bu} \xrightarrow{h\nu} {}^t\mathrm{BuX}\cdot \xrightarrow{\mathrm{Ar{-}P{=}P{-}Ar}\ (57)} \mathrm{Ar\dot{P}{-}X}{}^t\mathrm{Bu} $$

$X = O,S$ $\qquad$ $Ar = 2,4,6\text{-}{}^t\mathrm{Bu}_3\mathrm{C}_6\mathrm{H}_2$

$$ (\mathrm{RO})_3\mathrm{P} + {}^t\mathrm{BuOO}{}^t\mathrm{Bu} \xrightarrow{h\nu} {}^t\mathrm{BuO(RO)}_3\mathrm{P}\cdot $$

$R = Me, Et, {}^t\mathrm{Bu}$



58 $\qquad$ 59

$$ (\mathrm{RO})_3\mathrm{P} \xrightarrow{\gamma} (\mathrm{RO})_2\mathrm{P}\cdot + (\mathrm{RO})_4\mathrm{P}\cdot $$

$R = Me, Et$

$$ (\mathrm{EtO})_2\mathrm{PCl} \xrightarrow{\gamma} (\mathrm{EtO})_2\dot{\mathrm{P}} + (\mathrm{EtO})_2\dot{\mathrm{P}}\mathrm{Cl}_2 $$

LaCount and Griffin have shown that when trialkyl phosphites are irradiated, reasonable yields of the corresponding dialkyl alkylphosphonate are obtained, along with smaller quantities of the

$$(RO)_3P \xrightarrow{h\nu} (RO)_2P(O)R + (RO)_2P(O)H + (RO)_3PO$$

R = Me, Et, ^{i}Pr, ^{n}Bu

dialkyl phosphite and trialkyl phosphate.[126] A mechanism for this rearrangement reaction has been suggested[127,128] based on the reported detection of the oxy phosphite $\{(EtO)_2PO\cdot\}$ and diethoxyphosphinyl radicals $\{(EtO)_2\dot{P}(O)\}$ by e.s.r.[127] However the e.s.r. data has been reassigned to the phosphino $\{(EtO)_2P\cdot\}$ and phosphoranyl $\{(EtO)_3\dot{P}Et\}$ radicals.[125] Similarly the radiolysis of trialkyl phosphites in solution leads to the formation of products derived from C-H, C-O and P-O bond cleavage.[129] A mechanism has been suggested for the form-

$$(RO)_3P \xrightarrow{\gamma} ROH + (RO)_2P(O)H + (RO)_3PO + (RO)_2P(O)R$$

R = Me, Et, ^{i}Pr, ^{n}Pr

ation of the alkylphosphonate.[123] This involves β-scission from an excited state phosphite, followed by formation of and subsequent

$$(RO)_3P \xrightarrow{\gamma} (RO)_2PO\cdot + R\cdot$$

$$(RO)_3P + R\cdot \longrightarrow (RO)_3\dot{P}R$$

$$(RO)_3\dot{P}R \longrightarrow (RO)_2P(O)R + R\cdot$$

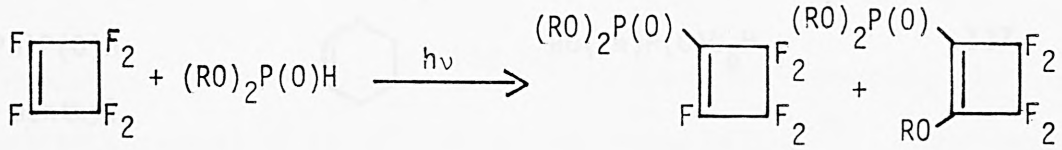
β-cleavage from a phosphoranyl radical$\{(RO)_3\dot{P}R\}$. With the identification of $(EtO)_2\dot{P}Et$ in the photolysis of $(EtO)_3P$[125,127] it is likely that the U.V. and γ-initiated reactions of $(EtO)_3P$ leading to diethyl ethylphosphonate occur by the same mechanism. That phosphoranyl radicals do undergo β-cleavage is shown by the formation of phosphine oxides when alkyl radicals, (generated from the photodecomposition of azoalkanes) add to methyl diphenylphosphinite.[130] Similarly phenyl radicals generated from phenylazotriphenylmethane add to phosphites

$$RN{=}NR \xrightarrow{h\nu} 2R\cdot + N_2$$

$$Ph_2POMe + R\cdot \longrightarrow [Ph_2(R)\overset{\cdot}{P}OMe] \longrightarrow Ph_2P(O)R + Me\cdot$$

to give phenylphosphonates.[131]

The phosphinyl radical, formed in the irradiation of dialkyl phosphites and alkyl alkylphosphonites has been found to add to unsaturated hydrocarbons, Table 2.4. The addition of the phosphinyl radical has been shown to proceed with retention of configuration at phosphorus[138] and not inversion as previously reported.[137] Additionally dialkyl phosphites have been found to add to polyfluorocyclobutenes on irradiation to give the unsaturated phosphonates 60 and 61.[135] Again the phosphinyl radical is the reactive intermediate.



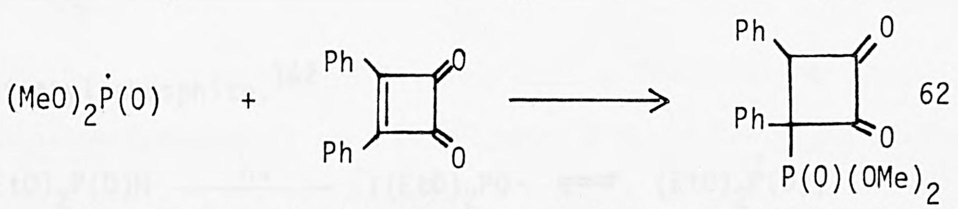
R = Me, Et, ^{n}Pr

60

61

The dimethoxyphosphino radical formed from the irradiation of trimethyl phosphite adds to 1,2-diphenylbut-1-ene-3,4-dione to give the phosphonate 62.[141]

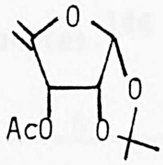
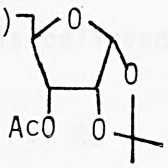
$$(MeO)_3P \xrightarrow{h\nu} (MeO)_2PO\cdot \rightleftharpoons (MeO)_2\overset{\cdot}{P}(O)$$



62

The interconversion of the oxy phosphite $\{(RO)_2PO\cdot\}$ and phosphinyl $\{(RO)_2\overset{\cdot}{P}(O)\}$ radicals is illustrated by the formation of both the hypophosphate, 63, and P(III)- P(V)anhydride, 64, on photolysis

Table 2.4. Addition of the phosphinyl radical to carbon carbon multiple bonds.

Phosphorus compound	Unsaturated hydrocarbon	Product	Reference.
$(RO)_2P(X)H$ X = O,S	RCH=CHR	$(RO)_2P(X)CHRCH_2R$	132,133,134.
$RO(R')P(X)H$ X = O,S	$RCH=CH_2$	$RCH_2CH_2P(X)(R')OR$	134
$(EtO)_2P(O)H$	$CH_2=CF_2$	$(EtO)_2P(O)CH_2CHF_2$	135
$(EtO)_2P(S)H$		$(EtO)_2P(S)$ 	136
$RO(Ph)P(O)H$ R = menthyl		$RO(Ph)P(O)C_6H_{11}$	137
$EtO(Ph)P(O)H$	$CH_2=CH_2$	$EtO(Ph)P(O)Et$	138
$^iPrO(Me)P(O)H$	C_7H_{13}	$^iPrO(Me)P(O)C_7H_{15}$	139
$(RO)_2P(X)H$ X = O,S	RC≡CH	$RCH=CHP(X)(OR)_2$	140
$RO(R')P(X)H$ X = O,S	RC≡CH	$RCH=CHP(X)(R')OR$	140

of diethyl phosphite.[142]

$$(EtO)_2P(O)H \xrightarrow{h\nu} [(EtO)_2PO\cdot \rightleftharpoons (EtO)_2\dot{P}(O)]$$

$$\longrightarrow \underset{63}{(EtO)_2P(O)P(O)(OEt)_2} + \underset{64}{(EtO)_2\ddot{P}OP(O)(OEt)_2}$$

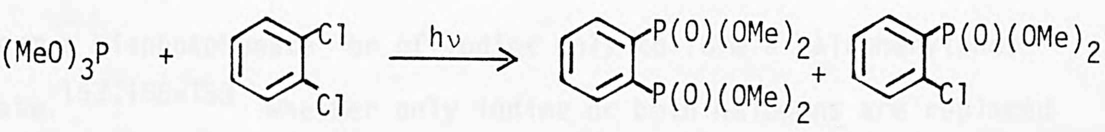
The photolysis of chloroacetone and triethyl phosphite has been shown by Tomioka et. al. to give both the ketophosphonate (Arbuzov product) and vinyl phosphate (Perkow product).[128] Such

$$(EtO)_3P + CH_3COCH_2Cl \xrightarrow{h\nu} CH_3COCH_2P(O)(OEt)_2 + CH_2{=}C(CH_3)OP(O)(OEt)_2$$

products are obtained via C-Cl bond fission to give the acetonyl radical which may then add to the phosphite. Triethyl phosphate and diethyl ethylphosphonate are also obtained,[128] formed from the excited phosphite.[126] Similarly Arbuzov products are obtained when aryl iodides are irradiated in the presence of trialkyl phosphites[143-145] or dialkyl alkylphosphonites.[146] The reaction is believed to involve

$$ArI + (RO)_3P \xrightarrow{h\nu} ArP(O)(OR)_2 + RI$$

a phosphoranyl intermediate.[144,147,148.] With haloiodobenzene, the iodide is displaced in preference to the second halide.[149] Additionally bisphosphonates may also be formed.[149,150] Thus the photoreaction of 1,2-dichlorobenzene with trimethyl phosphite gives 1,2-bis(dimethoxyphosphoryl)benzene as the major product along with smaller amounts



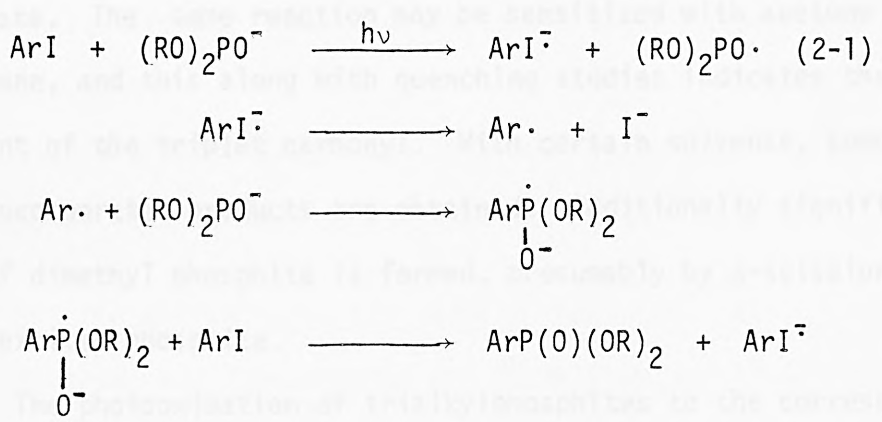
of dimethoxy o-chlorophenylphosphonate.[150] Phosphites in which the phosphorus atom is part of a ring system also undergo the photo-Arbuzov reaction with iodobenzene.[151]

α-Substituted phosphonates have been formed in the U.V. induced Michaelis-Becker reaction of dibromomethane with the sodium salt of several dialkyl phosphites.[152]

$$(RO)_2P(O)Na + CH_2Br_2 \xrightarrow{h\nu} (RO)_2P(O)CH_2P(O)(OR)_2 + NaBr$$

$R = Et, Pr, Bu, n\text{-}octyl$

Bunnett and Creary have reported the reaction of aryl iodides with the diethyl phosphite anion on irradiation to afford diethyl arylphosphonates.[153] The reaction is believed to occur by an $S_{RN}1$ radical chain mechanism. Fox et. al.[154] have shown that the initiation step



$$ArI + (RO)_2PO^- \xrightarrow{h\nu} ArI^{\dot{-}} + (RO)_2PO\cdot \quad (2\text{-}1)$$

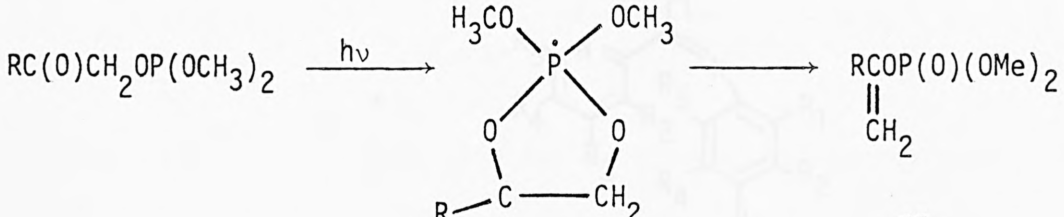
$$ArI^{\dot{-}} \longrightarrow Ar\cdot + I^-$$

$$Ar\cdot + (RO)_2PO^- \longrightarrow Ar\underset{\substack{|\\ O^-}}{\dot{P}}(OR)_2$$

$$Ar\underset{\substack{|\\ O^-}}{\dot{P}}(OR)_2 + ArI \longrightarrow ArP(O)(OR)_2 + ArI^{\dot{-}}$$

(2-1) involves an electron transfer within an excited charge transfer complex (<u>ie</u> $\{ArI\cdots\cdots{}^-OP(OR)_2\}$)as had been previously suggested.[155] Similarly alkyl and alkoxy substituted iodobenzenes react to form the corresponding aryl phosphonate.[153,156] With diiodobenzene, a bisphosphonate is obtained.[153] However the analagous reaction with o-, m- and p-haloiodobenzenes may bring about replacement of both halogens to form a bisphosphonate or of iodine only to form a halophenylphosphonate.[153,156-159] Whether only iodine or both halogens are replaced depends on the identity of the second halogen and its orientation with respect to iodine. With m-bromoiodobenzene formation of the bisphosphonate does not involve the successive replacement of the iodine and then bromine.[157,158] Instead the replacement of iodine initiates the replacement of bromine, such that the reaction occurs without the intermediacy of the bromophenylphosphonate.[157,158]

Griffin et. al. have reported the intramolecular photorearrangement of dimethyl β-ketoethyl phosphites to vinyl phosphates, 65.[160] The reaction is believed to occur via a cyclic biradical



65

intermediate. The same reaction may be sensitized with acetone or benzophenone, and this along with quenching studies indicates the involvement of the triplet carbonyl. With certain solvents, some solvent incorporated products are obtained. Additionally significant amounts of dimethyl phosphite is formed, presumably by β-scission from the excited phosphite.

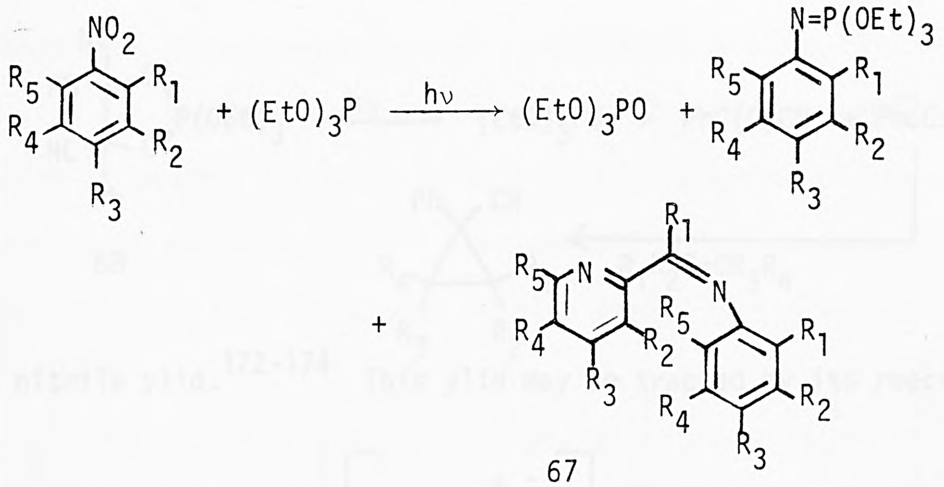
The photooxidation of trialkylphosphites to the corresponding phosphate by ground state oxygen has been reported by Plumb and Griffin.[161] A radical mechanism is suggested. Similarly Bolduc and Goe have shown that dye sensitized singlet oxygen may also oxidize phosphites to phosphates.[162] The photolysis of trialkyl phosphites in oxygenated solutions of aromatic hydrocarbons results in aromatic hydroxylation to give phenols, and with the formation of trialkyl phosphates.[163]

Hoffman et. al. reported the photoreaction of trialkyl phosphites with mercaptans to give thiophosphates.[164] Subsequently

$$(RO)_3P \ + \ R'SH \xrightarrow{h\nu} (RO)_3PS \ + \ R'H$$

this reaction was shown to occur via a radical chain mechanism.[165]

The photoinduced deoxygenation of aromatic nitro compounds by triethyl phosphite has been reported.[166,167] The major products are triethyl phosphate, triethyl N-arylphosphorimidates 66, and the



66

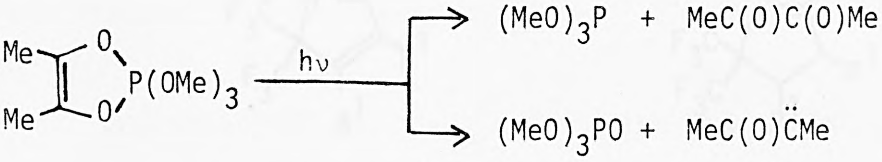
67

pyridine derivatives 67. The reaction is believed to occur via a nitrene intermediate.

Cyclic organic phosphites have been reported to be photostabilizers for polyolefins and polyvinylchloride.[168,169]

Quinquevalent Phosphorus Acids and Related Compounds.

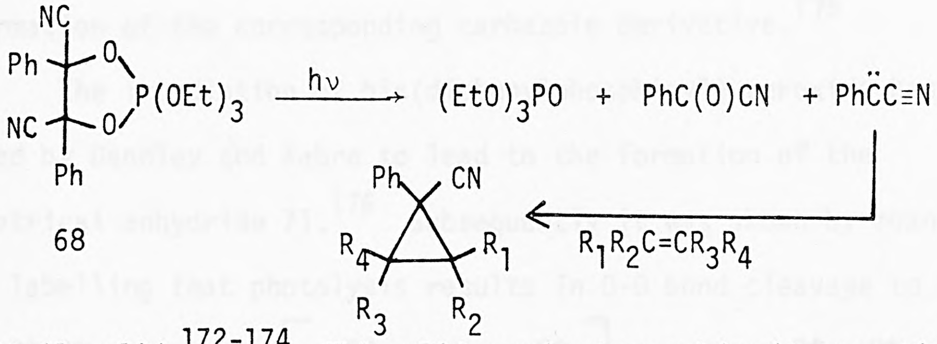
Bentrude has investigated the photochemistry of 4,5-dimethyl-0,0,0-trimethyl-1,3,2-dioxaphospholen and found that the distribution



of product formation is strongly wavelength dependent.[170] Thus at short wavelengths trimethyl phosphite and biacetyl are favoured. The phosphate is favoured at longer wavelengths along with a second product, suggested to be the keto-carbene, MeC(O)C̈Me. With the 4,5-diphenyl analogue only trimethyl phosphate is formed.

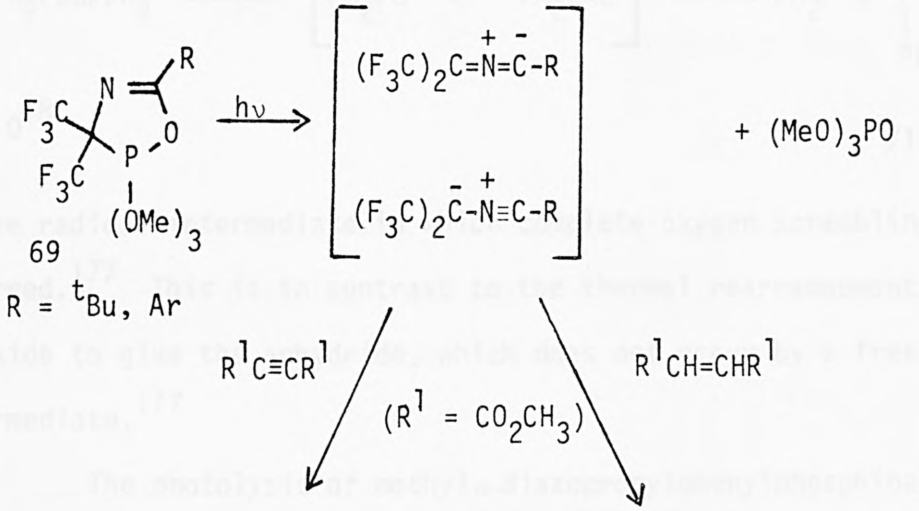
The photolysis of the 1,3,2-dioxaphospholan 68 has been found to give triethyl phosphate, benzoyl cyanide and phenylcyanocarbene.[171] This latter species can be trapped by its addition to olefins to give phenylcyanocyclopropanes.

The photolysis of the 1,3,5-oxazaphospholen 69 has been shown to result in expulsion of trimethyl phosphate and with formation



68

of a nitrile ylid.[172-174] This ylid may be trapped by its reaction

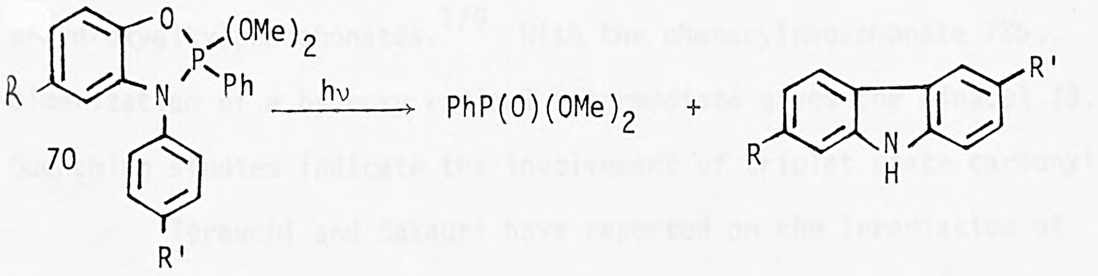


69

R = ^{t}Bu, Ar

with alkenes and alkynes.[172,173]

Cadogan et. al. have shown that irradiation of the 1,3,2-oxazaphospholine 70 leads to elimination of dimethyl phenylphosphonate



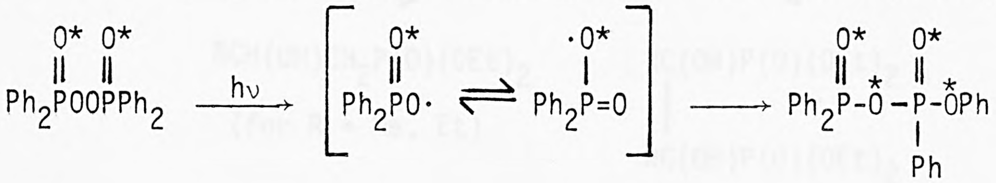
70

R = H, R' = H, OMe

R = Me, R' = OMe

and formation of the corresponding carbazole derivative.[175]

The irradiation of bis(diphenylphosphinyl) peroxide has been reported by Dannley and Kabre to lead to the formation of the unsymmetrical anhydride 71.[176] Subsequently it was shown by means of oxygen labelling that photolysis results in O-O bond cleavage to give



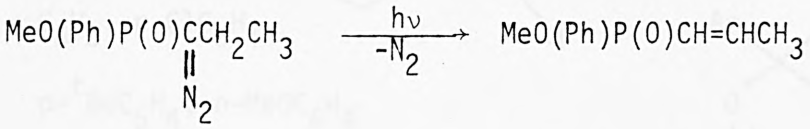
$$Ph_2P(O^*)OOP(O^*)Ph_2 \xrightarrow{h\nu} \left[Ph_2P(O^*)\cdot \rightleftharpoons Ph_2P(\cdot O^*)=O \right] \longrightarrow Ph_2P(O^*)\text{-}\overset{*}{O}\text{-}P(O^*)(Ph)\text{-}\overset{*}{O}Ph$$

$O^* = O^{18}$

71

a free radical intermediate in which complete oxygen scrambling had occurred.[177] This is in contrast to the thermal rearrangement of the peroxide to give the anhydride, which does not occur by a free radical intermediate.[177]

The photolysis of methyl α-diazopropylphenylphosphinate has been found to give methyl phenylpropenylphosphinate as an 89:11 trans-cis mixture.[178] The stereochemistry of the product is controlled by

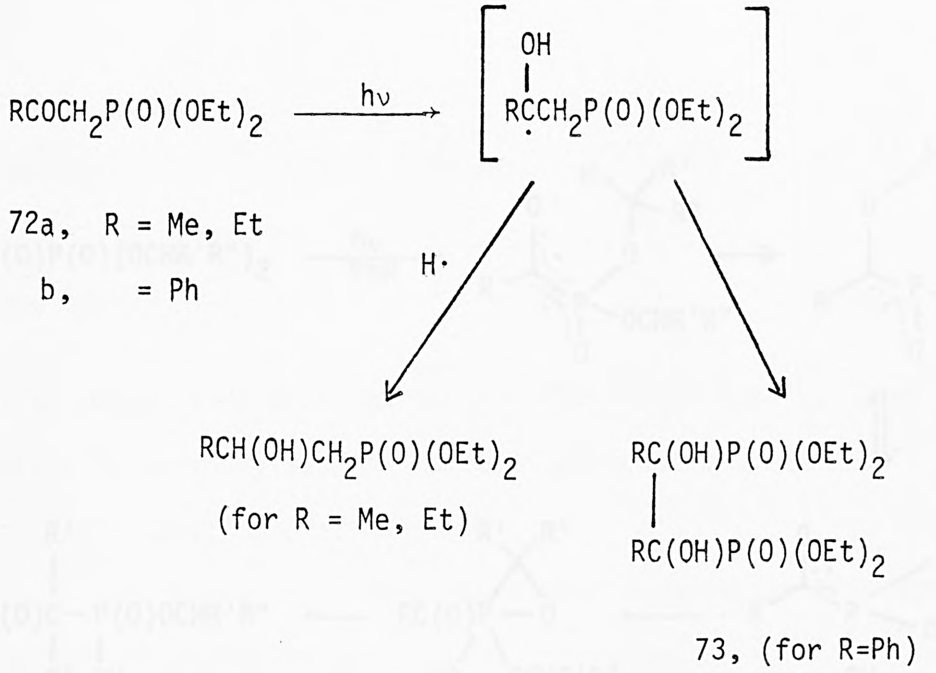


$$MeO(Ph)P(O)C(=N_2)CH_2CH_3 \xrightarrow[-N_2]{h\nu} MeO(Ph)P(O)CH=CHCH_3$$

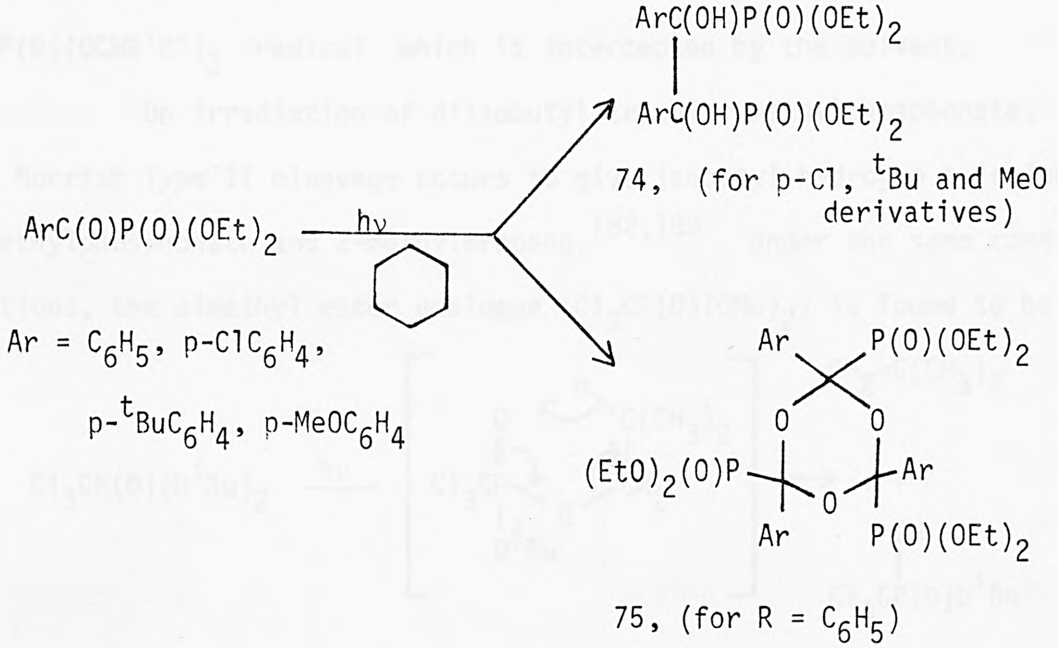
steric hindrance between the phosphorus and methyl fragments in a carbene intermediate.

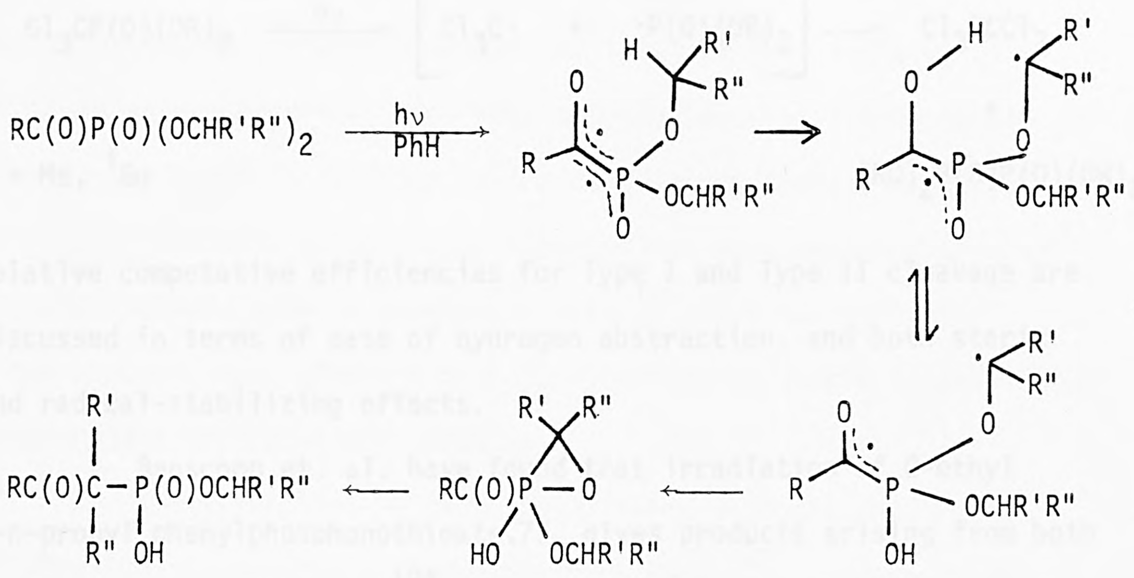
The photoreduction of β-ketoalkylphosphonates, 72a, has been shown by Tomioka et. al. to give high yields of the corresponding β-hydroxyalkylphosphonates.[179] With the phenacylphosphonate 72b, dimerization of a hydroxy radical intermediate gives the pinacol 73. Quenching studies indicate the involvement of triplet state carbonyl.

Terauchi and Sakauri have reported on the irradiation of some diethoxy benzoylphosphonates to yield either the pinacol 74 or the trioxan 75.[180] Similar product variation is observed on changing



the ethoxy function on the phosphoryl moiety. No clear explanation is given as to why both this, and the introduction of p-substituents into the aryl ring can drastically change the nature of the photoproducts formed. In contrast dialkyl α-ketophosphonates have been found to undergo a photoinduced rearrangement to give the β-ketophosphonates 76.[181] The reaction is suggested to occur via two diradical intermediates after initial intramolecular γ-hydrogen abstraction by triplet excited carbonyl. The formation of dialkyl phenylphosphonates {$PhP(O)(OCHR'R'')_2$} in addition to 76 is indicative

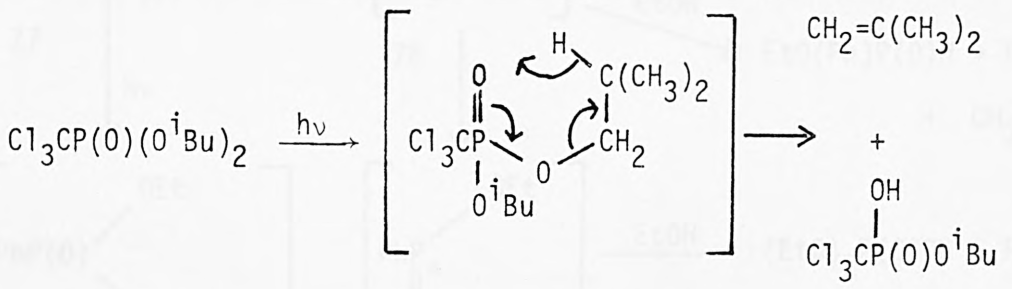




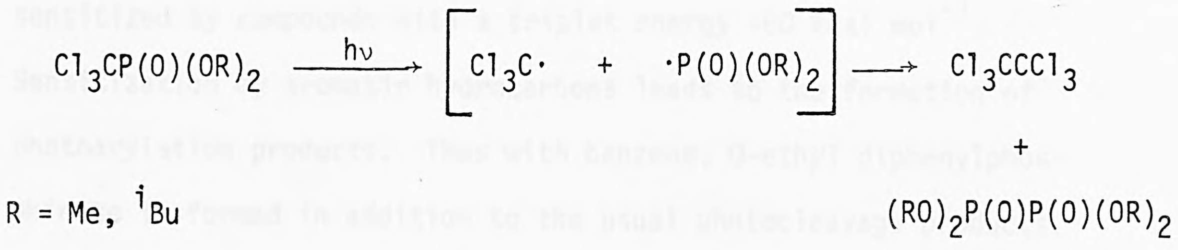
76

of some competitive Norrish Type I cleavage, giving rise to the $\cdot P(O)(OCHR'R'')_2$ radical which is intercepted by the solvent.

On irradiation of diisobutyl trichloromethylphosphonate, a Norrish Type II cleavage occurs to give isobutyl hydrogen trichloromethylphosphonate and 2-methylpropene.[182,183] Under the same conditions, the dimethyl ester analogue $\{Cl_3CP(O)(OMe)_2\}$ is found to be



photostable. This is attributed to its inability to participate in a 6-membered cyclic transition state required for hydrogen abstraction to occur. Additionally both these dimethyl and diisopropyl phosphonates are reported to give hexachloroethane and the corresponding tetraethylhypophosphate via a Norrish Type I cleavage.[183] Norrish Type II cleavage leading to the mono ester derivatives are reported for a number of other dialkyl trichloromethylphosphonates.[183] The

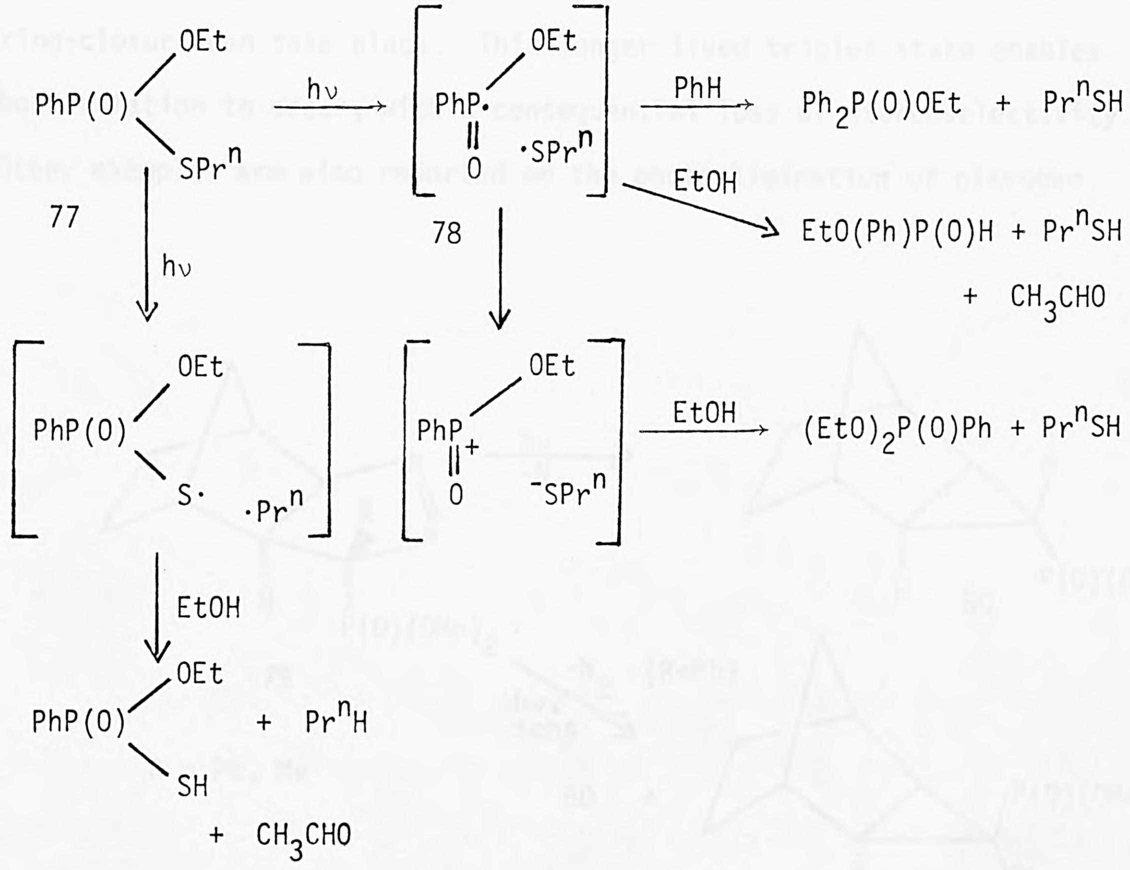


$$Cl_3CP(O)(OR)_2 \xrightarrow{h\nu} \left[Cl_3C\cdot \quad + \quad \cdot P(O)(OR)_2 \right] \longrightarrow Cl_3CCCl_3 + (RO)_2P(O)P(O)(OR)_2$$

R = Me, ^{i}Bu

relative competatative efficiencies for Type I and Type II cleavage are discussed in terms of ease of hydrogen abstraction, and both steric and radical-stabilizing effects.

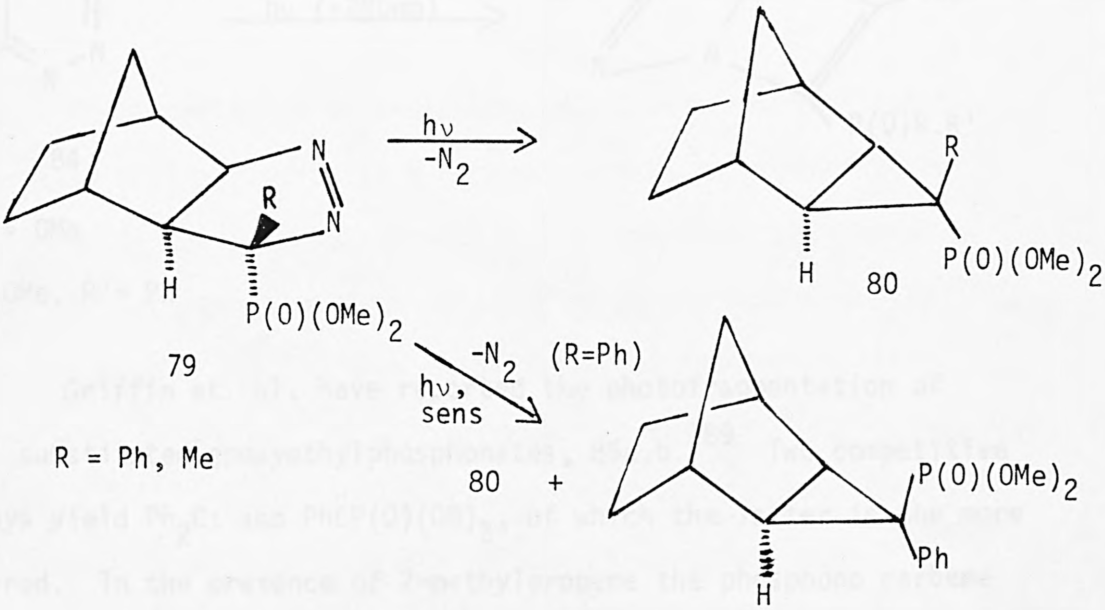
Benschop et. al. have found that irradiation of O-ethyl S-n-propyl phenylphosphonothioate,77, gives products arising from both α-cleavage and β-cleavage.[184] In ethanol, scission of the P-S bond gave O-ethyl phenylphosphinate and n-propanethiol as the major products, along with smaller amounts of O,O-diethyl phenylphosphonate as a photosolvolysis product. Spin trapping and e.s.r. confirm the intermediacy of the phosphinyl radical, 78. O-Ethyl phenylphosphonothioic acid is formed from S-C scission. The photoreduction of 77 can be



sensitized by compounds with a triplet energy >80 kcal mol^{-1}. Sensitization by aromatic hydrocarbons leads to the formation of photoarylation products. Thus with benzene, O-ethyl diphenylphosphinate is formed in addition to the usual photocleavage products.

Takahashi et. al. have reported the photodecomposition of phenylphosphonic acid to phosphoric acid.[185] Two stereoisomers of 4-hydroxybicyclo[3.1.0]hex-2-en-6-ylphosphonic acid were identified as intermediate decomposition products.

The pyrazoline 79 (R=Ph) eliminates nitrogen on direct irradiation to form the cyclopropane 80 (R=Ph).[186] Conversely its sensitized photolysis occurs non stereospecifically to give the cyclopropanes 80 and 81 (R=Ph). This is explained on the basis that direct irradiation proceeds via a short lived singlet state which can ring-close before bond rotation can occur, whilst sensitized irradiation proceeds from a triplet state, which must intersystem cross before ring-closure can take place. This longer lived triplet state enables bond rotation to occur, with a consequential loss of stereoselectivity. Other examples are also reported on the photoelimination of nitrogen



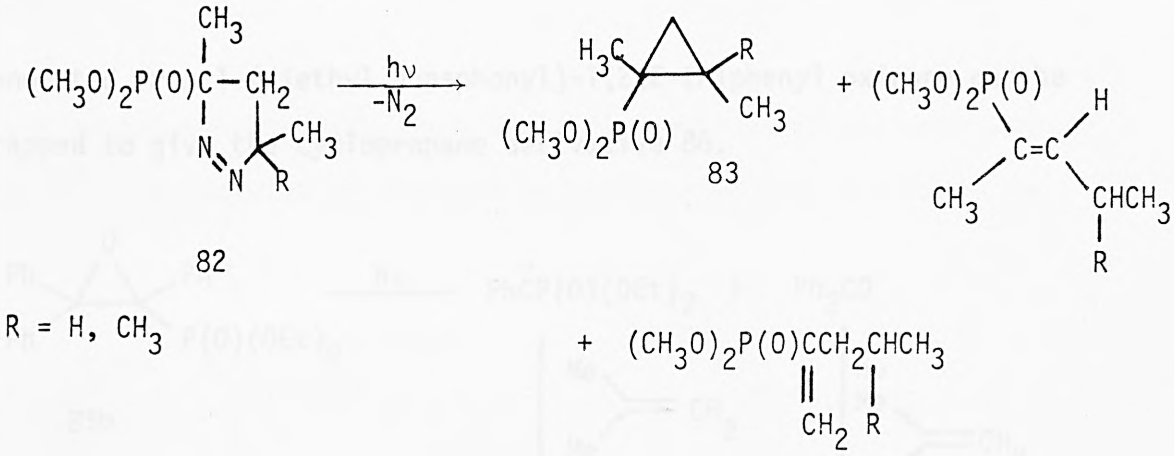
79

80

R = Ph, Me

81

from derivatives of 79 to give the corresponding cyclopropane derivative(s).[186] Similarly the pyrazolines 82 extrude nitrogen on photolysis to give stereoselectively the cyclopropane derivatives 83 as the major product.[187] This is believed to occur by rapid closure of a biradical intermediate in the singlet state. Intersystem crossing to give a secondary biradical intermediate in the triplet state is responsible for the formation of the olefinic phosphonates. The longer lived triplet state enables both 1,2- and 1,4-hydrogen shifts to occur.

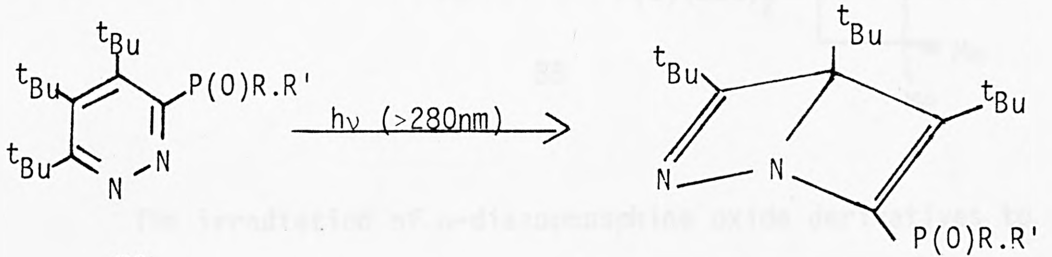


82

83

R = H, CH_3

Eisenbarth and Regitz have reported that irradiation of the pyridazine 84 leads to formation of the stable 1,2-Dewerpyridazine.[188]

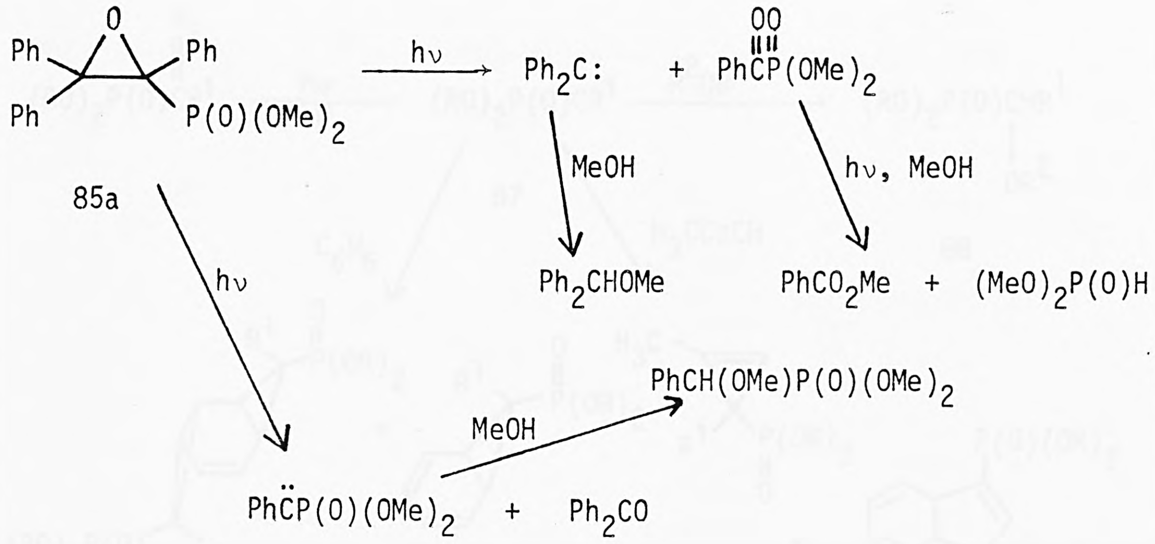


84

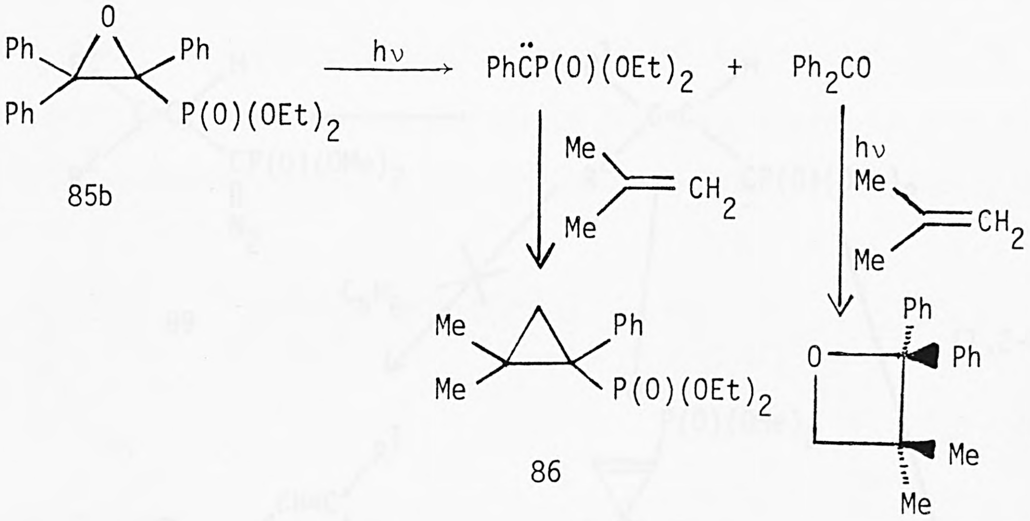
R=R'= OMe

R = OMe, R'= Ph

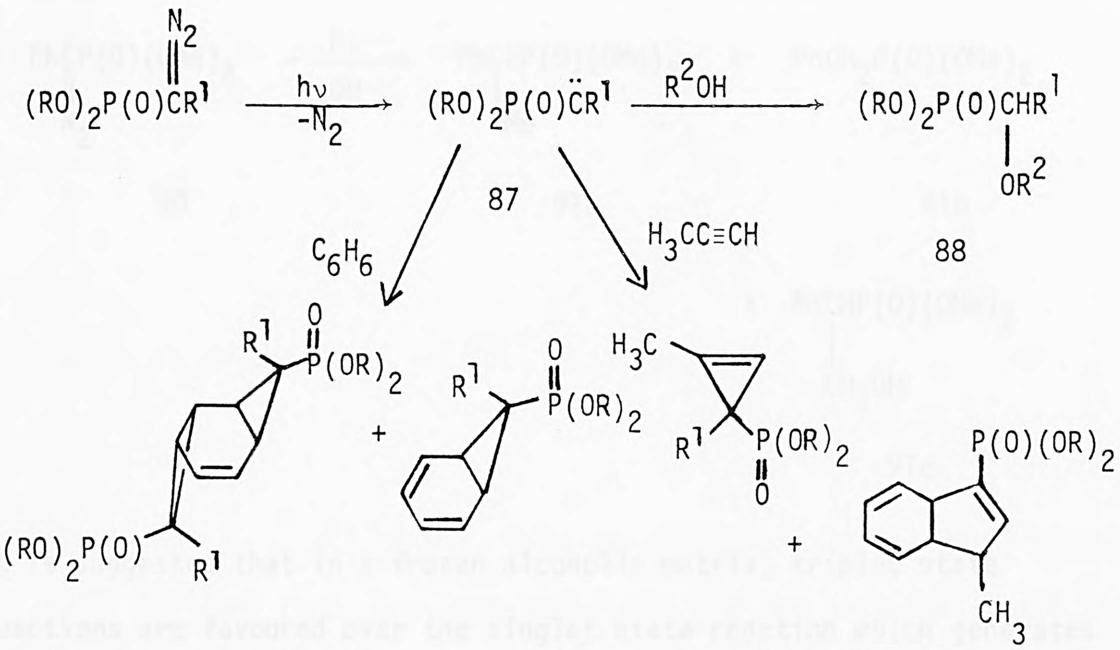
Griffin et. al. have reported the photofragmentation of phenyl substituted epoxyethylphosphonates, 85a,b.[189] Two competitive pathways yield Ph_2C: and $Ph\ddot{C}P(O)(OR)_2$, of which the latter is the more preferred. In the presence of 2-methylpropene the phosphono carbene



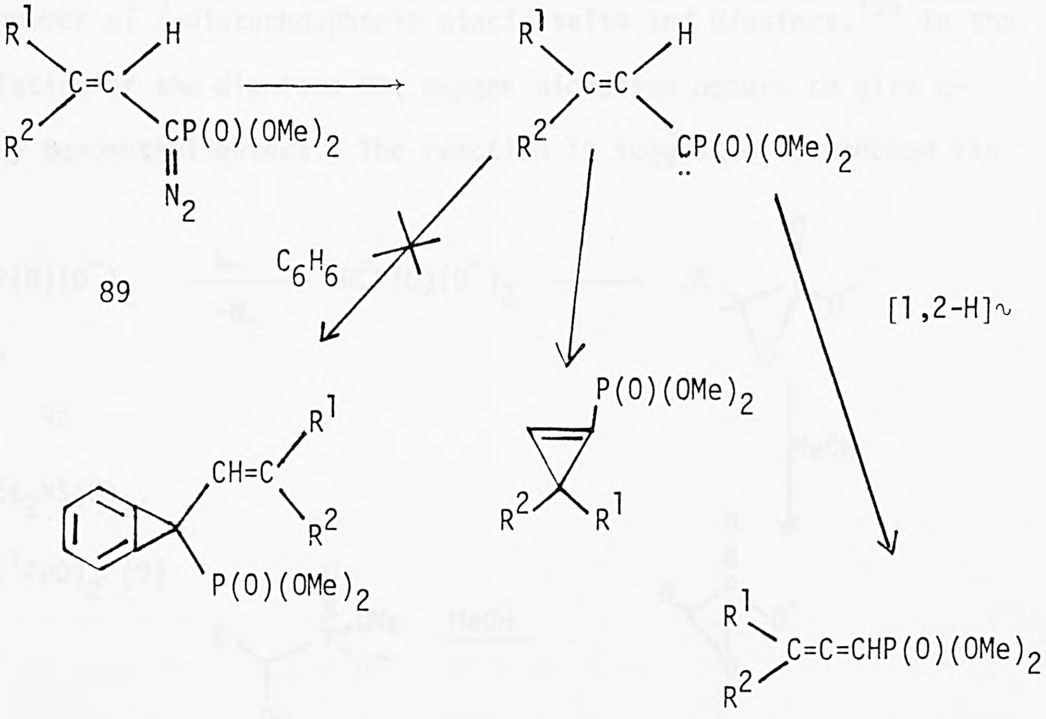
generated from 1-(diethyl phosphonyl)-1,2,2-triphenyl oxirane can be trapped to give the cyclopropane derivative 86.

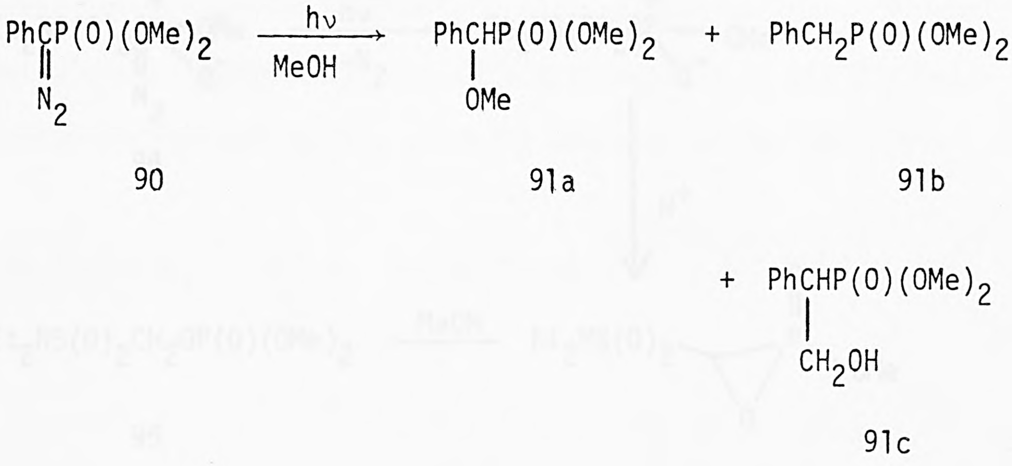


The irradiation of α-diazophosphine oxide derivatives to yield, after aryl migration to a carbene centre, an arylmethylene phosphine oxide has been mentioned.[109-112] Similarly phosphonyl-α-carbenes, 87, are produced from irradiation of the corresponding α-diazo precursor.[190,191] Such carbenes may be trapped by their reaction with alcohols,[192,193] olefins,[191] arenes[190,191,194] and acetylenes.[191,195] Additionally some α-phosphonylcarbenes are found to give products derived from intramolecular reactions only.[194,195] Thus irradiation of the α-diazophosphonate 89 affords predominantly



a cyclopropenephosphonate, with smaller amounts of an allenephosphonate.[195] The addition of alcohols to carbenes generally affords the corresponding ether derivative, 88. However Tomioka et. al. have shown that the formation of such O-H insertion products is temperature dependent.[193] Thus the carbene generated from 90 gives at -196°C, products derived from double hydrogen abstraction (91b) and C-H insertion (91c) at the expense of 91a. Sensitization reactions indicate that 91b and 91c are derived from the triplet state of the carbene.





90

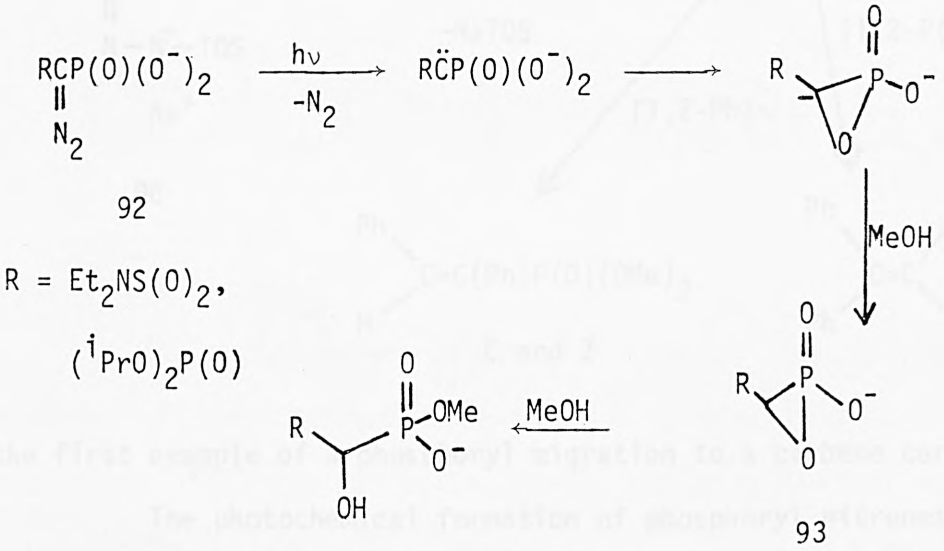
91a

91b

91c

It is suggested that in a frozen alcoholic matrix, triplet state reactions are favoured over the singlet state reaction which generates 91a.

Bartlett et. al. have examined the photochemical behaviour of a number of α-diazophosphonic diacid salts and diesters.[196] In the irradiation of the dianions 92, oxygen migration occurs to give α-hydroxy monomethyl esters. The reaction is suggested to proceed via

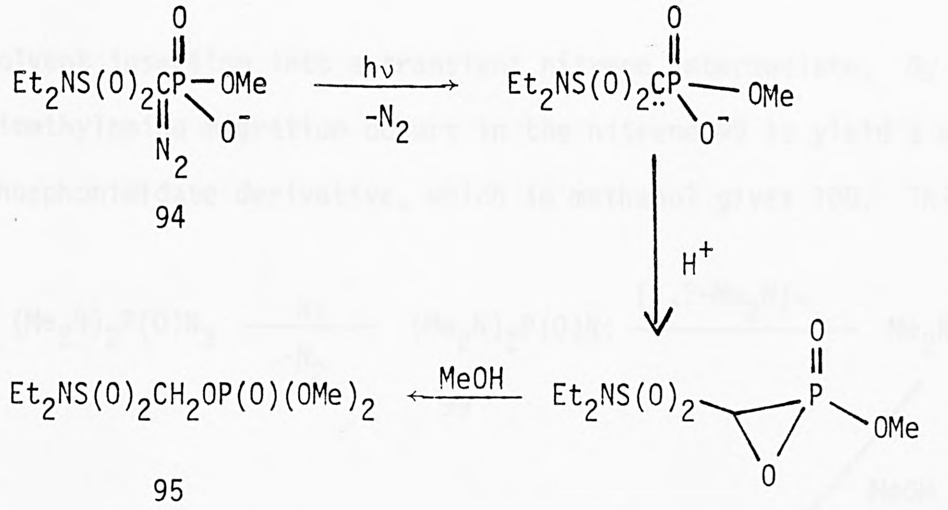


92

R = Et$_2$NS(O)$_2$,
(^{i}PrO)$_2$P(O)

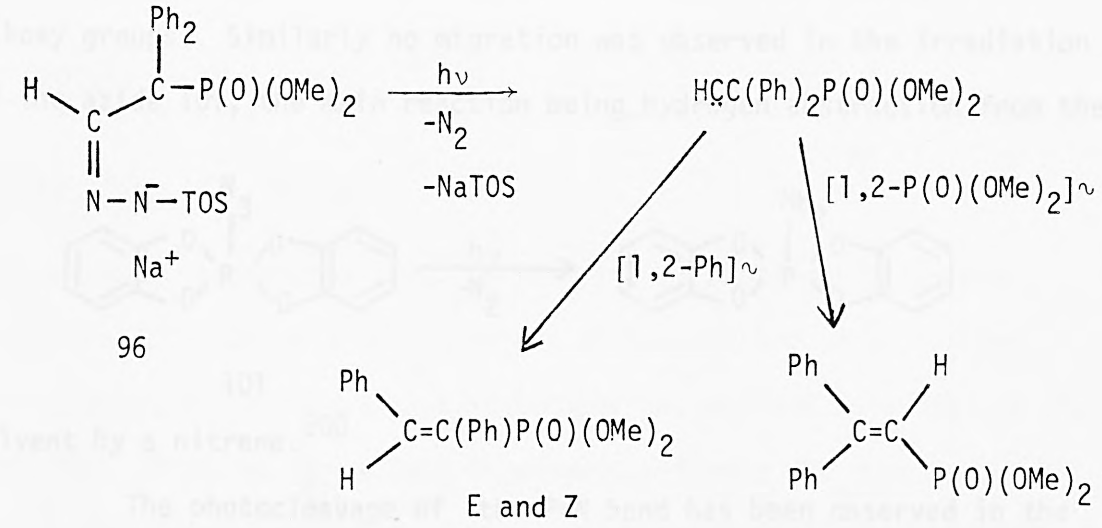
93

the oxaphosphirane intermediate 93. This represents the first reported example of a formal Wolff rearrangement of an oxygen substituent from phosphorus to an adjacent carbene centre. Subsequently it was reported that the mono ester 94 undergoes a similar migration to give an oxaphosphirane intermediate, which forms the phosphate 95 by oxygen insertion.[197] The analagous oxygen insertion products were identified



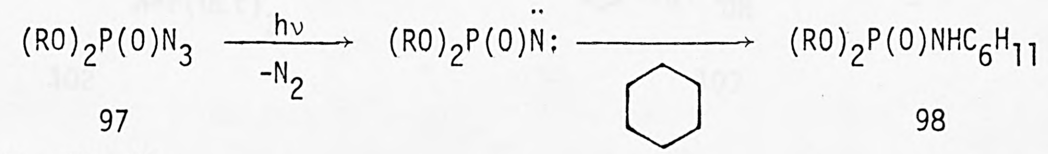
on re-examination of the results from the photolysis of the dianions 92.

Carbenes have also been generated from the irradiation of the sodium salts of β-phosphonyl tosylhydrazones.[198] Products are formed as a result of intramolecular rearrangements. Thus 96 affords products arising from both phenyl and phosphonyl migrations. This is



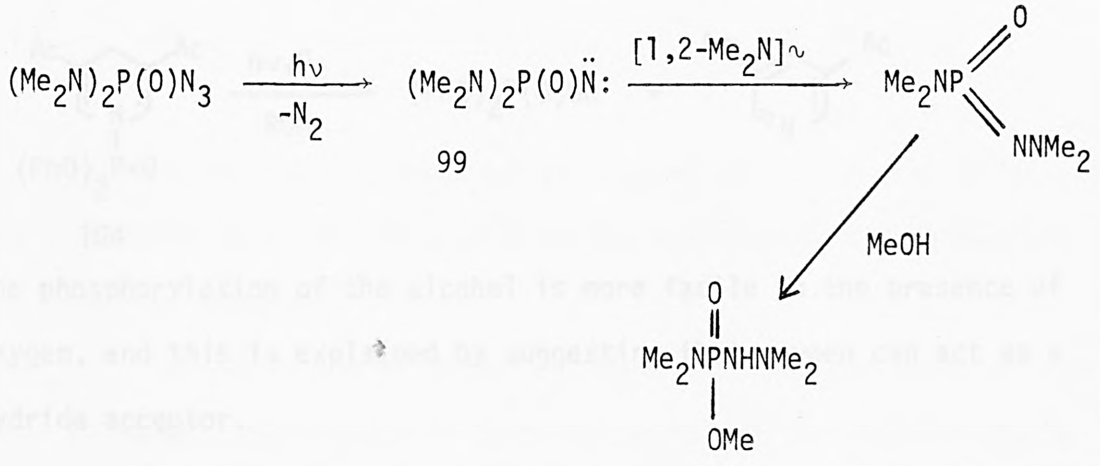
the first example of a phosphoryl migration to a carbene centre.

The photochemical formation of phosphoryl nitrenes has been investigated by Breslow et. al.[199] Irradiation of the phosphorylazide 97 gives predominantly the cyclohexylphosphoramidate 98 by



R = Et, Ph

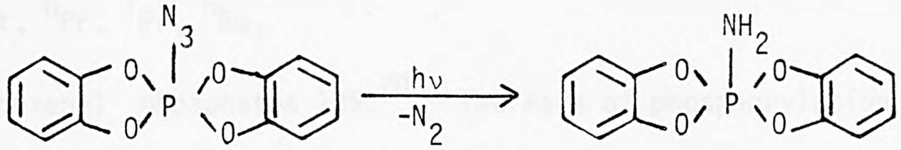
solvent insertion into a transient nitrene intermediate. By contrast, dimethylamino migration occurs in the nitrene 99 to yield a metaphosphonimidate derivative, which in methanol gives 100. This



99

100

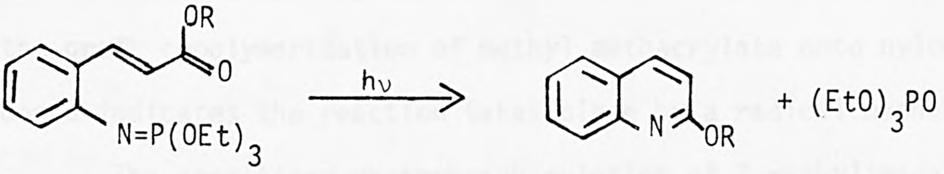
illustrates the greater migratory apptitude of amino groups over alkoxy groups. Similarly no migration was observed in the irradiation of the azide 101, the main reaction being hydrogen abstraction from the



101

solvent by a nitrene.[200]

The photocleavage of the P=N bond has been observed in the synthesis of α-substituted quinolines.[201] Irradiation of the phosphorimidate 102 leads to cyclization to the quinoline 103, with



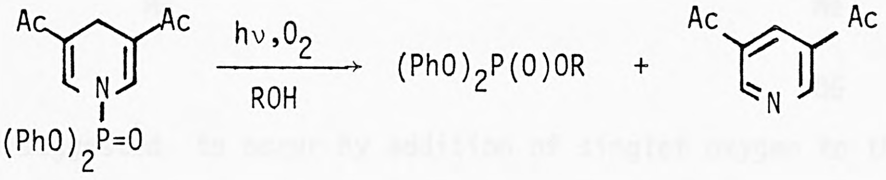
102

103

R = H, Me, Ph, C_6H_{11}

elimination of triethyl phosphate.

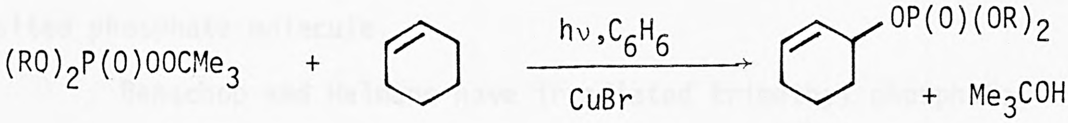
Irradiation of the phosphoramidate 104 in alcoholic solutions leads to P-N bond cleavage and formation of the corresponding phosphate.[202]



104

The phosphorylation of the alcohol is more facile in the presence of oxygen, and this is explained by suggesting that oxygen can act as a hydride acceptor.

Sosnovsky and Karas have reported that irradiation of dialkyl t-butylperoxy phosphates with cyclohexene in the presence of a catalytic amount of cuprous bromide leads to the formation of the



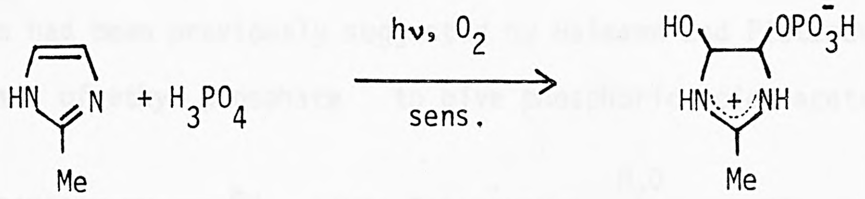
105

$R = Et, {}^nPr, {}^iPr, {}^nBu,$

cyclohexenyl phosphates 105.[203] The rate of phosphorylation was considerably enhanced in the presence of benzene and other triplet sensitizers, while the singlet sensitizer eosin-Y had no effect on the reaction. Addition of radical scavengers retarded the reaction, indicating a free radical mechanism. Similarly alkyl t-butylperoxy alkylphosphonates undergo the same photoreaction with cyclohexene to give the corresponding cyclohexenyl alkylphosphonates.

Potassium peroxydiphosphate has been used as a photoinitiator in the graft copolymerisation of methyl methacrylate onto nylon 6.[204] Evidence indicates the reaction takes place by a radical mechanism.

The sensitized photophosphorylation of 2-methylimidazole by irradiation in aqueous solution in the presence of inorganic phosphate has been reported to give the organic phosphate 106.[205] The reaction



106

is suggested to occur by addition of singlet oxygen to the imidazole, and subsequent nucleophilic attack on the 4,5-dioxetane intermediate by inorganic phosphate.

The photolysis of phenyl phosphate in aqueous solution has been found to yield phosphoric acid and phenol as the major products.[206] Smaller yields of phosphorous acid, benzene and dihydroxysubstituted biphenyls were also obtained. The initial step in the overall transformation is believed to involve the ejection of an electron from an excited phosphate molecule.

Benschop and Halmann have irradiated trimethyl phosphate under argon, and detected the formation of the bisphosphate 108.[207]

$$(MeO)_3PO \xrightarrow{h\nu} \underset{107}{(MeO)_2P(O)OCH_2\cdot} + H\cdot$$

$$(MeO)_2P(O)OCH_2\cdot \xrightarrow{Ar} \underset{108}{(MeO)_2P(O)OCH_2CH_2OP(O)(OMe)_2}$$

$$(MeO)_2P(O)OCH_2\cdot \xrightarrow{O_2} (MeO)_2P(O)OCH_2OO\cdot$$

$$(MeO)_2P(O)OCH_2OO\cdot \longrightarrow \longrightarrow (MeO)_2P(O)OH + CH_2O$$

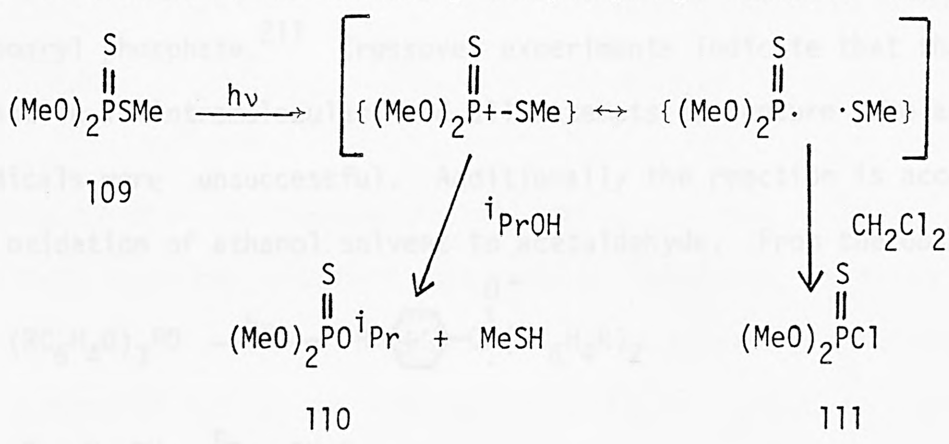
$$(MeO)_2P(O)OH \xrightarrow[O_2]{h\nu} \longrightarrow \longrightarrow MeOP(O)(OH)_2 \xrightarrow[O_2]{h\nu} \longrightarrow \longrightarrow H_3PO_4$$

Under oxygen, photolysis proceeds much faster to give formaldehyde and dimethyl phosphate as the initial products. Continual irradiation leads to further degradation to methyl phosphate and ultimately to phosphoric acid. In both cases the formation of the radical 107 is believed to be the primary photochemical reaction. A similar C-H bond scission had been previously suggested by Halmann and Platzner in the photolysis of ethyl phosphate to give phosphoric acid, acetaldehyde

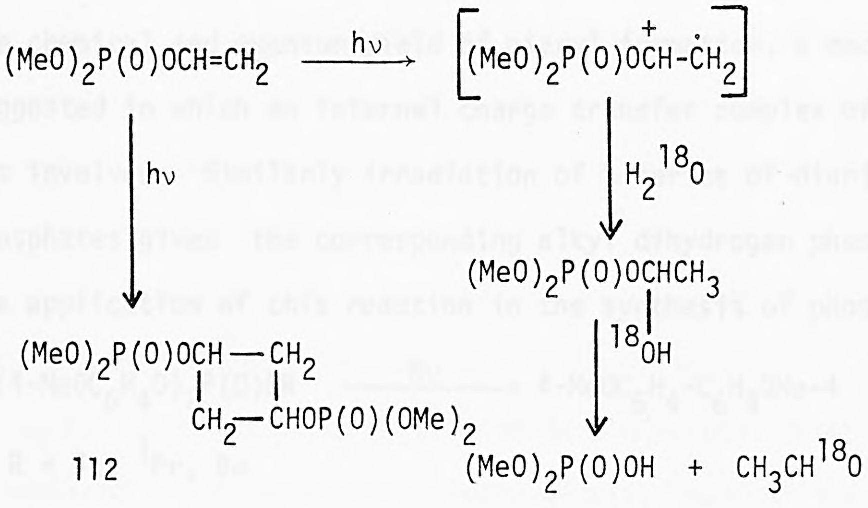
$$(HO)_2P(O)OCH_2CH_3 \xrightarrow[-H\cdot]{h\nu} [(HO)_2P(O)O\dot{C}HCH_3] \xrightarrow{H_2O} H_3PO_4 + CH_3CHO$$

and hydrogen.[208]

The irradiation of O,O,S-trimethyl phosphorodithioate, 109, gives decomposition products, the nature of which are dependent upon the solvent.[209] Thus irradiation of 109 in isopropanol gives the ionic photosolvolysis product 110, where as in dichloromethane the free radical product 111 is formed. It is suggested that the reaction occurs via an 'intimate radical-ion pair'. E.s.r. experiments indicate the involvement of the dimethoxy thiophosphinyl radical. The photosolvolysis of 109 can be sensitized by triplet sensitizers with E_T >80 kcal mol^{-1}. Other products formed from irradiation in ^{i}PrOH are obtained by thiono-thiolo isomerization and/or photoreduction reactions.

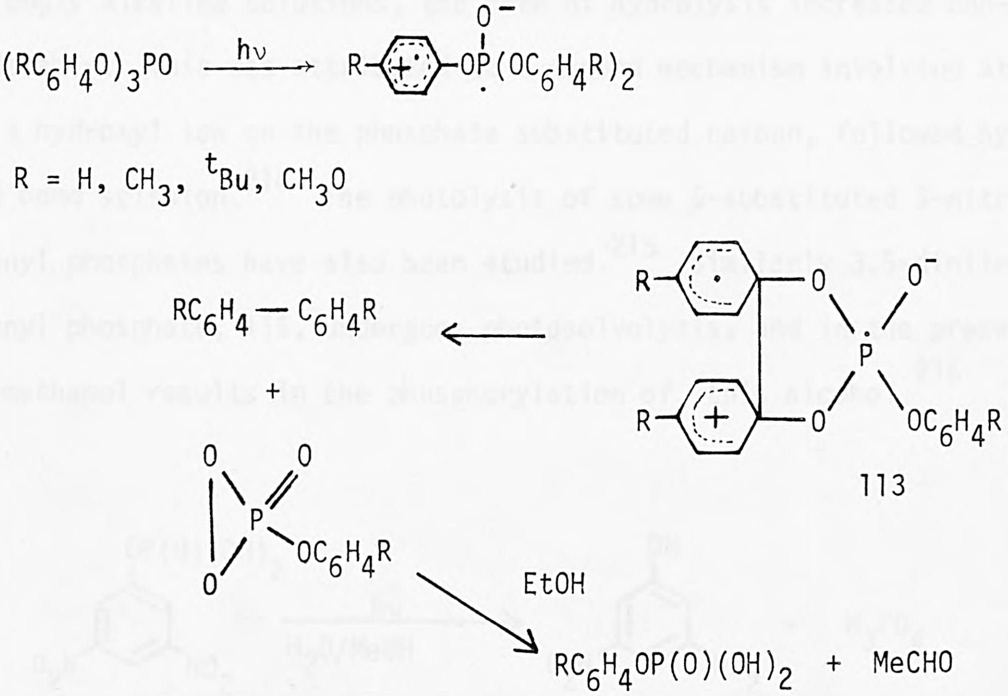


Gignoux et. al. have investigated the photolysis of dimethyl vinyl phosphate in aqueous solution.[210] In the absence of oxygen, products are formed arising from two equally important reaction pathways. The first leads to dimerization, to give what is believed to be the cyclobutane derivative 112. The second involves photosolvolysis



to dimethyl phosphate. Methyl phosphate and phosphoric acid are formed in secondary photosolvolysis reactions.

Finnegan and Matson have found that irradiation of triaryl phosphates may result in biaryl formation along with the corresponding monoaryl phosphate.[211] Crossover experiments indicate that the reaction is intramolecular, and all attempts to capture free aryl radicals were unsuccessful. Additionally the reaction is accompanied by oxidation of ethanol solvent to acetaldehyde. From the observation



that electron donating substituents in the aryl rings enhance both the chemical and quantum yield of biaryl formation, a mechanism was suggested in which an internal charge transfer complex of the type 113 was involved. Similarly irradiation of a series of dianisyl alkyl phosphates gives the corresponding alkyl dihydrogen phosphates.[212] The application of this reaction in the synthesis of phosphate mono-

$$(4\text{-}MeOC_6H_4O)_2P(O)OR \xrightarrow{h\nu} 4\text{-}MeOC_6H_4\text{-}C_6H_4OMe\text{-}4 + ROP(O)(OH)_2$$

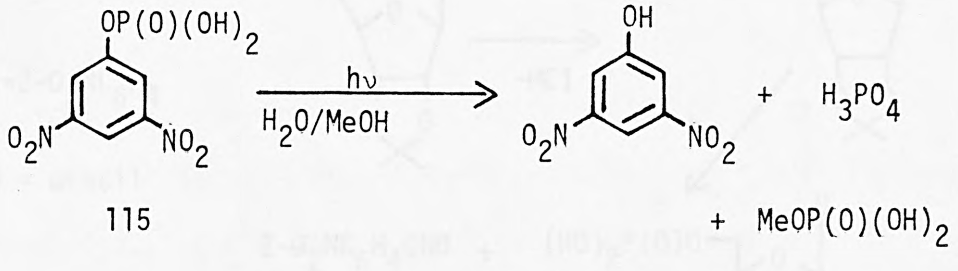
$$R = Et,\ {}^iPr,\ Bu$$

esters, with particular emphasis in nucleotide synthesis is discussed.

There have been a number of other reports on the photolysis of phosphate esters, often with particular reference to new photolabile phosphate protecting groups in nucleotide synthesis. Havinga et. al. reported the photohydrolysis of m-nitrophenyl phosphate, 114, to give m-nitrophenol.[213,214] A mechanism was suggested involving

$$\underset{114}{3\text{-}O_2NC_6H_4OP(O)(OH)_2} \xrightarrow[H_2O]{h\nu} 3\text{-}O_2NC_6H_4OH + H_3PO_4$$

attack by water on phosphorus, followed by P-O bond scission. In strongly alkaline solutions, the rate of hydrolysis increased considerably. This was attributed to a second mechanism involving attack by a hydroxyl ion on the phosphate substituted carbon, followed by C-O bond scission.[214] The photolysis of some 5-substituted 3-nitrophenyl phosphates have also been studied.[215] Similarly 3,5-dinitrophenyl phosphate, 115, undergoes photosolvolysis, and in the presence of methanol results in the phosphorylation of this alcohol.[216]

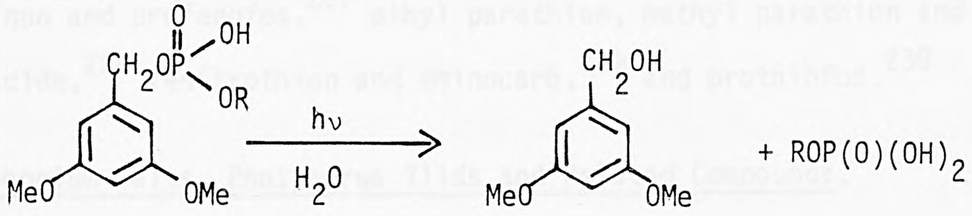


115

Additionally di-3,5-dinitrophenyl phosphate is hydrolysed on irradiation.[217] The application of the dinitrophenyl moiety as a photolabile protecting group is illustrated by its use in the synthesis of adenosine-5' phosphate.

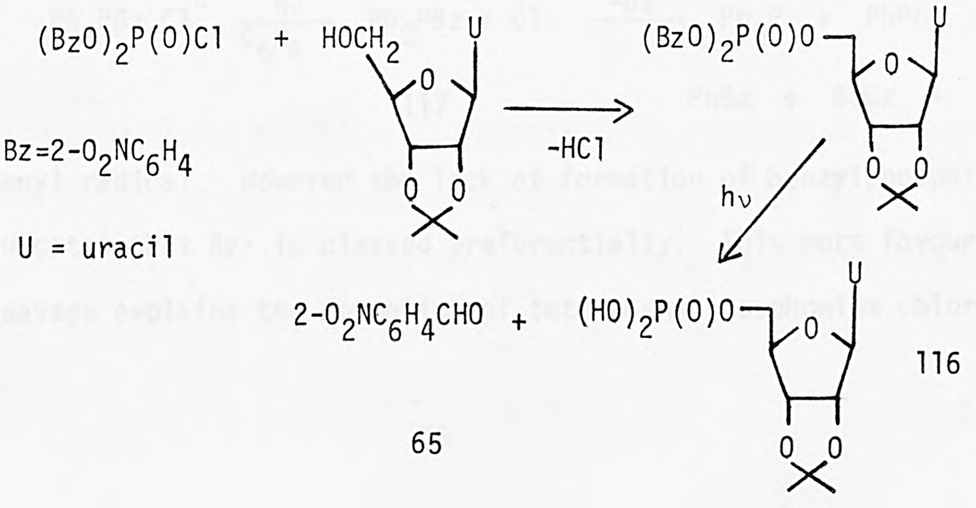
Arris et. al. have investigated the benzyl group as a possible protecting group in phosphate triester synthesis.[218] Irradiation of benzyl phosphates and pyrophosphates in alcohol leads to inorganic phosphates and pyrophosphates respectively. However the benzyl group in adenosine-5' benzyl phosphate was found not to be photolabile.

Clark et. al. have shown that irradiation of 3,5-dimethoxybenzyl phosphate in aqueous solution leads to inorganic phosphate and the corresponding benzyl alcohol.[219] The reaction is believed to proceed via a benzyl carbonium ion intermediate, formed from heterolytic C-O bond cleavage. Similarly 3,5-dimethoxybenzyl phenyl phosphate gave phenyl phosphate as the major product on irradiation.



R = H, Ph

Rubinstein et. al. have reported the synthesis of some mononucleotides using the o-nitrobenzyl moiety as a light sensitive protecting group.[220] The formation of 116 illustrates the steps in a typical preparation.



116

There have been several reports on the photolysis of glucose[221,222] and fructose phosphates.[223,224] In general, irradiation results in elimination of inorganic phosphate and decomposition of the phosphate free sugar.

The photochemistry of organophosphorus (O.P.) pesticides has received some attention because of their persistence in the environment. Eto has written briefly on this subject.[225] The principle transformations involving a change in functionality at phosphorus which can be brought about by UV light, include dealkyl and dearylation, and for thiophosphorus pesticides oxidative desulphurisation and thiono-thiolo isomerization. Recently the photodecomposition of the following O.P. pesticides have been reported. Pyrimithate,[226] methidathion, diazinon and profenofos,[227] ethyl parathion, methyl parathion and supracide,[228] fenitrothion and aminocarb,[229] and prothiofos.[230]

<u>Phosphonium Salts, Phosphorus Ylids and Related Compounds.</u>

The photochemical behaviour of phosphonium salts was originally investigated by Griffin and Kaufman.[231] They found that irradiation of benzyltriphenylphosphonium chloride resulted in the formation of triphenylphosphine along with products derived from phenyl and benzyl radicals. The primary process in this transformation is believed to be electron transfer to generate the phosphoranyl radical 117 and a chloride radical. The phosphoranyl radical may then suffer α-cleavage to give the corresponding phosphine with loss of either the benzyl or

$$Ph_3\overset{+}{P}Bz\ Cl^- \xrightarrow[C_6H_6]{h\nu} \underset{117}{Ph_3\dot{P}Bz} + Cl\cdot \xrightarrow{-Bz\cdot} Ph_3P \quad + \quad PhPh$$

$$PhBz \quad + \quad BzBz \quad + \quad Ph_2PH$$

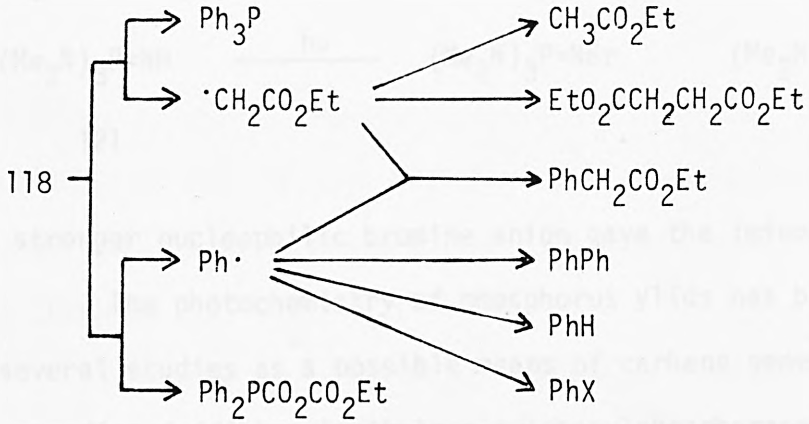
phenyl radical. However the lack of formation of benzylphosphines indicates that Bz· is cleaved preferentially. This more favoured cleavage explains the formation of tetraphenylphosphonium chloride from photolysis of a mixture of triphenylphosphine and benzyltriphenylphosphonium chloride.[60] Similarly tetraphenylphosphonium chloride gives products from a phosphoranyl radical intermediate along with products derived from the initially formed Ph_3P, (ie. Ph_2PH).[231]

$$Ph_4\overset{+}{P}\ Cl^- \xrightarrow[C_6H_6]{h\nu} Ph_4\dot{P} + Cl^{\cdot} \longrightarrow PhPh + Ph_3P + Ph_2PH$$

This elimination from a phosphoranyl radical intermediate confirms the reversible nature of the addition of radicals to trivalent phosphorus compounds.

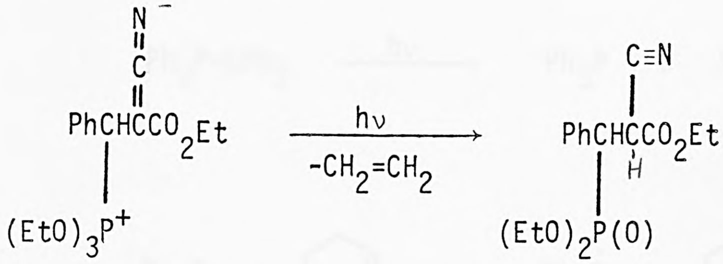
Nagao et. al. have similarly proposed a charge transfer process in the photolysis of (carboethoxymethyl)triphenylphosphonium salts.[232,233] Irradiation of such salts gives 118, which may decompose by either of two possible pathways. The formation of Ph_3P as the major phosphine (rather than (carboethoxymethyl)diphenylphosphine) indicates the preferential cleavage of the carboethoxymethyl radical.

$$Ph_3\overset{+}{P}CH_2CO_2Et\ \ X^- \xrightarrow{h\nu} \underset{118}{Ph_3\dot{P}CH_2CO_2Et} + Cl\cdot$$



The nature of the solvent and counter ion (X^-) were found to alter the photoreactivity of the phosphonium salt.

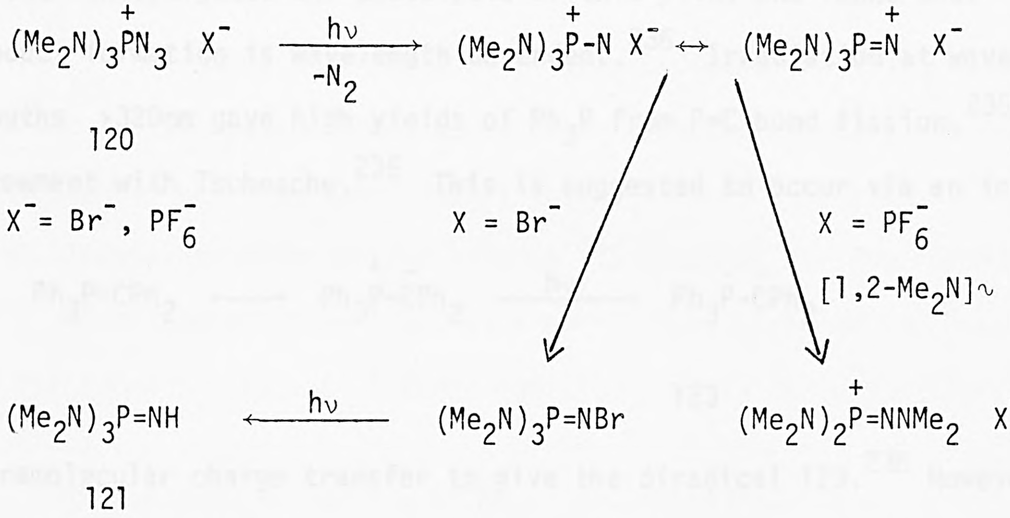
Shin et. al. have found that irradiation of the phosphonium salt 119 leads to the formation of a β-cyano phosphonate, accompanied



119

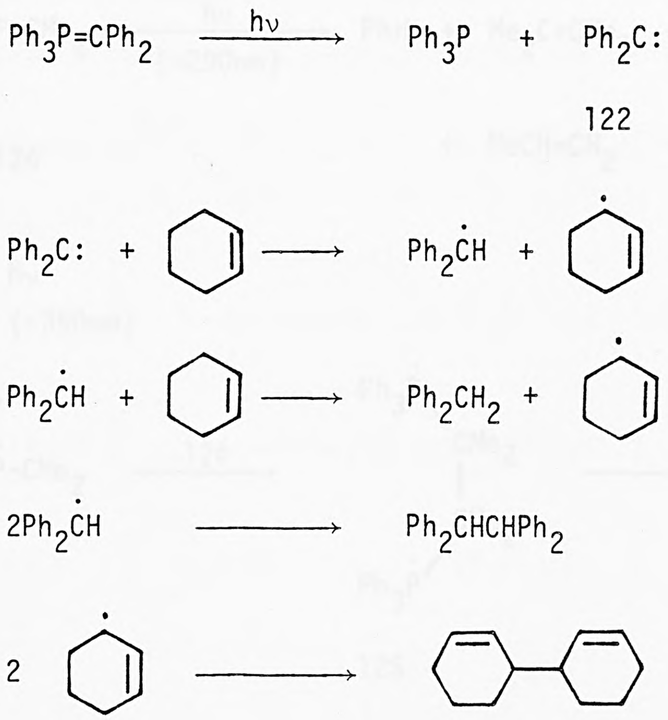
by elimination of ethylene.[234]

The photolysis of a number of phosphonium azides have been investigated by Majoral et. al.[200] Irradiation of 120 gives an initial phosphonium nitrene intermediate, which may ultimately form a number of possible products depending on the nucleophilicity of the anion. With the poorly nucleophilic PF_6^- anion an imino phosphonium salt was formed after the migration of a dimethylamino group, whilst



the stronger nucleophilic bromine anion gave the iminophosphorane 121.

The photochemistry of phosphorus ylids has been the subject of several studies as a possible means of carbene generation. Tschesche has irradiated (diphenylmethylene)triphenylphosphorane in cyclohexene, and isolated triphenylphosphine, diphenylmethane, tetraphenylethane and bicyclohex-2-enyl.[235] These are suggested to arise by P=C bond fission to generate the diradical 122. No cyclopropane derivatives were formed from cycloaddition with the solvent. Nagao et. al. has



122

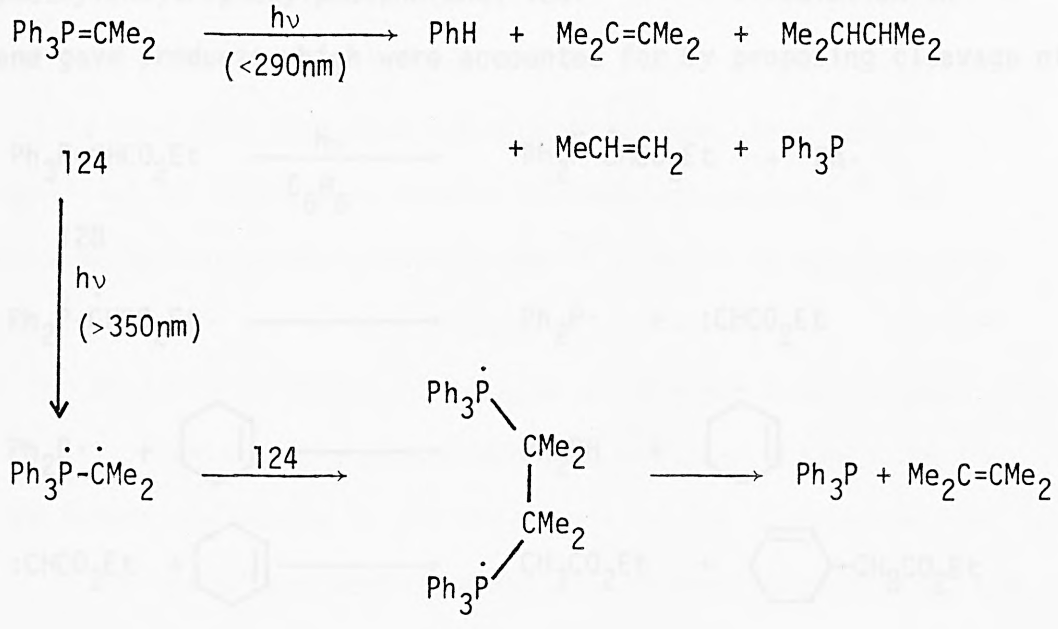
further investigated the photolysis of this ylid, and found that product formation is wavelength dependent.[236] Irradiation at wavelengths >320nm gave high yields of Ph_3P from P=C bond fission,[236] in agreement with Tschesche.[235] This is suggested to occur via an initial

$$Ph_3P{=}CPh_2 \longleftrightarrow Ph_3\overset{+}{P}-\overset{-}{C}Ph_2 \xrightarrow{h\nu} Ph_3\dot{P}-\dot{C}Ph_2$$

123

intramolecular charge transfer to give the diradical 123.[236] However irradiation at 253.7nm gave high yields of benzene, and no Ph_3P. This has been attributed to preferential P-Ph bond cleavage, prior to P=C bond cleavage.

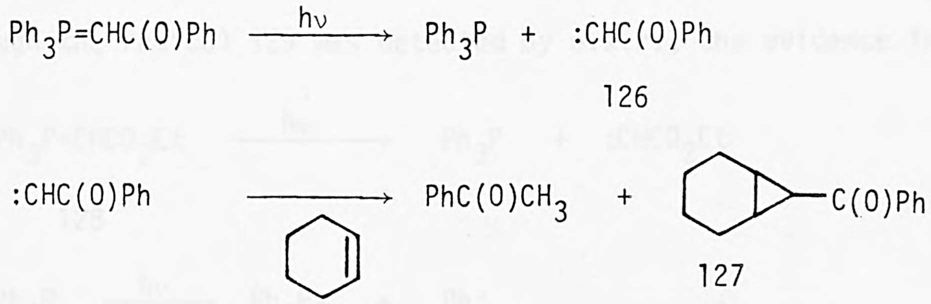
A similar wavelength dependency has been reported in the photolysis of (dimethylmethylene)triphenylphosphorane, 124.[237] Cleavage of Ph-P bonds to give benzene is favoured at low wavelengths (<290nm), while formation of 2,3-dimethylbut-2-ene is favoured at longer wavelengths (>350nm). Irradiation of 124 in isobutene does not lead to the formation of a cyclopropane. It is suggested therefore that 124



125

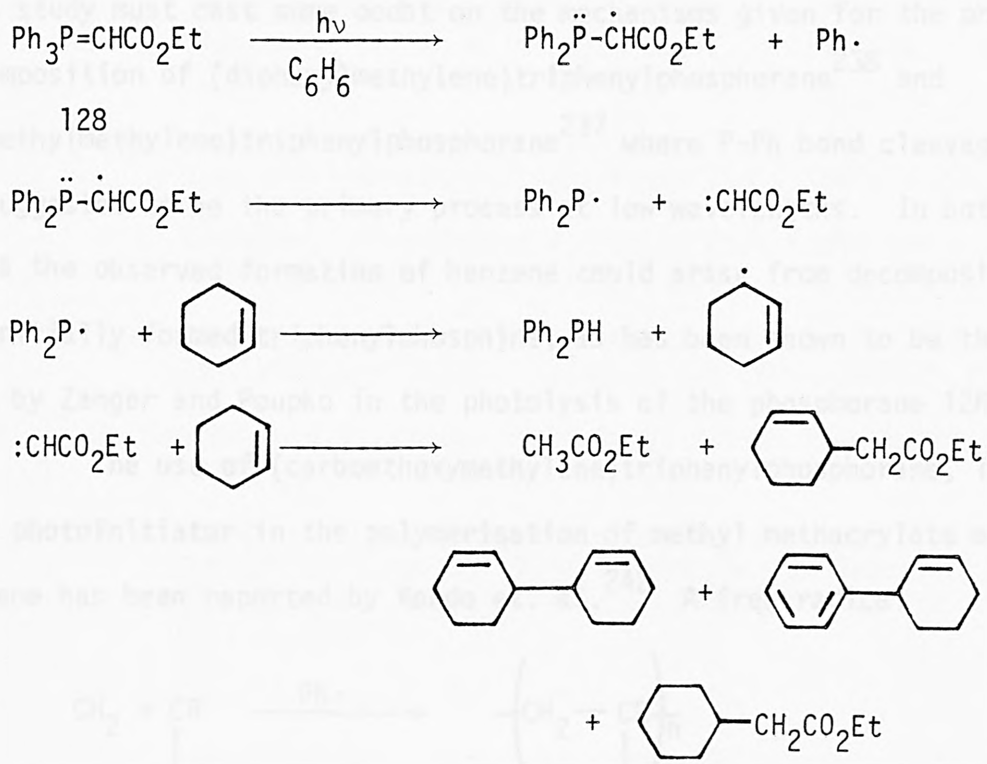
does not decompose via a carbene intermediate, but rather via the bisphosphoranyl radical 125.

In contrast irradiation of (benzoylmethylene)triphenylphosphorane in cyclohexene gave, among other products triphenyl phosphine, acetophenone and 7-norcaryl phenyl ketone, 127.[238] Initial P=C bond cleavage to generate the carbene 126 accounts for the formation of 127. Direct irradiation leads to a much larger yield of 127 compared to its formation on sensitized irradiation, which indicates that direct



irradiation produces the carbene 126 in the singlet state. On the other hand, sensitized irradiation leads preferentially to acetophenone which suggests the formation of 126 in its triplet state.

Nagao et. al. have reported the photodecomposition of (carboethoxymethylene)triphenylphosphorane, 128.[239,240] Irradiation in benzene gave products which were accounted for by proposing cleavage of



a P-Ph bond as the primary step in the reaction. However Zanger and Poupko have reexamined the photolysis of 128 using e.s.r., and found that the primary step is infact P=C bond cleavage and not P-Ph bond cleavage.[241] This gives triphenylphosphine and carboethoxymethylene. The formation of benzene arises from secondary photolysis of Ph_3P. Although the radical 129 was detected by e.s.r., the evidence indicates

$$Ph_3P{=}CHCO_2Et \xrightarrow{h\nu} Ph_3P + :CHCO_2Et$$

128

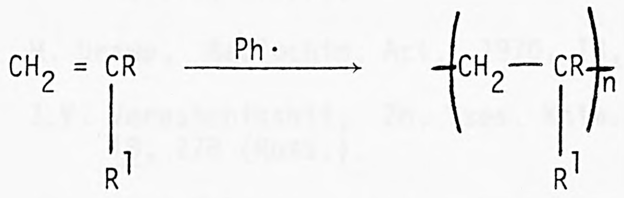
$$Ph_3P \xrightarrow{h\nu} Ph_2P\cdot + Ph\cdot$$

$$Ph_2P\cdot + :CHCO_2Et \longrightarrow Ph_2\dot{P}{=}CHCO_2Et$$

129

it is formed from a recombination reaction of the diphenylphosphino radical and carboethoxymethylene, and not from P-Ph bond scission. This study must cast some doubt on the mechanisms given for the photodecomposition of (diphenylmethylene)triphenylphosphorane[236] and (dimethylmethylene)triphenylphosphorane[237] where P-Ph bond cleavage is suggested to be the primary process at low wavelengths. In both cases the observed formation of benzene could arise from decomposition of initially formed triphenylphosphine, as has been shown to be the case by Zanger and Poupko in the photolysis of the phosphorane 128.[241]

The use of (carboethoxymethylene)triphenylphosphorane, 128, as a photoinitiator in the polymerisation of methyl methacrylate and styrene has been reported by Kondo et. al.[242] A free radical



$$CH_2 = \underset{R^1}{CR} \xrightarrow{Ph\cdot} \left(CH_2 - \underset{R^1}{CR} \right)_n$$

$R = H,\ R^1 = Ph$

$R = CH_3,\ R^1 = CO_2CH_3$

mechanism is suggested, involving Ph· as the radical initiator.

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THREE

THE PHOTOOXIDATION OF SOME ANTHRACENYL PHOSPHORUS COMPOUNDS

The Photooxidation Reaction.

Photooxidation (photooxygenation) is an oxygenation reaction in which a substrate A may be transformed, by molecular oxygen, into the addition product AO_2 only in the presence of light. It may take place as either;

(i) a direct process where light is absorbed by A or O_2

$$A + O_2 \xrightarrow{h\nu} AO_2$$

or (ii) an indirect (photosensitized) process where light is absorbed by molecules other than A or O_2. Such molecules are known as the sensitizer.

$$A + O_2 \xrightarrow{\text{sensitizer}/h\nu} AO_2$$

In general photooxidation reactions are divided into two types:

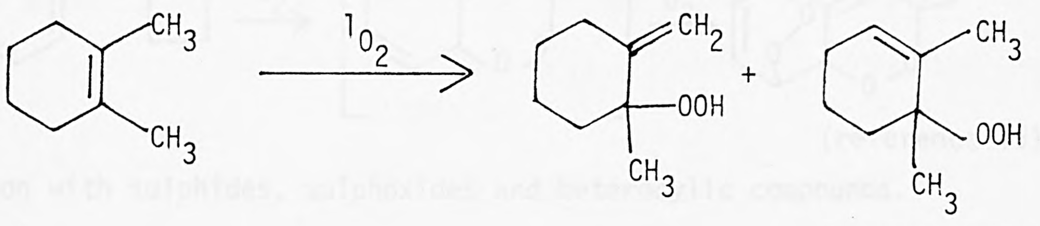
Type I processes, in which free radicals and electronically excited moleules are involved, and *Type II processes*, in which only electronically excited molecules occur as intermediates.[1]

Photochemical reactions of a variety of organic substrates with molecular oxygen have been studied, and several reviews on the various aspects of photooxidation reactions have appeared. Bowen[2] and Rigaudy[3] have reviewed Type II photooxidation reactions of polycyclic aromatic hydrocarbons. Livingston[4] has discussed Type I and Type II photooxidation reactions, paying particular attention to the mechanistic aspects. Hochstrasser and Porter[5] reported on 'Primary Processes in Photooxidation', a short review on direct photooxidation reactions, while Denny and Nickon[6] have written a comprehensive review of sensitized photooxidation reactions. From a preparative aspect, Type II direct and indirect photooxidation reactions of diene systems have been compiled in a review 'Oxygen as a Dienophile' by Gollnick and Schenck[7]. Arbuzov[8] has also reported on this topic along similar lines.

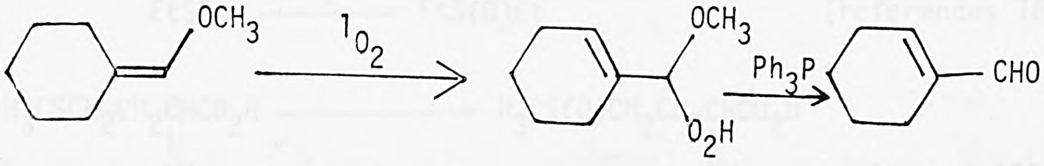
Briefly most of the known photooxidation reactions of molecular oxygen may be classified into one of the following two catagories.

Reactions with olefins and aromatic compounds.

Hydrogen abstraction and addition (the Ene reaction);

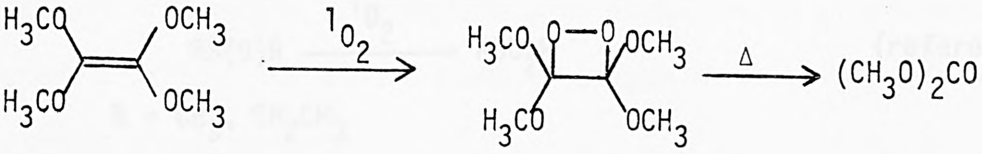


(reference 9)



(reference 10)

(2 + 2) - Cycloaddition with oxetane formation;



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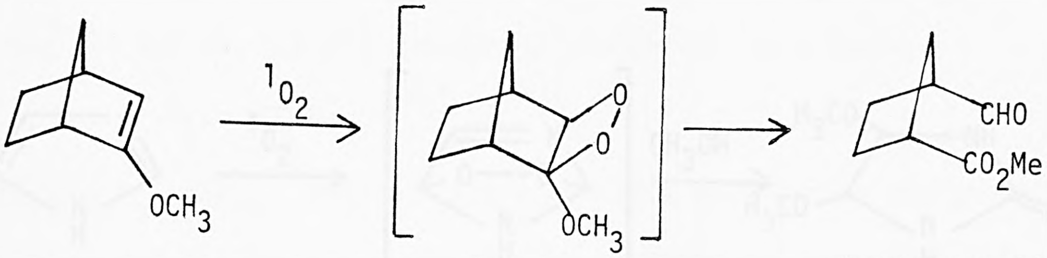
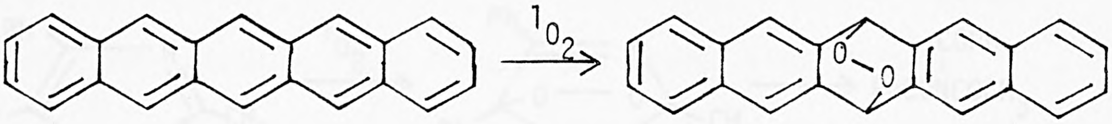


(reference 12)

(4 + 2) - Cycloaddition with endoperoxide formation;



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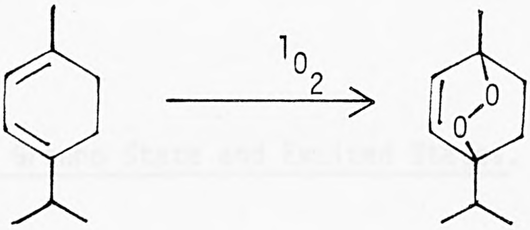

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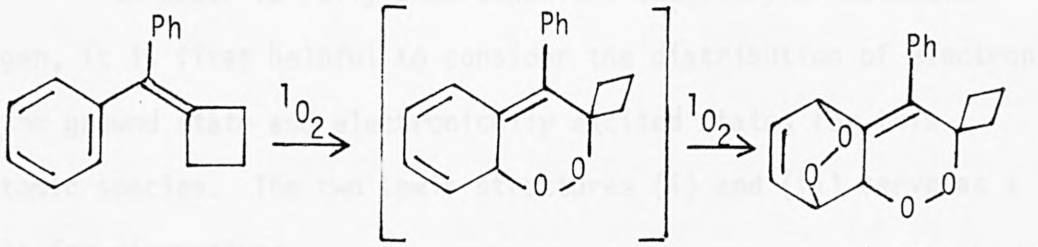
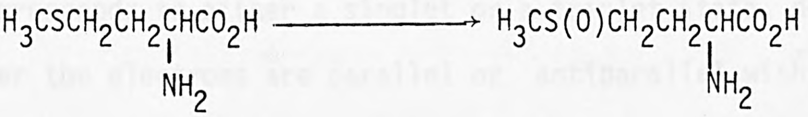


(reference 15)

Reaction with sulphides, sulphoxides and heterocylic compounds.

Oxidation of sulphides to sulphoxides;

$EtSEt \xrightarrow{^1O_2} EtS(O)Et$ (references 16,17)



$H_3CSCH_2CH_2CH(NH_2)CO_2H \longrightarrow H_3CS(O)CH_2CH_2CH(NH_2)CO_2H$

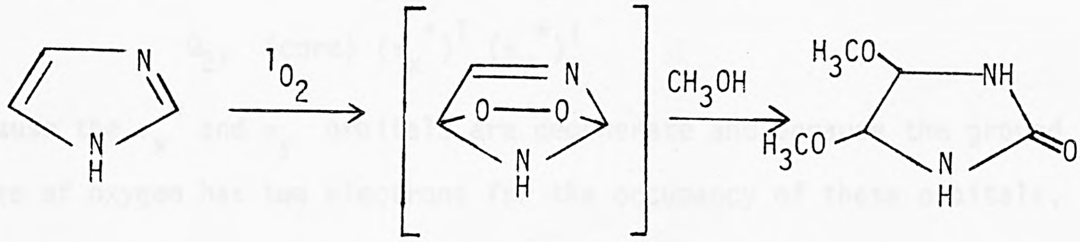
(reference 18)

Oxidation of sulphoxides to sulphones;

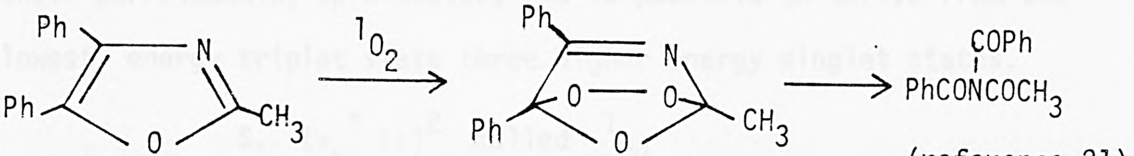
$$RS(O)R \xrightarrow{^{1}O_2} RSO_2R$$ (reference 19)

$R = CH_3, CH_2CH_3$

Reaction with heterocyclic compounds;



(reference 20)



(reference 21)

Molecular Oxygen: Ground State and Excited States.

In order to fully understand the chemistry of molecular oxygen, it is first helpful to consider the distribution of electrons in the ground state and electronically excited states for this diatomic species. The two Lewis structures (i) and (ii) serve as a basis for discussion:

$:\underset{\cdot\cdot}{\ddot{O}} = \underset{\cdot\cdot}{\ddot{O}}: \;\equiv\; O = O$ (i) electrons paired

$:\underset{\cdot\cdot}{\dot{O}} - \underset{\cdot\cdot}{\dot{O}}: \;\equiv\; \dot{O} = \dot{O}$ (ii) electrons unpaired.

Structure (i) in which all the electrons are paired corresponds to a singlet state, while structure (ii), in which two electrons are unpaired corresponds to either a singlet or a triplet state, depending on whether the electrons are parallel or antiparallel with respect to each other. If one considers the molecular orbital description of oxygen, it is possible to correlate each structure to a particular electronic state. The ground state of oxygen is described by the electronic configuration;

$$O_2,\ (\sigma_{1S})^2\ (\sigma_{1S}^*)^2\ (\sigma_{2S})^2\ (\sigma_{2S}^*)^2\ (\pi_{2p_x})^2\ (\pi_{2p_y})^2\ (\pi_{2p_z})^2\ (\pi_{2p_x}^*)^1\ (\pi_{2p_y}^*)^1.$$

Ignoring all but the two highest-energy electrons, this leaves,

$$O_2,\ (\text{core})\ (\pi_x^*)^1\ (\pi_y^*)^1$$

Because the π_x^* and π_y^* orbitals are degenerate and because the ground state of oxygen has two electrons for the occupancy of these orbitals, the ground state of molecular oxygen is a triplet, and is given the symbol $^3O_2$. From the orbital occupancies of the (π_x^*) (π_y^*) pair and their corresponding spin states, it is possible to derive from the lowest energy triplet state three higher energy singlet states.

$$S,\ (\pi_y^*\ \uparrow\downarrow)^2 \text{ called } {}^1\Delta_y$$

$$S,\ (\pi_x^*\ \uparrow\downarrow)^2 \text{ called } {}^1\Delta_x$$

$$S,\ (\pi_x^*\ \uparrow)\ (\pi_y^*\ \downarrow) \text{ called } {}^1\Sigma$$

$$T,\ (\pi_x^*\ \uparrow)\ (\pi_y^*\ \uparrow) \text{ called } {}^3\Sigma, \text{ ground state.}$$

These four states have the given spectroscopic notations of $^1\Delta_y$, $^1\Delta_x$, $^1\Sigma$, and $^3\Sigma$ respectively. The electron orbital occupancy corresponding to these four states gives rise to the electron distributions shown in Figure 3.1. The Δ state possess an electronic distribution such that the two π^* electrons are in one of two mutually perpendicular planes. Both these $^1\Delta_x$ and $^1\Delta_y$ states are degenerate, although the approach of another molecule may cause a splitting of the states to occur. The $^1\Delta$ state of molecular oxygen is commonly referred to as 'singlet oxygen', and given the symbol $^1O_2$: (c.f. ground state oxygen - $^3O_2$). Experimentally the energetic ordering of the lowest electronic states of molecular oxygen is found to be $^3\Sigma < {}^1\Delta$ (22.5 kcal mol^{-1})

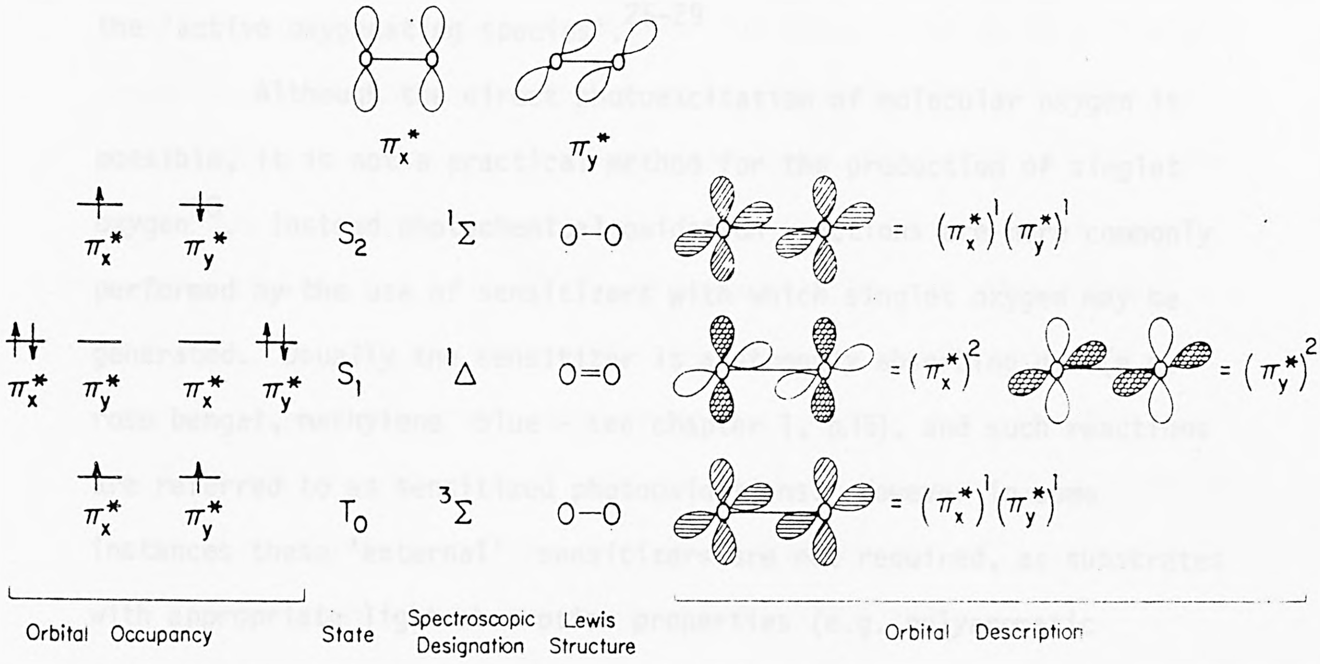


Figure 3.1. A qualitative description of the three lowest electronic orbital configurations and states of molecular oxygen.

$< {}^1\Sigma$ (37.5 kcal mol^{-1}). It is partly because of these relatively low energy excited states that accounts for molecular oxygen being an important participant in many photochemical reactions. The pure radiative life time of $^1\Delta$ molecular oxygen is found to be 2.7 x 10^{3}sec.[22] However such a long life time is not normally observed since, at ordinary pressures in the gas phase or in solution both collisional and chemical deactivation will occur effectively. The longest life times of $^1\Delta$ are ca. 10^{-3} sec when observed in solvents normally considered to be chemically inert (e.g. halogenated hydrocarbons).[23]

Photochemical Formation of Singlet Oxygen.

The identity of the reactive species in photooxidation reactions has been a subject of controversy for many years. However it has now been shown, in agreement with the original proposition of Kautsky[24], that for many photochemical reactions singlet oxygen in the 'active oxygenating species'.[25-29]

Although the direct photoexcitation of molecular oxygen is possible, it is not a practical method for the production of singlet oxygen[30]. Instead photochemical oxidation reactions are more commonly performed by the use of sensitizers with which singlet oxygen may be generated. Usually the sensitizer is a strongly absorbing dye (e.g. rose bengal, methylene blue - see chapter 1, p.15), and such reactions are referred to as sensitized photooxidations. However in some instances these 'external' sensitizers are not required, as substrates with appropriate light absorption properties (e.g. polyaromatic hydrocarbons) can also function as the sensitizer. Such reactions are known as direct or self-sensitized photooxidations. Because singlet oxygen has a low energy of excitation (22.5 kcal mol^{-1}), a vast number of compounds are able to sensitize its production. For aromatic hydrocarbons (ArH e,g. anthracene), Scheme 3.1 shows the important processes that are involved in a direct photooxidation reaction. Equations (2) → (5) represent the four major processes for oxygen quenching of the excited states of the hydrocarbon.

$$ArH_{S_0} \xrightarrow{h\nu} ArH_{S_1} \qquad (1)$$

$$ArH_{S_1} + {}^3O_2 \longrightarrow ArH_{T_1} + {}^1O_2 \qquad (2)$$

$$ArH_{S_1} + {}^3O_2 \longrightarrow ArH_{T_1} + {}^3O_2 \qquad (3)$$

$$ArH_{T_1} + {}^3O_2 \longrightarrow ArH_{S_0} + {}^1O_2 \qquad (4)$$

$$ArH_{T_1} + {}^3O_2 \longrightarrow ArH_{S_0} + {}^3O_2 \qquad (5)$$

$$ArH_{S_1} \xrightarrow{ISC} ArH_{T_1} \qquad (6)$$

$$ArH_{S_0} + {}^1O_2 \longrightarrow (ArHO_2)_{S_0} \qquad (7)$$

Scheme 3.1.

In addition to the normal route for ArH_{T_1} production, process (6), oxygen enhanced intersystems crossing (ISC), process (3), may also give rise to triplet aromatic hydrocarbon. For process (2) to be a feasible route to singlet oxygen production, the singlet-triplet splitting must exceed the excitation energy of singlet oxygen (22.5 kcal mol^{-1}). However there is considerable debate about the ability of process (2) to compete with process (3).[31-33] If processes (2) and (4) are both efficient, and process (5) inefficient, then the quantum yield of singlet oxygen production must approach a value of two, as observed for 9,10-dicyanoanthracene.[34] Alternatively if process (2) is inefficient, then singlet oxygen can only arise from process (4), and hence the quantum yield of its formation cannot exceed unity.

For indirect photooxidation reactions an 'external' sensitizer is used. Ideally the chosen sensitizer will have a high quantum yield of triplet production, and a triplet energy not far above that of singlet oxygen. This is because it is usually assumed that oxygen quenching of the triplet state is the only route to singlet oxygen production.

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

However by comparison with self-sensitized reactions, it can be seen

$$\mathrm{Sens}_{S_0} \xrightarrow{h\nu} \mathrm{Sens}_{S_1} \qquad (1)$$

$$\mathrm{Sens}_{S_1} + {}^3O_2 \longrightarrow \mathrm{Sens}_{T_1} + {}^1O_2 \qquad (2)$$

$$\mathrm{Sens}_{S_1} + {}^3O_2 \longrightarrow \mathrm{Sens}_{T_1} + {}^3O_2 \qquad (3)$$

$$\mathrm{Sens}_{T_1} + {}^3O_2 \longrightarrow \mathrm{Sens}_{S_0} + {}^1O_2 \qquad (4)$$

$$\mathrm{Sens}_{T_1} + {}^3O_2 \longrightarrow \mathrm{Sens}_{S_0} + {}^3O_2 \qquad (5)$$

$$\mathrm{Sens}_{S_1} \xrightarrow{ISC} \mathrm{Sens}_{T_1} \qquad (6)$$

Scheme 3.2.

that sensitizers with sufficient singlet-triplet splitting may also be capable of producing singlet oxygen. These processes are outlined in Scheme 3.2. It becomes apparent from Schemes 3.1 and 3.2 that the formation of singlet oxygen is a complex process dependent upon a number of competing reactions and their relative efficiencies with respect to each other.

While the photochemical generation of singlet oxygen is preferred for most synthetic work because of convenience, yield and ease of product isolation, there are also a number of non photochemical methods available. These include;

sodium hypochlorite - hydrogen peroxide,[25,28,29]

$$\mathrm{NaOCl} + \mathrm{H_2O_2} \longrightarrow {}^1\mathrm{O_2} + \mathrm{H_2O} + \mathrm{NaCl}$$

alkaline hydrogen peroxide - bromine,[35]

$$\mathrm{HO^-} + \mathrm{HOO^-} + \mathrm{Br_2} \longrightarrow {}^1\mathrm{O_2} + \mathrm{H_2O} + 2\mathrm{Br^-}$$

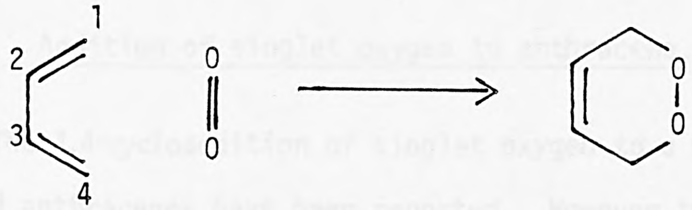
triphenyl phosphite - ozone adduct.[36,37]

$$(\mathrm{C_6H_5O})_3\mathrm{P} + \mathrm{O_3} \xrightarrow[\mathrm{CH_2Cl_2}]{-70^0} (\mathrm{C_6H_5O})_3\mathrm{P{-}O_3} \xrightarrow{-35^0} {}^1\mathrm{O_2} + (\mathrm{C_6H_5O})_3\mathrm{PO}$$

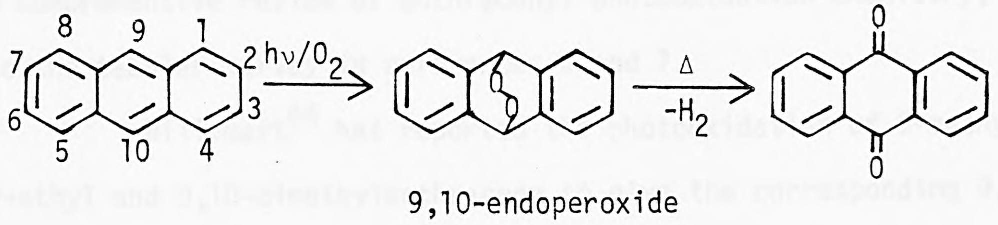
microwave or radiofrequency discharge[27,38]

<u>Type II Photooxidation Reactions of Anthracenyl Compounds.</u>

When a solution containing a polynuclear aromatic hydrocarbon is oxygenated and irradiated at a pertinent wavelength (with sensitizer if required), a 1,4-cyloaddition reaction may occur between photochemically generated singlet oxygen and the cisoid 1,3-diene system to yield a 1,4-endoperoxide with a double bond at the 2,3-position.



Thus anthracene is reported to yield the 9,10-endoperoxide[39,40,41] which on heating in solution oxidizes to anthraquinone.



This behaviour of singlet oxygen towards 1,3-π electron systems resembles that of dienes and olefins in the traditional Diels Alder reaction. Consequently the selection rules developed by Woodward and Hoffmann[42] for concerted thermal cycloaddition reactions are also applicable to 1,4-cyloaddition reactions involving singlet oxygen.[43] Such concerted cycloaddition reactions between anthracene and singlet oxygen are believed to occur by way of a six membered suprafacial (boat like) transition state as illustrated in Figure 3.2.

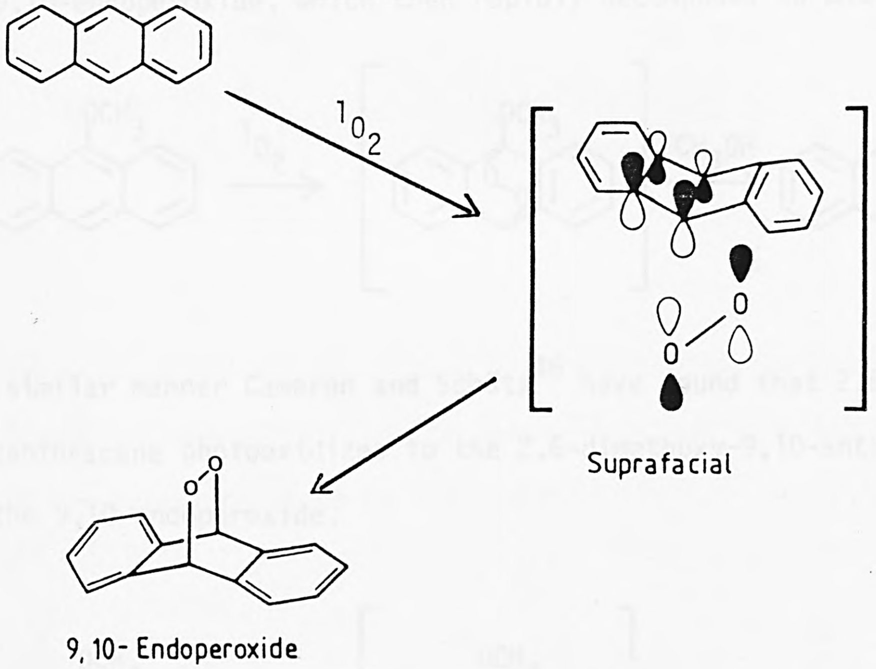
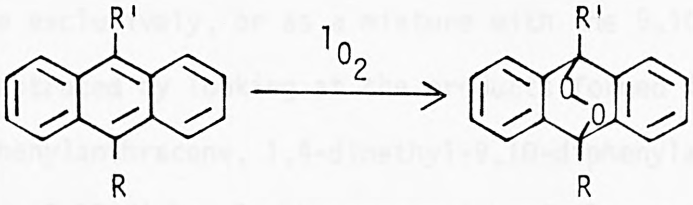


Figure 3.2. Addition of singlet oxygen to anthracene.

The 1,4-cycloaddition of singlet oxygen to a wide variety of substituted anthracenes have been reported. However to give just a brief introduction to this subject, the following examples will serve to illustrate the nature of oxidation products that may be formed. For a comprehensive review of anthracenyl photooxidation chemistry, refer to the tabular survey in references 6 and 7.

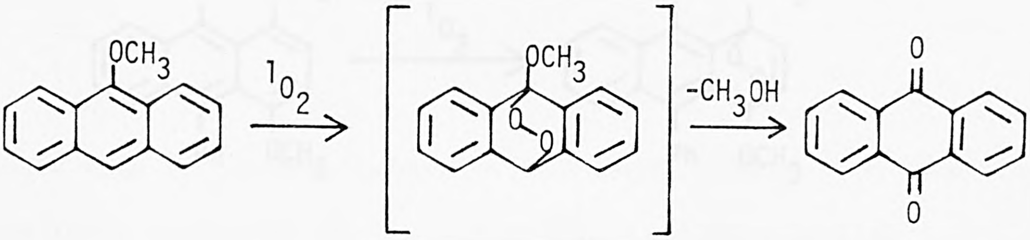
Willemart[44] has reported the photooxidation of 9-methyl, 9-ethyl and 9,10-dimethylanthracene to give the corresponding 9,10-endoperoxide.



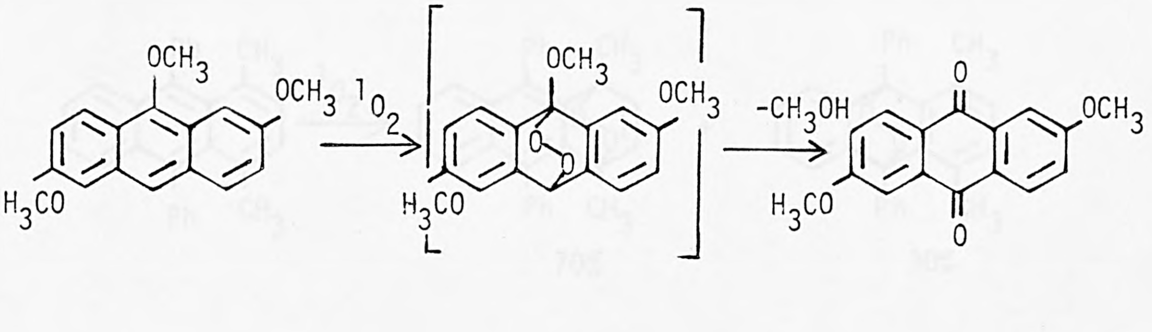
R = H, R' = CH_3, CH_2CH_3

R = R' = CH_3

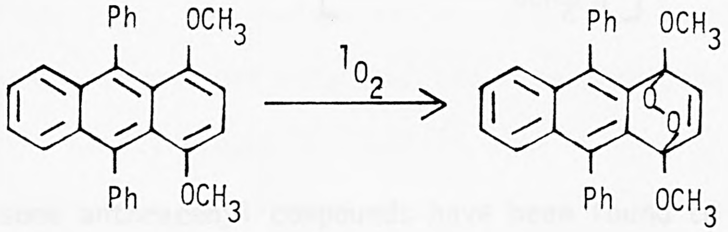
Similarly Lepage[45] showed that 9-methoxyanthracene is photooxidized to the 9,10-endoperoxide, which then rapidly decomposes to anthraquinone.



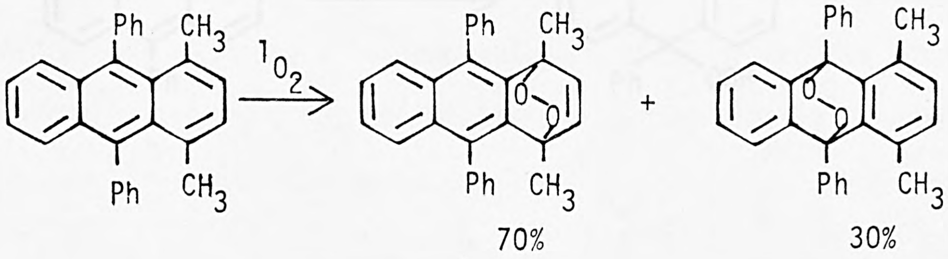
In a similar manner Cameron and Schütz[46] have found that 2,6,9-trimethoxyanthracene photooxidizes to the 2,6-dimethoxy-9,10-anthraquinone via the 9,10-endoperoxide.



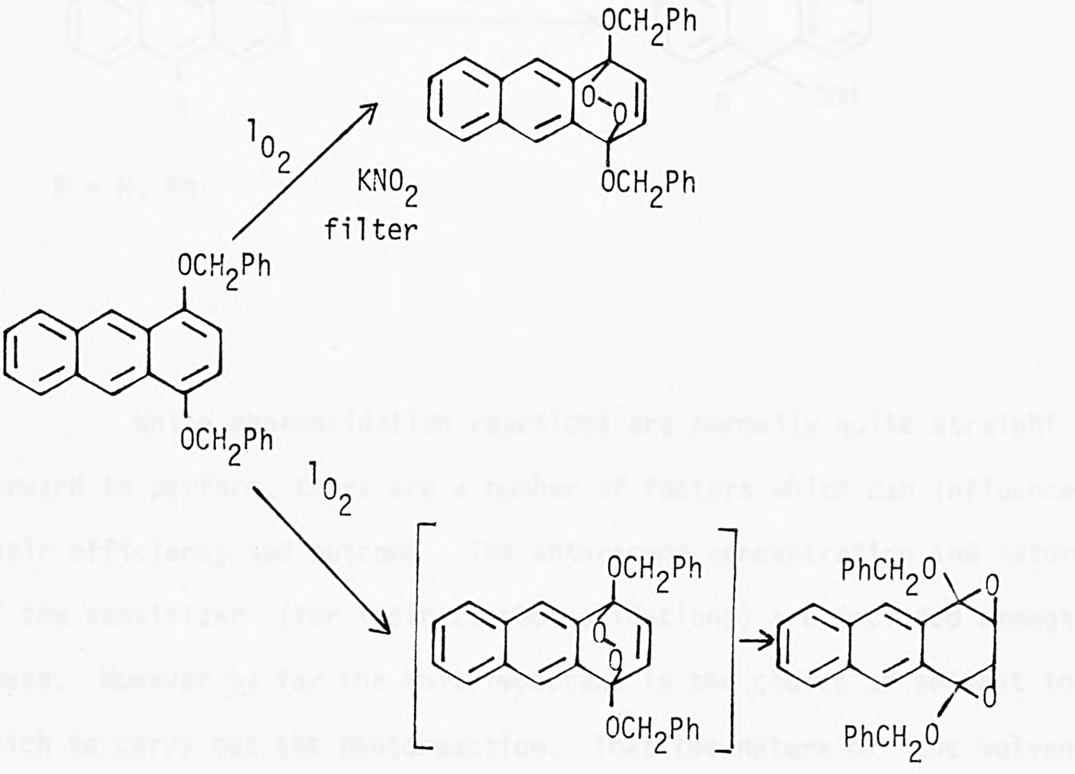
Even from these few examples it is clear that the outcome of an anthracenyl photooxidation reaction is influenced by the nature of the substituents on the anthracene nucleus. The presence of electron donating groups for example has been found to increase the reactivity of the 1,3-π systems, while conversely electron withdrawing groups decrease the reactivity of the diene system. It is thus possible by using appropriatly substituted anthracenes to form either the 1,4-endoperoxide exclusively, or as a mixture with the 9,10-isomer. This is well illustrated by looking at the products formed from the reaction of 9,10-diphenylanthracene, 1,4-dimethyl-9,10-diphenylanthracene and 1,4-dimethoxy-9,10-diphenylanthracene with singlet oxygen. 9,10-Diphenylanthracene is known to yield on photooxidation the 9,10-endoperoxide.[39,40,47] Alternatively Dufraisse et. al. have shown that by introducing methoxy groups into the 1,4-positions, photooxidation leads to the exclusive formation of the 1,4-endoperoxide.[48]



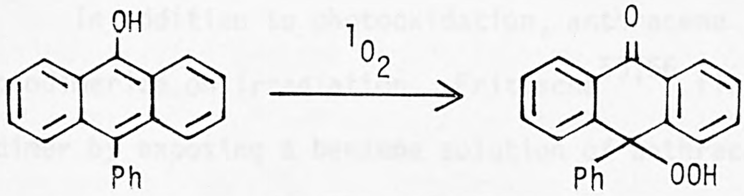
However Rigaudy et. al. have found that the photooxidation of the analagous compound containing the weaker electron donating methyl groups in the 1,4-positions leads to a mixture of the 1,4- and 9,10-endoperoxides.[49]



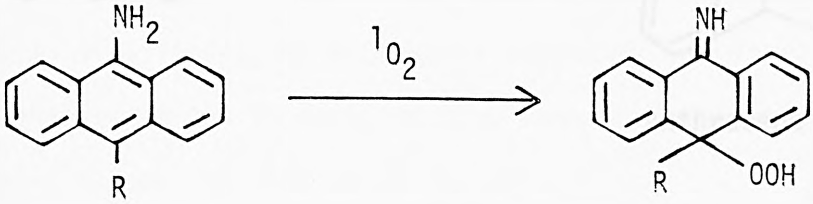
Similarly 1,4-dibenzyloxyanthracene photooxidizes to give the 1,4-endoperoxide.[50] However in the absense of any filter solution to remove light with a wavelength below 400nm, this endoperoxide will photoisomerize.



Finally some anthracenyl compounds have been found to form on photo-oxidation a hydroperoxide instead of the usual transannular endoperoxide. Thus Dufraisse et. al.[51,52] have reported the formation of an anthrone hydroperoxide from 9-hydroxy-10-phenylanthracene.



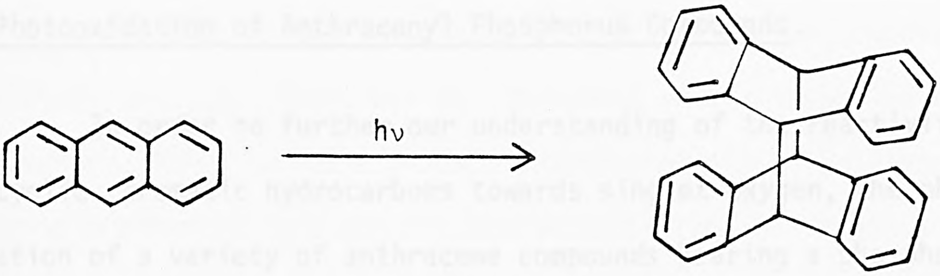
Rigaudy and Izoret[53] have also reported the formation of the imine analogue from the photooxidation of the 9-aminoanthracene.



R = H, Ph

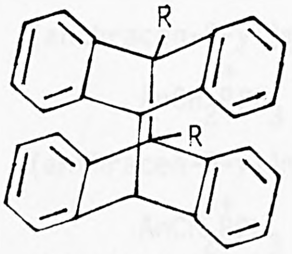
While photooxidation reactions are normally quite straight forward to perform, there are a number of factors which can influence their efficiency and outcome. The anthracene concentration and nature of the sensitizer (for indirect photooxidations) are included amongst these. However by far the most important is the choice of solvent in which to carry out the photoreaction. That the nature of the solvent can have a pronounced effect on the rate of endoperoxide formation can largely be attributed to the life time of singlet oxygen in the various solvents. Thus carbon disulphide in which singlet oxygen has a relatively long life time (200μ sec)[54] has been by far the most frequently used solvent for endoperoxide syntheses; (compare for example with, methanol - 7μ sec, ethanol - 12μ sec, benzene - 24μ sec, acetone - 26μ sec, acetonitrile - 30μ sec, chloroform - 60μ sec).[54]

In addition to photooxidation, anthracene is also known to photodimerize on irradiation. Fritzsche[55,56] first formed the photodimer by exposing a benzene solution of anthracene to sunlight. The correct structure for the photodimer was originally proposed by Linebarger[57] and Orndorff and Cameron[58].

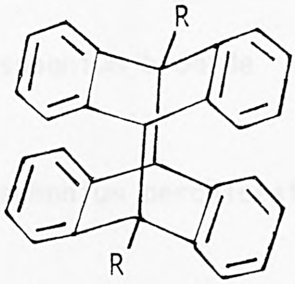


Anthracene Photodimer.

Many anthracene derivatives with substituents at the 1-, 2-, and 9-positions also form photodimers. A survey of such derivatives has been published by Greene et. al.[59] and Lalande and Calas[60]. 9-Monosubstituted anthracenes present an interesting problem in that they can give rise to dimers having either a cis (head to head) or trans (head to tail) structure. However currently only dimers of the latter type are known. Unlike photooxidation which involves triplet excited anthracene,



cisoid dimer



transoid dimer

photodimerization occurs via the first excited singlet state. However not all anthracenyl compounds will dimerize on irradiation. Steric and/or electronic effects may prevent photodimers being formed. Additionally irradiation of anthracenyl compounds under oxygen may lead to competition between photooxidation and photodimerization. Logically dilute solutions will favour photooxidation, as will compounds which possess a high rate for intersystem crossing into the triplet manifold.

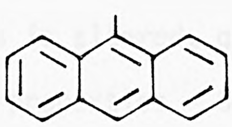
The Photooxidation of Anthracenyl Phosphorus Compounds.

In order to further our understanding of the reactivity of polycyclic aromatic hydrocarbons towards singlet oxygen, the photooxidation of a variety of anthracene compounds bearing a phosphorus functionality at the 9- position have been investigated. The compounds that were chosen for this study included,

an anthracenyl phosphate,

anthracen-9-yl diethyl phosphate,

$AnOP(O)(OCH_2CH_3)_2$ where An ≡



an anthracenyl phosphonate,

diethyl (anthracen-9-yl)methylphosphonate

$AnCH_2P(O)(OCH_2CH_3)_2$

and some anthracenyl phosphonium salts,

(anthracen-9-yl)methyltriphenylphosphonium bromide

$AnCH_2\overset{+}{P}Ph_3 \quad Br^-$

(anthracen-9-yl)methyltriphenylphosphonium perchlorate

$AnCH_2\overset{+}{P}Ph_3 \quad ClO_4^-$

1-(anthracen-9-yl)benzyltriphenylphosphonium chloride

$AnCH(Ph)\overset{+}{P}Ph_3 \quad Cl^-$

By choosing the appropriate wavelength of radiation with which to carry out these photoreactions, it was possible to observe both direct and indirect photooxidative transformations. For the direct irradiations, this required the use of black-light fluorescent lamps having a λ_{max} centered at approximately 350nm. The indirect irradiation utilized daylight fluorescent lamps, with rose bengal as the external sensitizer. A potassium chromate filter solution was also used in conjunction with the daylight lamps to remove any radiation emitted below 480nm which might otherwise have lead to some additional direct photooxidation. A full understanding of the photoreactivity of the chosen compounds under both these reaction conditions was dependent upon a number of differing approaches. These included product indentification, labelling studies, trapping experiments and kinetic measurements (solvent isotope effects). The photoreaction was easily followed by thin layer chromatography (t.l.c.), and UV absorption spectroscopy. Most anthracenyl compounds show a complex UV spectrum which frequently includes a quartet-like multiplet centered between 320nm and 400nm. As a photoreaction occurs, so the conjugation within the anthracene nucleus is altered, giving rise to a corresponding change in its absorption properties. On photooxidation, this change results in the loss of the quartet-like multi-

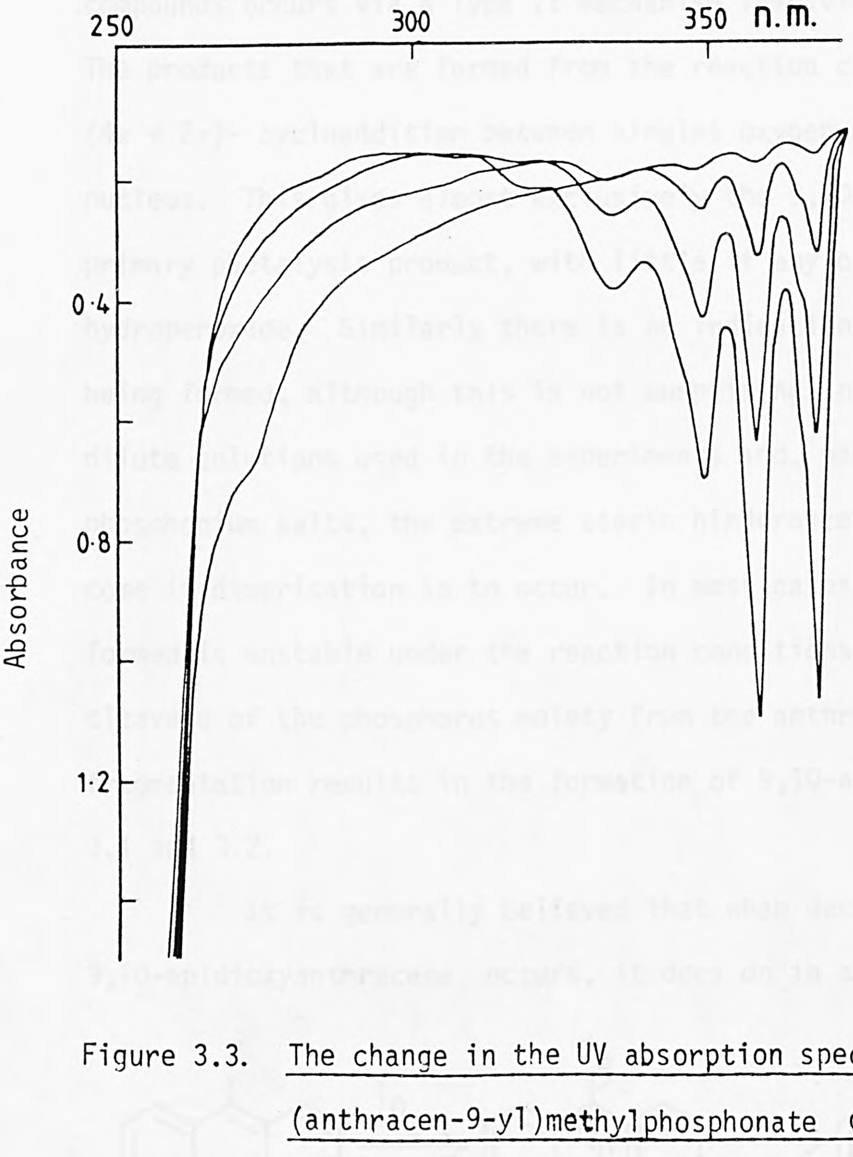


Figure 3.3. The change in the UV absorption spectrum for diethyl (anthracen-9-yl)methylphosphonate on its direct photooxidation.

plet from the spectrum. In some cases, new absorption bands appear which can be attributed to the product(s) formed. The direct photooxidation of diethyl (anthracen-9-yl)methylphosphonate, Figure 3.3. illustrates this perfectly. As the reaction proceeds, so there is a gradual disappearance of the bands at 334, 349, 366 and 386nm with the slow formation of a broad band at around 320nm. It will be seen that this latter band is due to the formation of anthraquinone. The reaction is taken as having gone to completion when the quartet-like multiplet has completely disappeared from the spectrum.

This work has found that as with anthracene and many of its derivatives, so also the photooxidation of these anthracenyl phosphorus compounds occurs via a Type II mechanism involving singlet oxygen. The products that are formed from the reaction clearly indicate a $(4\pi + 2\pi)$- cycloaddition between singlet oxygen and the anthracene nucleus. This gives almost exclusively the 9,10-endoperoxide as the primary photolysis product, with little if any of the 1,4-isomer or hydroperoxide. Similarly there is no indication of any photodimer being formed, although this is not surprising in view of the relatively dilute solutions used in the experiments and, particularly for the phosphonium salts, the extreme steric hinderance that must be overcome if dimerisation is to occur. In most cases the 9,10-endoperoxide formed is unstable under the reaction conditions, and fragments with cleavage of the phosphorus moiety from the anthracene nucleus. This fragmentation results in the formation of 9,10-anthraquinone, Tables 3.1 and 3.2.

It is generally believed that when decomposition of a 9,10-epidioxyanthracene occurs, it does do in a concerted fashion;

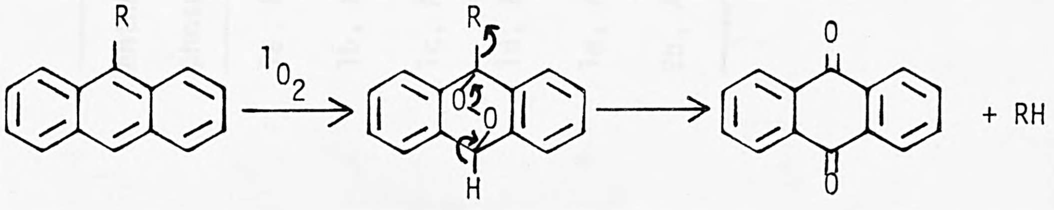


Table 3.1. Percentage yields of products obtained from the direct photooxidation of anthracenyl phosphorus compounds 1a - 1e and 2b.

Anthracenyl phosphorus compound	% yields of[a,b]	Anthraquinone 3	$(EtO)_2P(O)OH^c$ 4	$(EtO)_2P(O)Me$ 6	Ph_3PO 8	PhCHO 10	$PhCO_2H^c$ 11
1a, $AnOP(O)(OEt)_2$		46	84				
1b, $AnCH_2P(O)(OEt)_2$		76		75			
1c, $AnCH_2\overset{+}{P}Ph_3\ Br^-$		78			85		
1d, $AnCH_2\overset{+}{P}Ph_3\ ClO_4^-$		98			95		
1e, $AnCH(Ph)\overset{+}{P}Ph_3\ Cl^-$		70			80	19	42
2b, $An(O_2)CH_2P(O)(OEt)_2$		90		76			

a, % yields as determined by g.l.c.

b, all photolysis products identified by GCMS

c, determined as its methyl ester

Table 3.2. Percentage yields of products obtained from the indirect (rose bengal sensitized) photooxidation of anthracenyl phosphorus compounds 1a - 1e.

Anthracenyl phosphorus compound % yields of$^{a,b.}$	Anthraquinone 3	$(EtO)_2P(O)OH^c$ 4	$(EtO)_2P(O)Me$ 6	Ph_3PO 8	PhCHO 10	$PhCO_2H^c$ 11
1a, $AnOP(O)(OEt)_2$	95	87				
1b, $AnCH_2P(O)(OEt)_2$	0		0			
1c, $AnCH_2\overset{+}{P}Ph_3\ Br^-$	d			d		
1d, $AnCH_2\overset{+}{P}Ph_3\ ClO_4^-$	95			97		
1e, $AnCH(Ph)\overset{+}{P}Ph_3\ Cl^-$	59			61	49	<5

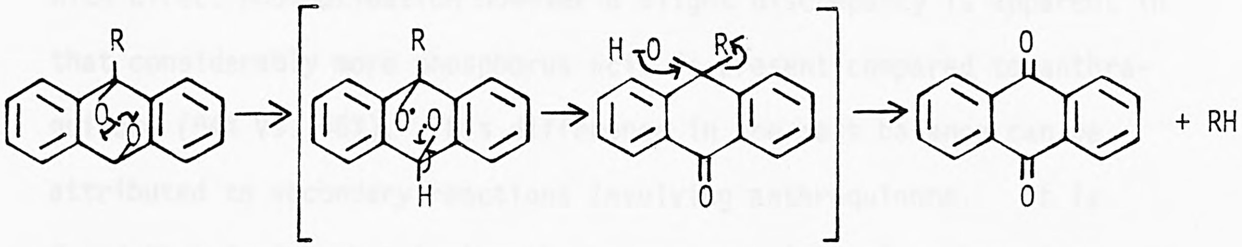
a, % yields as determined by g.l.c.

b, all photolysis products identified by GCMS

c, determined as its methyl ester

d, the precise % yield of formation of these compounds is unclear - refer to text.

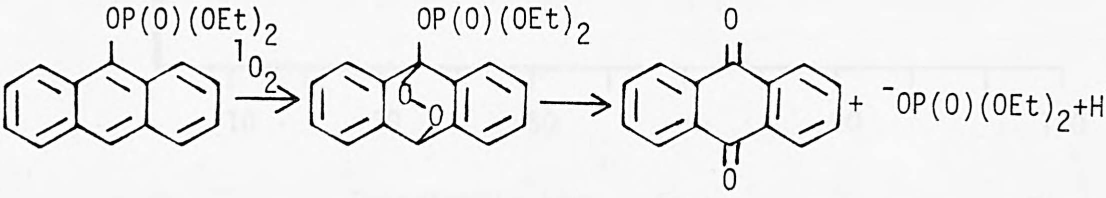
However it is also possible that the decomposition occurs not in a concerted manner, but by way of a transient hydroxy ketone intermediate;



Either way, the overall rearrangement and nature of the cleaved species are the same. It was found that where decomposition of the 9,10-epidioxyanthracenyl phosphorus compounds occurred the fate of the cleaved species varied with the nature of the phosphorus moiety. Since a variety of functionally different phosphorus compounds were investigated, this lead to a range of secondary, non photochemical, processes occurring. These, for each of the anthracenyl phosphorus compounds studied are discussed in the following pages.

Anthracen-9-yl diethyl phosphate.

The photooxidation of anthracen-9-yl diethyl phosphate, 1a, leads to the initial formation of the 9,10-endoperoxide 2a. Decomposition of this occurs under the photoreaction conditions with loss of the phosphorus moiety as the diethyl phosphate anion, which after methylation with diazomethane is readily detected by gas liquid chromatography, (g.l.c.). From Table 3.2 it can be seen that the indirect



1a 2a 3

photooxidation leads to the formation of diethyl phosphate and anthraquinone in correspondingly high yields (87% and 95% respectively). With direct photooxidation however a slight discrepancy is apparent in that considerably more phosphorus acid is present compared to anthraquinone (84% Vs. 46%). This difference in the mass balance can be attributed to secondary reactions involving anthraquinone. It is found that during photolysis, the percentage yield of anthraquinone rises in the early stages of the reaction to a maximum yield of 48% after 20 min., and then progressively decreases as illustrated in Figure 3.4. There is no clear reason why this fluctuation in yield should occur. Whether the anthraquinone is interacting in some way with the diethyl phosphate is unlikely, since irradiating a mixture

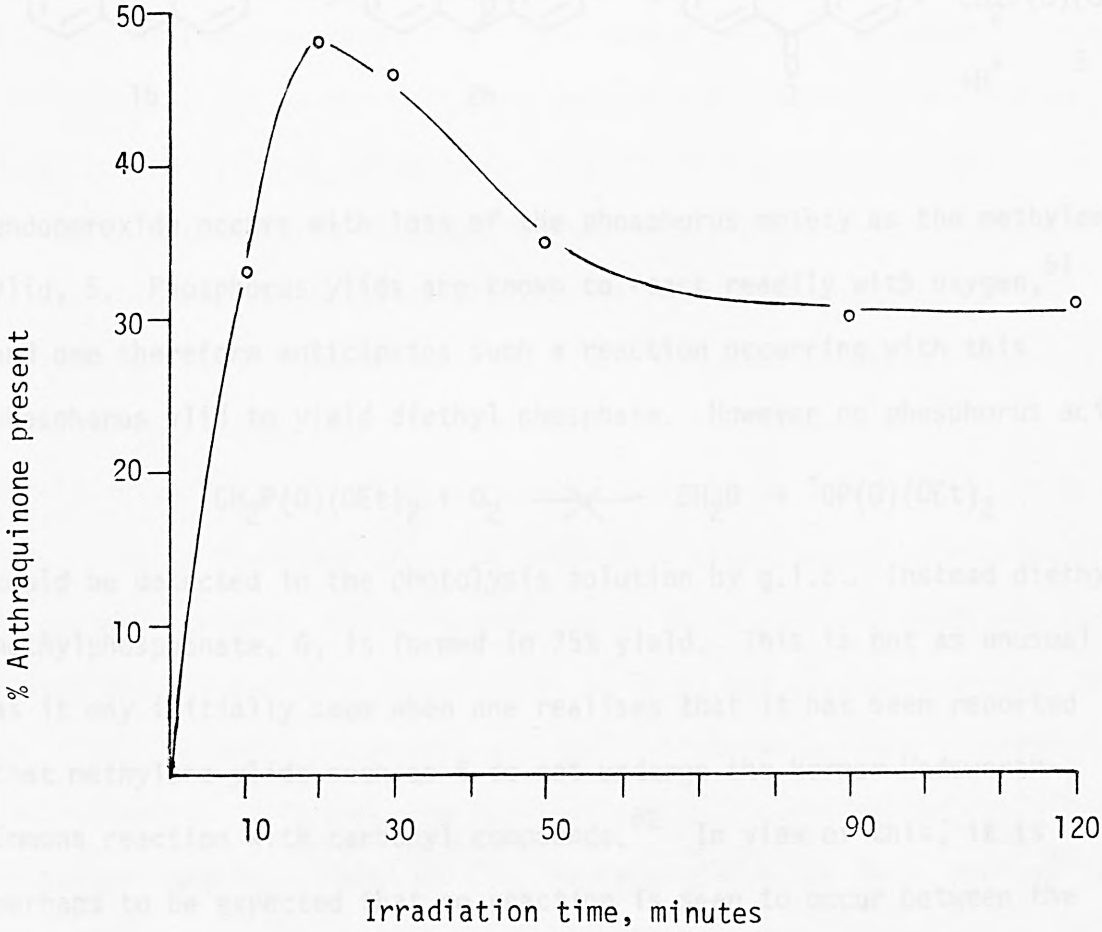
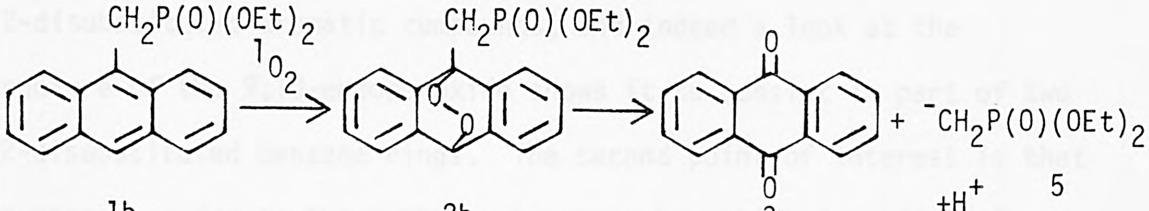


Figure 3.4. Fluctuation of anthraquinone concentration on photooxidation of anthracen-9-yl diethyl phosphate.

of anthraquinone and the phosphorus acid does not lead to a fall in anthraquinone concentration. Similarly it is also unlikely that anthraquinone is undergoing a secondary photochemical reaction, since for all the other anthracenyl phosphorus compounds which produce anthraquinone on irradiation, no similar fluctuation in anthraquinone concentration was observed.

Diethyl (anthracen-9-yl)methylphosphonate.

The direct photooxidation of diethyl (anthracen-9-yl)methylphosphonate, 1b, proceeds via the endoperoxide 2b, and leads to anthraquinone formation (76%). It is believed that the decomposition of this endoperoxide occurs with loss of the phosphorus moiety as the methylene ylid, 5. Phosphorus ylids are known to react readily with oxygen,[61] and one therefore anticipates such a reaction occurring with this phosphorus ylid to yield diethyl phosphate. However no phosphorus acid could be detected in the photolysis solution by g.l.c.. Instead diethyl methylphosphonate, 6, is formed in 75% yield. This is not as unusual as it may initially seem when one realises that it has been reported that methylene ylids such as 5 do not undergo the Horner-Wadsworth-Emmons reaction with carbonyl compounds.[62] In view of this, it is perhaps to be expected that no reaction is seen to occur between the methylene phosphonate ylid and oxygen. The formation of diethyl methylphosphonate, 6, from the protonation of the ylid is now easily rationalised.

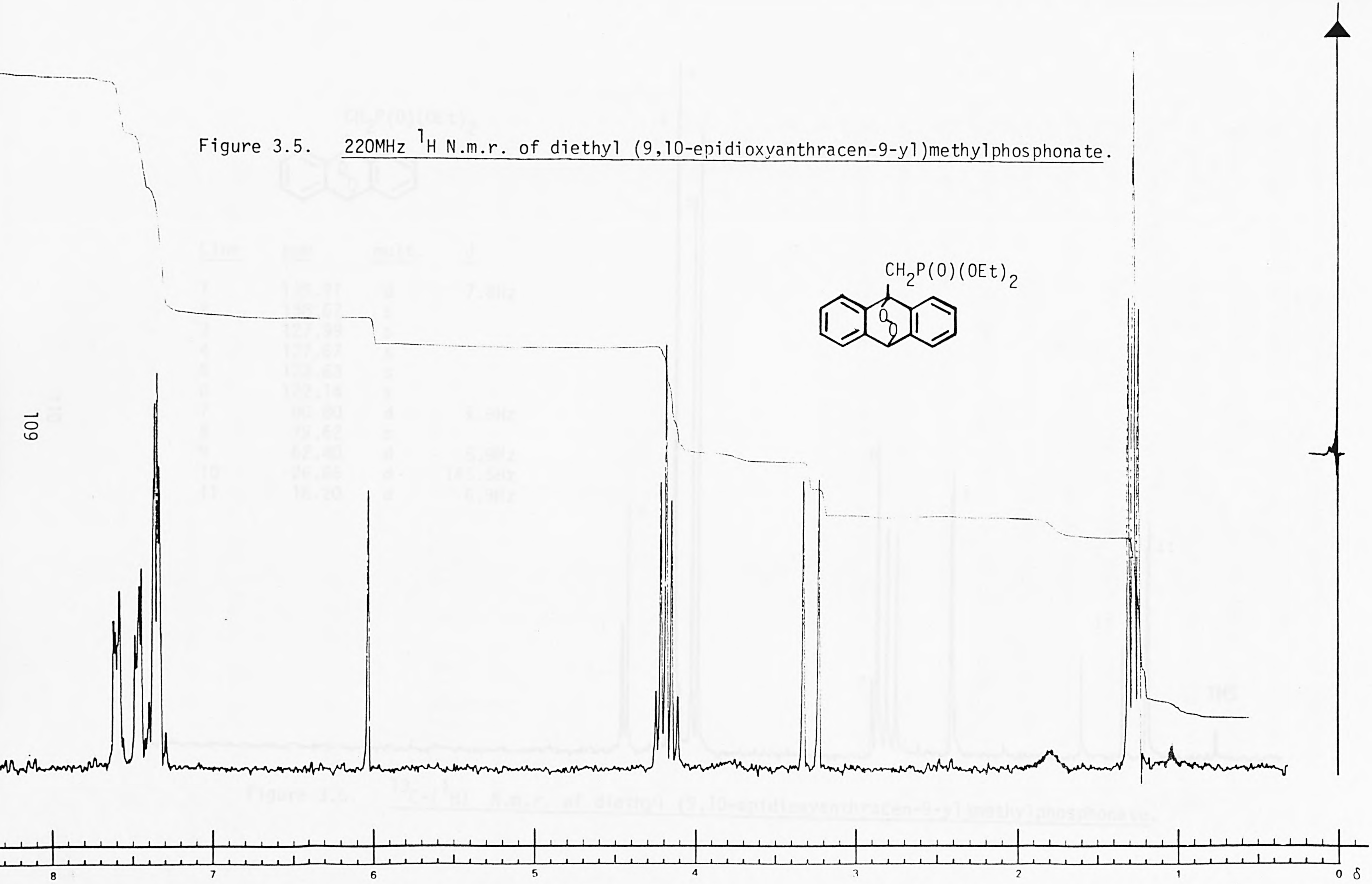


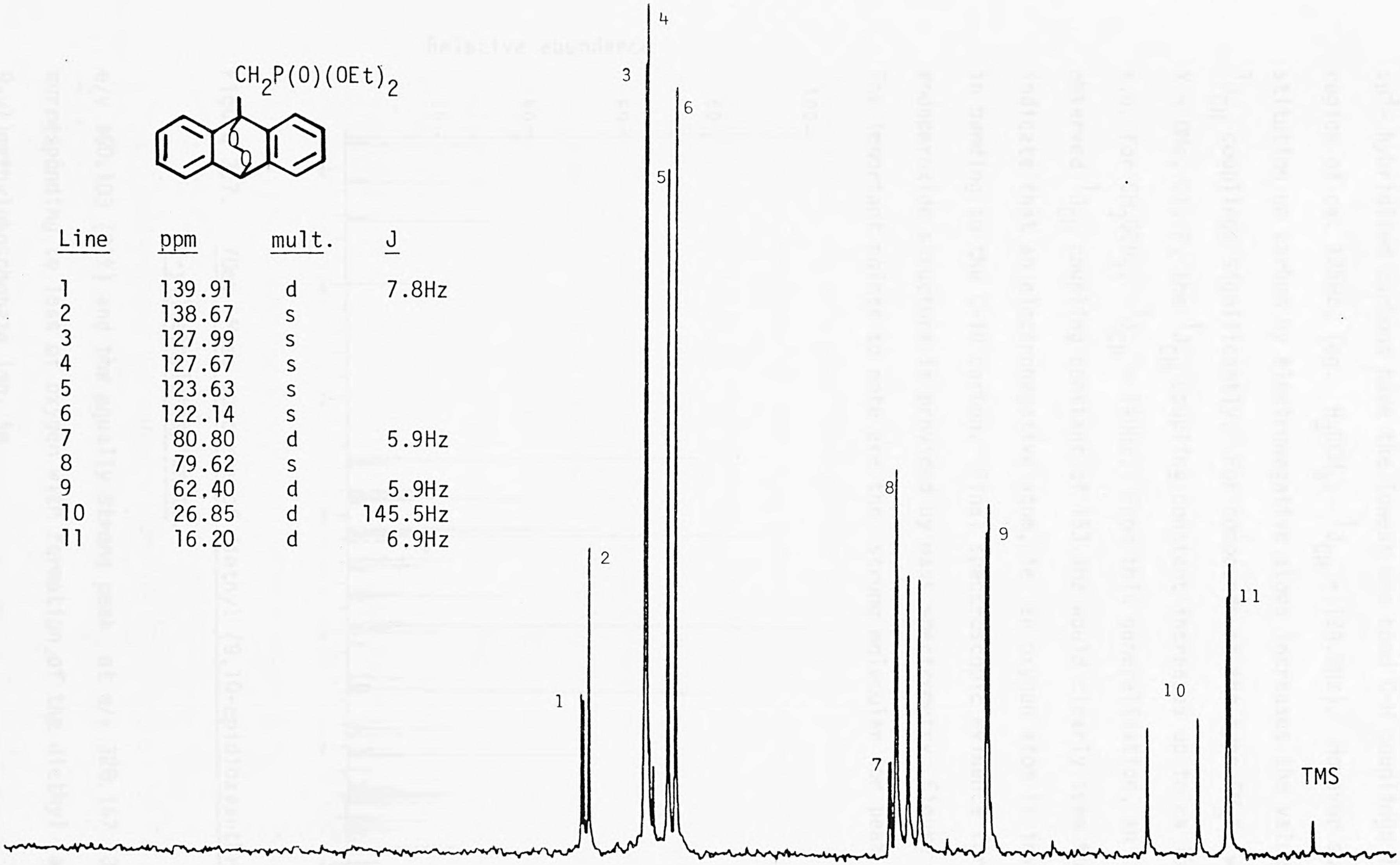
1b 2b 3 5

$$^-CH_2P(O)(OEt)_2 + O_2 \not\longrightarrow CH_2O + {}^-OP(O)(OEt)_2$$

The indirect, rose bengal sensitized photooxidation of diethyl (anthracen-9-yl)methylphosphonate, 1b, is also of particular interest in that it does not result in the formation of either anthraquinone or diethyl methylphosphonate. Instead chromatographic purification of the reaction mixture leads to the isolation of a novel compound (75% yield), which after spectroscopic analysis can be catagorically identified as the 9,10-endoperoxide, 2b. The ^{1}H n.m.r. of the endoperoxide, diethyl (9,10-epidioxyanthracen-9-yl)methylphosphonate is shown in Figure 3.5. There are two points of interest that are worth noting. The first is the pattern for the aromatic proton resonances. This pattern is similar to that usually obtained for 1,2-disubstituted aromatic compounds, and indeed a look at the structure of the 9,10-endoperoxide shows it to consist in part of two 1,2-disubstituted benzene rings. The second point of interest is that the resonance due to the methylene protons has shifted up field from 4.23δ in the starting phosphonate to 3.27δ in the endoperoxide, while a singlet has appeared at 6.02δ for the H-10 proton. These changes in the spectrum can be attributed to the loss of aromaticity in the 'B' ring of the anthracene nucleus. The ^{13}C n.m.r. spectrum, Figure 3.6. also indicates some loss of aromaticity in the compound whilst providing additional information which supports an endoperoxide structure. Clearly there are only six resonances which can be attributed to aromatic carbons, while in addition to those for the methylene and ethoxy carbons two other resonances at 79.6δ and 80.8δ are present in the region normally associated with sp^3 hybridized carbons. Indeed their chemical shift compares favourably with those reported for other epidioxyanthracenyl compounds.[63] The coupled spectra gives for the C-10 carbon a $^1J_{CH}$ coupling constant of 153.4Hz. From semi-empirical arguements, it is possible to estimate one bond C-H couplings in organic molecules.[64,65] In hydrocarbons, one bond ^{13}C-H couplings have

Figure 3.5. 220MHz ^1H N.m.r. of diethyl (9,10-epidioxyanthracen-9-yl)methylphosphonate.





Line	ppm	mult.	J
1	139.91	d	7.8Hz
2	138.67	s	
3	127.99	s	
4	127.67	s	
5	123.63	s	
6	122.14	s	
7	80.80	d	5.9Hz
8	79.62	s	
9	62.40	d	5.9Hz
10	26.85	d	145.5Hz
11	16.20	d	6.9Hz

Figure 3.6. ^{13}C-{^{1}H} N.m.r. of diethyl (9,10-epidioxyanthracen-9-yl)methylphosphonate.

been related to the amount of s character on the carbon nucleus. Thus sp^3- hybridized carbons have the lowest one bond C-H couplings in the region of ca. 125Hz; (eg. H_3CCH_3, ${}^1J_{CH}$ = 124.9Hz). However substitution on carbon by electronegative atoms increases the value for ${}^1J_{CH}$ couplings significantly. For compounds of the type CH_3X, where X = OMe, Cl, F, the ${}^1J_{CH}$ coupling constant increases up to ca 150Hz, e.g. for CH_3OCH_3, ${}^1J_{CH}$ = 140Hz. From this generalisation, an observed ${}^1J_{CH}$ coupling constant of 153.4Hz would clearly seem to indicate that an electronegative atom, ie an oxygen atom is involved in bonding to the C-10 carbon. Final spectroscopic evidence for an endoperoxide structure is provided by mass spectrometry, Figure 3.7. The important points to note are the strong molecular ion peak at

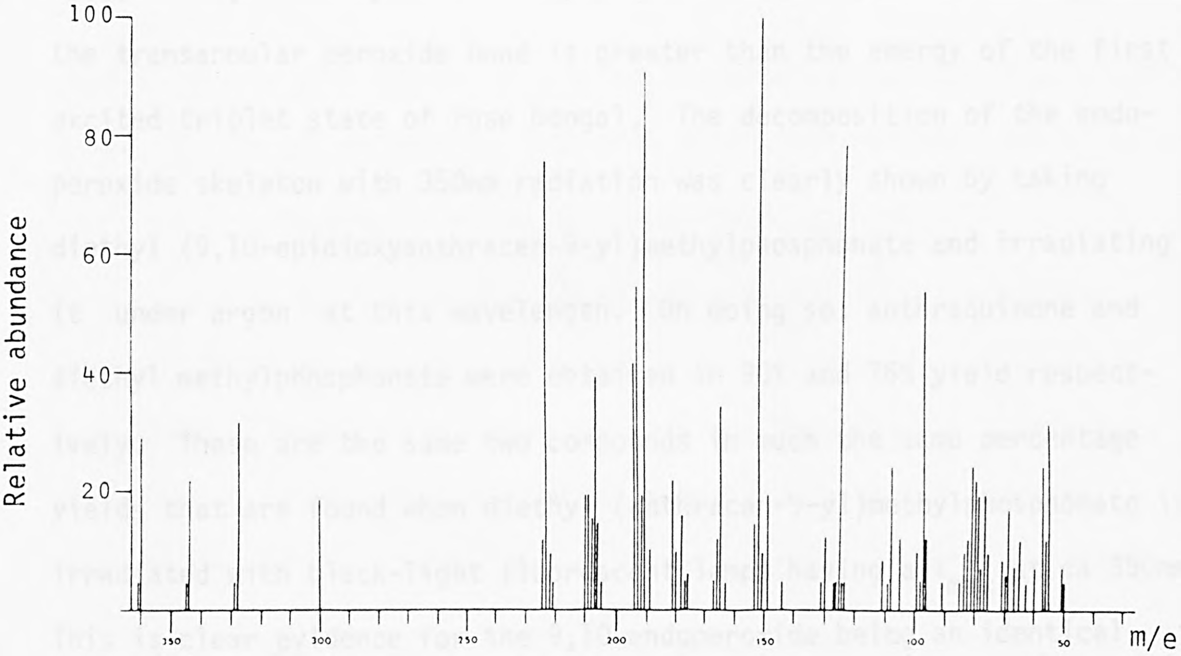
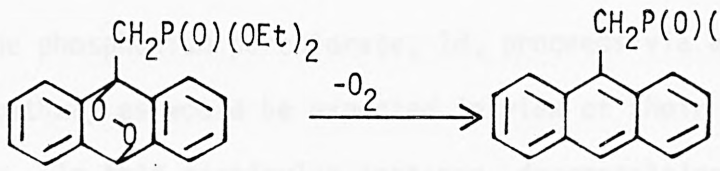


Figure 3.7. 70ev Mass spectrum of diethyl (9,10-epidioxyanthracen-9-yl)methylphosphonate.

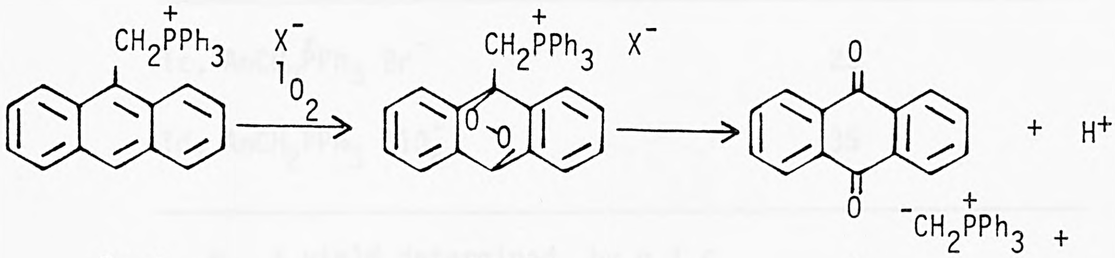
e/v 360.103 (31%) and the equally strong peak at e/v 328.167 (34%) corresponding to loss of oxygen with formation of the diethyl (anthracen-9-yl)methylphosphonate ion, ie.



The formation and stability of diethyl (9,10-epidioxyanthracen-9-yl)-methylphosphonate on indirect irradiation compared to its formation and subsequent decomposition on direct irradiation can be attributed to the relatively weak absorption of this compound in the 350nm region of the spectrum, (λ_{350nm}, log ε 2.08). Absorption of radiation leads to excitation into a higher electronic level, where clearly the rate of oxygen-oxygen bond cleavage must compare favourably with the rate for electronic deactivation if endoperoxide fragmentation is to occur. Above 480nm, not only does the compound not absorb, but the energy of the transannular peroxide bond is greater than the energy of the first excited triplet state of rose bengal. The decomposition of the endoperoxide skeleton with 350nm radiation was clearly shown by taking diethyl (9,10-epidioxyanthracen-9-yl)methylphosphonate and irradiating it under argon at this wavelength. On doing so, anthraquinone and diethyl methylphosphonate were obtained in 90% and 76% yield respectively. These are the same two compounds in much the same percentage yields that are found when diethyl (anthracen-9-yl)methylphosphonate is irradiated with black-light fluorescent lamps having a λ_{max} at ca 350nm. This is clear evidence for the 9,10-endoperoxide being an identical intermediate in both the direct and indirect photooxidation reactions.

(Anthracen-9-yl)methyltriphenylphosphonium bromide and (anthracen-9-yl)methyltriphenylphosphonium perchlorate.

In the case of the phosphonium salts, 1c and 1d product formation is again consistent with a 9,10-endoperoxide being the primary photoproduct. The direct photooxidation of the phosphonium bromide, 1c, and the phosphonium perchlorate, 1d, proceeds via an identical reaction pathway as would be expected in view of their structural similarity. In this particular instance, decomposition of the endoperoxide leads to loss of the phosphorus moiety as methylenetriphenylphosphorane, 7. Unlike the methylene phosphonate ylid, this phosphorane



1c,d. 2c,d. 3 7

c, x = Br

d, x = ClO_4^-

readily reacts with oxygen to produce formaldehyde and triphenylphoshine oxide, 8. In an attempt to trap this ylid intermediate, the direct

$$^-CH_2\overset{+}{P}Ph_3 + O_2 \longrightarrow CH_2O + \underset{8}{Ph_3PO}$$

irradiation of the phosphonium bromide and phosphonium perchlorate was carried out in the presence of hexaldehyde. If fragmentation of the endoperoxide 2c and 2d is occurring with the formation of a methylene phosphorane, then heptene should be formed from a Wittig reaction. On carrying out the photooxidation in this manner, heptene is indeed

$$CH_3(CH_2)_4CHO + {}^-CH_2\overset{+}{P}Ph_3 \longrightarrow CH_3(CH_2)_4CH{=}CH_2 + Ph_3PO$$

produced, Table 3.3. This clearly confirms the participation of a phosphorus ylid in the photooxidation of these types of anthracenyl phosphonium salts. Similarly the indirect irradiation of the phosphonium perchlorate occurs by the same mechanism to produce anthraquinone and triphenylphosphine oxide in high yields. The same however cannot be said for the sensitized photooxidation of the phosphonium

Table 3.3 Percentage yields of heptene obtained from the direct photooxidation of 1c and 1d when carried out in the presence of hexaldehyde.

Anthracenyl phosphonium salt	% yield [a] of $CH_3(CH_2)_4CH = CH_2$ [b]
1c, $AnCH_2\overset{+}{P}Ph_3\ Br^-$	23
1d, $AnCH_2\overset{+}{P}Ph_3\ ClO_4^-$	35

a, % yield determined by g.l.c.

b, confirmed by GCMS

bromide salt. That a 9,10-endoperoxide is formed is clear. Unfortunatly this particular endoperoxide does not appear to fragment cleanly in the usual manner. It is hard to say to what extent anthraquinone and triphenylphosphine oxide are formed, if at all, from the decomposition of the endoperoxide. They may be obtained though in yields of ca. 75% and 40% respectively by pyrolysis of the endoperoxide at 250°C in the injection port of the gas chromatograph prior to analysis. That 9,10-anthraquinone is obtained in such a high yield would seem to indicate the initial formation of a transannular peroxide across the 9,10-position of the anthracene nucleus. The possibility that the endoperoxide may be stable at room temperature does not appear to be so, since all attempts to isolate and purify this compound resulted only in a crude mixture containing (by t.l.c.) anthraquinone, triphenylphosphine oxide and a number of other unidentified compounds. ^1H And ^{31}P n.m.r. spectroscopy provide valuable information which supports an endoperoxide intermediate, while at the same time enabling its thermal instability to be clearly seen. The ^1H n.m.r. of the crude endoperoxide is shown in Figure 3.8. It shows a doublet at 5.12δ for the methylene protons (c.f. a doublet at 6.07δ with the starting phosphonium bromide 1c) and the appearance of a singlet at 5.90δ corresponding to the H-10 anthracenyl proton, (c.f. a singlet at 6.02δ for the same H-10 proton in diethyl (9,10-epidioxyanthracen-9-yl)-methylphosphonate. All these features are consistent with the loss

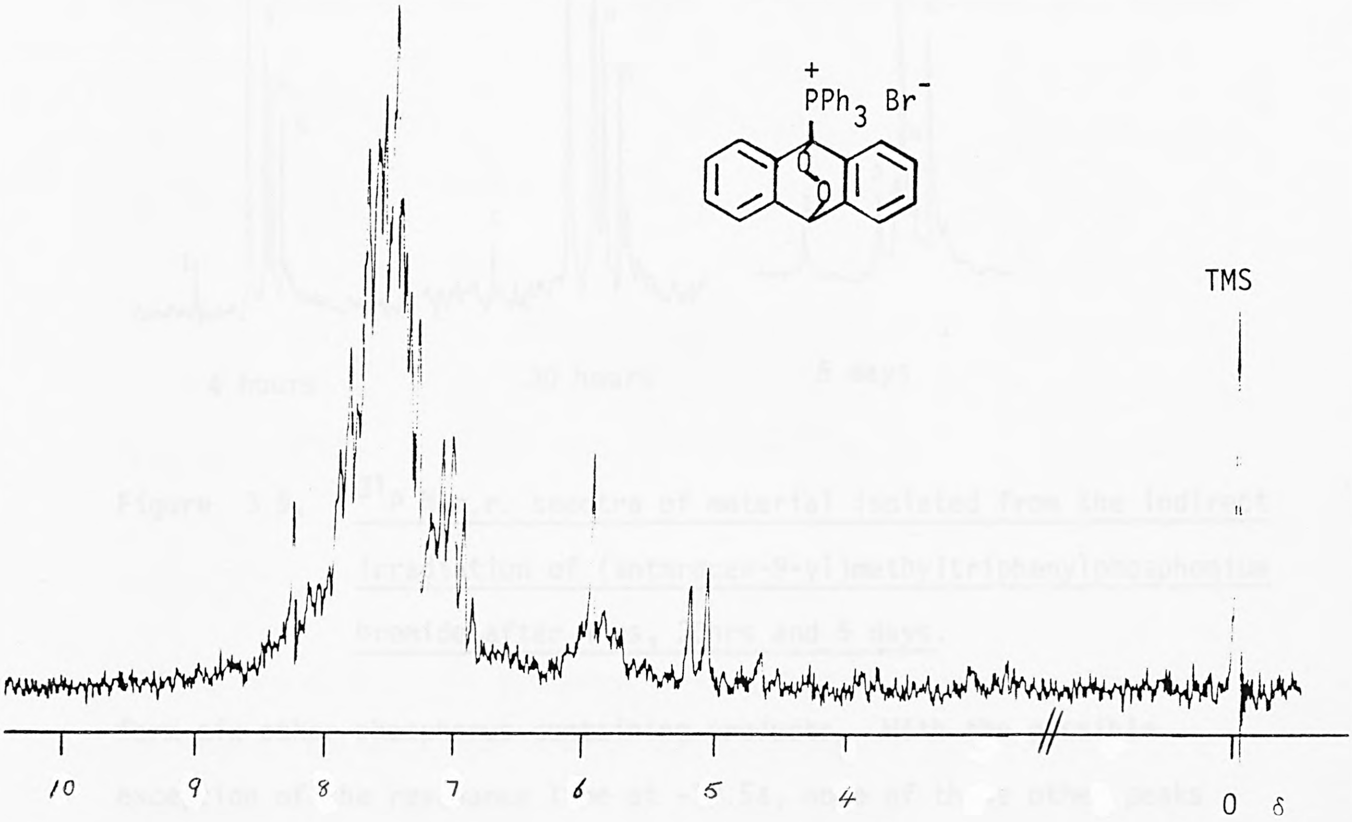
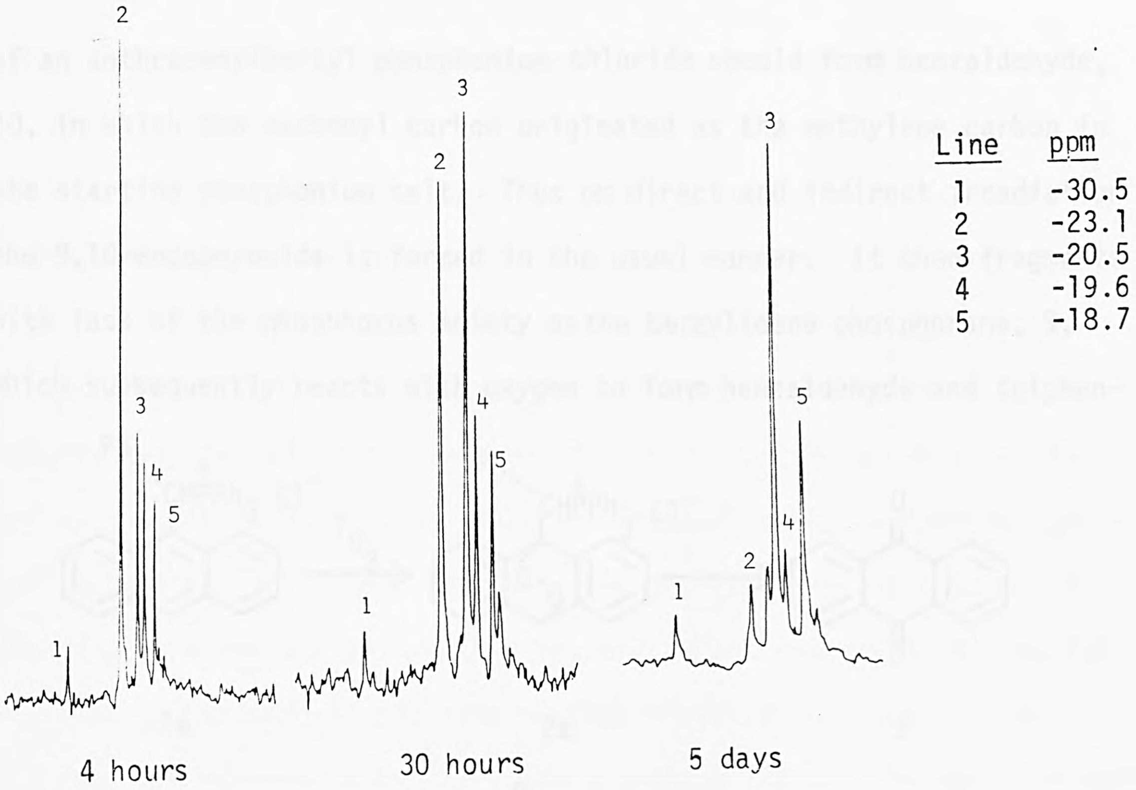


Figure 3.8. 100MHz ^{1}H N.m.r. of impure (9,10-epidioxyanthracen-9-yl)-methyltriphenylphosphonium bromide.

of aromaticity in the 'B' ring of the anthracene nucleus, as would be the case on forming a 9,10-endoperoxide. Experiments using ^{31}P n.m.r. spectroscopy have indicated that the sensitized photooxidation of this phosphonium bromide (^{31}P chemical shift, -20.2δ) leads to the formation of a transient peak at -23.1δ which then decreases in intensity over a period of days at room temperature, while other peaks of varying magnitude appear at -30.5δ, -21.4δ, -20.5δ, -19.6δ, -18.7δ, -17.8δ (all relative to H_3PO_4), Figure 3.9. The peak at -23.1δ is taken as being due to the endoperoxide intermediate which slowly decomposes to



4 hours

30 hours

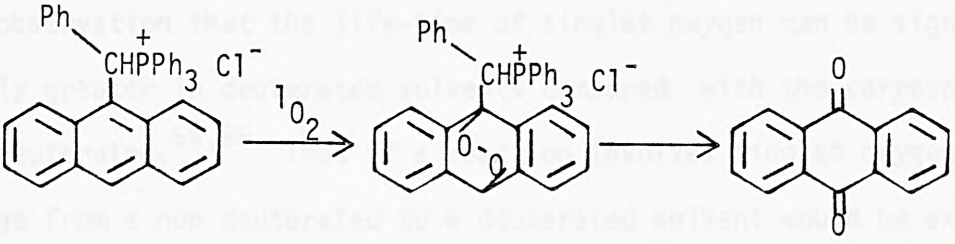
5 days

Figure 3.9. ^{31}P N.m.r. spectra of material isolated from the indirect irradiation of (anthracen-9-yl)methyltriphenylphosphonium bromide after 4hrs, 30hrs and 5 days.

form six other phosphorus containing products. With the possible exception of the resonance line at -30.5δ, none of these other peaks correspond to the phosphorus resonance for triphenylphosphine oxide (-29.5δ). The precise structure of the compounds which give rise to these remaining signals have not been elucidated.

1-(anthracen-9-yl)benzyltriphenylphosphonium chloride.

Finally the photooxidation of 1-(anthracen-9-yl)benzyltriphenylphosphonium chloride, 1e, has been investigated. It was initially prepared and studied so that the fate of the methylene carbon in compounds 1c and 1d could be catagorically determined. When the anthracenyl phosphonium bromide and phosphonium perchlorate salts are photooxidized, the methylene carbon is believed to become the carbon atom in a molecule of formaldehyde. Consequently the photooxidation of an anthracenylbenzyl phosphonium chloride should form benzaldehyde, 10, in which the carbonyl carbon originated as the methylene carbon in the starting phosphonium salt. Thus on direct and indirect irradiation the 9,10-endoperoxide is formed in the usual manner. It then fragments with loss of the phosphorus moiety as the benzylidene phosphorane, 9, which subsequently reacts with oxygen to form benzaldehyde and triphenylphosphine oxide. The formation of benzaldehyde clearly indicates the fate of the methylene carbon, and confirms the participation of a phosphorus ylid intermediate. The presence of benzoic acid on direct irradiation is a result of the autoxidation of the benzaldehyde initially formed. Interestingly there is no indication of any stilbene present (as determined by g.l.c.), formed from a Wittig reaction between the benzylidene phosphorane and benzaldehyde. The reason for



1e   2e   3

$$\underset{10}{\mathrm{PhCHO}} + \mathrm{Ph_3PO} \xleftarrow{O_2} \underset{9}{\mathrm{Ph\bar{C}H\overset{+}{P}Ph_3}}$$

$$\mathrm{PhCHO} \xrightarrow{h\nu\ 350\mathrm{nm}/O_2} \mathrm{PhCO_2H}$$

$$\mathrm{Ph\bar{C}H\overset{+}{P}Ph_3} + \mathrm{PhCHO} \longrightarrow \mathrm{PhCH{=}CHPh} + \mathrm{Ph_3PO}$$

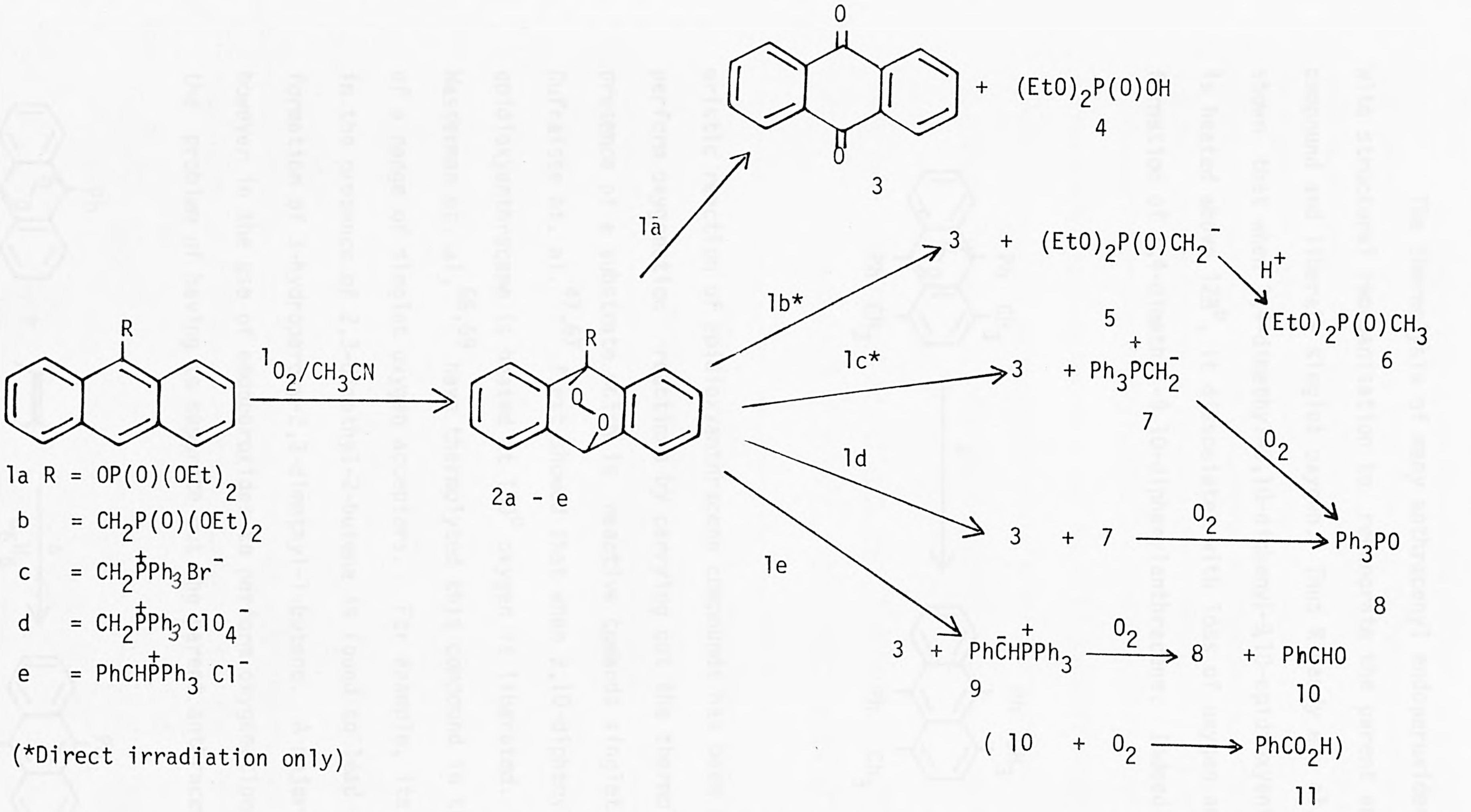
this is believed to be due to the approximately ten fold concentration excess of dissolved oxygen over that for benzaldehyde (1×10^{-2}M Vs. 1×10^{-3}M) Clearly the concentration of the aldehyde will be even lower during the early stages of the reaction, and thus the phosphorane will preferentially react with a molecule of oxygen.

A summary of the direct and rose bengal sensitized photooxidation reactions of all the anthracenyl phosphorus compounds discussed is shown in Scheme 3.1.

Throughout this work, the only evidence that has been proposed in support of these photooxidation reactions occurring by a Type II process involving singlet oxygen has been the nature of the products formed. However an important finding of recent years has been the observation that the life-time of singlet oxygen can be significantly greater in deuterated solvents compared with the corresponding non deuterated.[54,66] Thus if a reaction involves singlet oxygen, a change from a non deuterated to a deuterated solvent would be expected to cause an increase in the rate of photooxygenation. Such a change in rate is referred to as the solvent isotope effect. Measured solvent isotope effects for anthracen-9-yl diethyl phosphate and diethyl (anthracen-9-yl)methylphosphonate on direct photooxidation are reported in Table 3.4. This considerable increase in the rate of photooxidation on going from acetonitrile to deuteroacetonitrile clearly indicates the intermediacy of singlet oxygen in the photooxidation of anthracenyl phosphorus compounds.

Table 3.4. Solvent isotope effects for compounds 1a and 1b on direct photooxidation.

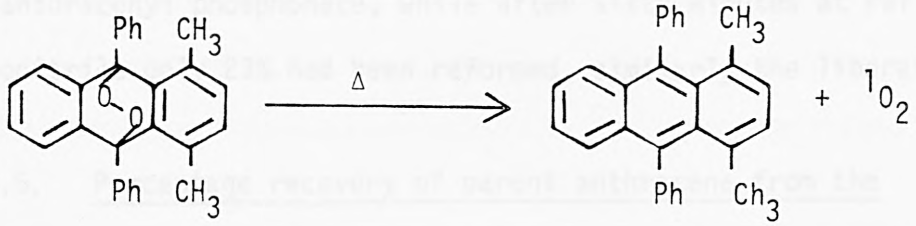
Anthracenyl phosphorus compound	Solvent isotope effect (CD_3CN/CH_3CN)
1a. $AnOP(O)(OEt)_2$	14
1b. $AnCH_2P(O)(OEt)_2$	12

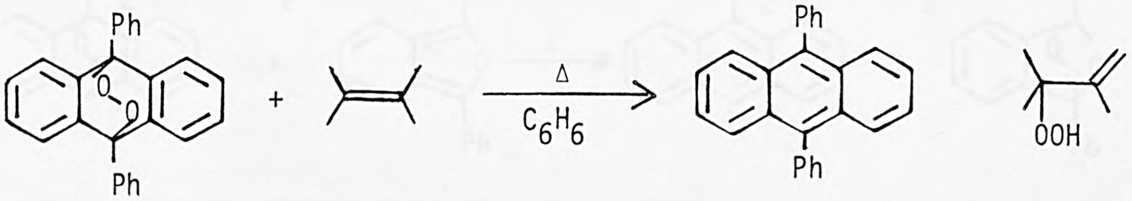


Scheme 3.1. A summary of the photooxidation reaction of the anthracenyl phosphorus compounds 1a - 1e.

The Thermolysis of Anthracenyl Endoperoxides.

The thermolysis of many anthracenyl endoperoxides proceeds with structural reorganisation to regenerate the parent anthracene compound and liberate singlet oxygen. Thus Rigaudy et. al.[49] have shown that when 1,4-dimethyl-9,10-diphenyl-9,10-epidioxyanthracene is heated above 128°, it dissociates with loss of oxygen and the formation of 1,4-dimethyl-9,10-diphenylanthracene. Indeed this characteristic reaction of epidioxyanthracene compounds has been used to perform oxygenation reactions by carrying out the thermolysis in the presence of a substrate which is reactive towards singlet oxygen. Dufraisse et. al.[47,67] first showed that when 9,10-diphenyl-9,10-epidioxyanthracene is heated at 180° oxygen is liberated. Thus Wasserman et. al.[68,69] have thermolysed this compound in the presence of a range of singlet oxygen acceptors. For example, its thermolysis in the presence of 2,3-dimethyl-2-butene is found to lead to the formation of 3-hydroperoxy-2,3-dimethyl-1-butene. A major disadvantage however in the use of endoperoxides to perform oxygenation reactions is the problem of having to separate out the parent anthracene compound



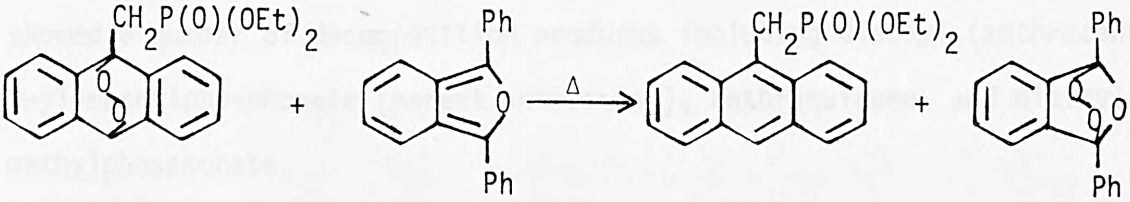


formed from the desired oxygenation product.

Agreement with these observations that many endoperoxides are thermally labile has come from the thermolysis of diethyl (9,10-epidioxyanthracen-9-yl)methylphosphonate. This compound when heated in a suitable solvent liberates singlet oxygen and reforms the parent anthracene, diethyl (anthracen-9-yl)methylphosphonate. Obviously, the rate of decomposition is temperature dependent. So diethyl (9,10-epidioxyanthracen-9-yl)methylphosphonate after five minutes at reflux temperature in tetralin was found to have reformed 53% of the parent anthracenyl phosphonate, while after sixty minutes at reflux in acetonitrile only 23% had been reformed, similarly the liberated singlet oxygen has been trapped when the epidioxyanthracenyl phosphonate was thermolysed in the presence of diphenylisobenzofuran, a known

Table 3.5. Percentage recovery of parent anthracene from the Thermolysis of diethyl (anthracen-9-yl)methylphosphonate.

Solvent,	Time at reflux temperature/min	% anthracenyl phosphonate, 1b, reformed
Tetralin	5	53
(bpt 207°C)	45	54
Acetonitrile	60	23
(bpt 82°C)	120	45



singlet oxygen acceptor.

In an attempt to determine the temperature at which rearrangement to the parent anthracene occurs, a differential thermal analysis (DTA) on the 9,10-epidioxyanthracenyl phosphonate was carried out. However from the DTA no single step corresponding to loss of oxygen was apparent. Instead at 133° a weak endothermic process began, which was immediately swamped by an exothermic process with an onset temperature of 142°C, peaking at 170°C and corresponding to a minimum 20% weight loss from the system, Figure 3.10. Compared to a theoretical weight loss of 8.9% based purely on the liberation of oxygen, it would seem that in addition to the regeneration of the parent anthracene, other decomposition processes are occurring. This is confirmed by chromatographic analysis (t.l.c.) of the residue from the DTA which showed a number of decomposition products including diethyl (anthracen-9-yl)methylphosphonate (parent anthracene), anthraquinone and diethyl methylphosphonate.

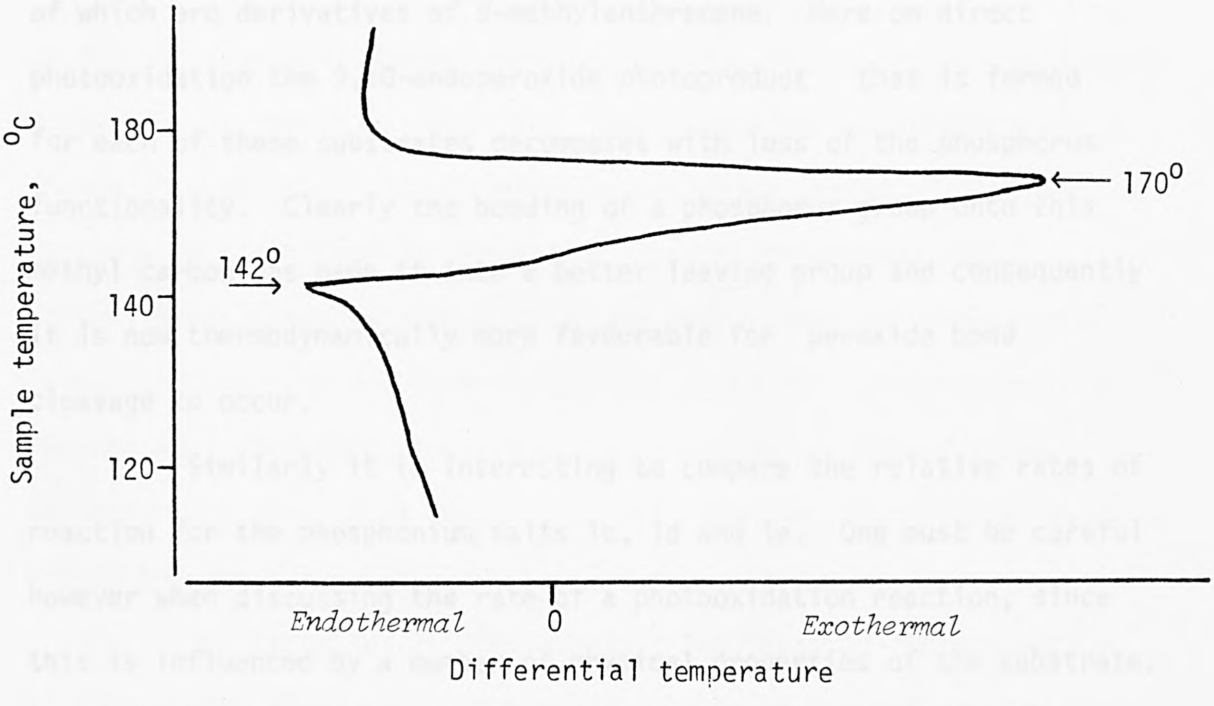


Figure 3.10. Differential thermal analysis trace for diethyl (9,10-epidioxyanthracen-9-yl)methylphosphonate.

Influence of Phosphorus on Anthracenyl Photooxidation Reactions.

It is interesting to observe the influence that phosphorus has on the outcome of anthracenyl photooxidation reactions. At first glance the presence of the phosphorus moiety would seem to be minimal. The photooxiation of anthracenyl phosphorus compounds occurs by a Type II mechanism involving singlet oxygen with the formation of a transannular peroxide bond across the 9,10-position. However it is on the 9,10-endoperoxide that the effect of the phosphorus moiety becomes apparent. 9-Methylanthracene forms on direct photooxidation the stable 9-methyl-9,10-epidioxyanthracene. Compare this with the methyl phosphonate 1b, and the methyl phosphonium salts 1c, 1d and 1e, all of which are derivatives of 9-methylanthracene. Here on direct photooxidation the 9,10-endoperoxide photoproduct that is formed for each of these substrates decomposes with loss of the phosphorus functionality. Clearly the bonding of a phosphorus group onto this methyl carbon has made it into a better leaving group and consequently it is now thermodynamically more favourable for peroxide bond cleavage to occur.

Similarly it is interesting to compare the relative rates of reaction for the phosphonium salts 1c, 1d and 1e. One must be careful however when discussing the rate of a photooxidation reaction, since this is influenced by a number of physical properties of the substrate. Additionally it is known from rate constants that for anythracenyl compounds, not every encounter with a singlet oxygen molecule will lead to a chemical reaction. Thus a compound may be an extremely efficient quencher of singlet oxygen, although its quantum yield of product formation may be very low. Taking the three phosphonium salts studied, all have similar molar absorption coefficients with respect to each other. Assuming they also have similar reaction efficiencies (as opposed to physical quenching) towards singlet oxygen, it is curious why on direct photooxidation the benzyl phosphonium chloride 1e, reacts (in terms of disappearance of starting material) some three times faster than either the methyl phosphonium bromide 1c, or methyl phosphonium perchlorate 1d. Possibly this is partly a reflection of the relative stabilities of the cleaved phosphorus species. With the phosphonium bromide and perchlorate salts the phosphorus moiety is lost as the methylene phosphorane, 7. This phosphorane is referred to as a reactive ylid, and can only be stabilized with resonance through one other canonical form;

$$Ph_3\overset{+}{P}C\overset{-}{H_2} \longleftrightarrow Ph_3P = CH_2$$

7

On the other hand the benzyl phosphonium salt, 1e, lo-ses its phosphorus moiety as the semistabilized ylid, benzylidenetriphenylphosphorane 9. In addition to stabilization with the methylene carbon, this ylid can also be stabilized by resonance through the benzene ring. Clearly this increased stability of the benzylidene phosphorane must lower the energy on the potential energy curve for product formation and may well therefore contribute to the greater rate of photooxidation for the benzyl phosphonium chloride over that for the two methyl phosphonium salts.

The formation of phosphorus ylids from the photooxidation of anthracenyl phosphorus compounds is worthy of special mention in view of the importance of such compounds in synthetic chemistry. If endoperoxides derived from an anthracenylmethyl phosphonate and an anthracenylmethyl phosphonium salt could be prepared non photochemically, say by the microwave discharge technique[27,38] they could be useful synthetic precursors in a 'photochemical Wittig' reaction. The range of compounds could be infinite bearing a variety of substituents on the carbon bonding to the 9- position of the anthracene nucleus. It is anticipated that the irradiation of such compounds in the presence of an aldehyde or ketone would ultimately result in a Wittig reaction between the carbonyl compound and the photochemically generated phosphorus ylid. Clearly it would be interesting to further investigate this aspect of anthracenyl phosphorus photooxidation chemistry.

Experimental.

For general experimental details see chapter 5.

Preparation of anthracen-9-yl diethyl phosphate.

Sodium hydride (50% oil dispersion, 6mmol, 0.288g) was washed (3x10ml) and finally covered with THF (10ml) under nitrogen. Anthrone (5mmol, 0.97g) dissolved in THF was added dropwise over 30 minutes to this sodium hydride suspension. The solution was stirred for 60 minutes (until hydrogen evolution ceased). A very dark yellow/brown colour resulted. Diethyl chlorophosphate (6mmol, 1.038g, 0.87ml) in THF was added dropwise over 15 minutes. Immediate precipitation of a solid occurred on addition. The solution was stirred for 5 hours at room temperature, diluted with ether (50ml), filtered and washed with a 10% $^{W}/v$ sodium hydroxide solution (20ml). The organic layer was dried and concentrated in vacuo to afford 1.52g of a yellow gummy. solid. Chromatographic purification (Kieselgel 60 GF254, Art 7730, diethyl ether as elluent) of 0.9g of this crude material gave 0.45g (46%) of the desired product as a creamy waxy solid.

Mpt. 81-82°C (lit. 84.5 - 85.5°C)[70]

Elemental Analysis

For $C_{18}H_{19}O_4P$ require : C,65.45; H,5.80; P,9.38.

found : C,65.52; H,5.72; P,9.32.

I.R. (nujol),

1620 (w), 1350 (m), 1295 (m), 1275 (m), 1020 (m), 965 (m), 905 (w), 885 (w), 835 (w), 735cm^{-1} (m).

U.V. (CH_3CN),

λ_{332nm} (log ε3.47), λ_{348} (3.78), λ_{364} (3.97), λ_{385} (3.93).

^1H n.m.r. (220MHz, $CDCl_3$),

1.25δ, (td, 6H, $^3J_{HCCH}$ 7.5Hz, $^4J_{HCCOP}$ 1Hz, $-CH_3$),

4.11-4.38δ, (m, 4H, $-OCH_2-$),

7.49-7.66δ, (m, 4H, H-2 H-3 H-6 H-7),

8.02δ, (d, 2H, $^3J_{HCCH}$ 8Hz, H-4 H-5),

8.36δ, (s, 1H, H-10),

8.50δ, (d, 2H, $^3J_{HCCH}$ 8Hz, H-1 H-8).

$^{31}P - \{^1H\}$ n.m.r. (24.1MHz, $CDCl_3$)

-4.84 (s),

M.S. (70ev),

m/e(rel.int.); 331.105 ($\overset{+}{M}$+1, 1.03%), 330.104 (M^+, 10.32%),302.070 (5.0%), 274.054 (9.5%) 194.078 (35.8%), 193.072 (24.5%), 180.863 (10.7%), 166.076 (5.8%), 165.071 (33.4%), 164.068 (5 8%), 163.059 (7.1%).

Preparation of 9-(bromomethyl)anthracene.

To 9-methylanthracene (10mmol, 1.92g) dissolved in carbon tetrachloride (30ml), freshly purified N-bromosuccinimide (10mmol, 1.78g) was added. With stirring and simultaneous irradiation from a 100W lamp, the solution was heated and maintained at reflux temperature for 30 minutes. The succinimide produced was filtered off, and the liquor reduced in vacuo to afford a yellow solid. Recrystallization from benzene gave 2.2g (81%) of the desired product as yellow needles.

Mpt. 138.5 - 139.5^{o}C (lit. 139 - 140^{o}C)[71]

Elemental Analysis

For $C_{15}H_{11}Br$ require : C, 66.44; H, 4.09; Br, 29.47.

found : C, 66.39; H, 4.06; Br, 29.47.

I.R. (nujol).

1620 (w), 1200 (m), 960 (w), 885 (m), 840 (w), 790 (m), 725cm^{-1} (m).

^1H n.m.r. (220MHz, $CDCl_3$),

5.52δ, (s, 2H, $-CH_2-$),

7.54δ, (ddd, 2H, $^3J_{HCCH_{5/4}}$ 9Hz, $^3J_{HCCH_{7/2}}$ 7Hz, $^4J_{HCCCH_{8/1}}$ 1Hz, H-3 H-6),

7.68δ, (ddd, 2H, $^3J_{HCCH_{8/1}}$ 9HZ, $^3J_{HCCH_{6/3}}$ 7Hz, $^4J_{HCCCH_{5/4}}$ 1Hz, H-2 H-7),

8.04δ, (dd, 2H, $^3J_{HCCH}$ 9Hz, $^4J_{HCCCH}$ 1Hz, H-4 H-5),

8.32δ, (dd, 2H, $^3J_{HCCH}$, 9Hz, $^4J_{HCCCH}$ 1Hz, H-1 H-8),

8.49δ, (s, 1H, H-10).

M.S. (70ev)

m/e (rel int.); 272.000 (M^+ ^{81}Br, 1.55%), 270.000 (M^+ ^{79}Br, 1.70%), 192.089(21.2%), 191.089 (100%), 190.071 (10.3%), 189.071 (33%), 165.072(8.1%), 163.057(5.3%).

Preparation of diethyl (anthracen-9-yl)methylphosphonate

9-(Bromomethyl)anthracene (2.5mmol, 0.67g) and triethyl phosphite (7.5mmol, 1.25g, 1.29ml) were heated together at 135-140°C for 1 hour. On cooling to room temperature a precipitate appeared. This was recrystallized from n-hexane to give 0.60g (73%) of the desired product as a yellow crystalline solid.

Mpt. 100-101°C (lit 103.5-104.5°C)[72]

Elemental Analysis.

For $C_{19}H_{21}O_3P$ require : C, 69.49; H, 6.46; P, 9.43.

found : C, 69.65; H, 6.61; P, 9.42.

I.R. (nujol)

1620 (w), 1240 (m), 1225 (m), 1055 (m), 1025 (m), 950 (m), 895 (w), 780^{-1} (w), 725cm^{-1} (m).

U.V. (CH_3CN)

λ_{334nm} (log ε 3.48), λ_{349} (3.80), λ_{366} (4.01), λ_{386} (4.00).

^1H n.m.r. (220 MHz, $CDCl_3$)

1.06δ, (t, 6H, $^3J_{HCCH}$ 7.5Hz, $-CH_3$), 3.74-4.04δ, (m, 4H, $-OCH_2-$),

4.23δ, (d, 2H, $^2J_{HCP}$ 22Hz, $-CH_2-$), 7.47-7.67δ, (m, 4H, H-2 H-3 H-6 H-7),

8.03δ, (d, 2H, $^3J_{HCCH}$ 8Hz, H-4 H-5),

8.39δ, (d, 2H, $^3J_{HCCH}$ 8.5Hz, H-1 H-8),

8.44δ, (s, 1H, H-10).

$^{31}P - \{^1H\}$ n.m.r. (24.1MHz, $CDCl_3$)

-25.82δ (s),

M.S. (70ev)

m/e, (rel.int.); 329.132 (M^++1, 4.7%), 328.130 (M^+, 21.6%), 192.093 (16.7%), 191.092 (100%), 190.084 (7.8%), 189.079 (20.6%), 165.077 (5.2%).

Preparation of (anthracen-9-yl)methyltriphenylphosphonium bromide.

To 9-(bromomethyl)anthracene (9.2mmol, 2.5g) in toluene (35ml), a solution of triphenyl phosphine (9.2mmol, 2.42g) in toluene (15ml) was added dropwise. The resulting solution was heated at reflux temperature for 30 minutes, cooled and stirred overnight. The precipitated solid was filtered off and washed with ether to afford 3.85g (79%) of the desired product as a yellow solid.

Mpt. 281-283°C (dec.) (lit. 280°C (dec))[71]

Elemental Analysis.

For $C_{33}H_{26}Br\,P$ require : C,74.29; H,4.92; Br, 14.98; P.5.81.

found : C,74.02; H,4.77; Br, 15.27; P,5.91.

I.R. (nujol),

1620 (w), 1590 (w), 1160 (w), 1110 (m), 995 (w), 910 (w), 865 (w), 800 (w), 780 (w), 760 (m), 735cm^{-1} (s), 725cm^{-1} (s), 695cm^{-1} (m).

U.V. (CH_3CN)

λ_{342}nm (log ε 3.39), λ_{359} (3.76), λ_{378} (3.97) λ_{398} (3.93).

^1H n.m.r. (220 MHz, $CDCl_3$),

6.07δ, (d, 2H, $^2J_{HCP}$ 14Hz, $-CH_2-$),

7.04-7.88δ, (m, 23H, C_6H_5's and H-1 to H-8),

8.29δ, (d, 1H, H 4Hz, H-10)*

*H-10 would be expected to be a singlet. A doublet is observed under conditions where TMS was a sharp singlet. The origin of the coupling is unknown, but the integration, chemical shift and peri-deshielding effect are all consistent with the assignment of the peak to H-10.

<u>$^{31}P - \{^1H\}$ n.m.r.</u> (24.1MHz, $CDCl_3$)

-20.22δ (s),

<u>Preparation of (anthracen-9-yl)methyltriphenylphosphonium perchlorate.</u>

A solution of silver perchlorate (2mmol, 0.42g) in water (10ml) was added to a stirred solution of (anthracen-9-yl)methyltriphenylphosphonium bromide (2mmol, 1.06g) in methanol (20ml). After stirring overnight at room temperature, a further portion of methanol (20ml) was added and the solution filtered. The liquor was reduced in vacuo to afford 0.9g (82%) of the desired product as a cream coloured solid.

<u>I.R.</u> (nujol)

1590 (w), 1160 (w), 1110 (w), 990 (w), 970 (w), 930 (w), 735cm^{-1} (m), 725cm^{-1} (m).

<u>U.V.</u> (CH_3CN)

λ_{341nm} (log ε 3.46), λ_{356} (3.76), λ_{375} (3.94), λ_{395} (3.90).

<u>^1H n.m.r.</u> (220MHz, $CDCl_3$)

5.67δ, (d, 2H, $^2J_{HCP}$ 14Hz, $-CH_2-$),

7.03-7.87δ, (m, 23H, C_6H_5's and H-1 to H-8),

8.28δ, (d, 1H, J 4Hz H-10)*

* The origin of this coupling is unknown. See comment concerning this in the spectral details for (anthracen-9-yl)methyltriphenylphosphonium bromide.

<u>$^{31}P - \{^1H\}$ n.m.r.</u> (24.1MHz, $CDCl_3$).

-20.12δ (s)

<u>Preparation of 9-benzoylanthracene</u>

The method by which this compound was prepared was adapted from that used in the preparation of 9-acetylanthracene.[73]

To anthracene (56mmol, 10g) suspended in benzene (32ml) under nitrogen, benzoyl chloride (336mmol, 47g, 39ml) was added. With vigorous stirring and whilst maintaining the temperature of the suspension between -5-0°C (ice/salt bath), the aluminium trichloride (112mmol, 15g) was added in small portions over 90 minutes. The suspension went dark purple in colour. After the addition was complete, the solution was stirred at 0°C for a further 60 minutes, and then allowed to rise slowly to room temperature. The purple complex formed was collected by suction onto a sintered glass funnel, and washed thoroughly with benzene. The complex was then added in small portions to a beaker (400ml) filled with ice and concentrated hydrochloric acid (1 : 1). The mixture was allowed to warm to room temperature and the crude ketone collected. This was recrystallized from benzene to give 7.9g (50%) of 9-benzoylanthracene as yellow crystals. Evaporation of the mother liquors and recrystalisation from benzene gave a second crop, 3.4g (22%) of the desired product as a crystaline yellow solid.

Mpt. 1st crop, 145-146°C, 2nd crop 144.5-145°C (lit. 146-147°C)[74]

Elemental Analysis

For $C_{21}H_{14}O$ require : C, 89.96; H, 5.04

found : C, 89.70; H, 4.90

I.R. (nujol).

1655 (s), 1590 (m), 1575 (w), 1265 (w), 1230 (s), 1170 (m), 895 (m), 880 (m), 775 (w).

^{1}H n.m.r. (100MHz, d_6- DMSO)

7.00-7.40δ, (m, 11H, C_6H_5, and H-2 to H-7),

7.80δ, (d, 2H, $^3J_{HCCH}$ 8Hz, H-1 H-8),

8.36δ, (s, 1H, H-10).

Preparation of 9-α-hydroxybenzylanthracene.

To a suspension of lithium aluminium hydride (74mmol, 2.80g) in ether (150ml), under nitrogen, 9-benzoylanthracene (20mmol, 5.65g) in ether (450ml) was added dropwise over 30 minutes. Very gentle refluxing of solution occurred during addition. The solution was stirred for a further thirty minutes. With cooling, water was slowly added, after which the ether layer was washed with a 10% ^{v}/v sulpuric acid solution (50ml) and water (2x100ml). The ether layer was separated, dried ($MgSO_4$) and evaporated in vacuo to give 5.58g (98%) of a gummy oil which crystallized into a yellow solid.

Mpt. 104-105°C (lit. 111-114°C)[75]

I.R. (nujol).

3500 (m), 3290 (m), 1615 (w), 1595 (w), 1170 (w), 1155 (w), 1040 (m), 1015 (w), 725cm^{-1} (m).

^{1}H n.m.r. (100MHz, d_6- DMSO).

6.05δ, (broad s, 1H, OH), 6.70-7.20δ (m, 11H, C_6H_5 and H-2 to H-7),

7.68δ, (d, 2H, $^3J_{HCCH}$ 8Hz, H-1 H-8),

8.06δ, (d, 1H, $^3J_{HCOH}$ 4Hz, >CH-),

8.16δ, (s, 1H, H-10).

Preparation of 9-α-chlorobenzylanthracene.

A solution of 9-α-hydroxybenzylanthracene (16.5mmol, 4.70g) and thionyl chloride (32mmol, 3.83g 2.35ml) in benzene (12ml) was refluxed under nitrogen for three hours. The solvent was then removed and the oil triturated with 40:60 petroleum ether. The precipitate was filtered to afford 4.30g of an olive green solid. This was recrystalised from benzene: 40:60 petroleum ether (1 : 1) to give a solid which was further recrystallized from benzene to afford 2.55g (51%) of yellow crystals.

Mpt. 132-134°C (lit 135-137°C)[76]

Elemental Analysis.

For $C_{21}H_{15}Cl$ require : C, 83.29, H, 5.00

found : C, 83.30, H, 5.00

I.R. (nujol),

1620 (w), 1595 (w), 1200 (w), 1030 (w), 890 (m), 840 (m), 785 (m), 760 (m), 735cm^{-1} (m).

^{1}H n.m.r. (100MHz, d_6-DMSO).

7.12δ, (s, 5H, C_6H_5),

7.24-7.34δ, (m, 4H, H-2 H-3 H-6 H-7),

7.92δ, (s, 1H, >CH-),

7.98δ, (m, 2H, H-4 H-5),

8.16δ, (m, 2H, H-1 H-8),

8.52δ, (s, 1H, H-10).

Preparation of 1-(anthracen-9-yl)benzyltriphenylphosphonium chloride.

To 9-α-chlorobenzylanthracene (5mmol, 1.51g) in toluene (80ml) a solution of triphenylphosphine (5.2mmol, 1.36g) in toluene (15ml) was added. The resulting solution was heated to reflux and held at this temperature for 2 hours. After cooling the solution was filtered and the collected precipitate washed with ether. This was recrystallized from ethanol - water (1 : 1, x3) to give 1.09 (39%) of the desired product as a pale cream solid.

Mpt. 170-172°C (dec)

Elemental Analysis.

For $C_{39}H_{30}ClP$ require : C, 82.88; H, 5.36; Cl, 6.27; P, 5.48.

found : C, 82.40; H, 5.34; Cl, 6.29; P, 5.07.

I.R. (nujol)

1625 (w), 1600 (w), 1590 (w), 1160 (w), 1105 (m), 1030 (w), 1000 (w), 960 (w), 860 (w), 780 (m), 755 (m) 725 (m), 690cm^{-1} (m)

U.V. (CH_3CN)

broad band, λ_{327nm} (log ε 3.96)

^{1}H n.m.r. (220MHz, $CDCl_3$),

6.40δ (s, 1H >CH-),

7.00-7.22δ (m, 5H C_6H_5),

7.26-7.84δ (m, 24H C_6H_5's and H-1 to H-8 & H-10),

$^{31}P - \{^1H\}$ n.m.r. (24.1MHz, $CDCl_3$)

-22.79δ (s).

Preparation of diethyl methylphosphonate.

Methyl iodide (50mmol, 7.10g, 3.12ml) was added dropwise to triethyl phosphite (50mmol, 8.31g, 8.57ml). Gentle warming of the mixture initiated the reaction, and once started the reaction refluxed spontaineously as addition proceeded. After addition was complete the mixture was fractionally distilled. This gave 4.5g (59%) of a colourless liquid.

B.pt. 40-41°C/.6mm (lit. 64°-65°C/2mm)[77]

Elemental Analysis

For $C_5H_{13}O_3P$ require : C, 39.47; H, 8.63.

found : C, 39.30, H, 8.73.

I.R.(liquid film)

3000 (m), 2940 (m), 1450 (w), 1390 (m), 1315 (m), 1245 (s), 1160 (m), 1055 (s), 1030 (s), 965 (s), 900 (m), 808 (m), $770cm^{-1}$ (m).

^1H n.m.r. (100MHz, $CDCl_3$)

1.32δ, (t, 6H, $^3J_{HCCH}$ 7Hz, $-CH_3$),

1.44δ, (d, 3H, $^2J_{HCP}$ 10Hz, $P-CH_3$),

4.07δ, (dq, 4H, $^3J_{HCOP}$ 9Hz, $-OCH_2-$).

Preparation of diethyl methyl phosphate.

To a solution of diethyl chlorophosphate (50mmol, 8.63g 7.23ml) in benzene (150ml) under nitrogen, methanol (60mmol, 1.92g, 2.43ml) and triethylamine (51mmol, 5.16g, 7.11ml) in benzene (50ml) was added dropwise over 15 minutes. The solution was refluxed for 4 hours and then stirred at room temperature overnight. The solution was filtered, concentrated to ca. ¼ of its volume, and washed with water (3x 25ml). The organic layer was then dried ($MgSO_4$) and evaporated in vacuo to give a pale yellow oil. Distillation of this material gave the desired product, 1.80g (21%), as a colourless liquid.

B.pt. 112-113^{o}C/16mm (lit. 100-102^{o}/24mm)[78]

Elemental Analysis

For $C_5H_{13}O_4P$ require : C, 35.71; H, 7.81.

found : C, 35.71; H, 7.81.

I.R. (liquid film)

2990 (s), 2920 (m), 2860 (m), 1500 (m), 1400 (m), 1370 (m), 1265 (s), 1170 (m), 1035 (s), 975 (s), 840 (s) 745cm^{-1} (m).

^{1}H n.m.r. (100MHz, $CDCl_3$)

1.44δ, (t, 6H, $^3J_{HCCH}$ 7Hz, $-CH_3$),

3.82δ, (d, 3H, $^3J_{HCOP}$ 11Hz, $-OCH_3$),

4.19δ, (dq. 4H, $^3J_{HCOP}$ 9Hz $-OCH_2-$).

Preparation of diethyl (9,10-epidioxyanthracen-9-yl)methylphosphonate.

Diethyl (anthracen-9-yl)methylphosphonate (1.22mmol, 0.40g) was taken up into acetonitrile (80ml) and rose bengal (0.035g) added. With water cooling, this solution was irradiated using daylight fluorescent lamps in conjunction with a 2% $^{w}/v$ potassium chromate filter solution. After 4 hours irradiation, the photolysis solution was passed through neutral alumina, (Aluminiumoxide 90 aktv, neutral, Art 1077). The alumina was washed with cooled ether, the liquors combined and evaporated in vacuo to afford a crude product. This was purified by preparative thin layer chromatography (Kieselgel 60 GF 254, Art 7730, ethyl acetate as elluent) to give 0.33g (75%) of the desired product as a cream crystallinesolid.

Mpt. 126-130^{o}C

Elemental Analysis.

For $C_{19}H_{21}O_5P$ require : C, 63.33; H, 5.87; P, 8.59.

found : C, 63.07; H, 5.91; P, 8.30.

I.R. (nujol)

1725 (m), 1600 (w), 1360 (w), 1230 (s), 1155 (m), 1045 (s), 1020 (s), 965 (s), 890 (m), 850 (w), 800 (m), 765cm^{-1} (s).

U.V. (CH_3CN)

broad band, λ_{350nm} (log ε 2.08),

^{1}H n.m.r. (220MHz, $CDCl_3$)

1.28δ, (t, 6H, $^3J_{HCCH}$ 7Hz, $-CH_3$),

3.27δ, (d, 2H, $^2J_{HCP}$ 20.5Hz, $-PCH_2-$),

4.18δ, (dq, 4H, $^3J_{HCOP}$ 8Hz),

6.02δ, (s, 1H, H-10),

7.34δ, (m, 4H, H-2 H-3 H-6 H-7),

7.45δ, (m, 2H, H-4 H-5),

7.59δ, (m, 2H, H-1 H-8).

$^{13}C-\{^1H\}$ n.m.r. (with additional multiplicity in SFORD).

16.2δ, (d, $^3J_{CCOP}$ 6.9Hz, $-CH_3$), (q, $^1J_{CH}$ 126.9Hz),

26.85δ, (d, $^1J_{CP}$ 145.5Hz, $-CH_2P$), (d, $^1J_{CH}$ 126.9Hz),

62.4δ, (d, $^2J_{COP}$ 5.9Hz, $-OCH_2-$), (tq, $^1J_{CH}$ 147.5Hz, $^2J_{CCH}$ 4.5Hz).

79.62δ, (s, C-10), ($^1J_{CH}$ 153.4Hz),

80.80δ, (d, $^2J_{CCP}$ 5.9Hz, C-9),

122.14 and 123.63δ (both s, C-1 and C-4)*,

127.67 and 127.99δ (both s, C-2 and C-3)*,

138.67δ (s, C-4a and C-10a),

139.91δ (d, $^3J_{CCCP}$ 7.8Hz, C-8a and C-9a).

*multiple couplings present in SFORD which were not analysed.

$^{31}P-\{^1H\}$n.m.r. (24.1MHz, $CDCl_3$)

-23.70δ (s),

M.S. (70ev)

m/e (rel. int.), 361.116 ($M^+ + 1$, 5.40%), 360.103 (M^+, 30.50%)

344.162 (22.5%), 328.167 (33.6%), 223.102 (76.4%),

209.087 (18.7%), 208.099 (15.5%), 207.101 (39.3%),

191.105 (90.2%),165.087 (34.6%), 152.072 (100%).

Direct photooxidation of anthracenyl phosphorus compounds.

The direct photooxidation of the anthracenyl phosphorus compounds was carried out by the following general procedure.

The substrate (0.01g) was dissolved in acetonitrile (10ml) and irradiated with black-light fluorescent lamps in pyrex vessels until UV spectroscopy indicated no starting material remaining. Through out the irradiation, the solution was continually flushed with dry, carbon dioxide free oxygen. After irradiation was complete the solution was removed and analysed by gas liquid chromatography, (g.l.c.).

The concentration of substrate used, its irradiation time and the yield of all the major photolysis products formed for each substrate are as follows.

1a, $AnOP(O)(OEt)_2$

Concentration of; 3.03×10^{-3} moles dm^{-3}.
Irradiation time; 30 minutes.
% Yield of, by g.l.c.; anthraquinone, 46%
diethyl phosphate (measured as its methyl ester after addition of diazomethane). 84%

1b, $AnCH_2P(O)(OEt)_2$

Concentration of; 3.05×10^{-3} moles dm^{-3}.
Irradiation time; 120 minutes.
% Yield of, by g.l.c.; anthraquinone, 76%
diethyl methylphosphonate. 75%

1c, $AnCH_2\overset{+}{P}Ph_3\ Br^-$

Concentration of; 1.87×10^{-3} moles dm^{-3}.
Irradiation time; 5 hours.
% Yield of, by g.l.c.; anthraquinone, 78%
triphenylphosphine oxide 85%

1d, $AnCH_2\overset{+}{P}Ph_3\ ClO_4^-$

Concentration of; 1.81×10^{-3} moles dm^{-3}.

Irradiation time; 4 hours.

% Yield of, by g.l.c.;	anthraquinone	98%
	triphenylphosphine oxide	95%

1e, $AnCH(Ph)\overset{+}{P}Ph_3\ Cl^-$

Concentration of; 1.77×10^{-3} moles dm^{-3}.

Irradiation time; 90 minutes.

% Yield of, by g.l.c.;	anthraquinone	70%
	triphenylphosphine oxide	80%
	benzaldehyde	19%
	benzoic acid (measured as its methyl ester after addition of diazomethane).	42%

The identity of each photolysis product was confirmed by GCMS. Their percentage yield of formation for each compound is also reported in Table 3.1.

Indirect photooxidation of anthracenyl phosphorus compounds.

The indirect photooxidation of the anthracenyl phosphorus compounds was carried out by the following general procedure.

The substate (0.01g) was dissolved in acetonitrile (10ml) and rose bengal (0.015g) added. The solution was then irradiated with daylight fluorescent lamps in conjunction with a 2% $^{w}/v$ potassium chromate filter solution. Through out the irradiation, the solution was continually flushed with dry, carbon dioxide free oxygen. After photooxidation was complete (as shown by UV spectroscopy). The solution was removed and analysed by g.l.c.

The concentration of each substrate used was identical to that reported in the direct photooxidation experiments. The irradiation time and yield of all the identified photolysis products for each substrate are as follows.

1a, $\underline{\mathrm{AnOP(O)(OEt)_2}}$

Irradiation time; 3 hours

% Yield of, by g.l.c; anthraquinone 95%

diethyl phosphate 87%

(measured as its methyl ester after addition of diazomethane).

1b, $\underline{\mathrm{AnCH_2P(O)(OEt)_2}}$

Irradiation time; 4 hours

The irradiation of this compound leads to the formation of diethyl (9,10-epidioxyanthracen-9-yl)methylphosphonate. By carrying out the photolysis on a larger scale to that used in these experiments, this endoperoxide can be isolated in 75% yield, - see earlier in this section amongst the preparative experimental details.

1c, $\underline{\mathrm{AnCH_2\overset{+}{P}Ph_3\ \ Br^-}}$

Irradiation time; 10 hours

The irradiation of this compound leads to the formation of (9,10-epidioxyanthracen-9-yl)methyltriphenylphosphonium bromide. This endoperoxide slowly decomposes at room temperature to a number of products, although it is unclear as to the extent to which anthraquinone and triphenylphosphine oxide are formed. By carrying out the photolysis of this phosphonium bromide on a larger scale, (0.1g substrate, 0.04g rose bengal, 100ml acetonitrile), and with water cooling of the solution throughout the irradiation (18 hours), it is possible to observe spectroscopically, (^{1}H, ^{31}P n.m.r., $\mathrm{CDCl_3}$ solvent, - see text), the 9,10-endoperoxide formed. However this endoperoxide cannot be isolated in its pure state.

1d, $\underline{\mathrm{AnCH_2\overset{+}{P}Ph_3\ \ ClO_4^-}}$

Irradiation time; 6 hours

% Yield of, by g.l.c.;	anthraquinone	95%
	triphenylphosphine oxide	97%

1e, <u>$\mathrm{AnCH(Ph)\overset{+}{P}Ph_3\ Cl^-}$</u>

Irradiation time;		4 hours
% Yield of, by g.l.c.;	anthraquinone	59%
	triphenylphosphine oxide	61%
	benzaldehyde	49%
	benzoic acid	<5%

(measured as its methyl ester after addition of diazomethane).

The identity of each photolysis product (where known) was confirmed by GCMS. Their percentage yield of formation for each compound is also reported in Table 3.2. For preparation of diazomethane see chapter 5.

<u>Direct photodecomposition of diethyl (9,10-epidioxyanthracen-9-yl) methylphosphonate.</u>

Apart from the fact that the solution (0.01g substrate/10ml acetonitrile) was flushed with argon and not oxygen, this experiment was performed in an identical manner to that for the direct photooxidation of the anthracenyl phosphorus compounds described earlier. The concentration, irradiation time and yield of product formation are reported below.

Concentration;		2.76×10^{-3} moles dm^{-3}
Irradiation time;		120 minutes.
% Yield of, by g.l.c.;	anthraquinone	90%
	diethyl methylphosphonate	76%

The percentage yield of formation for both of these compounds is reported in Table 3.1.

The direct photooxidation of (anthracen-9-yl)methytriphenylphosphonium bromide and (anthracen-9-yl)methyltriphenylphosphonium perchlorate in the presence of hexaldehyde - trapping experiments for an ylid intermediate.

These direct photooxidation experiments were carried out according to the general procedure for the direct photooxidation of anthracenyl phosphorus compounds given earlier. The photolysis solutions were prepared as follows;

0.2g	substrate (phosphonium bromide or perchlorate)
0.80g	hexaldehyde
100ml	acetonitrile

Direct irradiation for 10 hours followed by g.l.c. analysis for heptene.

These experiments gave the following percentage yields of heptene found to be present in the photolysis solution after irradiation;

Substrate	% yield of heptene
1c, $AnCH_2\overset{+}{P}Ph_3\ Br^-$	23%
1d, $AnCH_2\overset{+}{P}Ph_3\ ClO_4^-$	35%

The identity of the heptene formed was confirmed by GCMS. These results are also reported in Table 3.3.

Gas liquid chromatographic conditions.

The g.l.c. conditions used to identify and determine the products formed in these direct and indirect photooxidation experiments, the photodecomposition experiment and the trapping experiments are as follows.

9,10-Anthraquinone:

Column;	2m, 5% SE30
Oven temperature;	200°C

Carrier gas; N_2, 40ml min^{-1}

Retention time; ca. 3 min

Diethyl methyl phosphate: (for diethyl phosphate)

Column; 2m, 10% SE30

Oven temperature; 140^{o}C

Carrier gas; N_2, 30ml min^{-1}

Retention time; ca. 1 min

Diethyl methylphosphonate:

Column; 2m, 5% SE30

Oven temperature; 175^{o}C

Carrier gas; N_2, 25ml min^{-1}

Retention time; ca. 1 min

Triphenylphosphine oxide:

Column; 20", 10% UCW 982, (80-100WAW DMCS B-8)

Oven temperature; 270^{o}C

Carrier gas; 30ml min^{-1}

Retention time; ca. 1 min

Benzaldehyde:

Column; 2m, 5% SE30

Oven Temperature; 125^{o}C

Carrier gas; 15ml min^{-1}

Retention time; ca. 1½ min

Methyl benzoate: (for benzoic acid)

Column; 2m, 5% SE30

Oven temperature; 140^{o}C

Carrier gas; 15ml min^{-1}

Retention time; ca. 1½ min

1-Heptene:

Column; 2m, 15% carbowax (PEG 20M)

Oven temperature; 100^{o}C

Carrier gas; 30ml min^{-1}

Retention time; ca. 30sec.

Direct photooxidation of anthracen-9-yl diethyl phosphate and diethyl (anthracen-9-yl)methylphosphonate; - evidence for singlet oxygen intermediacy by solvent isotope measurements.

The following procedure was used in the determine of a solvent isotope effect (S.I.E.) for the photooxidation of anthracen-9-yl diethyl phosphate.

An acetonitrile solution of anthracen-9-yl diethyl phosphate was prepared to an optical density (o.d.) of 0.47 at the preselected wavelength of 364nm. A similar solution using deuteroacetonitrile was prepared to the same o.d. Both solutions were flushed with oxygen for three minutes, stoppered, and irradiated simultaneously with black-light fluorescent lamps. Absorbance readings at 364nm were taken every thirty seconds for the first three minutes, then every minute and subsequently every two and five minutes. The results were plotted and the relative rate of disappearance for the first 10-15% of the substrate taken from the slope of the curve. By ratioing these slopes for the two solvents the solvent isotope effect was obtained.

For anthracen-9-yl diethyl phosphate this procedure gave a solvent isotope effect of 14.

Similarly this was repeated for diethyl (anthracen-9-yl)methylphosphonate, again using acetonitrile/deuteroacetonitrile, and at a wavelength of 366nm.

For diethyl (anthracen-9-yl)methylphosphonate this procedure gave a solvent isotope effect of 12.

These results are also reported in Table 3.4.

Thermolysis of diethyl (9,10-epidioxyanthracen-9-yl)methylphosphonate.

Diethyl (9,10-epidioxyanthracen-9-yl)methylphosphonate (9.94×10^{-7} moles, 0.3582mg) was dissolved in tetralin (10ml) and heated rapidly to reflux temperature. After 5 minutes at this temperature a UV spectrum was recorded. The solution was then heated at reflux for a further 40 minutes where - after a second UV spectrum was recorded. From the molar absorption coefficient for diethyl (anthracen-9-yl)methylphosphonate at 386nm (log ε 4.01) and with the optical density at 386nm measured from the recorded UV spectra, the extent to which diethyl (anthracen-9-yl)methylphosphonate had been formed by liberation of singlet oxygen from the 9,10-epidioxyanthracene was calculated. It was found that after heating at reflux temperature for,

5 min	53% $AnCH_2P(O)(OEt)_2$ had been formed
45 min	54% $AnCH_2P(O)(OEt)_2$ had been formed.

Similarly when this experiment was repeated using acetonitrile in place of tetralin, it was found that after heating at reflux temperature for,

1 hour	23% $AnCH_2P(O)(OEt)_2$ had been formed
2 hours	45% $AnCH_2P(O)(OEt)_2$ had been formed.

Thermolysis of diethyl (9,10-epidioxyanthracen-9-yl)methylphosphonate; - trapping of singlet oxygen liberated with diphenylisobenzofuran.

Diethyl (9,10-epidioxyanthracen-9-yl)methylphosphonate (11.10×10^{-5} mol, 0.04g) and diphenylisobenzofuran (5.55×10^{-5} mol, 0.015g) were dissolved in toluene (10ml) and heated at reflux temperature for three hours. The toluene was then replaced with tetralin (10ml) and heated at reflux for a further one hour. At this stage a UV spectrum was run, and it showed,

i) The formation of the anthracenyl absorption bands at

334, 349, 366 and 386nm

and ii) The absence of the diphenylisobenzofuran absorption band at 412nm previously present at the start of the reaction.

Differential thermal analysis of diethyl (9,10-epidioxyanthracen-9-yl) methylphosphonate.

The decomposition of diethyl (9,10-epidioxyanthracen-9-yl)-methylphosphonate in the solid phase was studied using a Stanton Redcroft (780 series) thermal analysis equipped with a differential scanning calorimeter cell. The endoperoxide (4.87mg), with alumina as the packing material, was heated at a rate of 10°C per minute over the range 26° to 270°C in an atmosphere of air. An endotherm occurred at 133°C followed immediately by a large exotherm beginning at 142°C and peaking at 170°C. When heating ceased, the sample was found to have lost a total of 0.98mg (20%) in weight. Analysis (g.l.c.) of the residue (3.89mg) showed it to contain a number of decomposition products, including diethyl (anthracen-9-yl)methylphosphonate, anthraquinone and diethyl methylphosphonate.

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FOUR

PHOTOOXIDATIVE DESULPHURISATION AT PENTAVALENT PHOSPHORUS

Introduction.

A considerable proportion of organophosphorus chemistry is concerned with compounds in which a sulphur atom is associated with the central phosphorus atom as either the thionate moiety (P=S), or the thiolate moiety (P-S-). The thionate, or thiophosphoryl moiety as it is more commonly known, is perhaps the more frequently encountered of the two, and consequently the manner by which it may be converted into its phosphoryl analogue (P=O), and visa versa, is particularly important. This chapter is concerned primarily with the formation of the phosphoryl moiety by the photochemical oxidative desulphurisation of the thiophosphoryl group. However some novel non-photochemical methods by which this same transformation may also be achieved will be briefly mentioned. Additionally the oxidative desulphurisation of the thiolate moiety in phosphorus esters by photochemical methods will be discussed.

Chemical Oxidative Desulphurisation of Thiophosphorus Compounds.

There are a number of oxidizing systems that have been used to convert the thiophosphoryl moiety into the phosphoryl moiety. Whilst much of this work has been carried out on phosphine sulphides, many of these oxidation procedures are also applicable to the esters of P V oxyacids containing the thiophosphoryl moiety. By the use of optically active phosphine sulphides and thiophosphorus esters, the stereochemical and mechanistic details of these oxidation reactions are becoming clear.

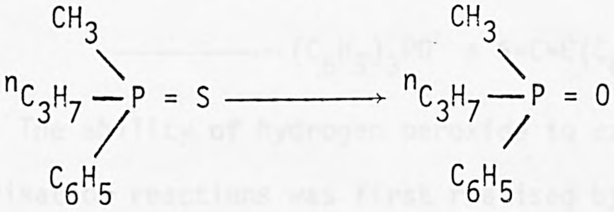
One of the earliest oxidative desulphurisation reactions was performed by Morgan and Herr[1] when they used a solution of potassium permanganate in pyridine to form di-(4-carboxyphenyl)phenylphosphine oxide from di-4-tolylphenylphosphine sulphide. Note how the tolyl

$$(H_3CC_6H_4)_2P(S)C_6H_5 \longrightarrow (HO_2CC_6H_4)_2P(O)C_6H_5$$

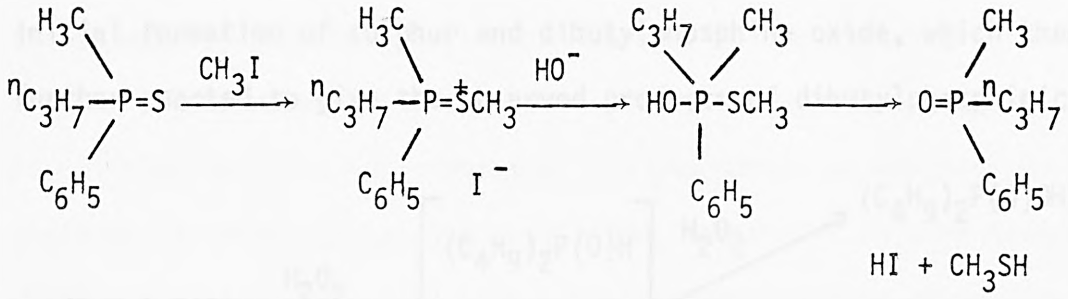
group is itself oxidized up to the carboxylic acid derivative. Similarly Maier[2] has used this same oxidizing system to convert tri-4-tolyphosphine sulphide to tri-4-carboxyphenylphosphine oxide.

$$(H_3CC_6H_4)_3PS \longrightarrow (HO_2CC_6H_4)_3PO$$

Horner,[3,4] in the oxidation of methylphenyl-n-propylphosphine sulphide with the permanganate pyridine mixture, has investigated the stereochemical course of the reaction and found it to occur with the retention of configuration at phosporus.



In contrast, oxidation with an alkaline methyl iodide solution resulted in inversion of configuration.[3,4]



Here the reaction is believed to occur via a trigonal bipyramidal intermediate, in which the entering and leaving groups occupy the two apical positions.

The use of thionyl chloride to achieve the oxidative desulphurisation of a variety of thiophosphoryl substrates has been elegantly shown by Harwood and Pollard.[5,6]

$$C_2H_5(CH_3)P(S)C_6H_5 + SOCl_2 \longrightarrow C_2H_5(CH_3)P(O)C_6H_5 + S_2Cl_2$$

$$(CH_3)_2P(S)Cl + SOCl_2 \longrightarrow (CH_3)_2P(O)Cl + S_2Cl_2$$

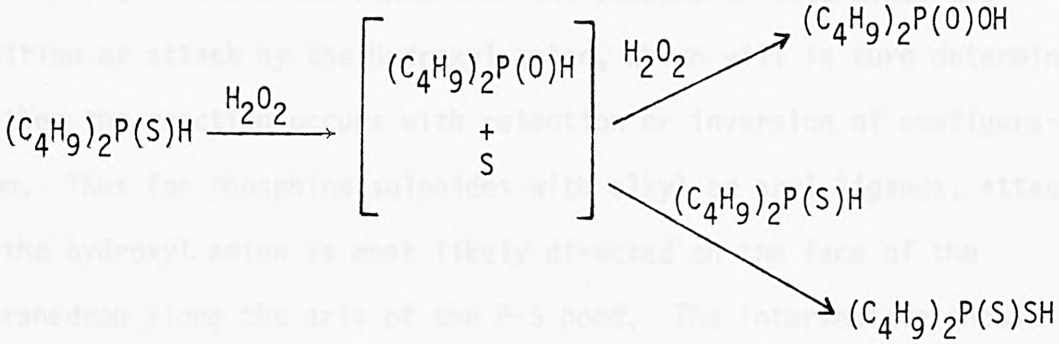
Although no reference was made as to the stereospecificity of the transformation, the influence of structure on the efficiency of the reaction was clearly shown. Thus the replacement of an alkyl group by an electronegative substituent such as a phenyl or a halogen markedly decreased the reactivity of the phosphorus towards sulphur-oxygen exchange.

A rather unusual oxidation of triphenylphosphine sulphide with diphenyl ketene was shown by Staudinger et. al.[7] The oxide and thioketene are isolated from the reaction.

$$(C_6H_5)_3PS + O{=}C{=}C(C_6H_5)_2$$

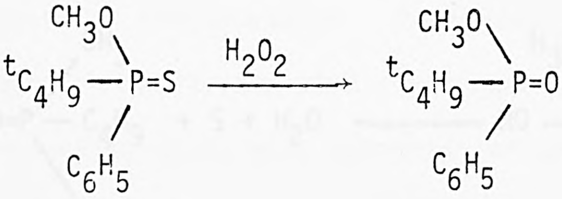
$$\longrightarrow (C_6H_5)_3PO + S{=}C{=}C(C_6H_5)_2$$

The ability of hydrogen peroxide to carry out oxidative desulphurisation reactions was first realised by Peters.[8] He reacted dibutylphosphine suphide with hydrogen peroxide and noticed the initial appearance and subsequent disappearance of colloidal sulphur as the reaction proceeded. From this he concluded that oxidation lead to the initial formation of sulphur and dibutylphosphine oxide, which then further reacted to give the observed products of dibutylphosphinic acid

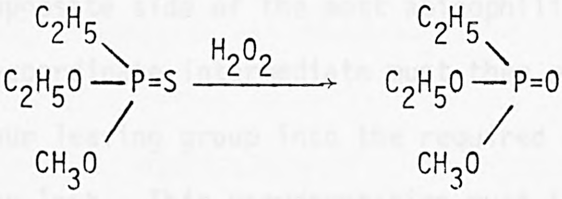


and dibutyldithiophosphinic acid.

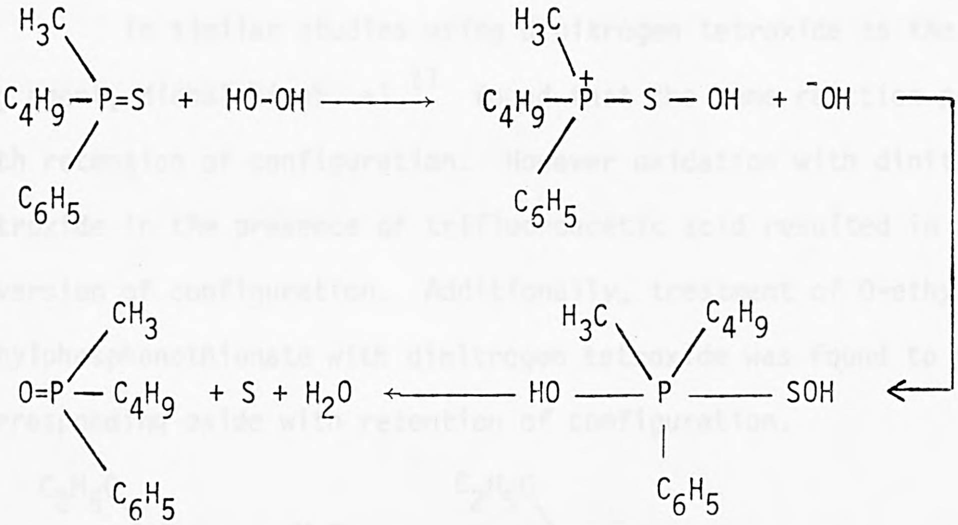
Trippett et. al.[9] have reported the oxidation of O-methyl t-butylphenylphosphinothionate with hydrogen peroxide and noted that the reaction proceeded with retention of configuration.



Agreement with this stereospecificity of hydrogen peroxide oxidation has come from Michalski et. al.[10] They observed that the reaction of O-ethyl O-methyl ethylphosphonothionate proceeded with retention of configuration. However Michalski et. al.[10] also reported that contrary



to this, the oxidation of methylphenyl-n-propylphosphine sulphide with hydrogen peroxide resulted in the formation of the corresponding oxide, but with the reaction proceeding with inversion of configuration. To account for this, Michalski et. al.[10] proposed a mechanism which involves initial nucleophilic attack by sulphur on the oxygen of hydrogen peroxide. Subsequent nucleophilic attack by the hydroxyl anion at the phosphorus atom to give a five-coordinate intermediate, followed by loss of the sulphur fraction will give the observed products. It is believed that the environment of the phosphorus determines the position of attack by the hydroxyl anion, which will in turn determine whether the reaction occurs with retention or inversion of configuration. Thus for phosphine sulphides with alkyl or aryl ligands, attack by the hydroxyl anion is most likely directed on the face of the tetrahedron along the axis of the P-S bond. The intermediate should

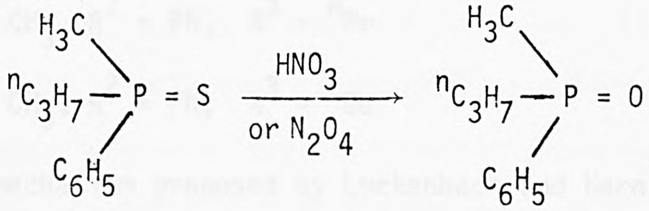


then decompose giving the oxide with inversion of configuration. For compounds with at least one alkoxy group attached to the phosphorus atom, attack from the hydroxyl anion now occurs along the P-O axis from the opposite side of the most apicophilic oxo ligand. The resultant five-coordinate intermediate must then pseudorotate once to bring the sulphur leaving group into the required apical position from where it can be lost. This pseudorotation must inconsequence lead to retention of configuration at phosphorus.

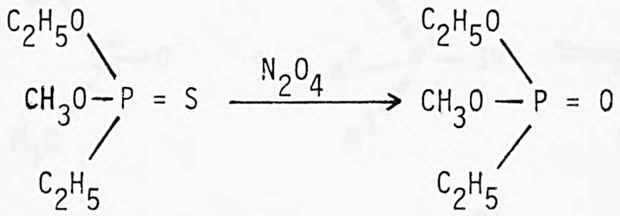
Nitric acid has also been used to perform oxidative desulpurisation reactions. Maier[2] first oxidized triphenylphosphine sulphide to the phosphine oxide, although aromatic nitration also occurred.

$$(C_6H_5)_3PS \xrightarrow{HNO_3} (3\text{-}NO_2C_6H_4)_3PO$$

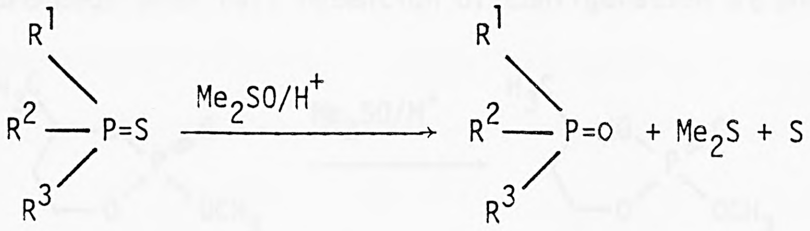
Stereochemical details on this method of oxidation have been provided by Michalski and his co-workers.[11] They found that the oxidation of methylphenyl-n-propylphosphine sulphide by nitric acid lead to the formation of methylphenyl-n-propylphosphine oxide with inversion of configuration.



In similar studies using dinitrogen tetroxide as the oxidizing agent, Michalski et. al.[11] found that the same reaction proceeded with retention of configuration. However oxidation with dinitrogen tetroxide in the presence of trifluoroacetic acid resulted in partial inversion of configuration. Additionally, treatment of O-ethyl O-methyl ethylphosphonothionate with dinitrogen tetroxide was found to form the corresponding oxide with retention of configuration.



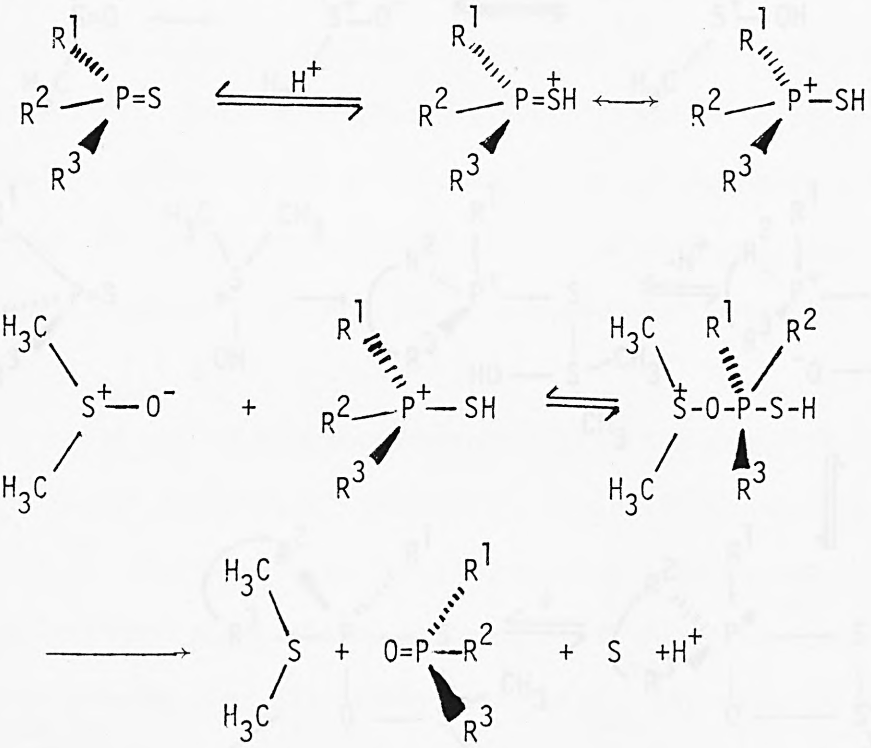
The oxidative desulphurisation of thiophosphorus acids by dimethyl sulphoxide was first reported by Mikolajczyk.[12] Since then the use of dimethyl sulphoxide in the presence of a strong acid has been used to oxidize a wide range of phosphine sulphides and thiophosphorus esters. By starting with optically active thiophosphorus compounds, the reaction has been shown to proceed in a stereospecific manner. Thus both methylphenyl-n-propylphosphine sulphide[13,14] and t-butylmethylphenylphosphine sulphide[14] give rise to their respective oxides with inversion of configuration.



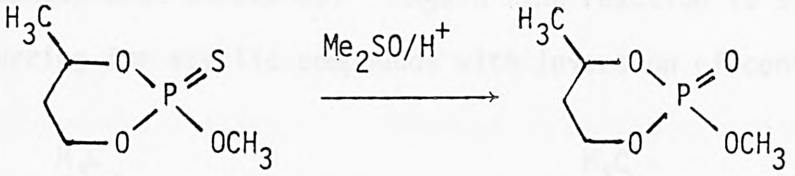
$R^1 = CH_3$, $R^2 = Ph$, $R^3 = {}^nPr$

$R^1 = CH_3$, $R^2 = Ph$, $R^3 = {}^tBu$

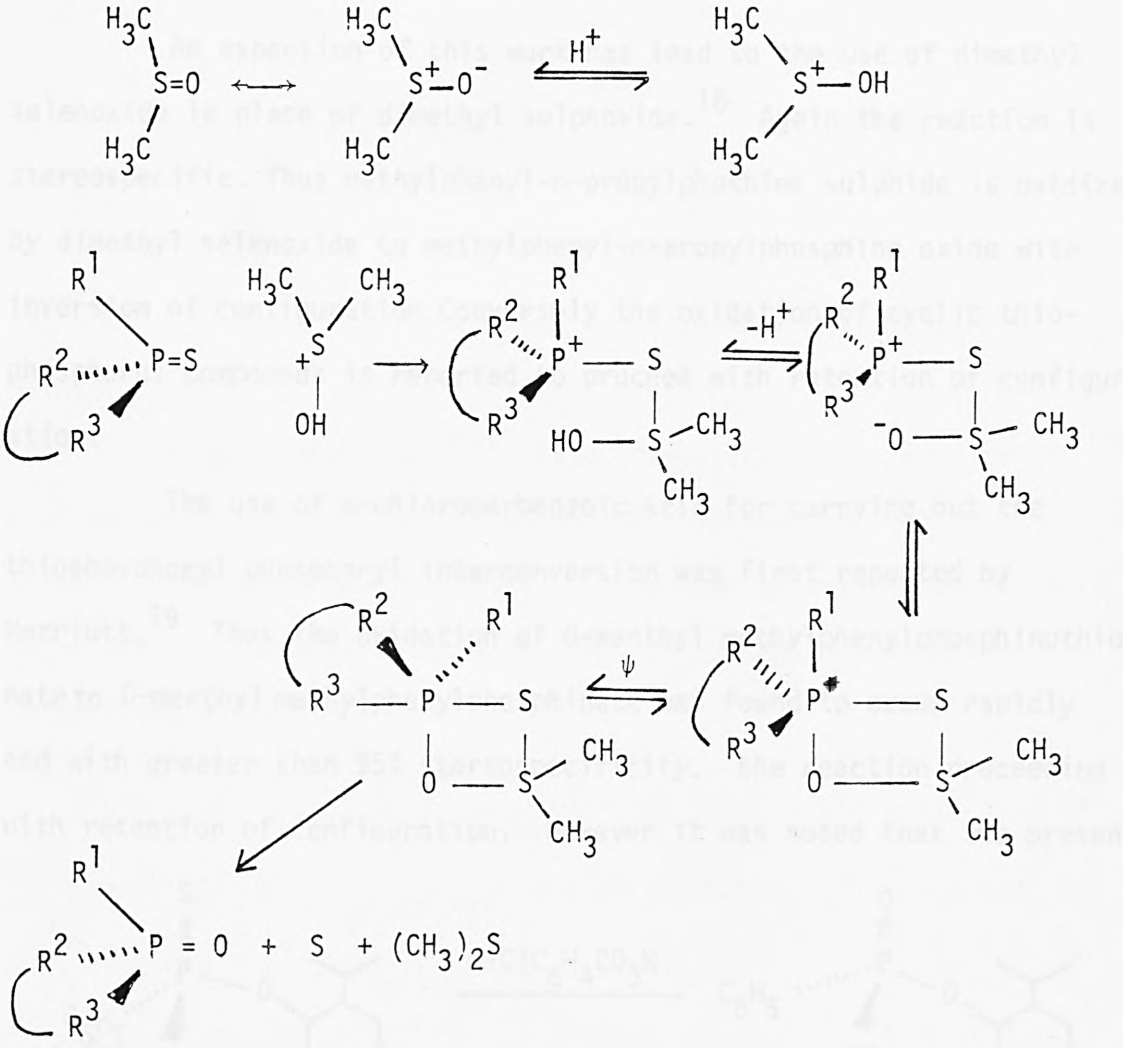
The mechanism proposed by Luckenbach and Kern[15] to account for this inversion of configuration is for the reaction to proceed via a trigonal bipyramidal intermediate.



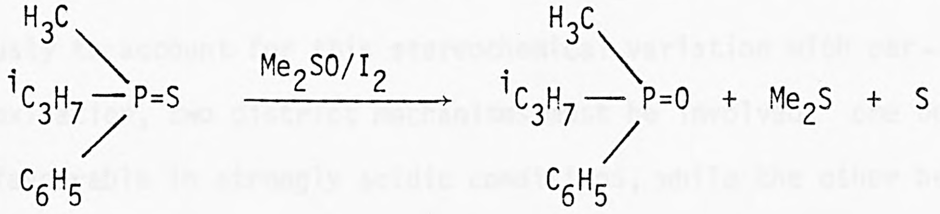
Clearly there is great similarity between this mechanism and that proposed by Michalski et. al.[10] to account for inversion of configuration of phosphine sulphides when oxidized with hydrogen peroxide. It is most likely that the nitric acid oxidation of acylic thiophosphorus compounds which proceeds with inversion also occurs by this same mechanism. In contrast to this, the oxidation of both cis and trans 2-methoxy-2-thio-4-methyl-1,3,2-dioxaphosphorinan by dimethyl sulphoxide proceeds with full retention of configuration at phosphorus.



Six-membered cyclic systems are less susceptible to nucleophilic attack at phosphorus. Consequently the formation and intramolecular decomposition of a 'betaine type' intermediate should be favoured, and would involve retention at phosphorus.[13]



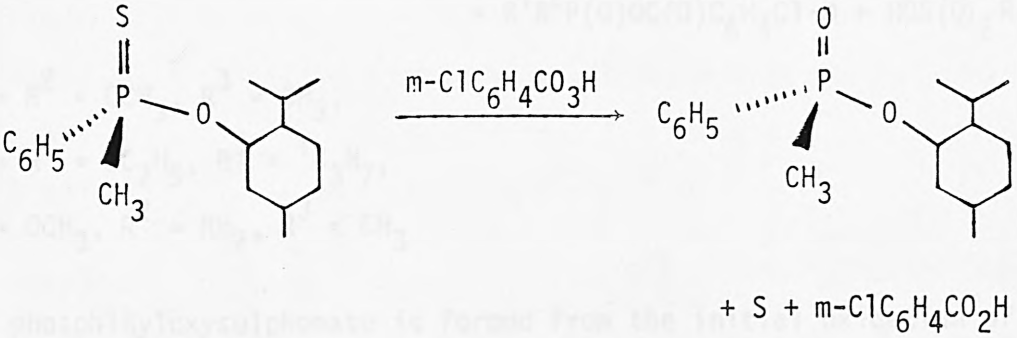
Recently however the oxidation of cis and trans 2-hydroxy-2-thiono-4-methyl-1,3,2-dioxaphosphorinan with (^{18}O)-dimethyl sulphoxide was found to proceed with inversion of configuration and with the formation of (^{18}O)-phosphate.[16] The use of iodine in place of a strong acid has also been found to catalyse the dimethyl sulphoxide oxidation of thiophosphorus compounds.[17] Again the reaction is stereospecific occurring for acyclic compounds with inversion of configuration.



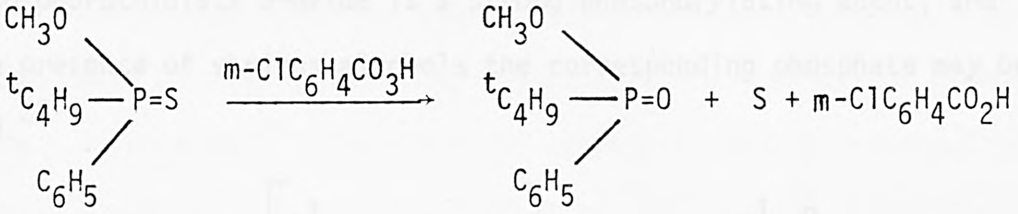
Clearly the steric course of the dimethyl sulphoxide oxidations catalysed by acids and iodine are the same.

An expansion of this work has lead to the use of dimethyl selenoxide in place of dimethyl sulphoxide.[18] Again the reaction is stereospecific. Thus methylphenyl-n-propylphoshine sulphide is oxidized by dimethyl selenoxide to methylphenyl-n-propylphosphine oxide with inversion of configuration. Conversely the oxidation of cyclic thiophosphorus compounds is reported to proceed with retention of configuration.

The use of m-chloroperbenzoic acid for carrying out the thiophosphoryl phosphoryl interconversion was first reported by Herriott.[19] Thus the oxidation of O-menthyl methylphenylphosphinothionate to O-menthyl methylphenylphosphinate was found to occur rapidly and with greater than 95% stereospecificity, the reaction proceeding with retention of configuration. However it was noted that the presence



of stronger acids such as trifluoroacetic acid lead to a reversal of the stereospecificity with the reaction now occurring predominantly with inversion of configuration. Clearly there is a close analogy between this reaction and that for dinitrogen tetroxide[11] where oxidation normally occurred with retention, but in the presence of trifluoroacetic acid some inversion of configuration was observed. Obviously to account for this stereochemical variation with per-acid oxidation, two district mechanisms must be involved, one being more favourable in strongly acidic conditions, while the other being more favourable in the absence of any acid. The oxidation of O-methyl t-butylphenylphosphinothionate to O-methyl t-butylphenylphosphinate using m-chloroperbenzoic acid has been briefly mentioned by Trippett



et. al.[9] The reaction was reported to occur with retention of configuration.

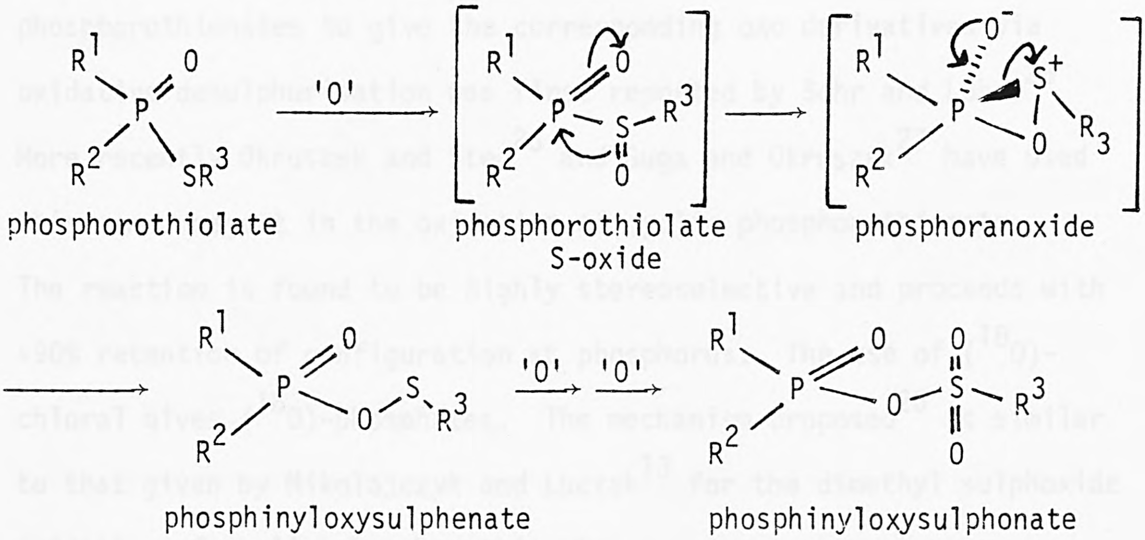
Segal and Casida [20,21] have investigated the reaction of m-chloroperbenzoic acid with a number of compounds containing the S-alkyl phosphorothiolate moiety. The phosphinyloxysulphonate is the major product isolated along with some pyrophosphate and m-chlorobenzoyl anhydride.

$$R^1R^2P(O)SR^3 \xrightarrow{m\text{-}ClC_6H_4CO_3H} R^1R^2P(O)OS(O)_2R^3 + R^1R^2P(O)OP(O)R^1R^2$$

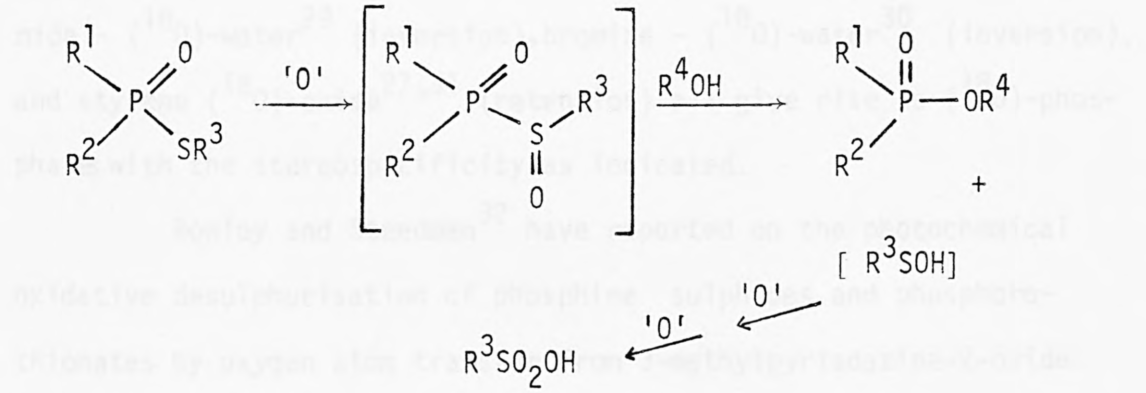
$$+ R^1R^2P(O)OC(O)C_6H_4Cl\text{-}m + HOS(O)_2R_3$$

$R^1 = R^2 = OCH_3$, $R^3 = CH_3$,
$R^1 = R^2 = OC_2H_5$, $R^3 = {}^iC_3H_7$,
$R^1 = OCH_3$, $R^2 = NH_2$, $R^3 = CH_3$

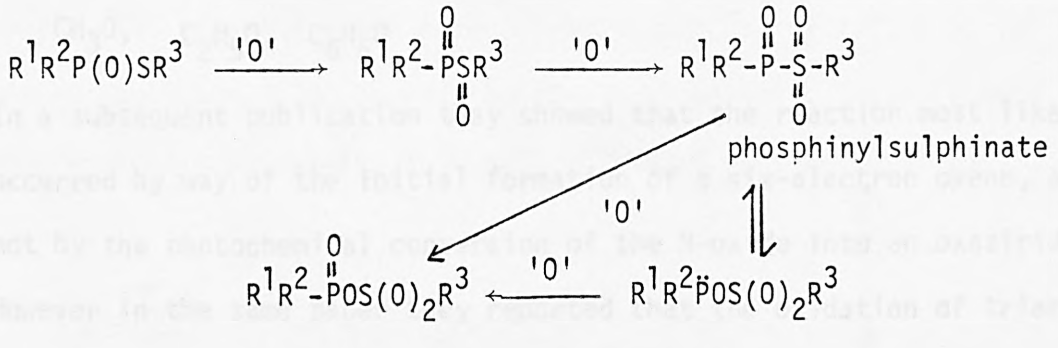
The phosphinyloxysulphonate is formed from the initial oxidation of the phosphorothiolate to give the S-oxide, rearrangement to the phosphinyloxysulphenate and subsequent oxidation.



The phosphorothiolate S-oxide is a strong phosphorylating agent, and in the presence of various alcohols the corresponding phosphate may be formed.[22]



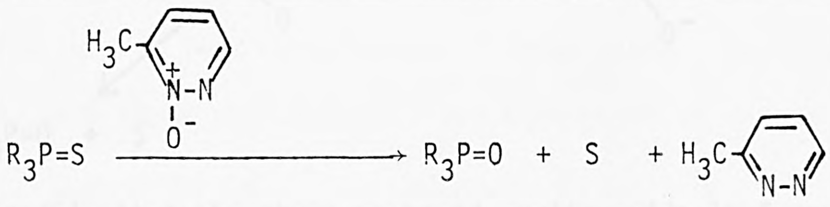
However Michalski et. al. have suggested[23,24] that the formation of the phosphinyloxysulphonate occurs via oxidation of the S-oxide to the phosphinylsulphinate and then either, insertion of oxygen into the phosphorus sulphur bond, or alternatively oxidation of the P III anhydride which is believed to be in equilibrium with the sulphinate.



The reaction of trichloroacetaldeyhyde (chloral) with phosphorothionates to give the corresponding oxo derivatives via oxidative desulphurisation was first reported by Sohr and Lohs.[25] More recently Okruszek and Stec[26] and Guga and Okruszek[27] have used this same reagent in the oxidation of cyclic phosphorothionates. The reaction is found to be highly stereoselective and proceeds with >90% retention of configuration at phosphorus. The use of (^{18}O)-chloral gives (^{18}O)-phosphates. The mechanism proposed[26] is similar to that given by Mikolajczyk and Luczak[13] for the dimethyl sulphoxide oxidation of cyclic phosphorothionates.

Other reports on the stereospecific oxidation of phosphorothionates have of late appeared in the literature. The use of cyanogen bromide - (^{18}O)-water[28] (inversion of configuration), N-bromosuccinimide - (^{18}O)-water[29] (inversion), bromine - (^{18}O)-water[30] (inversion), and styrene (^{18}O)-oxide[27,31] (retention) all give rise to (^{18}O)-phosphates with the stereospecificity as indicated.

Rowley and Steedman[32] have reported on the photochemical oxidative desulphurisation of phosphine sulphides and phosphorothionates by oxygen atom transfer from 3-methylpyriadazine-2-oxide.

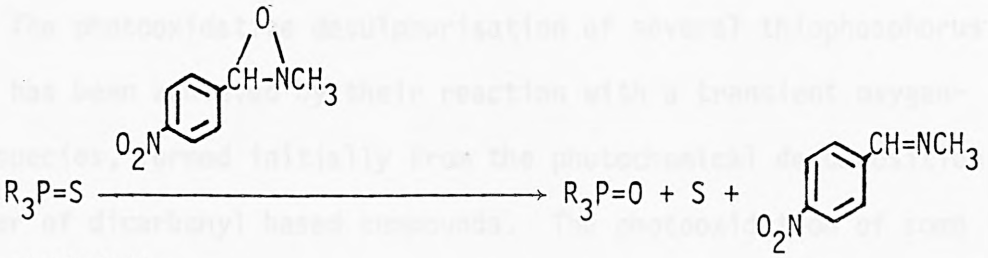


R = C_6H_5, 4-$CH_3C_6H_4$,

4-$CH_3OC_6H_4$, 4-ClC_6H_4

CH_3O, C_2H_5O, C_6H_5O

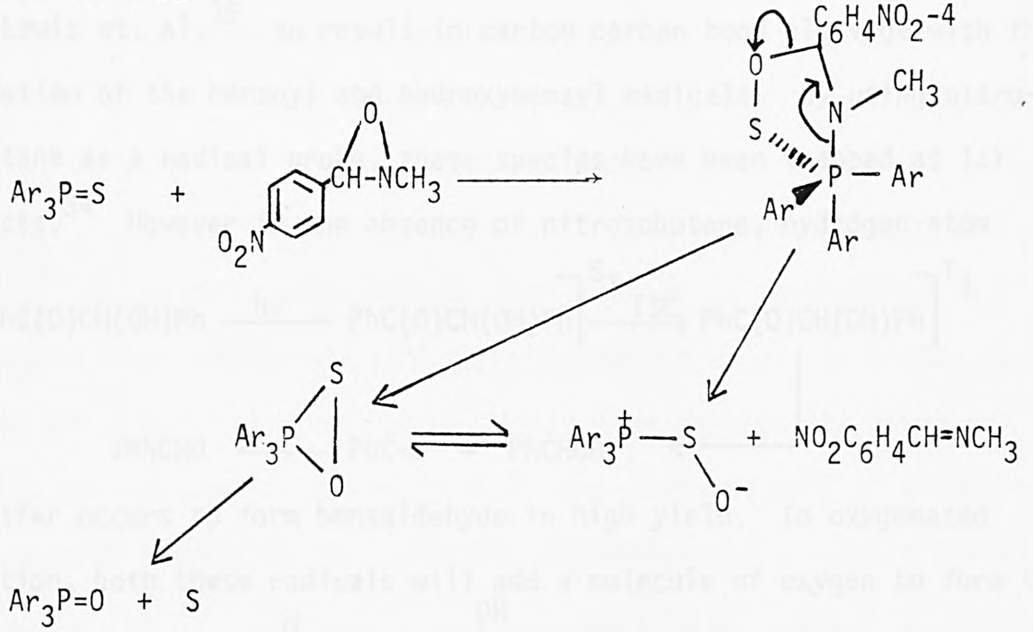
In a subsequent publication they showed that the reaction most likely occurred by way of the initial formation of a six-electron oxene, and not by the photochemical conversion of the N-oxide into an oxaziridine.[33] However in the same paper they reported that the oxidation of triaryl-phosphine sulphides can be achieved using 3-methyl-3-p-nitrophenyloxaziridine.



R = C_6H_5, 4-$CH_3C_6H_4$,

4-$CH_3OC_6H_4$, 4-ClC_6H_4

Using methylphenyl-n-propylphosphine sulphide the reaction was found to proceed with >90% retention of configuration. A mechanism was proposed involving initial attack of the thiophosphoryl sulphur on the oxaziridine oxygen.

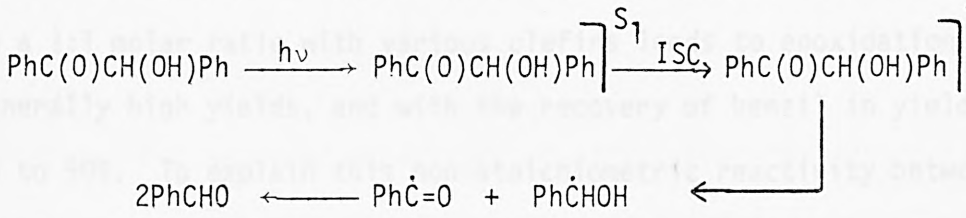


It is possible that the three membered cyclic oxide is formed without the participation of the 1,3-dipolar species, but directly from the trigonal pyramidal intermediate. This may lead to enhanced stereospecificity. On the other hand the photochemical oxidation of the chiral phosphine sulphide with 3-methylpyriadazine-2-oxide is much less stereospecific proceeding with <60% retention of configuration.

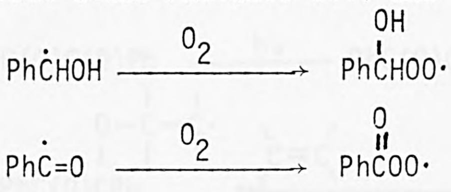
Photochemical Generation of Peroxy Radicals from 1,2-Diketones.

The photooxidative desulphurisation of several thiophosphorus compounds has been achieved by their reaction with a transient oxygen-transfer species, formed initially from the photochemical decomposition of a number of dicarbonyl based compounds. The photooxidation of some of these dicarbonyl compounds, particularly benzoin, benzil and biacetyl have been investigated in relation to their ability to epoxidize olefins. However the structure of the oxygen-transfer species, its formation and precise involvement in such photoepoxidation reactions still remains in some instances most unclear.

The photolysis of benzoin has been shown by Ledwith et. al.[34] and Lewis et. al.[35] to result in carbon carbon bond cleavage with the formation of the benzoyl and hydroxybenzyl radicals. By using nitrosobutane as a radical probe, these species have been trapped as 1:1 adducts.[34] However in the absence of nitrosobutane, hydrogen atom transfer occurs to form benzaldehyde in high yield. In oxygenated solution, both these radicals will add a molecule of oxygen to form the corresponding peroxy radical.



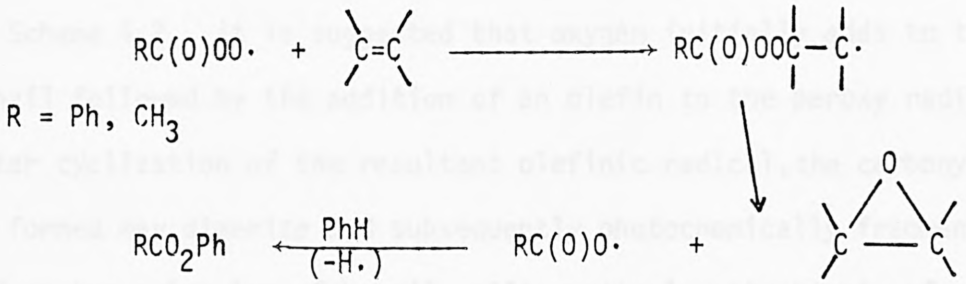
$$\mathrm{PhC(O)CH(OH)Ph} \xrightarrow{h\nu} \left[\mathrm{PhC(O)CH(OH)Ph}\right]^{S_1} \xrightarrow{ISC} \left[\mathrm{PhC(O)CH(OH)Ph}\right]^{T_1} \rightarrow \mathrm{Ph\dot{C}{=}O} + \mathrm{Ph\dot{C}HOH} \rightarrow 2\mathrm{PhCHO}$$



$$\mathrm{Ph\dot{C}HOH} \xrightarrow{O_2} \mathrm{Ph\overset{OH}{C}HOO\cdot}$$

$$\mathrm{Ph\dot{C}{=}O} \xrightarrow{O_2} \mathrm{Ph\overset{O}{\overset{\|}{C}}OO\cdot}$$

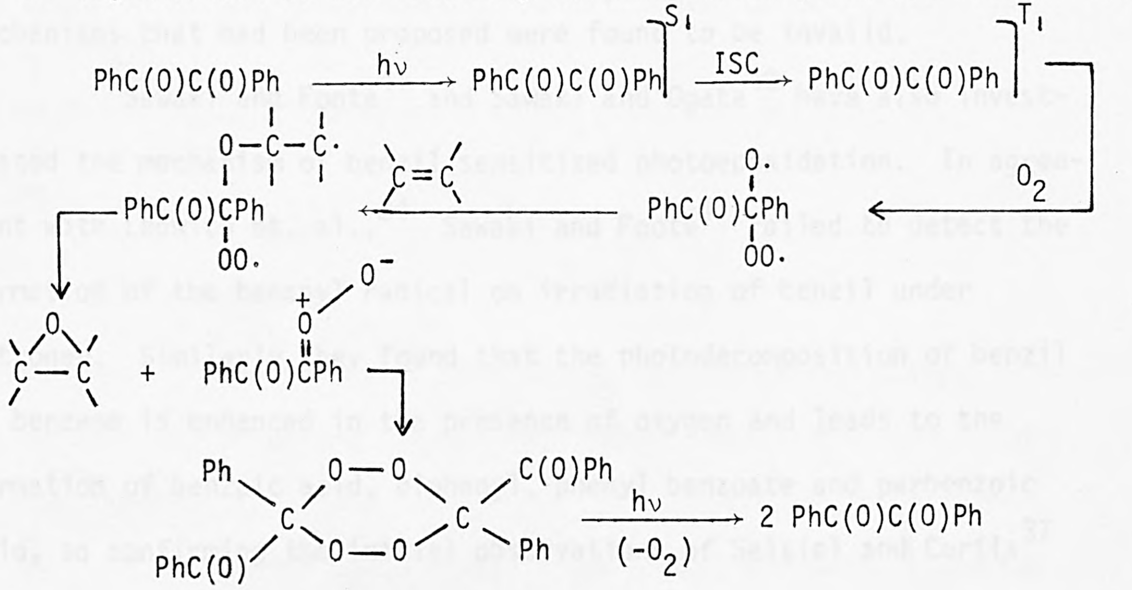
Sawaki and Ogata[36] have suggested that it is the formation of the benzoylperoxy radical which is responsible for the epoxidation of olefins, Scheme 4.1 (R=Ph). Although the intramolecular cyclization of the olefinic radical is fast, the rotation around the carbon carbon bond is much faster and thus both cis and trans olefins give predominantly trans epoxides. Epoxidation



Scheme 4.1.

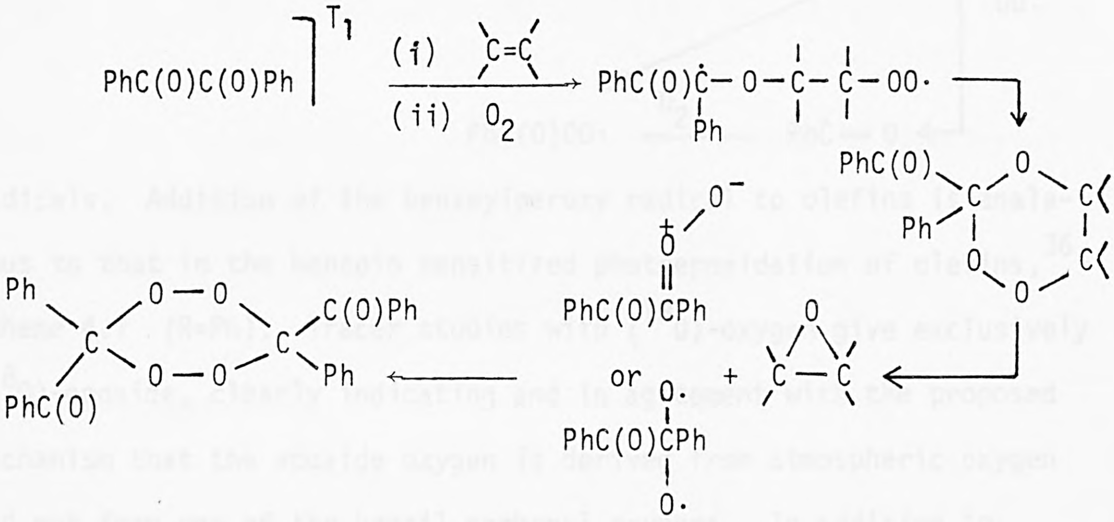
occurring from the peracid was discounted by the authors as the yield of epoxide was not affected by the presence of dimethyl sulphoxide, a much more reactive substrate towards peracids.

The epoxidation of olefins by benzil and biacetyl has similarly been investigated, although there remains much to be clarified about the mechanism of the photoreaction. Saltiel and Curtis[37] and Gream et. al.[38] have shown that in benzene, benzil is photooxidized to benzoic acid, phenyl benzoate, benzoyl peroxide, phenol and biphenyl. However Shimizu and Bartlett[39] have reported that benzil in a 1:1 molar ratio with various olefins leads to epoxidation in generally high yields, and with the recovery of benzil in yields of up to 90%. To explain this non-stoichiometric reactivity between benzil and the olefin, two mechanisms were proposed both of which result in the regeneration of the initially consumed benzil, Schemes 4.2 and 4.3.



Scheme 4.2.

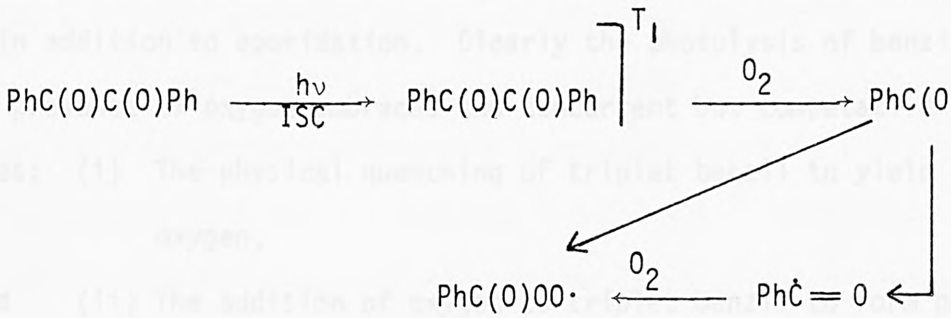
In Scheme 4.2. it is suggested that oxygen initially adds to triplet benzil followed by the addition of an olefin to the peroxy radical. After cyclization of the resultant olefinic radical, the carbonyl oxide so formed may dimerize and subsequently photochemically fragment to reform two molecules of benzil. Alternatively attachment of oxygen to the alkene carbon radical may lead to cyclization and fragmentation to epoxide, Scheme 4.3. Subsequently however a retraction was made



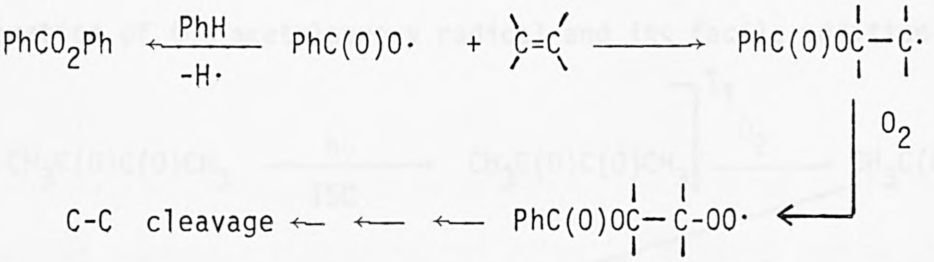
Scheme 4.3.

concerning the reported recoveries of benzil from the epoxidation reactions.[40] The recoveries of benzil were found to be much lower than those originally published[39] and as such the chain like reaction mechanisms that had been proposed were found to be invalid.

Sawaki and Foote[41] and Sawaki and Ogata[42] have also investigated the mechanism of benzil sensitized photoepoxidation. In agreement with Ledwith et. al.,[34] Sawaki and Foote[41] failed to detect the formation of the benzoyl radical on irradiation of benzil under nitrogen. Similarly they found that the photodecomposition of benzil in benzene is enhanced in the presence of oxygen and leads to the formation of benzoic acid, biphenyl, phenyl benzoate and perbenzoic acid, so confirming the initial observations of Saltiel and Curtis[37] and Gream et. al.[38] To account for this Sawaki and Foote have suggested that the primary process in the irradiation of an oxygenated benzil solution is a direct interaction between a molecule of oxygen and triplet state benzil, as previously proposed.[37] This is followed by carbon carbon bond cleavage to form the benzoyl and benzoylperoxy



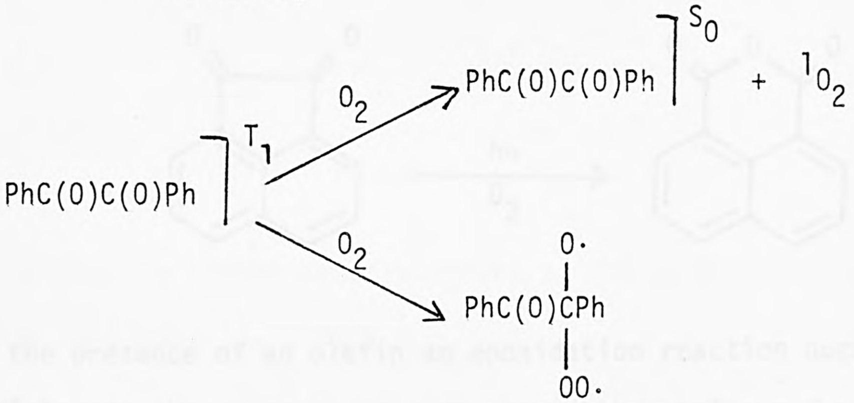
radicals. Addition of the benzoylperoxy radical to olefins is analagous to that in the benzoin sensitized photoepoxidation of olefins,[36] Scheme 4.1 (R=Ph). Tracer studies with (^{18}O)-oxygen give exclusively (^{18}O)-epoxide, clearly indicating and in agreement with the proposed mechanism that the epoxide oxygen is derived from atmospheric oxygen and not from one of the benzil carbonyl oxygens. In addition to epoxidation, competative reactions involving olefinic carbon carbon bond cleavage are also observed. Sawaki and Ogata[42] have shown that such reactions arise from the addition of the benzoyloxy radical to olefins. However since this addition is not as rapid compared to the addition of the benzoylperoxy radical, lower concentrations of



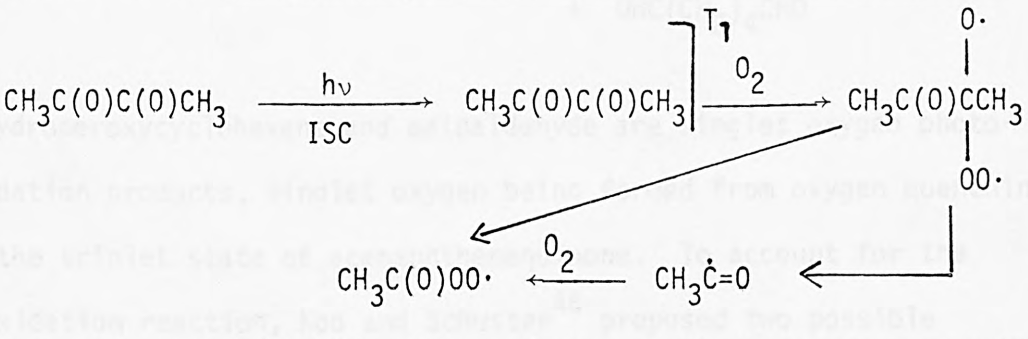
olefin leads to preferential reaction of the benzoyloxy radical with the solvent and therefore favours epoxidation over carbon carbon bond cleavage reactions.

Both Shimizu and Bartlett[39] and Sawaki and Foote[41] are in agreement that benzil is also able to sensitize the production of singlet oxygen. This is not surprising since the triplet energy of benzil[43] is much greater than the energy of singlet oxygen, (53 kcal. mol^{-1} Vs. 22.5 kcal. mol^{-1}). Thus for olefinic substrates having a high reactivity towards singlet oxygen, hydroperoxide formation is observed in addition to epoxidation. Clearly the photolysis of benzil in the presence of oxygen embraces two concurrent but competative processes; (i) The physical quenching of triplet benzil to yield singlet oxygen,

and (ii) The addition of oxygen to triplet benzil to form peroxy radicals,



As for benzoin and benzil, the photo-oxidation of biacetyl is known to proceed through the triplet state.[44] Similarly in the presence of olefins photoepoxidation may occur.[39,41,42] The mechanism is believed to be the same as for benzil, involving the initial generation of the acetylperoxy radical and its facile addition to

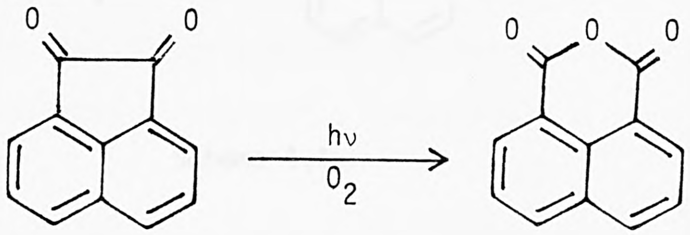


olefins, Scheme 4.1 (R=CH_3). The acetyloxy radical formed on epoxidation is known to rapidly decarboxylate to give the methyl radical,[45] which may subsequently add a molecule of oxygen to form the methylperoxy radical. It is this methylperoxy radical which is believed to

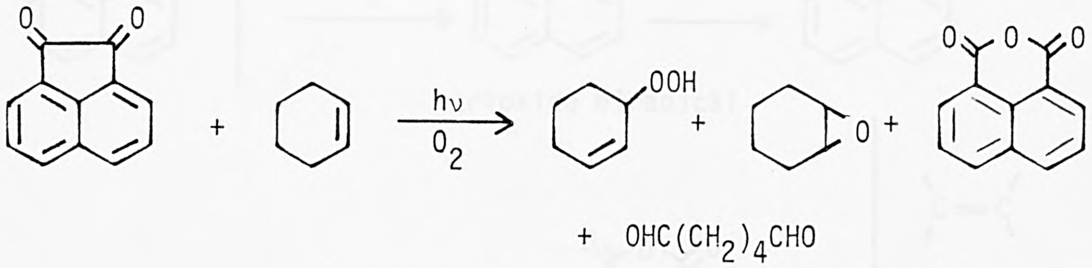
$$CH_3C(O)O\cdot \xrightarrow{-CO_2} CH_3\cdot \xrightarrow{O_2} CH_3OO\cdot$$

be responsible for the formation of carbon carbon bond cleavage products in the biacetyl sensitized photoepoxidation of olefins.[42]

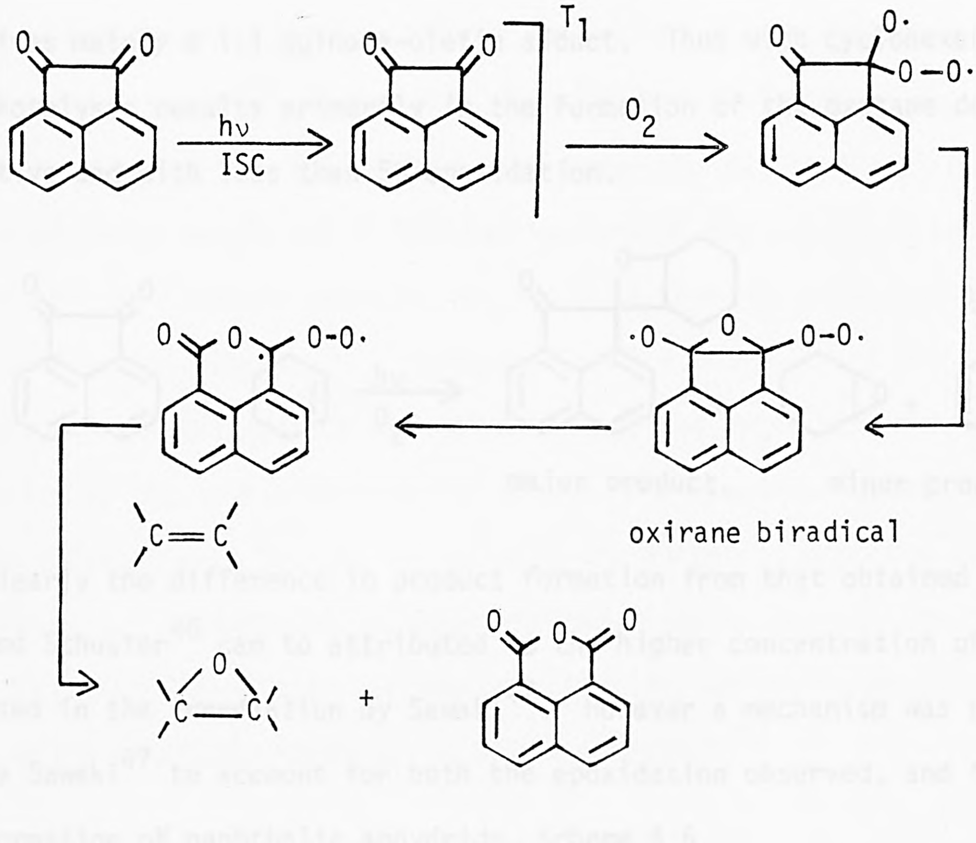
The mechanism for the photooxidation of and photoepoxidation by cyclic α-diketones, particularly acenaphthenequinone has also been investigated. Both Koo and Schuster[46] and Sawaki[47] have found that the photooxidation of acenaphthenequinone leads almost exclusively to the formation of the 1,8-naphthalic anhydride.



In the presence of an olefin an epoxidation reaction occurs.[46] Thus cyclohexene when photolysed with acenaphthenequinone forms the cyclohexene oxide.

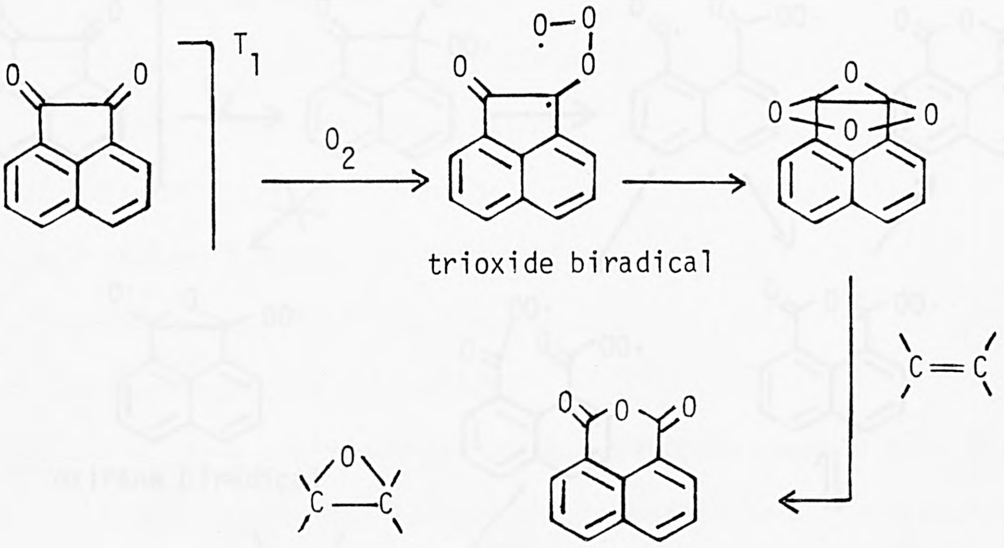


3-Hydroperoxycyclohexene and adipaldehyde are singlet oxygen photooxidation products, singlet oxygen being formed from oxygen quenching of the triplet state of acenaphthenequinone. To account for the epoxidation reaction, Koo and Schuster[46] proposed two possible mechanisms. The first involves oxygen bonding to the carbonyl carbon followed by cyclization to an oxirane biradical, Scheme 4.4.



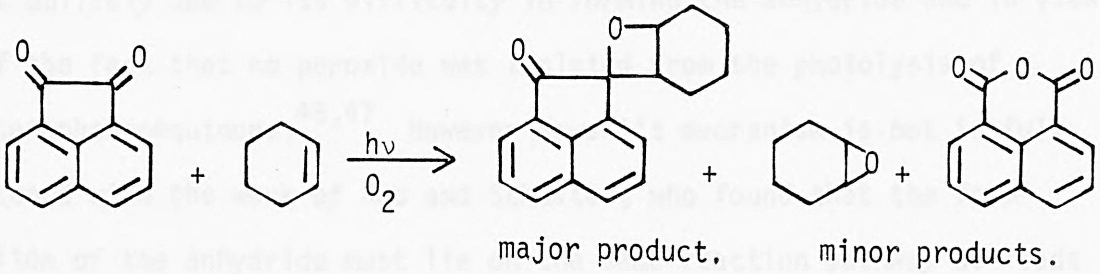
Scheme 4.4.

Alternatively oxygen bonding occurs at the carbonyl oxygen to give a trioxide biradical, Scheme 4.5.

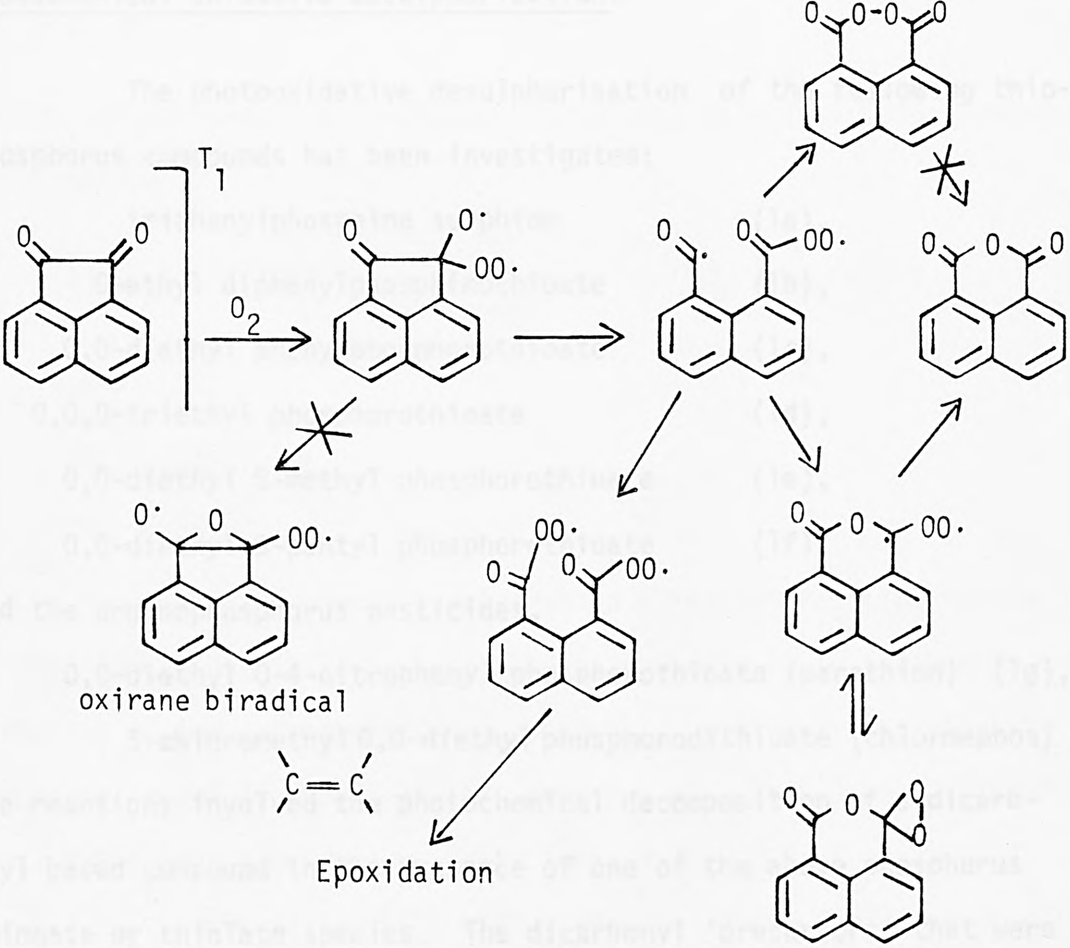


Scheme 4.5.

In contrast to this Sawaki[47] has reported that the photooxidation of acenaphthenequinone in the presence of various olefins gives mainly a 1:1 quinone-olefin adduct. Thus with cyclohexene, photolysis results primarily in the formation of the oxetane derivative and with less than 5% epoxidation.



Clearly the difference in product formation from that obtained by Koo and Schuster[46] can to attributed to the higher concentration of olefin used in the irradiation by Sawaki[47]. However a mechanism was proposed by Sawaki[47] to account for both the epoxidation observed, and the formation of naphthalic anhydride, Scheme 4.6.



Scheme 4.6.

Sawaki discounts the formation of an oxirane biradical as proposed by Koo and Schuster[46] on the basis that the ketone diradical should be much more stable. Additionally the formation of the diacyl peroxide is unlikely due to its difficulty in forming the anhydride and in view of the fact that no peroxide was isolated from the photolysis of acenaphthenequinone.[46,47] However Sawaki's mechanism is not in full accord with the work of Koo and Schuster, who found that the formation of the anhydride must lie on the same reaction pathway as leads to epoxidation. This is not so with the mechanism depicted in Scheme 4.6. Additionally phenanthrenequinone is reported to be an inefficient sensitizer for photoepoxidation, while its photolysis with olefins similarly leads to 1:1 adduct formation.[47]

Photochemical Oxidative Desulphurisation.

The photooxidative desulphurisation of the following thiophosphorus compounds has been investigated;

triphenylphosphine sulphide (1a),
O-ethyl diphenylphosphinothioate (1b),
O,O-diethyl phenylphosphonothioate (1c),
O,O,O-triethyl phosphorothioate (1d),
O,O-diethyl S-methyl phosphorothioate (1e),
O,O-diethyl S-pentyl phosphorothioate (1f),

and the organophosphorus pesticides,

O,O-diethyl O-4-nitrophenyl phosphorothioate (parathion) (1g),
S-chloromethyl O,O-diethyl phosphorodithioate (chlormephos) (1h).

The reactions involved the photochemical decomposition of a dicarbonyl based compound in the presence of one of the above phosphorus thionate or thiolate species. The dicarbonyl 'precursors' that were used in this study included benzoin, benzil, biacetyl, acenaphthene-9,10-quinone (AcQ), phenanthrene-9,10-quinone (PhQ), pyruvic acid, methyl pyruvate, t-butyl pyruvate, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and tetrachloro-1,4-benzoquinone (p-chloranil). The reactions were performed by irradiating an acetonitrile solution of the thiophosphorus compound and dicarbonyl precurser under oxygen with black-light fluorescent lamps. The disappearance of starting material and formation of products was monitored by g.l.c. For the thiophosphoryl compounds the formation of the phosphoryl analogue was anticipated,

$$R'_{3-n}P(S)(OCH_2CH_3)_n \xrightarrow[\text{precursor}]{h\nu/O_2} R'_{3-n}P(O)(OCH_2CH_3)_n$$

1a, $R' = C_6H_5$ $n=0$
1b, $=1$
1c, $=2$
1d, $=3$
1g, $R'=4\text{-}NO_2C_6H_4O$ $n=2$

whilst for the thiolate compounds, phosphorus thioalkyl bond cleavage was expected.

$$(CH_3CH_2O)_2P(X)SR'' \xrightarrow[\text{precursor}]{h\nu/O_2} (CH_3CH_2O)_2P(O)OH$$

1e, $X=O$ $R''=CH_3$
1f, $=O$ $=(CH_2)_4CH_3$
1h, $=S$ $=CH_2Cl$

It was found that by carrying out such an oxidation reaction in the manner indicated does, for the thionate compounds 1a to 1d lead to the formation of the oxon derivative, Table 4.1. Similarly the thiolate compounds 1e and 1f result in the formation of the phosphorus acid for all but one of the precursors used, Table 4.2.

In view of the information concerning the formation of peroxy radicals from the decomposition of α-dicarbonyl compounds, it is not unreasonable to suppose that such radicals are responsible for the

Table 4.1. Photooxidative desulphurisation of the phosphorus thionate compounds 1a, 1b, 1c and 1d.

Phosphorus thionate compound*		percentage yield of †	
		recovered st. material :	oxidized product
$R'_{3-n}P(S)(OEt)_n$	precursor	$R'_{3-n}P(S)(OEt)_n$	$R'_{3-n}P(O)(OEt)_n$
1a, Ph_3PS ^{x}	benzoin, 2equ	0	98
1b, $Ph_2P(S)OEt$		0	88
1c, $PhP(S)(OEt)_2$		0	86
1d, $(EtO)_3PS$		0	95
1a,	benzil, 2equ	0	85
1b,		17	72
1c,		35	53
1d,		42	44
1a,	biacetyl, 4equ	0	84
1b,		0	84
1c,		13	69
1d,		17	63
1a,	AcQ, 2equ	2	96
1b,	1.4equ	26	68
1c,	1.2equ	29	67
1d,	1equ	39	39
1a,	PhQ, 2equ	91	4
1a,	DDQ, 2equ	0	95
1b,		33	53
1c,		56	24
1d,		73	17
1a,	p-chloranil, 2equ	65	31
1b,		88	12

Table 4.1. continued.

Phosphorus thionate compound* $R'_{3-n}P(S)(OEt)_n$	precursor	percentage yield of † recovered st. material : $R'_{3-n}P(S)(OEt)_n$	oxidized product $R'_{3-n}P(O)(OEt)_n$
1a,	pyruvic acid, 4equ	0	88
1b,		0	92
1c,		20	68
1d,		52	38
1a,	methyl pyruvate, 4equ	0	94
1b,		2	86
1c,		30	62
1d,		39	44
1a,	t-butylpyruvate, 4equ	46	48
1b,		54	39
1c,		72	14
1d,		77	16
1a,^{y}	DCA, 0.3equ	53	34

* irradiated in CH_3CN under oxygen with black-light fluorescent lamps for 10 hours unless stated.

† determined by g.l.c.

x irradiated for 1 hour

y irradiated for 80 hours

Table 4.2. Photooxidative desulphurisation of the phosphorus thiolate compounds le and 1f.

Phosphorus thiolate compound* $(EtO)_2P(O)SR''$	precursor	percentage yield of + recovered st. material : $(EtO)_2P(O)SR''$	oxidized product $(EtO)_2P(O)OH$ †
le, $(EtO)_2P(O)SCH_3$	benzoin, 2equ	0	77
1f, $(EtO)_2P(O)S(CH_2)_4CH_3$		0	90
le,	benzil, 4equ	57	42
1f,		51	41
1f,	biacetyl, 6equ	5	93
le,	AcQ, 0.6equ	68	11
1f,		84	14
le,	DDQ, 6equ	64	0
1f,		73	0
le,	pyruvic acid, 6equ	53	25
1f,		13	67
le,	methyl pyruvate, 6equ	55	31
1f		54	41

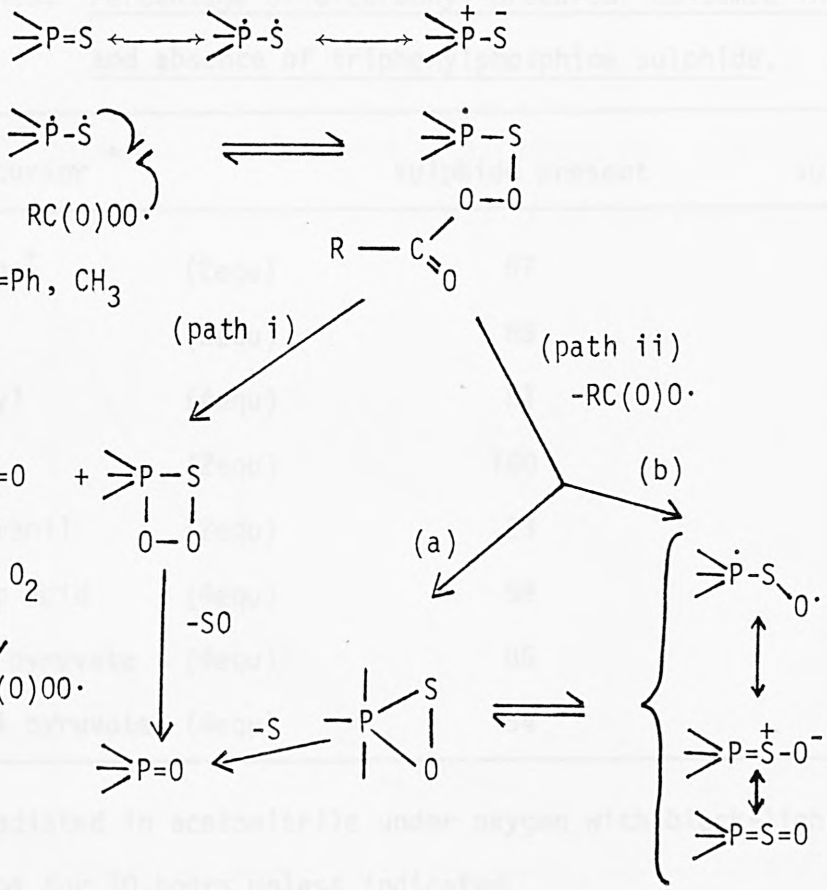
* irradiated in CH_3CN under oxygen with black-light fluorescent lamps for 10 hours.

\+ determined by g.l.c.

† determined as its methyl ester after treatment with diazomethane.

observed oxidative desulphurisation of thiophosphorus compounds. Thus for benzoin whose photofragmentation under oxygen produces the benzoylperoxy and hydroxybenzylperoxy radicals,[34] one can invoke the following mechanism for the oxidation of the thiophosphoryl moiety, Scheme 4.7 (R=Ph). Addition of the benzoylperoxy radical and cyclization can occur to give either a four membered 'betaine type' intermediate (path i), or a three membered cyclic S-oxide intermediate (possibly via its acyclic isomer), (path ii). With the formation of a four

⋟P=S represents $R'_{3-n}P(S)(OCH_2CH_3)_n$



Scheme 4.7.

membered intermediate, this must result in the regeneration of the benzoyl radical which may subsequently reform the benzoylperoxy radical. Consequently it is possible that the presence of a thiophosphoryl compound, by regenerating the benzoyl radical, may retard the initial photofragmentation of the benzoin. However for benzoin and all the other precursors used this is not so. Decomposition of the precursor was found to occur regardless of the presence of any thiophosphoryl compound, Table 4.3 and Figure 4.1. Alternatively the formation of either the cyclic phosphorus oxythionate (path ii, a) or its acyclic S-oxide isomer (path ii, b) involves loss of the benzoyloxy radical, a more favourable leaving group than the benzoyl radical. A similar S-oxide intermediate and its associated resonance structures was proposed by Herriott in the peracid oxidation of phosphinothioates[19] and by Kamataki et. al. in the enzymic metabolism of parathion.[48] Additionally the hydroperoxy radical formed from the photodecomposition of benzoin may also lead to oxidative desulphurisation via either a three

Table 4.3. Percentage of dicarbonyl precursor consumed in the presence and absence of triphenylphosphine sulphide.

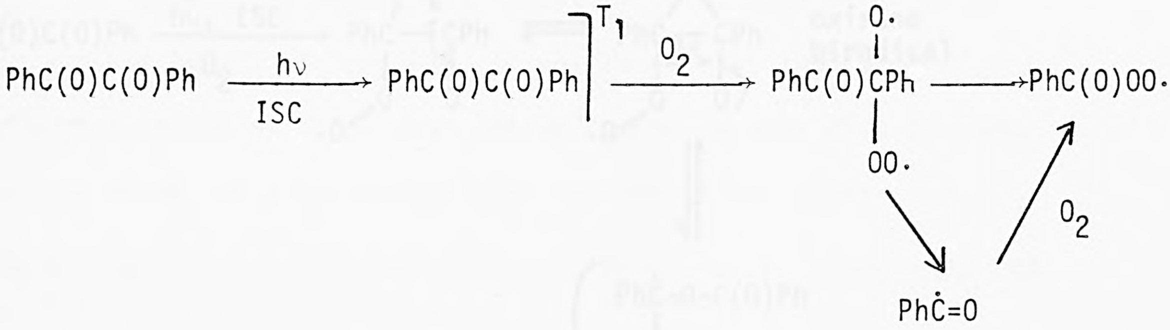
Precursor [*][†]		sulphide present	sulphide absent.
Benzoin [+]	(2equ)	67	76
Benzil	(2equ)	89	88
Biacetyl	(4equ)	81	91
AcQ	(2equ)	100	100
p-Chloranil	(2equ)	23	26
Pyruvic acid	(4equ)	98	96
Methyl pyruvate	(4equ)	85	86
t-butyl pyruvate	(4equ)	54	65

[*] irradiated in acetonitrile under oxygen with black-light fluorescent lamps for 10 hours unless indicated.

[†] number of equivalents relative to sulphide present and at the same concentration in absence of sulphide.

[+] irradiated 20 minutes.

or four membered cyclic intermediate. With benzil, it is likely that the benzoylperoxy radical is again responsible for the oxidative desulphurisation of the thiophosphoryl moiety. The formation of the benzoylperoxy radical from addition of oxygen to triplet benzil and subsequent fragmentation is as proposed by Sawaki and Foote[41] and Saltiel and Curtis.[37] Addition of this radical and cyclization to



either a three or four membered intermediate may now occur as depicted for benzoin in Scheme 4.7 (R=Ph). Bird has reported that the

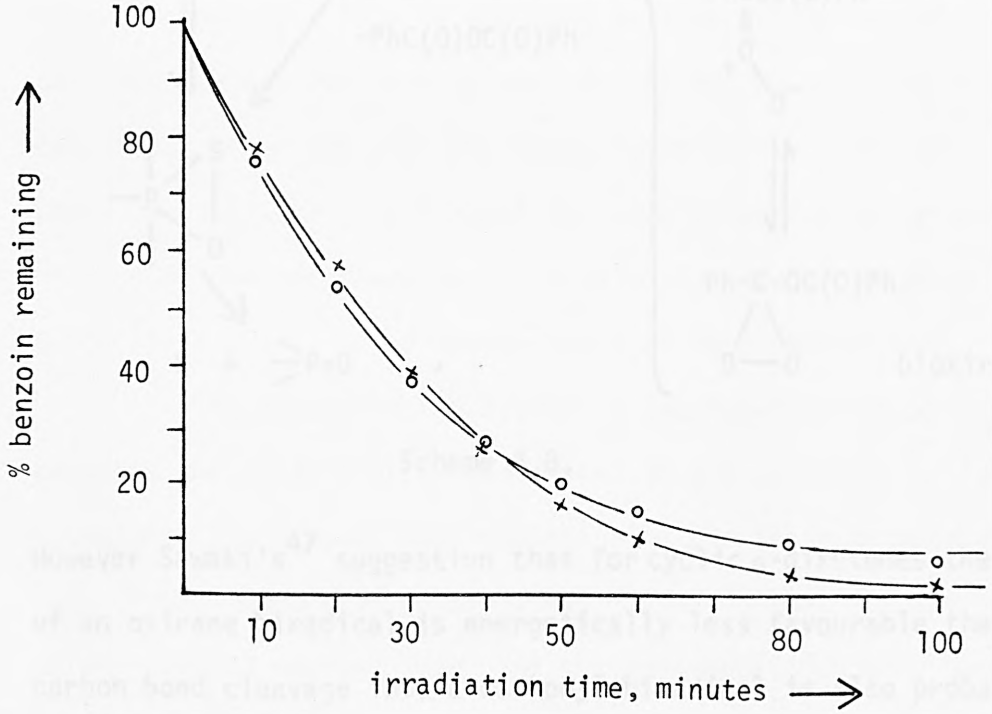
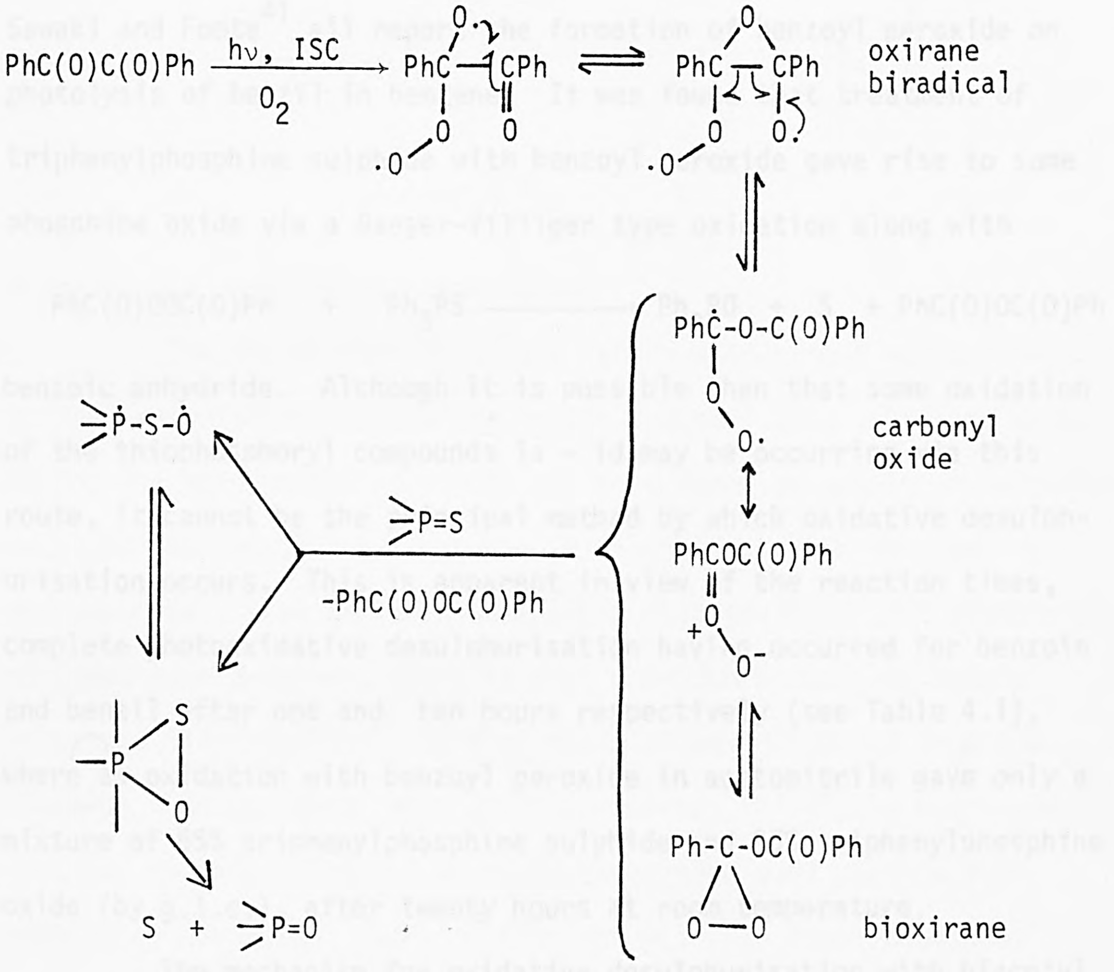


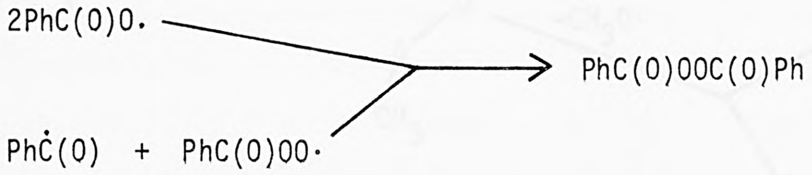
Figure 4.1. The relative loss of benzoin on irradiation in the presence (o) and absence (x) of O,O,O-triethyl phosphorothioate.

photooxidation of benzil in acetonitrile gives rise to benzoic anhydride.[49] It is possible that the formation of this carboxylic anhydride occurs via a bioxirane or a carbonyl oxide intermediate, either of whose participation in an oxidative desulphurisation reaction cannot be ruled out, Scheme 4.8.



Scheme 4.8.

However Sawaki's[47] suggestion that for cyclic α-diketones the formation of an oxirane biradical is energetically less favourable than carbon carbon bond cleavage into a carbonyl biradical is also probably true for acyclic α-diketones. Further more Sawaki et. al.[50] have shown that carbonyl oxides are relatively poor oxygen atom transfer reagents in comparison to acylperoxy radicals. An alternative route to oxidative desulphurisation involves the formation of benzoyl peroxide via radical recombination reactions from the photooxidation of both benzoin and benzil. Infact Saltiel and Curtis,[37] Gream et. al.[38] and

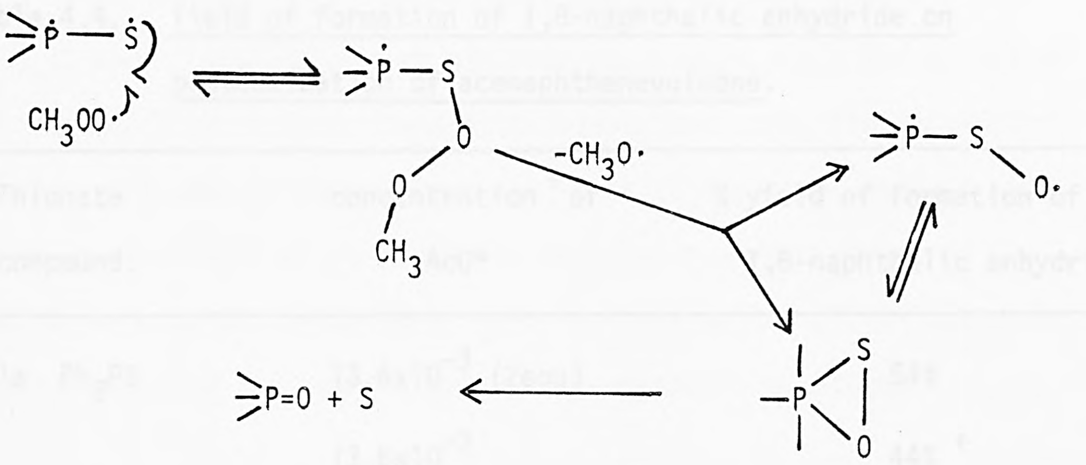


Sawaki and Foote[41] all report the formation of benzoyl peroxide on photolysis of benzil in benzene. It was found that treatment of triphenylphosphine sulphide with benzoyl peroxide gave rise to some phosphine oxide via a Baeyer-Villiger type oxidation along with

$$PhC(O)OOC(O)Ph \quad + \quad Ph_3PS \longrightarrow Ph_3PO \quad + \quad S \quad + PhC(O)OC(O)Ph$$

benzoic anhydride. Although it is possible then that some oxidation of the thiophosphoryl compounds 1a → 1d may be occurring via this route, it cannot be the principal method by which oxidative desulphurisation occurs. This is apparent in view of the reaction times, complete photooxidative desulphurisation having occurred for benzoin and benzil after one and ten hours respectively (see Table 4.1), where as oxidation with benzoyl peroxide in acetonitrile gave only a mixture of 65% triphenylphosphine sulphide and 26% triphenylphosphine oxide (by g.l.c.), after twenty hours at room temperature.

The mechanism for oxidative desulphurisation with biacetyl requires the photochemical generation of the acetylperoxy radical. Subsequent reaction of this radical with the thionate moiety, Scheme 4.7. ($R=CH_3$) occurs in an analagous manner to that for the benzoylperoxy radical derived from the photodecomposition of benzoin and benzil. Additionally it is also possible that the methylperoxy radical, formed from the methyl radical after decarboxylation of the acetyloxy radical, is also able to carry out the oxidative desulphurisation of the thiophosphoryl moiety, Scheme 4.9. Again it is suggested that the reaction proceeds with elimination of sulphur from



Scheme 4.9.

a phosphorus oxythionate intermediate.

The photooxidation of the cyclic α-diketones acenaphthenequinone and phenanthrenequinone in the presence of a substrate containing the thiophosphoryl moiety has been found to result in oxidative desulphurisation of the substrate, although in rather contrasting efficiencies. With acenaphthenequinone high yields of the phosphoryl analogue were obtained, where as with phenanthrenequinone mainly unchanged thiophosphoryl starting material was recovered from the reaction. In agreement with earlier reports,[46,47,49] it was found that the photooxidation of acenaphthenequinone gave rise to 1,8-naphthalic anhydride. Additionally it was also found that the presence of a thiophosphoryl compound resulted in greater yields of formation of the anhydride than in the absence of any thionate compound, Table 4.4. In other words, oxidative desulphurisation would seem to facilitate the formation of 1,8-naphthalic anhydride. Clearly this would be so if anhydride formation and oxidative desulphurisation were to lie on the same reaction pathway. As with the acyclic α-dicarbonyl precursors, a number of mechanisms for oxidative desulphurisation can be proposed. The first is similar to that given by Koo and Schuster[46] for the photoepoxidation of olefins, and

Table 4.4. Yield of formation of 1,8-naphthalic anhydride on photooxidation of acenaphthenequinone.

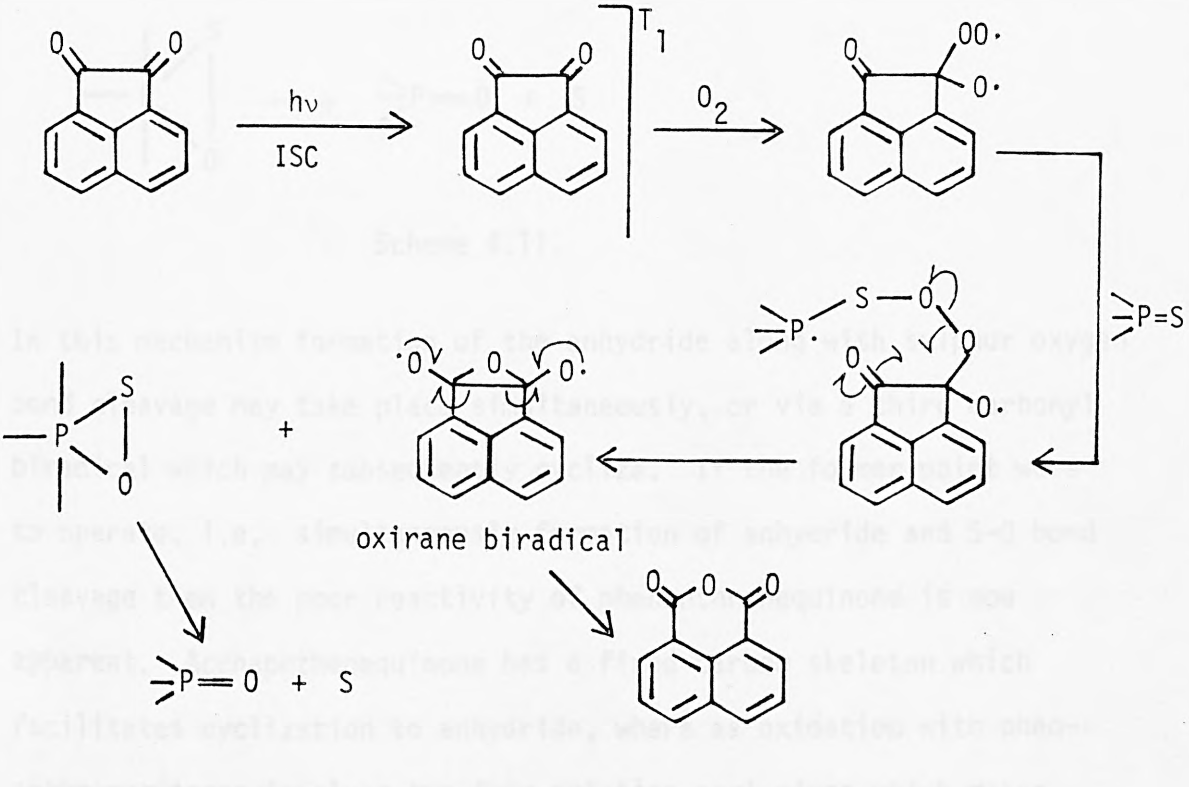
Thionate compound.	concentration† of AcQ*	% yield of formation of 1,8-naphthalic anhydride
1a Ph_3PS	13.6×10^{-3} (2equ)	54%
	13.6×10^{-3}	44% +
1d $(EtO)_3PS$	20.5×10^{-3} (1equ)	60%
	20.5×10^{-3}	42% +

* irradiated in CH_3CN under oxygen with black-light fluorescent lamps for 10 hours.

† concentration in mol dm^{-3}

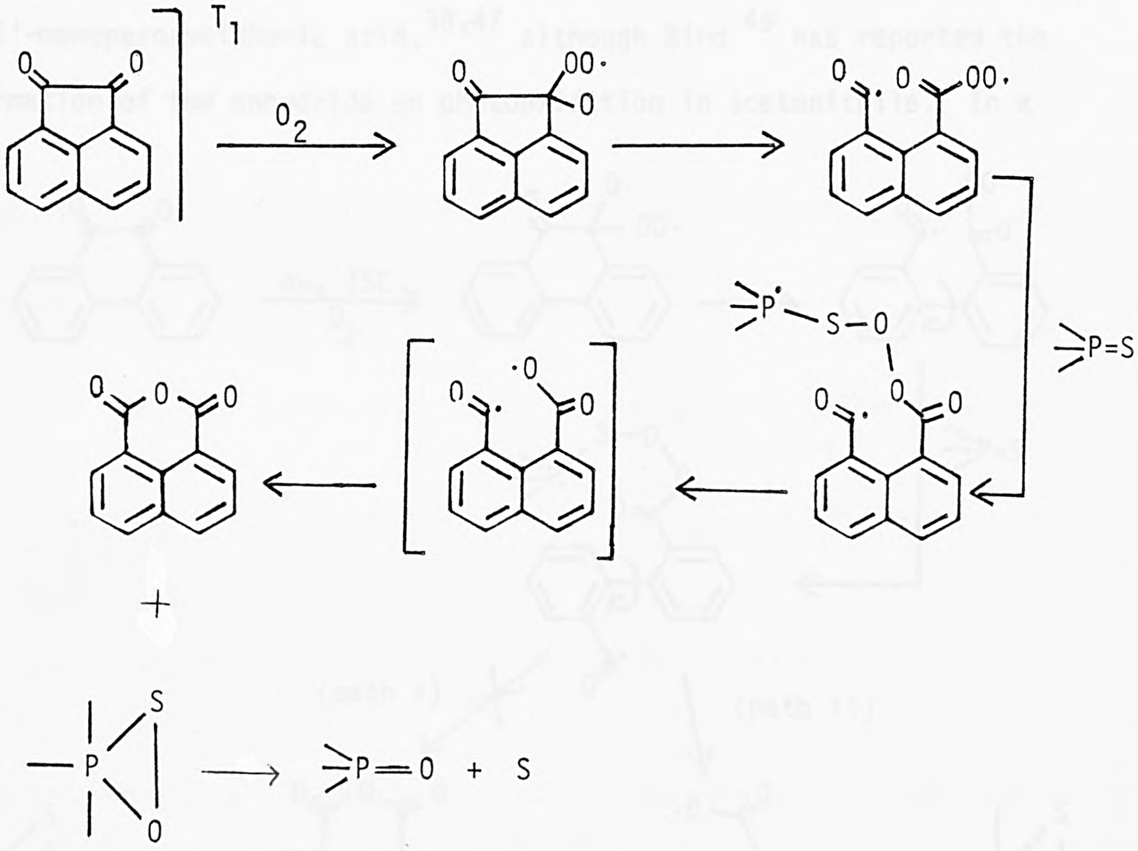
+ % yield of formation in the absence of any ⋛P=S compound.

involves the reaction occurring via an oxirane intermediate, Scheme 4.10.



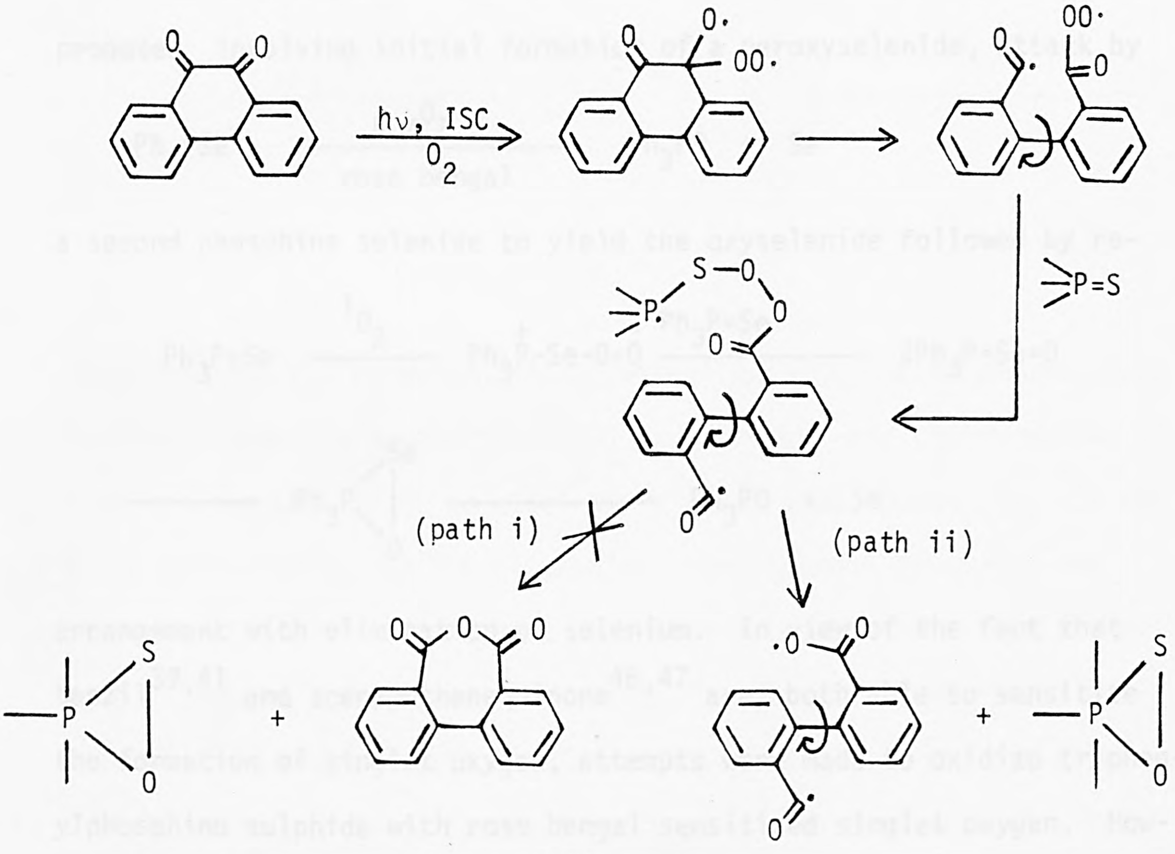
Scheme 4.10.

If this is the actual mechanism operating, then apart from the fact that it would require a seven membered transition state for formation of the cyclic anhydride, there is no reason why oxidative desulphurisation with phenanthrenequinone should be so sluggish. However this could be explained if the mechanism were to involve cleavage of the appropriate carbon carbon bond prior to cyclization of the anhydride and formation of the cyclic phosphorus oxythionate, Scheme 4.11.



Scheme 4.11.

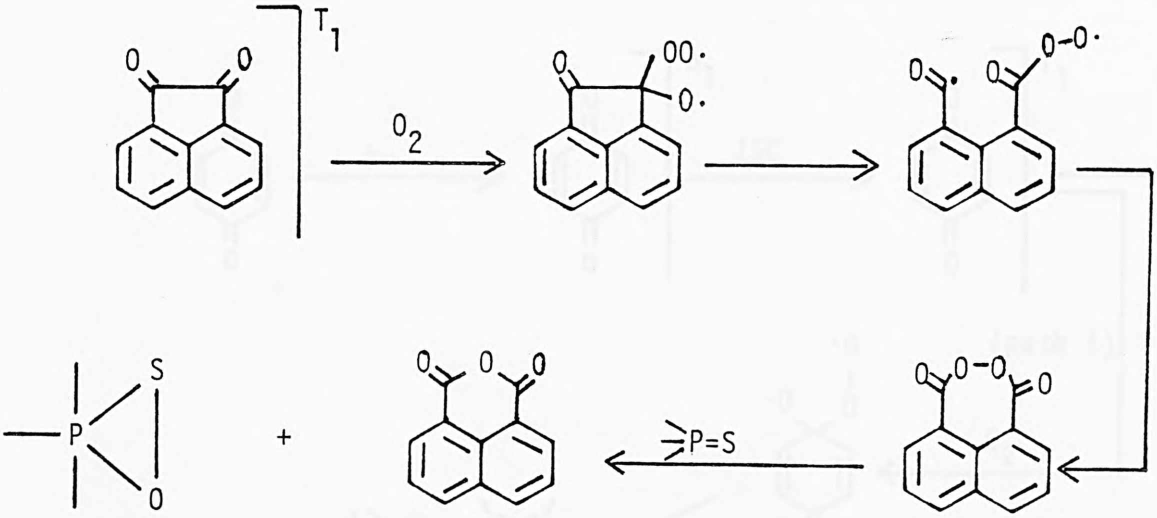
In this mechanism formation of the anhydride along with sulphur oxygen bond cleavage may take place simultaneously, or via a third carbonyl biradical which may subsequently cyclize. If the former point were to operate, i.e. simultaneously formation of anhydride and S-O bond cleavage then the poor reactivity of phenanthrenequinone is now apparent. Acenaphthenequinone has a fixed carbon skeleton which facilitates cyclization to anhydride, where as oxidation with phenanthrenequinone involves two free rotating aryl rings which makes simultaneous cyclization much more unlikely, Scheme 4.12 (path i). However the rigidity of the carbon skeleton cannot be used to account for the poor reactivity of phenanthrenequinone if the reaction were to occur either without the simultaneous formation of biphenic anhydride, Scheme 4.12 (path ii) or indeed without the formation of biphenic anhydride at all. In fact the photooxidation of phenanthrenequinone has been found to yield predominantly 2,2'-biphenic acid and 2,2'-monoperoxybiphenic acid,[38,47] although Bird [49] has reported the formation of the anhydride on photooxidation in acetonitrile. In a



Scheme 4.12.

similar manner to that for benzoyl peroxide, it is possible that some reaction may be occurring via 1,8-naphthaloyl peroxide, although it is again very unlikely that this is the major route to oxidative desulphurisation, Scheme 4.13.

Tamagaki and Akatsuka[51] have reported the photooxygenation of triphenylphosphine selenide by singlet oxygen. A mechanism was



Scheme 4.13.

proposed involving initial formation of a peroxyselenide, attack by

$$Ph_3PSe \xrightarrow[\text{rose bengal}]{h\nu/O_2} Ph_3PO + Se$$

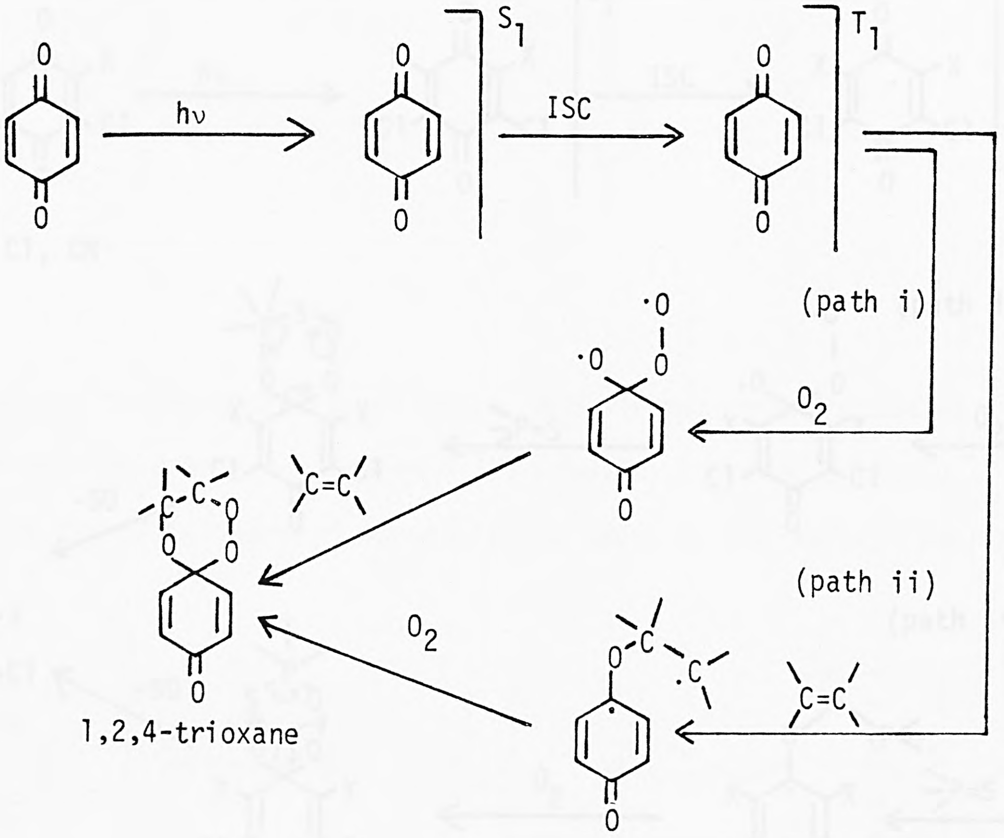
a second phosphine selenide to yield the oxyselenide followed by re-

$$Ph_3P{=}Se \xrightarrow{^1O_2} Ph_3\overset{+}{P}\text{-}Se\text{-}O\text{-}\overset{-}{O} \xrightarrow{Ph_3P=Se} 2Ph_3P{=}Se{=}O$$

$$\longrightarrow Ph_3P\begin{matrix}Se\\|\\O\end{matrix} \longrightarrow Ph_3PO + Se$$

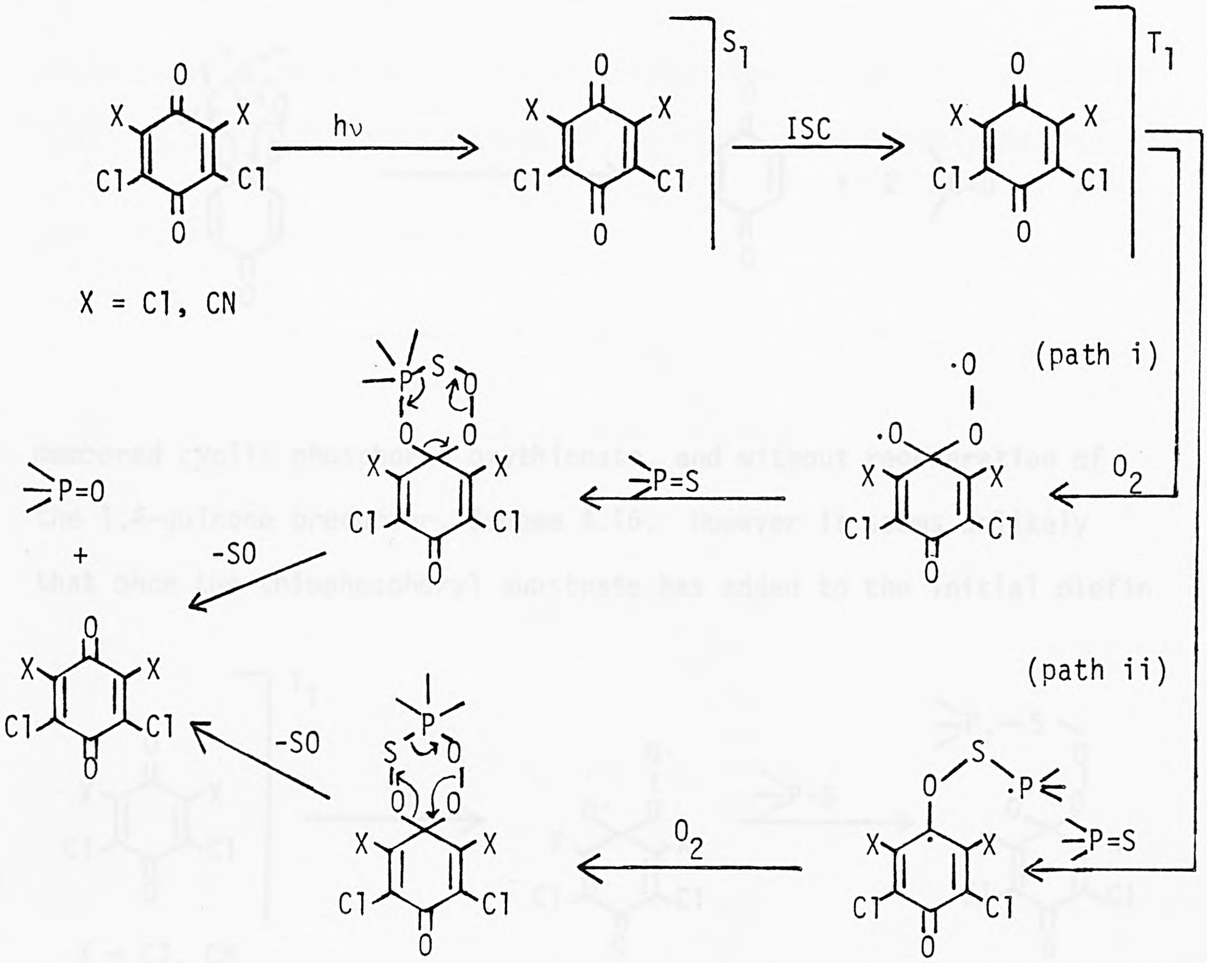
arrangement with elimination of selenium. In view of the fact that benzil[39,41] and acenaphthenequinone[46,47] are both able to sensitize the formation of singlet oxygen, attempts were made to oxidize triphenylphosphine sulphide with rose bengal sensitized singlet oxygen. However in all attempts no oxidation was observed, the phosphine sulphide being recovered quantitatively. Clearly therefore the formation of singlet oxygen from α-diketones does not participate in the oxidative desulphurisation of compounds bearing the thionate moiety.

Wilson et. al.[52] have studied the photoaddition of olefins to p-benzoquinone in the presence of oxygen to form 1,2,4-trioxanes. Two of the possible routes to trioxane formation are shown in Scheme 4.14.



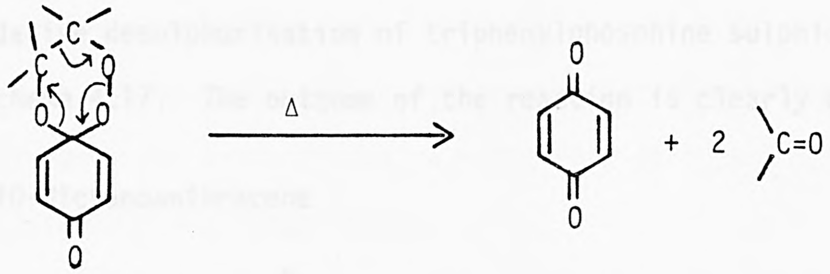
Scheme 4.14.

These involve the formation of an initial quinone-olefin adduct which is then trapped by oxygen (path i), or alternatively the formation of a quinone-oxygen adduct to which the olefin adds, (path ii). On the basis of quenching studies of triplet benzoquinone by oxygen and styrene, Wilson et. al. suggest that path i is much less likely than path ii leading to trioxane formation. Additionally they found that with some olefins the quinone-olefin adduct is frequently not a pre-oxetane biradical but a charge transfer exciplex intermediate. From the results in Table 4.1 it can be seen that the 1,4-dicarbonyl compounds, dichlorodicyano-1,4-benzoquinone and p-chloranil are both able to sensitize the oxidative desulphurisation of the thiophosphoryl moiety. Possible mechanisms all involve addition to the triplet carbonyl of the quinone. However in analogy with trioxane formation[52] two possible modes of addition are possible, Scheme 4.15 (paths i and ii). Which is the initial adduct formed (i.e. addition via path i or

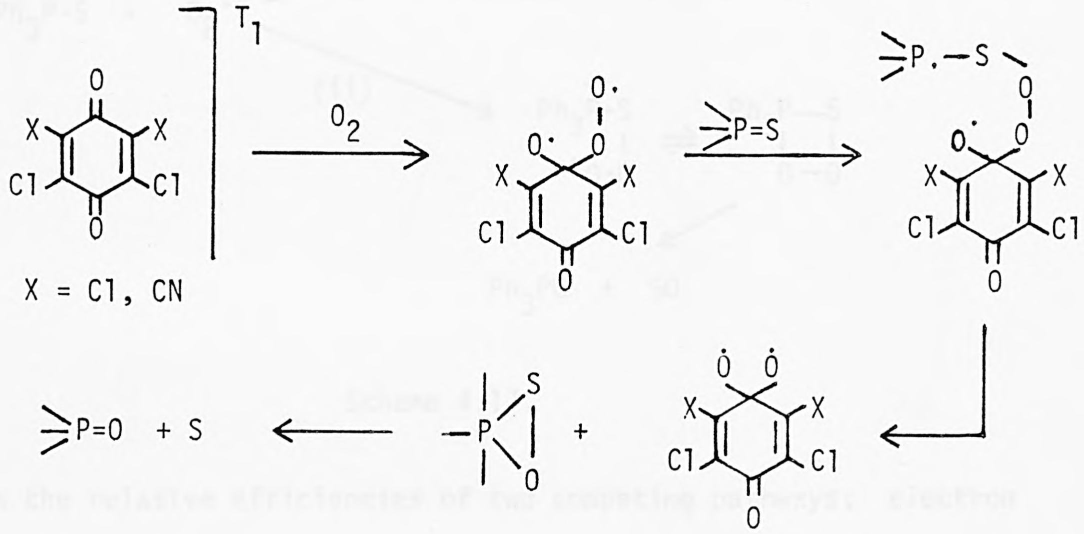


Scheme 4.15.

ii) is dependent upon the relative ability of oxygen and the thiophosphoryl compound to quench the triplet carbonyl. However once the initial adduct is formed it is tempting to propose the formation of a six membered cyclic intermediate. Collapse of either of the two possible cyclic intermediates would give rise to identical products and with oxidative desulphurisation of the thiophosphoryl moiety. This decomposition of the cyclic intermediate is not without justification. 1,2,4-Trioxanes undergo an identical rearrangement on thermolysis to give the analagous carbonyl decomposition products.[52] In the case of the phosphorus derivatives, the formation of the phosphoryl oxygen bond would without doubt be the driving force for the decomposition reaction. Alternatively the mechanism given in Scheme 4.15 may not be operating at all. Instead the reaction may proceed via the formation of a three



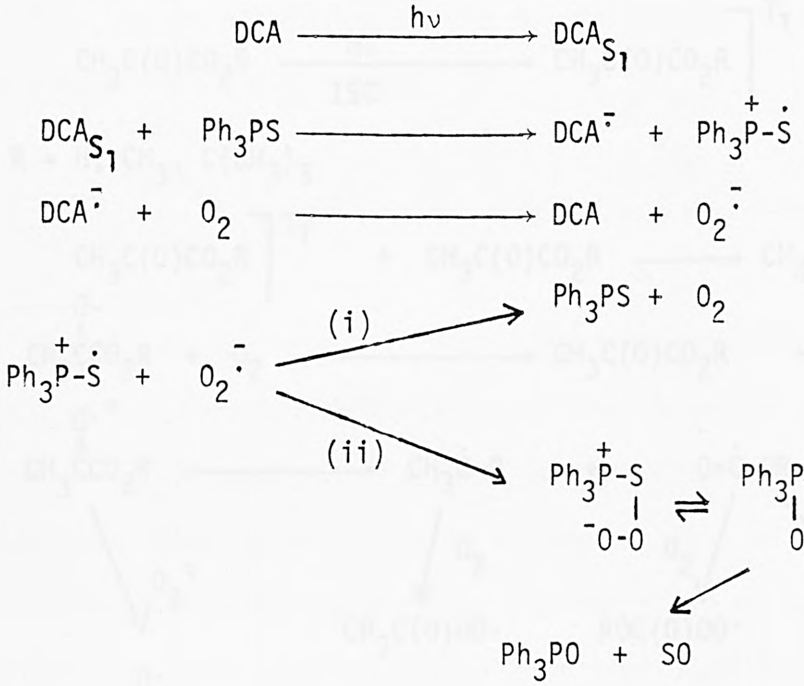
membered cyclic phosphorus oxythionate, and without regeneration of the 1,4-quinone precursor, Scheme 4.16. However it seems unlikely that once the thiophosphoryl substrate has added to the initial olefin



Scheme 4.16.

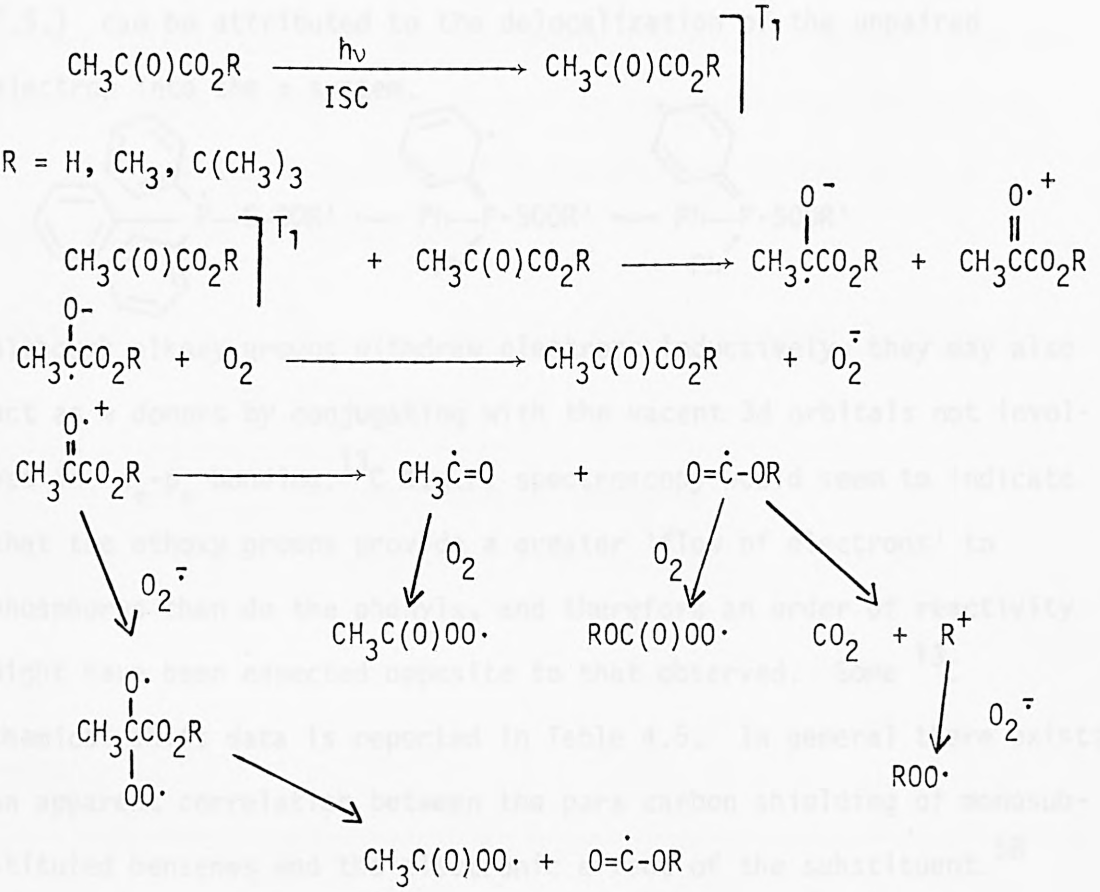
oxygen adduct it does not find it energetically more favourable to cyclize to a six membered intermediate as in Scheme 4.15 rather than the cyclic phosphorus oxythionate as depicted in Scheme 4.16. The formation of the superoxide anion from DDQ and p-chloranil is also a pathway by which oxidative desulphurisation may occur. A number of 1,4-quinones are powerful electron acceptors and may participate in electron transfer reactions. 9,10-Dicyanoanthracene (DCA) is known to sensitize the formation of the superoxide anion via an electron transfer reaction,[53] and has been used in this context to carry out the photooxidative desulphurisation of triphenylphosphine sulphide (Table 4.1), Scheme 4.17. The outcome of the reaction is clearly dependent on the relative efficiencies of two competing pathways; electron transfer back to phosphine sulphide (path i) and radical combination, cyclization and decomposition to phosphine oxide (path ii). However should DDQ and p-chloranil be able to sensitize the formation of the superoxide anion, it is likely, in view of the long reaction time required for appreciable oxidation to occur with dicyanoanthracene, that this would only be a minor route to oxidative desulphurisation.

DCA = 9,10-dicyanoanthracene



Scheme 4.17.

The photooxidation of pyruvic acid and pyruvate esters has been extensively studied by Davidson et. al.[54-57] They have shown that the reaction involves an electron transfer from triplet excited pyruvic acid (or its ester) to a second ground state pyruvic acid (or ester) molecule. Decomposition of the resultant radical ions can in the presence of oxygen lead to the formation of a number of both acylperoxy and alkylperoxy radicals, Scheme 4.18. The formation of such species and their reaction with the thiophosphoryl moiety is, particularly for pyruvic acid, a relatively efficient process which leads to oxidative desulphurisation.

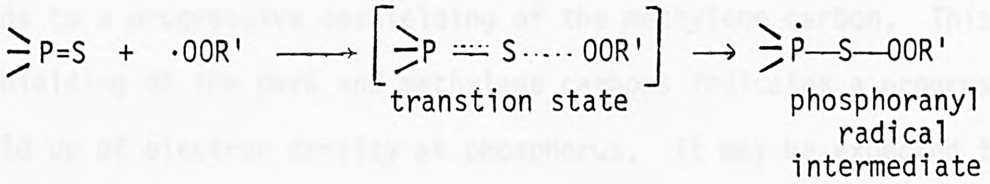


Scheme 4.18.

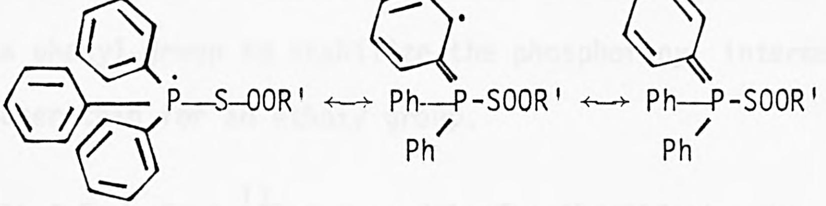
From the data in Table 4.1 it would appear that for all the dicarbonyl precursors used there is a specific order of reactivity for the thiophosphoryl moiety towards oxidative desulphurisation. That is;

$$Ph_3PS \; > \; Ph_2P(S)OEt \; > \; PhP(S)(OEt)_2 \; > \; (EtO)_3PS.$$

This decrease in reactivity on going from a phosphine sulphide to a phosphorothionate parallels the loss in stabilization of the phosphoranyl intermediate as phenyl groups are replaced by ethoxy groups at phosphorus. Such a loss in stabilization reflects a higher activattion energy for the transition state, (T.S.). The ability of the phenyl groups to stabilize the radical intermediate (and therefore the



T.S.) can be attributed to the delocalization of the unpaired electron into the π system.



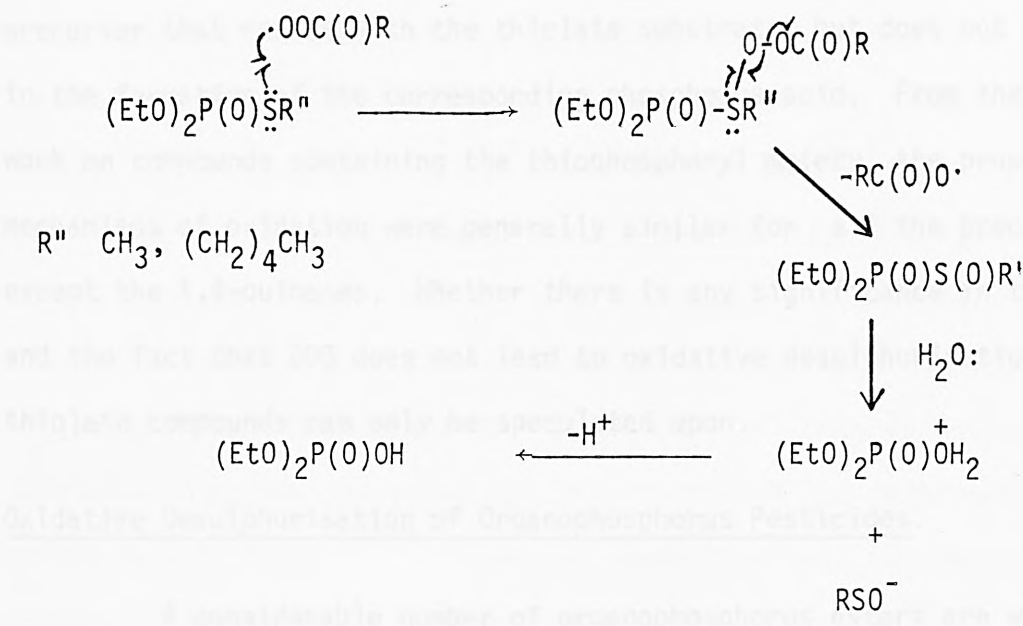
Although alkoxy groups withdraw electrons inductively, they may also act as π donors by conjugating with the vacent 3d orbitals not involved in d_π-p_π bonding. ^{13}C N.m.r. spectroscopy would seem to indicate that the ethoxy groups provide a greater 'flow of electrons' to phosphorus than do the phenyls, and therefore an order of reactivity might have been expected opposite to that observed. Some ^{13}C chemical shift data is reported in Table 4.5. In general there exists an apparent correlation between the para carbon shielding of monosubstituted benzenes and the electronic effect of the substituent.[58] Electron withdrawing groups tend to deshield the para carbon while electron donating groups shield this nucleus. From the data in Table 4.5 it can be seen that for these four thiophosphoryl compounds the chemical shift of the para carbon has moved down field relative to benzene (-128.5ppm from TMS). This clearly indicates that the thiophosphoryl moiety is withdrawing electrons from the aryl ring(s). Further, the more ethoxy groups present, the greater is the deshielding of the para carbon. Retcofsky and Griffin have similarly shown that the phosphoryl and thiophosphoryl moieties are weak electron attractors and will deshield the para carbon in monosubstituted benzene.[59] A similar trend is observed for the methylene carbon of the ethoxy group(s). The introduction of one, two and then three ethoxy groups leads to a progressive deshielding of the methylene carbon. This deshielding of the para and methylene carbons indicates a progressive build up of electron density at phosphorus. It may be expected that this increase in electron density at phosphorus would lead to a greater stabilization of the phosphoranyl radical. However from the observed trend in reactivity it must be concluded that the ability of a phenyl group to stabilize the phosphoranyl intermediate is greater than for an ethoxy group.

Table 4.5. Some ^{13}C n.m.r. data for the thiophosphoryl compounds 1a to 1d inclusive.

^{13}C *	Thiophosphoryl compound			
	Ph_3PS	$Ph_2P(S)OEt$	$PhP(S)(OEt)_2$	$(EtO)_3PS$
$\delta_{POCH_2CH_3}$		61.26	62.84	64.31
$\delta_{C_{para}}$	131.77	132.00	132.34	

* in ppm from TMS

The photooxidative desulphurisation of the phosphorus thiolate compounds 1e and 1f leads in most cases to cleavage of the thioalkyl group with formation of the corresponding phosphorus acid, Table 4.2. For the α-dicarbonyl precursors and pyruvate compounds, the reaction is again believed to involve the photochemical generation of acylperoxy and alkylperoxy radicals. Although acylperoxy radicals are unreactive towards sulphides and sulphoxides,[34,40] it is suggested that the presence of the phosphorus atom can enhance the reactivity of sulphur towards oxidation and lead to formation of the thiolate S-oxide. The formation of the phosphorus acid from this intermediate would occur rapidly in the presence of water, with loss of the sulphenic



Scheme 4.19.

acid anion, Scheme 4.19. Although A.R. grade acetonitrile was used for these experiments, it was subsequently found that at the concentration at which these reactions were performed there is sufficient water present in the solvent for it to become an important reactive intermediate in the overall oxidation process. Segal and Casida[22] have shown that thiolate S-oxides are powerful phosphorylating agents. Therefore this mechanism could be confirmed if the reaction in methanol were found to lead to the formation of diethyl methyl phosphate. That the presence of the phosphorus atom can alter the reactivity of the sulphur is clear. For example, sulphides are readily oxidized to sulphoxides by singlet oxygen. However rose bengal sensitized singlet oxygen was found to have no effect on 0,0-diethyl S-methyl phosphorothioate. Additionally cleavage of the phosphorus sulphur bond with loss of the thioalkyl moiety as the thiol anion (RS^-) is unlikely since in the photooxidative desulphurisation of 0,0-diethyl S-pentyl phosphorothioate, no pentanethiol could be detected in the reaction mixture, (by g.l.c.). This would seem to indicate that oxidation of the sulphur atom is occurring prior to its cleavage from the phosphoryl moiety. Interestingly dichlorodicyanoquinone is the only precursor that reacts with the thiolate substrate, but does not result in the formation of the corresponding phosphorus acid. From the earlier work on compounds containing the thiophosphoryl moiety, the proposed mechanisms of oxidation were generally similar for all the precursors except the 1,4-quinones. Whether there is any significance in this and the fact that DDQ does not lead to oxidative desulphurisation of thiolate compounds can only be speculated upon.

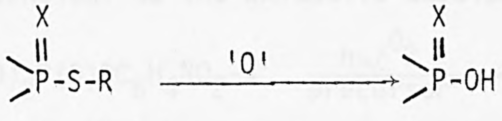
Oxidative Desulphurisation of Organophosphorus Pesticides.

A considerable number of organophosphorus esters are widely used as pesticides, and in many instances are found to contain either the thionate and/or the thiolate moiety.[60,61] They act as pesticides because of their ability to inhibit cholinesterase and therefore prevent the hydrolysis of the neurotransmitter acetylcholine.[62] Oxidative desulphurisation plays an important role in both activation and detoxication of organophosphorus pesticides, although in general activation can be regarded as a process resulting finally in degradation. The two most important biochemical processes which are involved in the metabolism of organophosphorus pesticides containing the thionate and/or thiolate moiety are,

i) the oxidative desulphurisation of the thionate moiety

$$>P{=}S \xrightarrow{'O'} >P{=}O$$

and ii) the oxidative deesterification of the thiolate moiety,



$$>\overset{X}{\overset{\|}{P}}\text{-S-R} \xrightarrow{'O'} >\overset{X}{\overset{\|}{P}}\text{-OH}$$

X = O,S

Several thiophosphorus pesticides such as parathion and malathion are poor inhibitors of cholinesterase, whereas the corresponding oxon analogues are highly potent cholinesterase agents. This biotransformation of essentially non toxic organophosphorus compounds into toxic metabolites involves oxidative desulphurisation of the thiophosphoryl moiety.[63] It is generally considered that in mammals the enzymes known as mixed function oxidazes are responsible for the conversion of the thionate moiety into its oxon analogue. In particular the microsomal metabolism of parathion has been extensively studied.[48,64,65] Similarly in the environment the dissipation of thiophosphorus pesticides involves oxidative desulphurisation of the thiophosphoryl moiety by U.V. light.[66-68] Numerous cases have been reported concerning poisoning by organophosphorus pesticides in man.[69-71] It is known that peroxy radicals and the superoxide anion are present in mammalian tissue,[72-74] and although superoxide is controlled enzymatically by superoxide dismutase,[75,76] it has been suggested to be involved along with peroxy radicals, in diverse events of biological importance ranging from cancer to heart disease and ageing.[73,74] Additionally pyruvic acid and other α-ketocarboxylic acids are important biochemical intermediates involved in the metabolism of carbohydrates and certain amino acids.[77] In view of the presence of such chemical species in mammalian tissue, it is possible that they may be involved, in conjunction with microsomal oxidation, in the metabolism of organophosphorus pesticides. With this in mind the oxidative desulphurisation of parathion, lg, by photochemically generated peroxy radicals was investigated. The reactions were performed in a manner identical to the oxidative desulphurisation of the thiophosphorus compounds previously discussed. It can be seen from the results in Table 4.6. that, as expected, oxidative desulphurisation leads to the formation of the more potent anticholinesterase agent, paraoxon.

$$(EtO)_2P(S)OC_6H_4NO_2\text{-}4 \xrightarrow[\text{precursor}]{h\nu/O_2} (EtO)_2P(O)OC_6H_4NO_2\text{-}4$$

lg, parathion paraoxon

Table 4.6. The photooxidative desulphurisation of parathion with formation of paraoxon.

Precursor *	percentage yield of †	
	recovered parathion	paraoxon
a,	81	0
benzoin, 2equ	0	38
benzil, 2equ	35	29
AcQ, 1equ	38	44
DDQ, 2equ	64	17
biacetyl, 4equ	27	23
pyruvic acid, 4equ	46	11
methyl pyruvate, 4equ	66	7

* irradiated in CH_3CN with parathion under oxygen using black-light fluorescent lamps for 10 hours.

† as determined by g.l.c.

a, parathion irradiated in absence of any precursor.

The non quantitative yields of phosphorus material detected (by g.l.c.), as illustrated by the irradiation in the absence of any dicarbonyl precursor, can be attributed to the direct photodecomposition of parathion and paraoxon. Both these compounds absorb between 235 and 370nm, and it is probable that their photodecomposition involves O-dearylation as suggested by Grunwell and Erickson.[78] Frawley et. al.[79] and Grunwell and Erickson[78] have shown that paraoxon is formed from the photolysis of parathion, although singlet oxygen was found not to be the oxidizing species.[78] However it is clear from the data obtained that the presence of dicarbonyl precursors and therefore peroxy radicals considerably enhances the yield of oxidative desulphurisation

Table 4.7. Oxidative desulphurisation of chlormephos by photochemically generated peroxy radicals.

Precursor*	percentage yield of †		
	$(EtO)_2P(S)SCH_2Cl^b$	$(EtO)_2P(S)OH^{c,d}$	$(EtO)_2P(O)OH^c$
a,	100	0	0
benzoin, 2equ	30	15	46
benzil, 2equ	68	12	10
biacetyl, 6equ	18	<2	66
pyruvic acid, 6equ	58	12	28
methyl pyruvate, 6equ	61	8	26

* irradiated in CH_3CN with chlormephos under oxygen using black-light fluorescent lamps for 10 hours.

† as determined by g.l.c., identity of all photolysis products confirmed by GCMS.

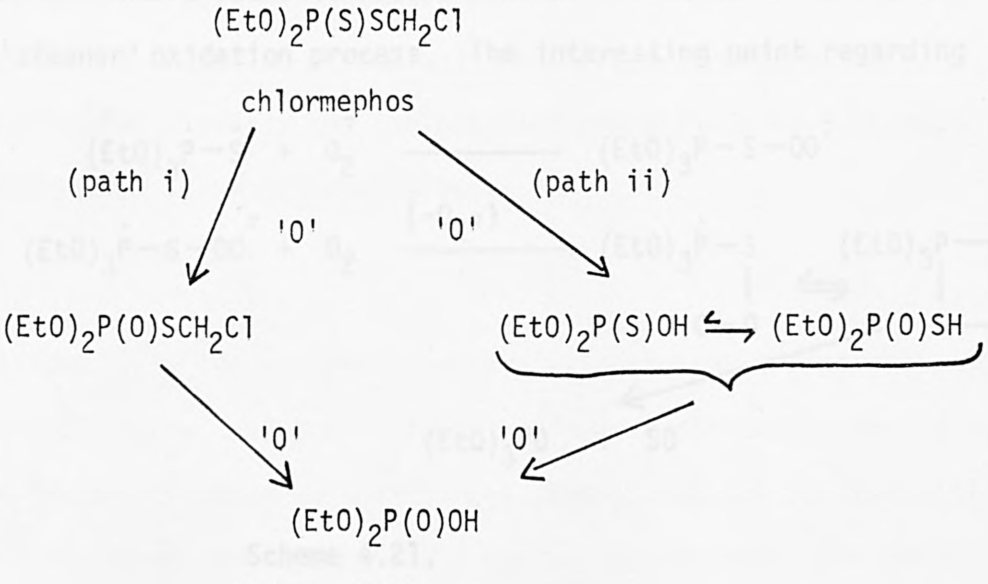
b, GCMS indicates this compound is present as a mixture with $(EtO)_2P(O)CH_2Cl$.

c, determined as its methyl ester after addition of diazomethane.

d, in equilibtrium with its thiolate isomer; recorded yields represent total acid content.

$$(EtO)_2P(S)OH \rightleftharpoons (EtO)_2P(O)SH$$

products, i.e. paraoxon. Similarly the effect of peroxy radicals upon chlormephos, 1h, has been found to lead to oxidative desulphurisation. However in this instance oxidative desulphurisation results in detoxication of the organophosphorus pesticide, as opposed to activation in the case of parathion. Under the irradiation conditions employed and in the absence of any dicarbonyl precursor, chlormephos is found to be photostable. Irradiation in the presence of dicarbonyl based precursors leads to the formation of a number of oxidation products, depending on whether desulphurisation occurs at the thionate (path i) or thiolate moiety (path ii), Table 4.7, Scheme 4.20. The percentage yields of material attributed to chlormephos (Table 4.7) were infact found to be due to a mixture of chlormephos and S-chloromethyl 0,0-diethyl phosphorothiolate. Under the g.l.c. conditions used for quantitative analysis, these two compounds were not resolved. With benzoin and biacetyl, GCMS data indicates that the yield of material (i.e. 30% and 16% respectively) is due mainly (>90%) to the phosphoryl compound rather than its thiophosphoryl analogue. For the remaining precursors however it is the thiophosphoryl derivative (chlormephos) which is the predominant species present. Additionally oxidative desulphurisation of the thiolate moiety leads to the formation of 0,0-diethyl phosphorothionic acid, which may isomerise to its more stable thiolo isomer. Treatment with diazomethane results in alkylation at both oxygen and sulphur. Again these two isomers were not resolved by g.l.c. although GCMS shows that methylation occurs predominantly at sulphur. Clearly it is not possible without further investigation to say whether oxidative desulphurisation occurs preferentially at the thionate moiety or the thiolate moiety. Ultimately however, in the

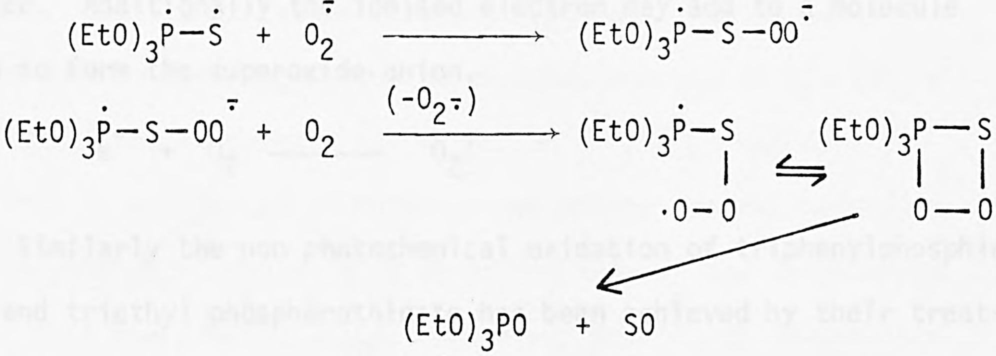


Scheme 4.20.

presence of sufficient dicarbonyl precursor, total oxidative desulphurisation leading to O,O-diethyl phosphate will result. Clearly this work has demonstrated the ability of peroxy radicals to either activate or detoxicate thiophosphorus pesticides, and the importance of these chemical intermediates in the metabolism of such pesticides is worthy of further investigation.

Chemical Oxidative Desulphurisation.

The oxidative desulphurisation of triphenylphosphine sulphide by photochemically generated superoxide has been demonstrated. In view of this, the reactivity of this same phosphine sulphide and triethyl phosphorothioate towards potassium superoxide was investigated. Such reactions were performed by treating a chloroform solution of the thiophosphoryl compound with potassium superoxide using 18-crown-6-ether as a phase transfer catalyst, (PTC). As expected this was found to lead to the formation of the corresponding phosphoryl analogue, Table 4.8, Scheme 4.21. However several molar excess of potassium superoxide was required for oxidation to occur to any appreciable extent. Whilst the application of ultrasound to facilitate a chemical reaction has been shown,[80] in this particular instance sonication of the reaction mixture seems to have a minimal effect other than promoting a 'cleaner' oxidation process. The interesting point regarding



Scheme 4.21.

Table 4.8. Oxidation of the thiophosphoryl compounds 1a and 1d with potassium superoxide.

Thiophosphoryl compound	KO_2/equ.	conditions*	percentage yield of recovered st. material	: oxidized prod.
1a, Ph_3PS	3	sonicated	68	31
	40	sonicated	0	97
	40	stirred	0	63
	0	sonicated †	85	10
1d, $(EtO)_3PS$	15	sonicated	20	55
	40	sonicated	4	78
	40	stirred	2	79

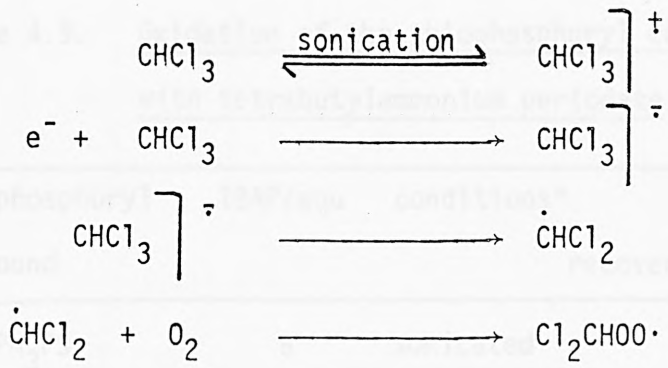
* $CHCl_3$ as solvent, all solutions contain 18-crown-6-ether (0.2equ) as PTC, reaction time 20 hours unless stated.

† reaction time 80 hours.

the use of the ultrasound technique is that sonication of a chloroform solution of triphenylphosphine sulphide in the absence of any conventional oxidizing agent (i.e. KO_2) leads to oxidative desulphurisation, albeit in low yields. This may possibly arise through ionisation of the solvent, the formation of radicals and thence peroxy radicals, Scheme 4.22. Additionally the ionised electron may add to a molecule of oxygen to form the superoxide anion.

$$e^- + O_2 \longrightarrow O_2^{\cdot -}$$

Similarly the non photochemical oxidation of triphenylphosphine sulphide and triethyl phosphorothioate has been achieved by their treatment with tetrabutylammonium perchlorate (TBAP), Table 4.9. The oxidizing properties of periodic acid and sodium metaperiodate are well



Scheme 4.22.

known.[81] However the application of quaternary ammonium salts as phase transfer catalysts has lead to the development of a number of tetraalkylammonium periodate compounds as selective oxidizing agents towards a variety of organic substrates. Thus tetrabutylammonium periodate has been shown to oxidize sulphides to sulphoxides in good yields.[82] The ability of tetrabutylammonium periodate to oxidatively desulphurise the thiophosphoryl moiety is enhanced by sonication of the reaction mixture. As with the potassium superoxide reactions, sonication leads to a gradual rise in temperature of the aqueous medium surrounding the reaction vessel up to a maximum of 45-47°C after 1½ to 2 hours, where it remains until sonication has ceased. Consequently some of the observed acceleration of the reaction may be due in part to the higher reaction temperature. Again sonication of a solution of the thiophosphoryl compound in the absence of any conventional oxidizing agent (TBAP) leads to oxidative desulphurisation. Additionally the presence of chloro-meso-tetraphenylporphinatomanganese (III), (MnTPP(III)Cl) was found to promote the oxidation of the thiophosphoryl moiety. This is attributed to coordination of the central manganese atom in the porphyrin complex with an oxygen atom in the perchlorate molecule. This coordination must in some way facilitate oxygen atom transfer to the thiophosphoryl compound.

Table 4.9. Oxidation of the thiophosphoryl compounds 1a and 1d with tetrabutylammonium periodate.

Thiophosphoryl compound	TBAP/equ	conditions*	percentage yield of recovered st. material :	oxidized prod.
1a, Ph_3PS	6	sonicated	20	75
	6	sonicated†	0	99
	6	stirred †	28	72
	0	sonicated†	93	5
1d, $(EtO)_3PS$	6	sonicated	83	15
	6	sonicated†	75	25
	6	stirred †	90	8
	0	sonicated†	94	6

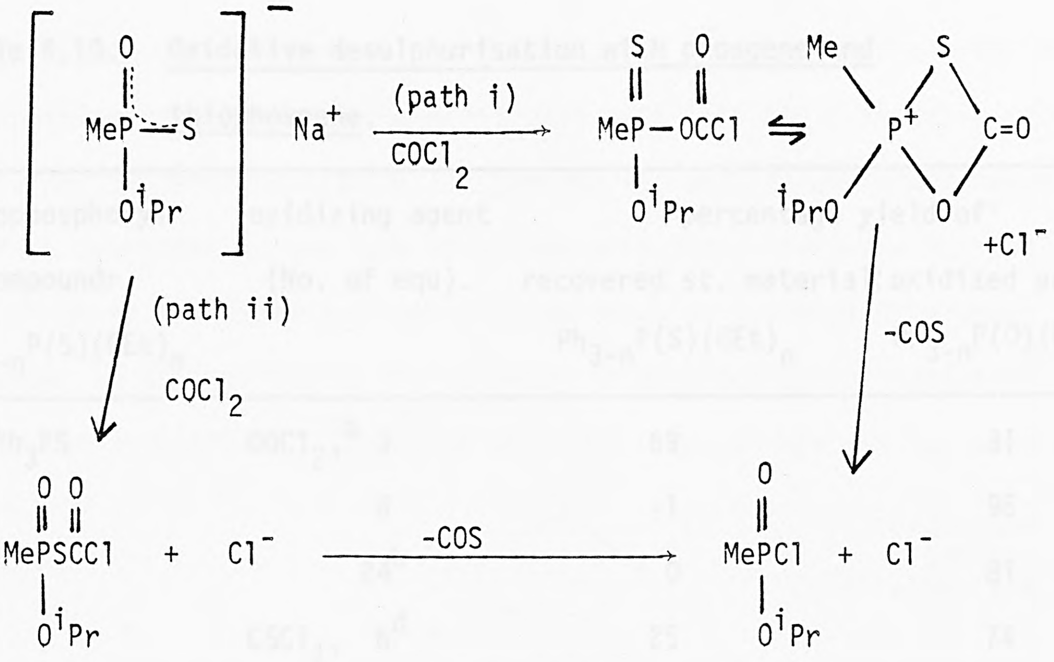
* $CHCl_3$ as solvent, reaction time 20 hours.

† These solutions contain MnTPP(III)Cl (0.02 equ).

The use of phosgene as a chlorinating agent for the conversion of phosphite esters,[83,84] phosphinate esters[85] and phosphonate esters[85,86,87] into their corresponding chloridates is well known. Cadogan has shown that for phosphorus thionate compounds, reaction with phosgene will form the phosphorus chloridate but with oxidative desulphurisation of the thiophosphoryl moiety.[87] Thus O,O-diethyl methylphosphonothioate is converted into O-ethyl methylphosphonochloridate, with loss of sulphur as carbon oxysulphide. Similarly Aaron has shown that

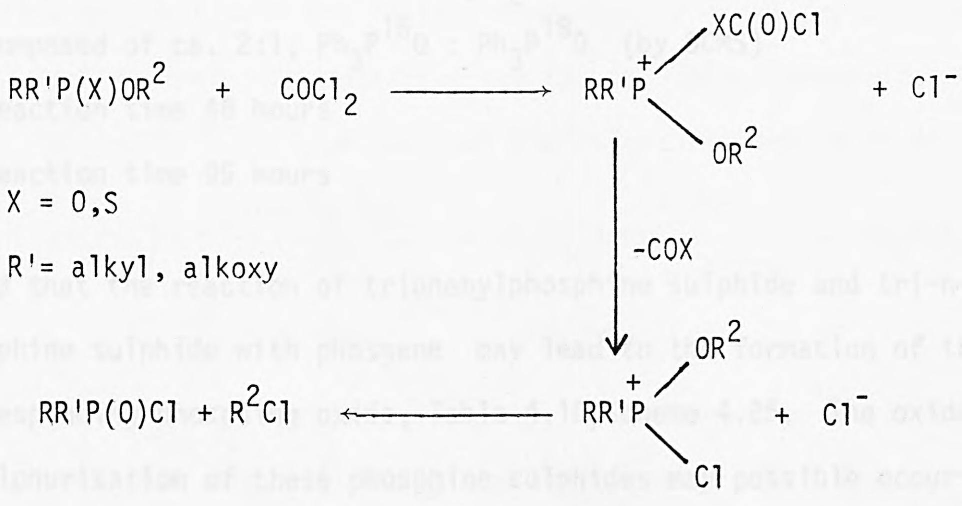
$$(EtO)_2P(S)Me \ + \ COCl_2 \longrightarrow EtO(Me)P(O)Cl \ + \ EtCl \ + COS$$

treatment of the sodium salt of O-isopropyl methylphosphonothioic acid with phosgene gives rise to the formation of O-isopropyl methylphosphonochloridate.[88] It was postulated that the reaction occurred via a four membered 'betaine type' intermediate, Scheme 4.23, (path i).



Scheme 4.23.

However Hudson and Green[89] noted that such a mechanism should occur with retention of configuration at phosphorus, where as inversion of configuration was observed. They suggested that the reaction proceeds with nucleophilic attack by the chloride ion on an acyclic anhydride, (path ii). In the reaction of neutral esters (e.g. benzyl methylphenylphosphinate[85] O,O-diethyl methylphosphonothioate[87]) it is proposed that the phosphoryl oxygen or sulphur (in thionate compounds) behaves as the nucleophilic centre, Scheme 4.24.[85,89,90] It has been



Scheme 4.24.

Table 4.10. Oxidative desulphurisation with phosgene and thiophosgene.

Thiophosphoryl compound†	oxidizing agent (No. of equ).	percentage yield of* recovered st. material:	oxidized prod.
$Ph_{3-n}P(S)(OEt)_n$		$Ph_{3-n}P(S)(OEt)_n$	$Ph_{3-n}P(O)(OEt)_n$
1a Ph_3PS	$COCl_2$,[a] 3	69	31
	6	<1	95
	24[b]	0	81
	$CSCl_2$, 6[d]	25	74
1i n-Bu_3PS	$COCl_2$,[a] 3	0	99
	$CSCl_2$ 6	<2	95
1b $Ph_2P(S)OEt$	$COCl_2$[a] 6[d],	26	25
1c $PhP(S)(OEt)_2$	$COCl_2$,[a] 6[d]	92	0
1d $(EtO)_3PS$	$COCl_2$,[a] 12[e],	96	0

* as determined by g.l.c. (all compounds identified by GCMS)

† CH_3CN as solvent, reaction time 24 hours unless stated.

a used as a 20% $^{w}/w$ solution in toluene

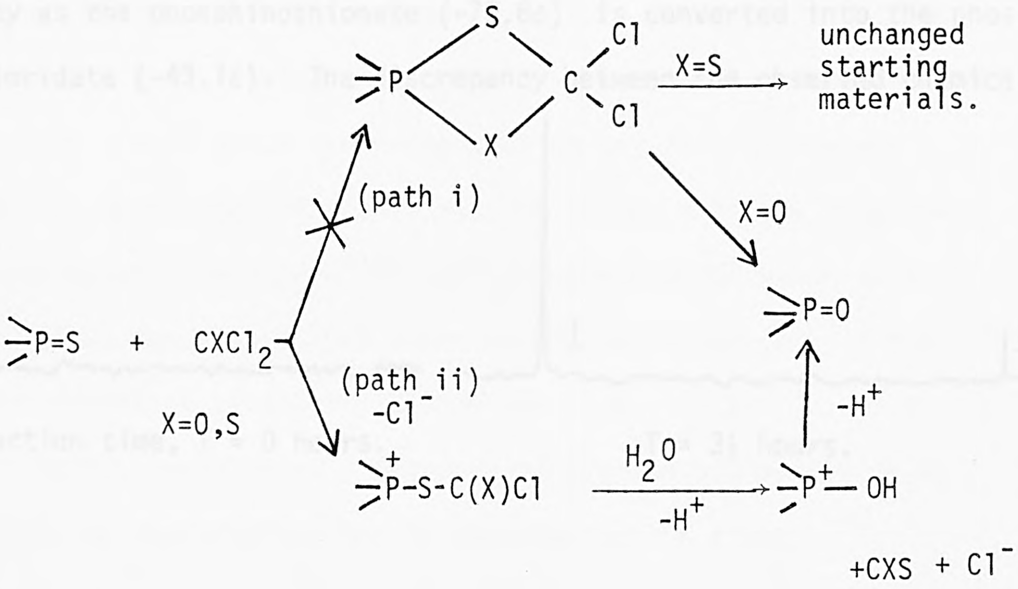
b reaction doped to 0.2% $^{v}/v$ with $H_2{}^{18}O$

c composed of ca. 2:1, $Ph_3P^{16}O$: $Ph_3P^{18}O$ (by GCMS)

d reaction time 48 hours

e reaction time 95 hours

found that the reaction of triphenylphosphine sulphide and tri-n-butylphosphine sulphide with phosgene may lead to the formation of the corresponding phosphine oxide, Table 4.10, Scheme 4.25. The oxidative desulphurisation of these phosphine sulphides may possible occur in an analagous manner to oxidative desulphurisation by thionyl chloride,[5,6] (path i), or via the formation and subsequent hydrolysis of a transient phosphonium intermediate, (path ii). That path i is not a feasable route to oxidative desulphurisation is shown by the ability of thiophosgene to form phosphine oxides from phosphine sulphides. Evidence for the formation of a phosphonium intermediate which is hydrolysed by water (present as an impurity in the solvent) is provided by the formation of triphenylphosphine (^{18}O)-oxide when the reaction mixture is doped

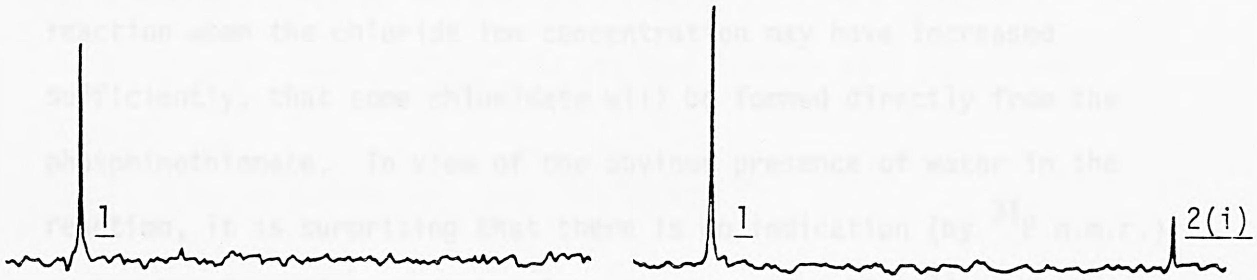


Scheme 4.25.

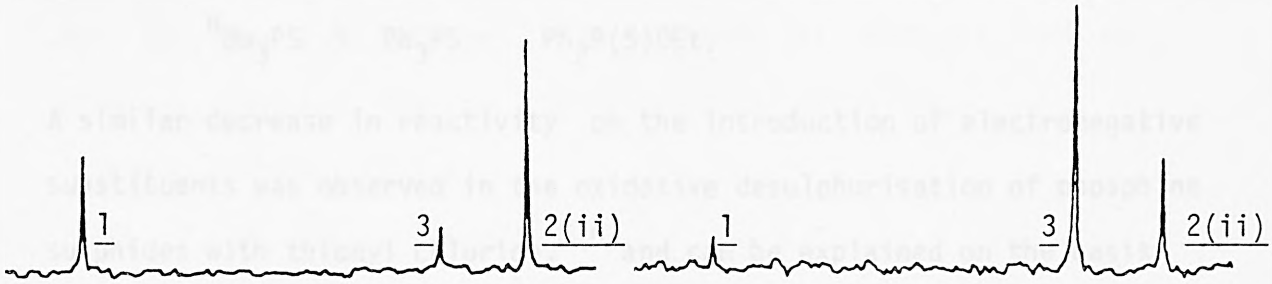
with (^{18}O)-water. In the case of ethyl diphenylphosphinothionate the reaction proceeds with the initial formation of ethyl diphenylphosphinate, which is then subsequently converted to diphenylphosphinochloridate. Although it is expected that the chloridate should be formed

$$Ph_2P(S)OEt \xrightarrow[\substack{-HCl \\ -COS}]{COCl_2/H_2O} Ph_2P(O)OEt \xrightarrow[\substack{-EtCl \\ -CO_2}]{COCl_2} Ph_2P(O)Cl$$

directly from the phosphinothionate by the mechanism given in Scheme 4.24, (X=S, R=R' =Ph, R^2= Et), the formation of ethyl diphenylphosphinate confirms the presence of water in the solvent. Further more, although water would be expected to hydrolyse some of the phosgene, it must be present in a sufficiently greater concentration than the more nucleophilic chloride ion for it to compete successfully for the phosphonium intermediate. By following the reaction with ^{31}P n.m.r. it is possible to observe the formation and subsequent reaction of ethyl diphenylphosphinate, Figure 4.2. The peak at -34.2δ is attributed to this phosphinate. It can be seen to increase and then decrease in intensity as the phosphinothionate (-79.8δ) is converted into the phosphinochloridate (-43.1δ). The discrepancy between the observed chemical



Reaction time, T = 0 hours. T = 3½ hours.



T = 28 hours. T = 100 hours.

1, -79.8δ (phosphinothionate); 2(i) -33.0δ and 2(ii) -34.2δ (ethyl diphenylphosphinate)*; 3, -43.1δ (phosphinochloridate)
(* variation in chem. shift due to protonation of >P=O by HCl)

Figure 4.2. ^{31}P n.m.r. for the reaction of phosgene with ethyl diphenylphosphinothionate.

shifts and the chemical shifts for the pure compounds (-28.9δ for ethyl diphenylphosphinate and -42.7δ for the phosphinochloridate[91]) is due to the protonation of the phosphoryl oxygen atom by hydrochloric acid (generated either in the reaction or from the hydrolysis of phosgene). Additionally the poor mass balance as regards the total percentage phosphorus material detected by g.l.c. (51% - see Table 4.10) can be attributed to the formation of diphenylphosphinochloridate. No quantitative analysis by g.l.c. was carried out for this product. It is likely, particularly in the latter stages of the reaction when the chloride ion concentration may have increased sufficiently, that some chloridate will be formed directly from the phosphinothionate. In view of the obvious presence of water in the reaction, it is surprising that there is no indication (by ^{31}P n.m.r.) as to the formation of diphenylphosphinic acid (-25.2δ[91]). As in the photochemical reactions, a sequence of decreasing reactivity towards oxidative desulphurisation is observed in the order,

$$^{n}Bu_3PS > Ph_3PS > Ph_2P(S)OEt.$$

A similar decrease in reactivity on the introduction of electronegative substituents was observed in the oxidative desulphurisation of phosphine sulphides with thionyl chloride,[5,6] and can be explained on the basis of a decrease in stabilization of the initially formed phosphonium intermediate. The apparent non reactivity of triethyl phosphorothionate towards phosgene is in agreement with the earlier work of Cadogan.[87]

Experimental

For general experimental details see chapter 5.

Preparation of O-ethyl diphenylphosphinite.

Under a nitrogen atmosphere, a mixture of absolute ethanol (55mmol, 3.2ml) and triethylamine (55mmol, 7.67ml), in benzene (50ml) was added dropwise over 60 minutes to an ice cooled solution of P-chlorodiphenylphosphine (50mmol, 11.04g, 8.98ml), in benzene (150ml). After stirring at ice bath temperature for a further 2 hours, the solution was filtered and reduced in vacuo to give a crude oil. Distillation gave 10.4g (90%) of the desired product as a colourless liquid.

B.pt. 158-160^{o}C/15mm Hg, (lit. 179^{o}/14mm)[92]

Elemental Analysis.

For $C_{14}H_{15}OP$ require : C, 73.03; H, 6.57; P, 13.45.
found : C, 73.31; H, 6.61; P, 13.24.

I.R. (liquid film)

3055 (m), 2980 (m), 2900 (w), 1590 (m), 1480 (m), 1440 (s), 1390 (m), 1130 (s), 1030 (s), 945 (s), 750 (s), 725 (s) 695cm^{-1}(s).

^{1}H n.m.r. (100MHz, $CDCl_3$)

1.22δ, (t, 3H, $^{3}J_{HCCH}$ 7Hz $-CH_3$),
3.69δ, (dq, 2H, $^{3}J_{HCCH}$ 7Hz, $^{3}J_{HCOP}$ 10Hz, $-OCH_2-$),
7.14δ, (m, 6H, H-meta & H-para),
7.33δ, (ddd, 4H, H-ortho).

Preparation of O-ethyl diphenylphosphinothioate.

To an ice cooled solution of ethyl diphenylphosphinite (45mmol, 10.4g) in benzene(50ml), sulphur (135mmol, 4.33g) was added in small portions over 15 minutes. The suspension was stirred for 1 hour under nitrogen with ice cooling, and then for a further hour at room temperature. The excess sulphur was removed and the solvent reduced in vacuo to afford a crude oil. This was purified by column chromatography (Kieselgel 60, Art 9385, elluting with dichloromethane). The material collected was treated with decolourising charcoal, filtered and reduced in vacuo to give 7.8g (66%) of the desired product as colourless crystals.

M.pt. 35-37^{o}C (lit. 42-43^{o}C)[93]

Elemental Analysis:

For $C_{14}H_{15}OPS$ require : C,64.10; H,5.78; P, 11.81; S, 12.44.

found : C,64.12; H,5.78; P, 11.60; S, 12.24.

I.R. (melt).

3050 (m), 2980 (m), 2895 (m), 1590 (w), 1575 (w), 1480 (m), 1435 (s), 1390 (m), 1310 (m), 1160 (m), 1110 (s), 1020 (s), 940 (s), 780 (s), 720 (s), 685cm^{-1} (s).

^{1}H n.m.r. (220MHz, $CDCl_3$),

1.33δ, (t, 3H, $^{3}J_{HCCH}$ 7Hz, $-CH_3$),

4.14δ, (dq, 2H, $^{3}J_{HCCH}$ 7Hz, $^{3}J_{HCOP}$ 9Hz, $-OCH_2-$),

7.50δ, (m, 6H, H-meta & H-para),

7.94δ, (ddd, 4H, $^{3}J_{HCCP}$ 13Hz, $^{3}J_{HCCH}$ 8Hz, $^{4}J_{HCCCH}$2Hz, H-ortho)

^{13}C-{^{1}H} n.m.r. ($CDCl_3$, with additional multiplicity in SFORD).

16.26δ, (d, $^{3}J_{CCOP}$ 7.93Hz, CH_3), (qt, $^{1}J_{CH}$ 126.95Hz $^{2}J_{CCH}$ 2.44Hz),

61.26δ, (d, $^{2}J_{COP}$ 5.49Hz, $-OCH_2-$), (tq, $^{1}J_{CH}$ 147.10Hz $^{2}J_{CCH}$ 4.27Hz),

128.66δ, (d, $^{3}J_{CCCP}$13.43Hz, C-meta), (*),

131.406δ, (d, $^{2}J_{CCP}$ 11.60Hz, C-ortho), (*),

132.00δ, (d, $^{4}J_{CCCCP}$ 3.05Hz, C-para), (*),

135.04δ, (d, $^{1}J_{CP}$ 110.47Hz, C-ipso), (*),

* multiple couplings present in SFORD which were not analysed,

^{31}P-{^{1}H}n.m.r. (36.2MHz, CH_3CN)

-79.8δ (s),

M.S. (70ev),

m/e (rel.int.); 262.048 (M^+, 6.18%), 218.022 (18.2%), 201.037 (69%), 185.044 (8.5%), 139.981 (8.9%), 84.943 (58.7%), 82.947 (100%).

Preparation of O-ethyl diphenylphosphinate.

To an ice cooled solution of ethyl diphenylphosphinite (10 mmol, 2.30g) in dichloromethane (20ml), m-chloroperbenzoic acid (11mmol, 1.90g) in dichloromethane (30ml) was added dropwise with stirring over 15 minutes. The solution was stirred at ice bath temperature for 2 hours and filtered. After washing with a 10% sodium hydroxide soluton (4 x 25ml) and water (3 x 25ml), the organic layer was dried ($MgSO_4$) and reduced in vacuo to afford a yellow oil. This was purified by flash chromatography (Kieselgel 60H, Art 7736, ethyl acetate (3)-dichloromethane (2) as elluent), to give 1.45g (59%) of the desired product as a colourless oil.

Elemental Analysis.

For $C_{14}H_{15}O_2P$ require : C,68.28; H, 6.15.

found : C,67.88; H, 6.26.

I.R. (liquid film),

3050 (m), 2980 (m), 2900 (w), 1735 (m), 1590 (m), 1480 (m), 1440 (s), 1390 (m), 1225 (s), 1130 (s), 1030 (s), 950 (s), 780 (m), 750 (s), 730 (s), 695cm^{-1} (s).

^1H n.m.r. (220MHz, $CDCl_3$),

1.38δ, (t, 3H, $^3J_{HCCH}$ 7Hz, $-CH_3$)

4.15δ, (dq, 2H, $^3J_{HCCH}$ 7Hz, $^3J_{HCOP}$ 7Hz, $-OCH_2-$),

7.54δ, (m, 6H, H-meta & H-para),

7.88δ, (ddd, 4H, $^3J_{HCCH}$ 7Hz, $^4J_{HCCCH}$ 2Hz, $^3J_{HCCP}$ 12Hz, H-ortho).

$^{13}C-\{^1H\}$ n.m.r. ($CDCl_3$, with additional multiplicity in SFORD).

16.54δ, (d, $^3J_{CCOP}$ 6.71Hz, CH_3), (qt, $^1J_{CH}$ 126.95Hz, $^2J_{CCH}$ 2.44Hz).

61.26δ, (d, $^2J_{COP}$ 5.49Hz, $-OCH_2-$), (tq, $^1J_{CH}$ 146.48Hz, $^2J_{CCH}$ 4.27Hz),

128.78δ, (d, $^3J_{CCCP}$ 13.43Hz, C-meta), (*),

131.91δ, (d, $^2J_{CCP}$ 9.77Hz, C-ortho), (*), 132.04δ, (d, $^1J_{CP}$ 136.72Hz, C-ipso), (*),

132.34δ, (d, $^4J_{CCCCP}$ 3.05Hz, C-para), (*),

* multiple couplings present in SFORD which were not analysed

^{31}P-{^{1}H}n.m.r. (36.2MHz, CH_3CH)

-28.9δ (s),

M.S. (70ev)

m/e (rel. int.); 246.075 (M^+,4.04%), 218.050 (7.9%), 217.052 (20.9%), 202.052 (7.7%), 142.012 (1.1%), 125.013 (1.6%), 104.055 (15.2%) 84.943 (59.9%), 82.947 (100%), 78.044 (1.2%).

Preparation of O,O-diethyl phenylphosphonite.

To an ice cooled solution of P,P-dichlorophenylphosphine (50mmol, 8.95g, 6.79ml) in ether (150ml) under a nitrogen atmosphere a mixture of absolute ethanol (110-mmol, 5.07g, 6.46ml) and triethylamine (110mmol, 11.13g, 15.34ml) in ether (50ml) was added dropwise over 1 hour. The reaction mixture was stirred at ice bath temperature for a further 2 hours. The white precipitate formed was removed by filtration, and the clear etheral solution of diethyl phenylphosphonite used directly in the next reaction. It is preferable to use the diethyl phenylphosphonite immediatly and without prior isolation. Attempted distillation of this material repeatedly resulted in its decomposition to O-ethyl phenylphosphinate.

Preparation of O,O-diethyl phenylphosphonothioate.

To an ice cooled etheral solution of diethyl phenylphosphonite, prepared from dichlorophenylphosphine (50mmol) as described earlier, sulphur (150mmol, 4.81g) was added in small portions over 15 minutes. The suspension was then stirred at ice bath temperature for a further 2 hours. Filtration and subsequent removal of the solvent gave an oil, which on distillation gave 8.1g (70% from dichlorophenylphosphine) of the desired product as a colourless liquid.

B.pt. 137-140°C/15mm. Hg, (lit. 72-73°C/0.02mm)[94]

Elemental Analysis.

For $C_{10}H_{15}O_2PS$ require : C, 52.15; H, 6.58; S, 13.92; P, 13.45
found : C, 52.42; H, 6.51; S, 13.82; P, 13.50.

I.R. (liquid film)

3060 (w), 2980 (s), 2900 (m), 1590 (w), 1475 (m), 1440 (s), 1390 (m), 1310 (w), 1160 (m), 1120 (s), 1035 (s), 950 (s), 790 (s), 735 (s), 690cm^{-1} (s)

^{1}H n.m.r. (220MHz, $CDCl_3$)

1.31δ, (t, 6H, $^3J_{HCCH}$ 7Hz, $-CH_3$),
4·04-4.33δ,(ddq, 4H $^3J_{HCCH}$ 7Hz, $^3J_{HCOP}$ 10Hz, HCH')*
7.46-7.64δ,(m, 3H, H-meta & H-para),
7.97δ, (ddd, 2H, $^3J_{HCCH}$ 8Hz, $^4J_{HCCCH}$ 2Hz, $^3J_{HCCP}$ 14Hz, H-ortho).

* These two methylene protons are diasteriotopic, although their individual chemical shift and geminal coupling constant were not determined.

^{13}C-{^{1}H} n.m.r. ($CDCl_3$, with additional multiplicity in SFORD).

16.11δ, (d, $^3J_{CCOP}$ 7.3Hz, CH_3), (qt, $^1J_{CH}$126.9Hz $^2J_{CCH}$ 1.8Hz),
62.85δ, (d, $^2J_{COP}$ 5.5Hz, $-OCH_2-$), (tq, $^1J_{CH}$ 147.7Hz $^2J_{CCH}$ 4.3Hz),
128.52δ, (d, $^3J_{CCCP}$ 15.3Hz, C-meta), (*),
131.14δ, (d, $^2J_{CCCP}$ 12.2Hz, C-ortho), (*),
132.34δ, (d, $^4J_{CCCCP}$ 3.1Hz, C-para), (*),
133.83δ, (d, $^1J_{CP}$ 151.4Hz, C-ipso), (*),

* multiple couplings present in SFORD which where not analysed

^{31}P-{^{1}H} n.m.r. (36.2MHz, $CDCl_3$).

-85.8δ (s),

M.S. (70ev)

m/e (rel. int.); 231.085 (M^++1, 1.92%), 230.065 (M^+, 22.29%) 201.053 (10.6%), 186.037 (11.0%), 169.054 (18.7%), 156.993 (12.6%), 153.056 (19.9%), 142.015 (18.8%), 141.019 (61.5%), 125.022 (29.9%)

124.014 (7.6%), 110.028 (9.2%), 109.022 (26.1%), 77.040 (100%).

Preparation of 0,0-diethyl phenylphosphonate.

To diethylphenylphosphonite, prepared as a solution in benzene from dichlorophenylphosphine (50mmol) using the method described earlier, m-chloroperbenzoic acid (55mmol, 9.49g) in benzene (150ml) was added dropwise over 30 minutes with ice bath cooling. The solution was stirred at this temperature for a further 2 hours and then concentrated to approximatly 1/5th of its volume. After washing with a 10% sodium hydroxide solution (4 x 25ml) and water (3 x 25ml), the organic layer was dried ($MgSO_4$) and reduced in vacuo to afford a crude oil which on distillation gave 5.50g (51% from dichlorophenylphosphine) of the desired product as a colourless liquid.

B.pt. 159-160°C/20mm Hg (lit. 97°/0.1mm)[95]

Elemental Analysis.

For $C_{10}H_{15}O_3P$ require : C, 56.06; H, 7.07; P, 14.46.

found : C, 55.56; H, 6.96; P, 14.14.

I.R. (liquid film)

3060 (m), 2980 (s), 2900 (m), 1595 (m), 1460 (w), 1440 (s), 1390 (m), 1365 (w), 1250 (s), 1160 (s), 1130 (s), 1035 (s), 955 (s), 790 (s), 750 (s), 695cm^{-1} (s)

^{1}H n.m.r. (220MHz, $CDCl_3$)

1.33δ, (t, 6H, $^3J_{HCCH}$ 7Hz, CH_3),

4.02-4.32δ, (ddq, 2H, $^3J_{HCCH}$ 7Hz, $^3J_{HCOP}$ 8Hz, HCH')*

7.47-7.68δ, (m, 3H, H-meta & H-para),

7.88δ, (ddd, 2H, $^3J_{HCCP}$ 13Hz, $^3J_{HCCH}$ 8Hz, $^4J_{HCCCH}$ 1.5Hz H-ortho).

* These two methylene protons are diasteriotopic, although their individual chemical shift are geminal coupling constant were not determined.

^{13}C-{^{1}H} n.m.r. (CDCl$_3$, with additional multiplicity in SFORD).

16.38δ, (d, $^{3}J_{CCOP}$ 6.7Hz, CH$_3$), (qt, $^{1}J_{CH}$ 126.9Hz, $^{2}J_{CCH}$ 1.8Hz),

62.23δ, (d, $^{2}J_{COP}$ 5.5Hz, -OCH$_2$-), (tq, $^{1}J_{CH}$ 147.1Hz, $^{2}J_{CCH}$ 4.3Hz),

128.743δ, (d, $^{3}J_{CCCP}$ 14.7Hz, C-meta), (*),

128.78δ, (d, $^{1}J_{CP}$ 188.0Hz, C-ipso), (*),

132.08δ, (d, $^{2}J_{CCP}$ 9.8Hz, C-ortho), (*),

132.63δ, (d, $^{4}J_{CCCCP}$ 3.1Hz, C-para), (*),

* Multiple couplings present in SFORD which were not analysed.

^{31}P-{^{1}H} n.m.r. (36.2MHz, CDCl$_3$).

-18.3δ (s),

M.S. (70ev).

m/e (rel. int.); 215.078 (M^{+}+1, 4.61%), 214.069 (M^{+}, 33.37%), 186.053 (14.3%), 170.051 (9.1%), 169.043 (9.2%), 159.017 (44.4%), 158.016 (100%), 143.023 (7.1%), 142.012 (57.1%), 141.011 (91.6%), 77.031 (85.6%).

Preparation of O,O,O-triethyl phosphorothioate.

To ice cooled triethyl phosphite (40mmol, 6.46g, 6.84ml), sulphur (120mmol, 5.76g) was added in small portions over 15 minutes. The solution was stirred at room temperature for 1 hour and then at 100°C for a further 30 minutes. The mixture was cooled, diluted with dichloromethane (50ml) and filtered. Removal of the solvent gave an oil which on distillation gave 6.20g (80%) of the desired product as a colourless liquid.

B.pt. 119-121°C/22mm Hg (lit. 50-51/0.9mm)[94]

Elemental Analysis.

For $C_6H_{15}O_3PS$ require : C, 36.35; H, 7.64; P, 15.62; S, 16.17.
found : C, 36.56; H, 7.41; P, 15.66; S, 16.15.

I.R. (liquid film)

2980 (m), 2930 (w), 2900 (w), 1470 (w), 1440 (w), 1390 (m), 1160 (m), 1020 (s), 960 (m), 820 (m), 790cm^{-1} (m),

^{1}H n.m.r. (100MHz, $CDCl_3$)

1.38δ, (t, 9H $^{3}J_{HCCH}$ 7.5Hz, CH_3),

4.27δ, (dq, 6H $^{3}J_{HCCH}$ 7.5Hz, $^{3}J_{HCOP}$ 10Hz, $-OCH_2-$)

^{13}C-{^{1}H}n.m.r. ($CDCl_3$, with additional multiplicity in SFORD).

15.95δ, (d, $^{3}J_{CCOP}$ 7.32Hz, CH_3), (qt, $^{1}J_{CH}$ 126.95Hz, $^{2}J_{CCH}$ 2.44Hz),

64.31δ, (d, $^{2}J_{COP}$ 5.49Hz, $-OCH_2-$), (tq, $^{1}J_{CH}$ 147.71Hz, $^{2}J_{CCH}$ 4.27Hz).

^{31}P-{^{1}H}n.m.r. (36.2MHz, $CDCl_3$).

-67.2δ (s)

Preparation of 0,0-diethyl-0-4-nitrophenyl phosphorothioate.[96]

Diethyl chlorothiophosphate (25mmol, 4.72g, 3.2ml) was added under nitrogen to a solution of sodium 4-nitrophenoxide (25mmol, 4.03g) in chlorobenzene (12.5ml). The solution was heated to 120°C and maintained at this temperature for 20 hours. It was then cooled, filtered and the precipitate washed with toluene. The solvent was removed in vacuo to give an oil which on distillation gave 3.2g (44%) of the desired product as a pale yellow liquid.

B.pt. 125-130°C/0.01mm Hg (lit. 170-171°/1mm)[96]

^{1}H n.m.r. (100MHz, $CDCl_3$).

1.44δ (t, 6H, $^{3}J_{HCCH}$ 7Hz, CH_3),

4.44δ (dq, 4H, $^{3}J_{HCCH}$ 7Hz, $^{3}J_{HCOP}$ 11Hz),

7.64δ (d, 2H, J 9Hz, H-2, H-6),

8.56δ (d, 2H, J 9Hz, H-3, H-5)

Preparation of tri-n-butylphosphine sulphide.

Sulphur (22mmol, 0.71g) was added in small portions over 15 minutes to an ice cold solution of tri-n-butylphosphine (22mmol, 4.4g, 5.4ml) in dichloromethane (50ml). The solution was left to stir for 2 hours at room temperature. The solvent was then removed and the crude oil filtered and distilled. Treatment of this oil with activated charcoal gave 3.9g (76%) of the desired product as a colourless liquid.

B.pt. 166-167°C/22mm Hg (lit. 137-138/1.1mm)[97]

Elemental Analysis.

For $C_{12}H_{27}PS$ require : C, 61.48; H, 11.63; P. 13.21; S, 13.68

found : C, 60.85; H, 11.82; P. 13.07; S, 13.67

I.R. (liquid film)

2940 (s), 2860 (s), 1460 (s), 1405 (m), 1380 (m), 1300 (w), 1210 (m), 1095 (s), 1050 (m), 1005 (m), 970 (m), 910 (s), 790 (s), 735cm^{-1}(s)

^{1}H n.m.r. (100MHz, $CDCl_3$)

0.96δ, (distorted t, 9H, $^{3}J_{HCCH}$ 6.5 Hz, CH_3),

1.20-2.00δ, (m, 6H, $-(CH_2)_3-$).

$^{31}P-\{^{1}H\}$ n.m.r. (36.2 MHz, CH_3CN)

-48.3δ, (s).

M.S. (70ev).

m/e (rel. int.); 234.119 (M^+, 8.80%), 178.072 (19.0%), 122.015 (100%), 93.991 (5.13%), 87.023 (10.3%), 79.980 (17.3%), 57.061 (24.5%).

Preparation of Tri-n-butylphosphine oxide.

To a solution of tri-n-butylphosphine (22mmol, 4.4g, 5.4ml) in dichloromethane (20ml) m-chloroperbenzoic acid (24mmol, 4.14g) in dichloromethane (100ml) was added dropwise over 30 minutes with ice bath cooling. After stirring for 2 hours at room temperature the solution was washed with a 10% sodium hydroxide solution (3 x 50ml) water (4 x 25ml) and dried ($MgSO_4$). Filtration and removal of the solvent gave an oil which was distilled to give a colourless liquid which on cooling solidified to give colourless crystals of the desired product.

B.pt. 165-166°C/20mm Hg (lit. 300°C)[98]

I.R. (melt).

2940 (s), 2860 (s), 1460 (s), 1405 (m), 1375 (m), 1345 (w), 1300 (m), 1275 (m), 1220 (s), 1150 (s), 1090 (s), 1040 (m), 1005 (m), 965 (m), 900 (s), 800 (s), 725cm^{-1} (m).

^{1}H n.m.r. (100MHz, $CDCl_3$)

0.94δ, (distorted t, 9H, $^3J_{HCCH}$ 7Hz),

1.16-1.88δ, (m, 6H, $-(CH_3)_3-$).

^{31}P-{^{1}H} n.m.r. (36.2MHz, CH_3CN)

-45.7δ (s).

M.S. (70ev).

m/e (rel. int.); 218.138 (M^+, 0.61%), 189.109 (22.3%), 162.084 (12.9%), 161.081 (11.6%), 147.071 (15.2%), 134.063 (12.7%), 120.051 (27.9%), 92.025 (100%), 78.016 (75.9%), 62.993 (27.1%), 55.043 (22.3%).

Preparation of tetrabutylammonium periodate.[82]

A solution of sodium periodate (50mmol, 10.7g), in water (75ml) was added dropwise with vigorous stirring to a solution of tetrabutylammonium hydrogen sulphate (50mmol, 17.0g) in water (25ml) over 15 minutes. The precipitate was filtered and dried over phosphorus pentoxide to give 18.6g (86%) of the desired product as a white powder. Contrary to the literature[82] this material does not recrystalise from diisopropyl ether. It was used without further purification.

M.pt. 166-167°C, (lit. 158-159°C).[82]

Preparation of di-t-butyl sulphone.

Hydrogen peroxide (30% aq. solution, 9.6ml) in glacial acetic acid (8ml) was added dropwise over 15 minutes to an ice cooled solution of di-t-butyl sulphide (27mmol, 4.92ml) in glacial acetic acid (28ml). The mixture was allowed to warm to room temperature and stirred for 10 hours. The solution was evaporated to near dryness under reduced pressure to leave a white solid. This was partitioned between dichloromethane (20ml) and water (20ml), and sodium bicarbonate added till the aqueous phase was basic. The dichloromethane layer was separated, washed with water (2 x 5ml) and reduced in vacuo to give a solid which was recrystalised from ethanol-water (1:1) to give 4.35g (89%) of the desired product as white needles.

M.pt. 127-128°C, (lit. 127-128°C)[99]

Elemental Analysis.

For $C_8H_{18}O_2S$ require : C, 53.88; H, 10.20.

found : C, 54.09; H, 10.00.

I.R. (nujol).

1270 (s), 1180 (m), 1090 (s), 1010 (w), 800 (m), 685cm^{-1} (m).

^{1}H n.m.r. (100MHz, $CDCl_3$).

1.48δ, (s, $-CH_3$).

Preparation of dimethyl sulphone.

Dimethyl sulphide (50mmol, 3.1g, 3.7ml) was treated with hydrogen peroxide (30% aq. solution, 15ml) in glacial acetic acid (20ml + 15ml) as for the preparation of di-t-butyl sulphone. The solid obtained was recrystalised from ethanol-water (1:1) to give white needles, 2.49g (53%).

M.pt. 106-108°C (lit.109°C)[100]

Elemental Analysis.

For $C_2H_6O_2S$ require : C, 25.52; H, 6.44.

found : C, 25.61; H, 6.35.

I.R. (nujol).

1410cm^{-1} (w), 1140 (m), 935 (m), 765 (m), 725 (m), 700cm^{-1} (m).

^{1}H n.m.r. (100MHz, $CDCl_3$).

3.00δ (s, $-CH_3$).

Photooxidative desulphurisation, - a general procedure.

The following general procedure was used in the photooxidative desulphurisation of thiophosphorus compounds 1a, 1b, 1c, 1d, 1e, 1f, 1g and 1h.

A stock solution of the thiophosphorus compound was prepared, (see below). To 5ml of this stock solution, a known amount of precursor was added. This solution was then irradiated for 10 hours (unless stated otherwise below) in pyrex vessels using black-light fluorescent lamps. Throughout the irradiation the solution was continually flushed with dry, carbon dioxide free oxygen. After irradiation, the solutions containing compounds 1a, 1b, 1c, 1d and 1g were analysed for any unreacted thiophosphorus compound and its corresponding phosphoryl analogue. The solutions containing compounds 1e and 1f were treated with an etheral solution of diazomethane, and then analysed by g.l.c. for diethyl phosphate (as its methyl ester). For 1h, the photolysis solution was preconcentrated prior to addition of diazomethane. Subsequent g.l.c. analysis was carried out to determine the presence of diethyl phosphate and diethyl phosphorothioic acid (as their methyl esters). The solutions containing compound 1f was also analysed for 1-pentanethiol. However in all cases no thiol was detected. Finally for 1e, 1f and 1h the solutions were analysed by g.l.c. for any unreacted thiophosphorus compound prior to addition of diazomethane. The stock solution for each thiophosporus substrate was prepared to the following concentration. Irradiation times are given if other than 10 hours.

1a, Ph_3PS; concentration 6.79×10^{-3} mol dm^{-3},
0.20g Ph_3PS + 0.10g Ph_2SO_2 in 100ml CH_3CN,
irradiation time 1 hour with benzoin as precursor,
80 hours for DCA as precursor and 10 hours for all other precursors used.

1b, $Ph_2P(S)OEt$; concentration 15.25×10^{-3} mol dm^{-3},
0.40g $Ph_2P(S)OEt$ + 0.20g Ph_2SO_2 in 100ml CH_3CN.

1c, $PhP(S)(OEt)_2$; concentration 17.37×10^{-3} mol dm^{-3},
0.40g $PhP(S)(OEt)_2$ + 0.20g ${}^tBu_2SO_2$ in 100ml CH_3CN.

1d, $(EtO)_3PS$; concentration 20.18×10^{-3} mol dm^{-3},

0.40g $(EtO)_3PS$ + 0.20g Me_2SO_2 in 100ml CH_3CN.

1e, $(EtO)_2P(O)SCH_3$; concentration 32.57×10^{-3} mol dm^{-3},

1.50g $(EtO)_2P(O)SCH_3$ + 1.0g 1-bromodecane in 250ml CH_3CN

1f, $(EtO)_2P(O)S(CH_2)_4CH_3$; concentration 32.45×10^{-3} mol dm^{-3},

1.95g $(EtO)_2P(O)S(CH_2)_4CH_3$ + 1.0g $^tBu_2SO_2$ in 100ml CH_3CN.

1g, $(EtO)_2P(S)OC_6H_4NO_2$-4; concentration 13.73×10^{-3} mol dm^{-3},

0.40g parathion in 100ml CH_3CN.

1h, $(EtO)_2P(S)SCH_2Cl$; concentration 68.17×10^{-3} mol dm^{-3},

0.80g chlormephos in 50ml CH_3CN.

The internal standards used, that is Ph_2SO_2 (for Ph_3PS and $Ph_2P(S)OEt$), $^tBu_2SO_2$ (for $PhP(S)(OEt)_2$ and $(EtO)_2P(O)S(CH_2)_4CH_3$), Me_2SO_2 (for $(EtO)_3PS$) and 1-bromodecane (for $(EtO)_2P(O)SCH_3$) were added in the preparation of the appropriate stock solution, and were therefore present during the irradiation. The following amounts of each precursor used were as follows:

benzoin,	2 equivalents for compounds 1a to 1h inclusive.
benzil,	2 equivalents for compounds 1a to 1d inclusive and 1g, and 6 equivalents for 1e, 1f and 1h.
biacetyl,	4 equivalents for compounds 1a to 1d inclusive and 1g, and 6 equivalents for 1e, 1f and 1h.
acenaphthenequinone,	2 equivalents for 1a, 1.4 equivalents for 1b, 1.2 equivalents for 1c, 1.0 equivalent for 1d and 1g and 0.64 equivalents for 1e and 1f, (solutions saturated with AcQ).
phenanthrenequinone,	2 equivalents for 1a.
DDQ	2 equivalents for compounds 1a to 1d inclusive and 1g, and 6 equivalents for 1e, 1f and 1h.
p-chloranil,	2 equivalents for compounds 1a and 1b.

pyruvic acid,	4 equivalents for compounds 1a to 1d inclusive and 1g, and 6 equivalents for 1e, 1f and 1h.
methyl pyruvate,	4 equivalents for compounds 1a to 1d inclusive and 1g, and 6 equivalents for 1e, 1f and 1h.
t-butyl pyruvate,	4 equivalents for compounds 1a to 1d inclusive and 6 equivalents for 1e and 1f.
9,10-DCA,	0.3 equivalents for 1a (solution saturated with DCA).

The results of these photooxidative desulphurisation experiments are reported in Tables 4.1 (for compounds 1a to 1d inclusive), 4.2 (1e and 1f), 4.6 (1g) and 4.7 (1h).

Photooxidation of precursor in presence and absence of any thiophosphorus compound.

The photooxidation of the following precursors were investigated in an identical manner to the photooxidative desulphurisation experiments described earlier; benoin, benzil, biacetyl, acenaphthenequinone, p-chloranil, pyruvic acid, methyl pyruvate and t-butyl pyruvate. Two solutions for each precursor (ie. pure precursor and precursor + triphenylphosphine sulphide mixture, both solutions containing an identical concentration of precursor) in acetonitrile were irradiated simultaneously for 10 hours under oxygen, (1 hour for benzoin). The concentration (number of equivalents) of precursor used were the same as in the desulphurisation reactions relative to compound 1a. After irradiation was complete the solutions were then analysed for the percentage of precursor remaining. With pyruvic acid, diazomethane was added to form the methyl ester prior to g.l.c. analysis. In all cases it was found that the presence of triphenylphosphine sulphide had no apparent effect on the photooxidation of the precursor. The precise results are reported in Table 4.3. This was similarly repeated for acenaphthenequinone with triethyl phosphorothioate, only here samples were taken for g.l.c. analysis during the course of the photoreaction. The results obtained are illustrated graphically in Figure 4.1. In the case of acenaphthenequinone, for both triphenylphosphine sulphide and triethyl phosphorothioate, the solutions were also analysed for 1,8-naphthalic anhydride (using acenaphthenequinone as the standard solution). These results are reported in Table 4.4.

Oxidative desulphurisation of triphenylphosphine sulphide with benzoyl peroxide.

To 5ml of a stock solution containing triphenylphosphine sulphide (6.79×10^{-3} mol dm^{-3}) and phenyl sulphone in acetonitrile, benzoyl peroxide (2 equivalents) was added. This solution was then stirred at room temperature for 20 hours. Subsequent g.l.c. analysis indicated the presence in solution of,

65% unreacted Ph_3PS
26% yield of Ph_3PO
and 48% yield of benzoic anhydride.

Attempted photooxidative desulphurisation with singlet oxygen.

Triphenylphosphine sulphide (0.034 mmol, 10mg) phenyl sulphone (0.01g) and rose bengal (0.002g) were all dissolved up in 10ml of the following solvent mixtures; methanol, chloroform : methanol (1:1), dichloromethane : methanol (1:1) and benzene : methanol (1:1). These solutions were then irradiated for 10 hours under oxygen using daylight lamps in conjunction with a 2% $^{W}/v$ potassium chromate filter solution. After irradiation the solutions were analysed for any phosphine sulphide and phosphine oxide. They all gave quantitative recovery of Ph_3PS with no formation of Ph_3PO, (by g.l.c.).

Similarly O,O-diethyl S-methyl phosphorothioate (30mg) when irradiated with tetraphenylporphine (2mg) in deuterochloroform under oxygen using daylight lamps for 67 hours gave only unreacted starting material (as shown by ^{1}H n.m.r.). Again O,O-diethyl S-methyl phosphorothioate (200mg) and rose bengal(10mg) in acetonitrile (10ml) under oxygen gave only unreacted starting material after 22 hours irradiation (as shown by ^{1}H n.m.r.).

Oxidative desulphurisation with potassium superoxide.

The following general procedure was used in the chemical oxidative desulphurisation of triphenylphosphine sulphide and triethyl phosphorothioate.

A stock solution of the thiophosphorus compound was prepared, (see below). Into a r.b. flask containing 5ml of this stock solution, a known amount of potassium superoxide was added, taking care to prevent unecessary exposure of the grannules to the atmosphere. Once covered by the chloroform, the grannules of superoxide were ground to a fine powder. The flask was then stoppered, and either sonicated or stirred at room temperature for 20 hours. After this time, the reaction mixture was analysed by g.l.c. for any unreacted thiophosphorus compound and its phosphoryl analogue. The stock solution for each thiophosphorus substrate was prepared to the following concentration.

1a, Ph_3PS; concentration 13.59 x 10^{-3} mol dm^{-3},
0.10g Ph_3PS + 0.050g Ph_2SO_2 (internal standard) + 0.018g PTC, (0.2 equivalents) in 25ml $CHCl_3$

1d, $(EtO)_3PS$; concentration 20.18 x 10^{-3} mol dm^{-3}, 0.20g $(EtO)_3PS$ + 0.10g Me_2SO_2 (internal standard) + 0.053g PTC (0.2 equivalents) in 50ml $CHCl_3$.

The following amounts of potassium superoxide were used;
0.0145g (3 equivalents) and 0.1933g (40 equivalents) for reaction with 1a,
0.1076g (15 equivalents) and 0.2870g (40 equivalents) for reaction with 1d.

The results for these reactions, both on sonication and without sonication are reported in Table 4.8.

Oxidative desulphurisation with tetrabutylammonium periodate.

The following general procedure was used in the oxidative desulphurisation of triphenylphosphine sulphide and triethyl phosphorothioate with tetrabutylammonium periodate.

A stock solution of the thiophosphorus compound was prepared, (see below). To a known amount of tetrabutylammonium periodate (and chloro-meso-tetraphenylporphinatomanganese (III) if used), 5ml of the thiophosphorus stock solution was added. The flask was then stoppered, and either sonicated or stirred at room temperature for 20 hours. After this time, the reaction mixture was analysed by g.l.c. for any unreacted thiophosphorus compound and its phosphoryl analogue. The stock solution for each thiophosphorus substrate was prepared to the following concentration.

1a, Ph_3PS; concentration 13.59×10^{-3} mol dm^{-3}, 0.20g Ph_3PS + 0.10 Ph_2SO_2 (internal standard) in 50ml $CHCl_3$.

1d, $(EtO)_3PS$; concentration 20.18×10^{-3} mol dm^{-3} 0.20g $(EtO)_3PS$ + 0.10g Me_2SO_2 (internal standard) in 50ml $CHCl_3$.

The following concentrations of tetrabutylammonium periodate were used;

0.1766g (6 equivalents) for reaction with 1a,

0.236g (6 equivalents) for reaction with 1d,

The following concentrations of MnTPP(III)Cl were used.

0.001g (0.02 equivalents) for reaction with 1a,

0.0014g (0.02 equivalents) for reaction with 1d.

The results for these reactions, both on sonication and without sonication and in the presence and absence of MnTPP(III)Cl are reported in Table 4.9.

Oxidative desulphurisation with phosgene and thiophosgene.

The following general procedure was used in the oxidative desulphurisation of a number of thiophosphorus compounds with phosgene and thiophosgene.

A stock solution of the thiophosphorus compound was prepared (see below). To a known amount of either phosgene or thiophosgene, 5ml of the thiophosphorus stock solution was added. The reaction vessel was then stoppered and left at room temperature for a predetermined time period. After this had elapsed, the solutions were analysed by g.l.c. for any unreacted thiophosphorus compounds and its phosphoryl analogue. The stock solution of each thiophosphorus substrate was prepared to the following concentration, and had a reaction time as indicated below.

1a, Ph_3PS; concentration 6.79×10^{-3} mol dm^{-3}, 0.10g Ph_3PS + 0.030g Ph_2SO_2 in 50ml CH_3CN.
Reaction time, 24 hours (with phosgene),
48 hours (with thiophosgene).

1b, $Ph_2P(S)OEt$; concentration 15.25×10^{-3} mol dm^{-3}, 0.10g $Ph_2P(S)OEt$ + 0.050g Ph_2SO_2 in 25ml CH_3CN.
Reaction time, 48 hours (with phosgene).

1c, $PhP(S)(OEt)_2$; concentration 17.37×10^{-3} mol dm^{-3}, 0.10g $PhP(S)(OEt)_2$ + 0.050g $^tBu_2SO_2$ in 25ml CH_3CN.
Reaction time, 48 hours (with phosgene).

1d, $(EtO)_3PS$; concentration 20.18×10^{-3} mol dm^{-3}, 0.080g $(EtO)_3PS$ + 0.080g Me_2SO_2 in 20ml CH_3CN.
Reaction time, 95 hours (with phosgene).

1i, $^nBu_3PS$; concentration 17.06×10^{-3} mol dm^{-3}, 0.10g $^nBu_3PS$ + 0.10g Ph_2SO_2 in 25ml CH_3CN.
Reaction time, 24 hours (with both phosgene and thiophosgene).

The sulphones (ie. Ph_2SO_2 for Ph_3PS, $Ph_2P(S)OEt$ and $^nBu_3PS$, $^tBu_2SO_2$ for $PhP(S)(OEt)_2$ and Me_2SO_2 for $(EtO)_3PS$) were employed as internal standards for the reaction.

Phosgene was added as a 20% $^w/w$ solution in toluene. The following concentrations were used;

0.0504g (3 equivalents) and 0.1008g (6 equivalents) for reaction with 1a,

0.2263g (6 equivalents) for reaction with 1b,

0.2581g (6 equivalents) for reaction with 1c,

0.5987g (12 equivalents) for reaction with 1d,

0.1266g (3 equivalents) for reaction with 1i.

The following concentrations of thiophosgene were used;

0.0234g (6 equivalents) for reaction with 1a,

0.0590g (6 equivalents) for reaction with 1i.

Similarly the oxidative desulphurisation of triphenylphosphine sulphide with phosgene in the presence of $H_2{}^{18}O$ was investigated. Here 5ml of a stock solution (0.050g Ph_3PS + 0.015g Ph_2SO_2 + 0.10ml $H_2{}^{18}O$: $H_2{}^{16}O$ {isotopic ratio 1:1} in 24.9ml CH_3CN) was reacted with phosgene (0.4032g, 24 equivalents) in the manner described earlier. After 24 hours GCMS of the reaction mixture gave molecular ion peaks at the following m/e values, (with relative intensities);

280.0606 (16.44%), corresponding to $Ph_3P^{18}O$

278.0680 (34.39%), corresponding to $Ph_3P^{16}O$

This and the results of the reaction of substrate 1a to 1d and 1i with phosgene and thiophosgene are reported in Table 4.10.

Additionally the reaction of $Ph_2P(S)OEt$ with phosgene was investigated by ^{31}P n.m.r. as follows;

To 0.01g $Ph_2P(S)OEt$ in 2.5ml CH_3CN, 0.2262g (12 equivalents) of phosgene was added. ^{31}P n.m.r. spectra run at T=0 (ie. prior to additon of phosgene), 3½, 28 and 100 hours. The spectra obtained are illustrated in Figure 4.2.

The g.l.c. conditions used to identify and determine the compounds discussed on the topic of oxidative desulphurisation (photochemical and non photochemical) are as follows;

Triphenylphosphine sulphide and triphenylphosphine oxide reaction mixture, (with diphenyl sulphone internal standard):

Column; 20", 10% UCW 982 (80-100 WAW DCMS B-8)
Oven temperature; 245^{o}C
Carrier gas; 30ml min^{-1}
Retention times; Ph_2SO_2 ca. 30 seconds
Ph_3PO ca. 2 minutes 10 seconds
Ph_3PS ca. 2 minutes 40 seconds

Ethyl diphenylphosphinothionate and ethyl diphenylphosphinate reaction mixture, (with diphenyl sulphone internal standard):

Column; 20", 10% UCW 982 (80-100 WAW DCMS B-8)
Oven temperature; 185^{o}C
Carrier gas; 45ml min^{-1}
Retention times; Ph_2SO_2 ca. 2 minutes
$Ph_2P(O)OEt$ ca. 2 minutes 30 seconds
$Ph_2P(S)OEt$ ca. 3 minutes 15 seconds

Diethyl phenylphosphonothionate and diethyl phenylphosphonate reaction mixture, (with di-t-butyl sulphone internal standard):

Column; 20",10% UCW 982 (80-100 WAW DCMS B-8)
Oven temperature; 140^{o}C
Carrier gas; 45ml min^{-1}
Retention times; $^{t}Bu_2SO_2$ ca. 45 seconds
$PhP(O)(OEt)_2$ ca. 2 minutes 10 seconds
$PhP(S)(OEt)_2$ ca. 2 minutes 50 seconds

Triethyl phosphorothionate and triethyl phosphate reaction mixture, (with dimethyl sulphone internal standard):

Column; 2m, 1.5% OV225

Oven temperature; 150°C

Carrier gas; 45ml min^{-1}

Retention times; $(EtO)_3PS$ ca. 1 minute 15 seconds

$(EtO)_3PO$ ca. 1 minute 35 seconds

Me_2SO_2 ca. 2 minutes 10 seconds

Diethyl S-methyl phosphorothioate, (with 1-bromodecane internal standard);

Column; 2m, 1.5% OV225

Oven temperature; 155°C

Carrier gas; 45ml min^{-1}

Retention times; 1-bromodecane ca. 1 minute 30 seconds

$(EtO)_2P(O)SMe$ ca. 2 minutes 50 seconds

Diethyl S-pentyl phosphorothioate, (with di-t-butyl sulphone internal standard):

Column; 2m 1.5% OV225

Oven temperature; 200°C

Carrier gas; 30ml min^{-1}

Retention times; ${}^tBu_2SO_2$ ca. 1 minute 20 seconds

$(EtO)_2P(O)S(CH_2)_4CH_3$ ca. 2 minutes 40 seconds

Parathion and paraoxon reaction mixture:

Column; 20", 10% UCW 982 (80-100 WAW DCMS B-8)

Oven temperature; 190°C

Carrier gas; 45ml min^{-1}

Retention times; Paraoxon ca. 2 minutes 10 seconds

Parathion ca. 2 minutes 50 seconds

Chlormephos:

Column; 2m, 1.5% OV225

Oven temperature; 175°C

Carrier gas; 30ml min^{-1}

Retention times; ca. 2 minutes 30 seconds

Tri-n-butylphosphine sulphide and tri-n-butylphosphine oxide reaction mixture, (with diphenyl sulphone internal standard):

Column; 20", 10% UCW 982 (80-100 WAW DCMS B-8)

Oven temperature; 160°C

Carrier gas; 30ml min^{-1}

Retention times; $^nBu_3PO$ ca. 3 minutes 50 seconds

$^nBu_3PS$ ca. 4 minutes 40 seconds

Ph_2SO_2 ca. 7 minutes

Diethyl methyl phosphate, (for diethyl phosphate):

Column; 2m, 10% SE30

Oven temperature; 140°C

Carrier gas; 30ml min^{-1}

Retention time; ca. 1 minute 30 seconds

Diethyl methyl phosphorothioate, (for diethyl phosphorothioic acid):

Column, oven temperature and carrier gas as for diethyl methyl phosphate;

Retention time; ca. 2 minutes 40 seconds

Pentanethiol:

Column; 2m, 10% SE30

Oven temperature; 95°C

Carrier gas 35ml min^{-1}

Retention time; ca. 1 minute 20 seconds

Benzoin:

Column; 20", 10% UCW 982 (80-100 WAW DCMS B-8)

Oven temperature; 200°C

Carrier gas; 45ml min^{-1}
Retention time; ca. 45 seconds.

Benzil:

Column; 20", 10% UCW 982 (80-100 WAW DCMS B-8)
Oven temperature; 185^{o}C
Carrier gas; 45ml min^{-1}
Retention time; ca. 1 minute 10 seconds

Acenaphthenequinone:

Column; 20", 10% UCW 982 (80-100 WAW DCMS B-8)
Oven temperature; 200^{o}C
Carrier gas; 45ml min^{-1}
Retention time; ca. 1 minute

p-Chloranil:

Column; 20", 10% UCW 982 (80-100 WAW DCMS B-8)
Oven temperature; 170^{o}C
Carrier gas; 30ml min^{-1}
Retention time; ca. 1 minute

Methyl pyruvate:

Column; 2m, 15% B.B. Oxydipropionitrile
Oven temperature; 95^{o}C
Carrier gas; 60ml min^{-1}
Retention time; ca. 12 minutes

t-Butyl pyruvate:

Column; 2m, 15% B.B. Oxydipropionitrile
Oven temperature; 95^{o}C
Carrier gas; 60ml min^{-1}
Retention time; ca. 11 minutes 45 seconds

Pyruvic acid:

This was detected and measured as methyl pyruvate after methylation with diazomethane.

1,8-Naphthalic anhydride:

Column, oven temperature and carrier gas as for acenaphthenequinone.

Retention time; ca. 1 minute 40 seconds

Benzoic anhydride:

Column; 20", 10% UCW 982 (80-100 WAW DCMS B-8)

Oven temperature; 175^{o}C

Carrier gas; 45ml min^{-1}

Retention time; ca. 3 minutes

In all cases, nitrogen was the carrier gas used.

Biacetyl:

This was determined by measuring its U.V. absorption at 419 nm.

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FIVE

GENERAL EXPERIMENTAL DETAILS

Proton nuclear magnetic resonance (100MHz ^{1}H n.m.r.) spectra were recorded on a Jeol 100MHz continuous wave instrument, as ca. 10% solutions. Tetramethylsilane (TMS) was used as the internal standard, its resonance being assigned a value of zero on the delta scale. 220MHz ^{1}H n.m.r. spectra were recorded at the Physico-Chemical Measurements Unit, Harwell.

^{13}C N.m.r. were recorded on a Jeol FX60 spectrometer operating at 15.00 MHz using a dual ^{13}C/^{1}H probe. TMS was used as internal standard with D_2O as external lock.

The ^{31}P n.m.r. spectra in chapter three were run in the Analytical section, C.D.E. Porton Down, on a Jeol FX60 spectrometer operating at 24.1 MHz. ^{31}P Data in chapter four was obtained on a spectrometer operating at 36.2MHz, courtesy of Professor McFarlane and Dr. Wood at City of London Polytechnic. In all cases the chemical shift are recorded in ppm relative to 85% H_3PO_4.

All infrared spectra were obtained using a Perkin Elmer 157G infrared spectrophotometer.

Ultraviolet spectra were recorded on either a Perkin Elmer 402 U.V. spectrophotometer or (for solvent isotope measurements) on a Cecil CE 272 U.V. spectrophotometer.

Mass spectra were recorded on a Kratos MS 30 mass spectrometer, with sample introduction via either a probe or GCMS interface.

Gas liquid chromatography data were obtained on a Perkin Elmer Sigma 3 Gas Chromatograph (F.I.D.), with a Pye Unicam DP 88 integrator.

Melting point data was determined using a Gallenkamp melting point apparatus, and are reported uncorrected.

In experiments requiring the use of ultrasound, a Dawe Sonicleaner (Type 6453A) sonic bath was used.

Dry benzene and diethyl ether were obtained by standing over sodium wire. Dichloromethane was predried over P_2O_5 and distilled before use. Tetrahydrofuran was distilled from lithium aluminium hydride and collected at 63-65^{o}C. Analytical reagent (A.R.) grade solvents were used in all photolysis experiments.

Preparative t.l.c. plates were prepared using Kieselgel 60 GF 254, Art 7730 (Merck). A slurry of 130g silica in 240ml distilled water was spread on five 20 x 20cm plates to give a film of ca. 1mm thickness. The plates were backed at 120^{o}C overnight and storred in a dry atmosphere. For column chromatography, either Kieselgel 60, Art 9385 (Merck), {gravity chromatography}, or Kieselgel 60H, Art 7736 (Merck), {flash chromatography}[1] was used. Analytical t.l.c. plates were prepared using Kieselgel 60G, Art 7731 (Merck). Here plates were obtained by spreading a slurry of 30g silica and 65ml distilled water over 60 2 x 10cm microscope slides, and left to dry overnight at room temperature. Compounds were visualized on analytical t.l.c. plates by either U.V. light (254nm, 375nm), by iodine vapour absorption, or by use of any of the following spray reagents;

(i) $[PdCl_4]^{2-}$, (0.5% $^w/v$ $PdCl_2$ and 0.7% $^v/v$ HCl in water; shows P-SR and P=S as yellow/orange/black/pink spots).

(ii) 'CO', (0.7g $CO(NO_3)_2 \cdot 6H_2O$ + 4.5g NH_3SCN in ethanol (80ml)-water (20ml); shows most tetracoordinate O.P's as white on blue or blue on blue).

(iii)Ninhydrin, (0.3% ninhydrin in ethanol; shows phosphorus acids and phosphorus chloridates as pink on white blackground.

(iv) Bromocresol green, (shows many O.P's as yellow on blue).

Dry, carbon dioxide free oxygen as used in all photooxidation experiments was obtained by flushing a stream of oxygen through a saturated barium hydroxide solution, and then passing the gas over molecular sives (3A and 4A).

Preparation of diazomethane.

Diazomethane was used to methylate phosphorus acids and carboxylic acids prior to g.l.c. analysis. The quantities given represent a typical preparation.

Potassium hydroxide (0.96g) was dissolved in water (1.94ml) and added to ice cold diethyl ether (7ml). To this stirred solution, N,N-nitrosomethyl urea (0.0058 mol, 0.6g) was added in small portions over 15 minutes, with ice-bath cooling throughout. Ten minutes after addition was complete, the resultant yellow solution was decanted onto potassium hydroxide (0.5g), and left for a further 15-20 minutes. After decanting into a second flask, the etheral diazomethane solution was now ready for use.

Preparation of N,N-nitrosomethyl urea.

This was prepared using the procedure of Arndt,[2] with the exception that a 40% aqueous methylamine solution (120g) was used. Cooling of the reaction mixture was achieved using an ice-acetone bath. The yield was 130g (82%).

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