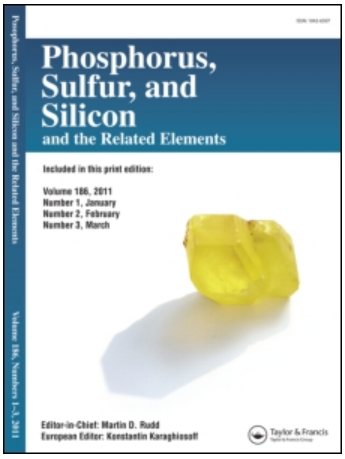

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The Photooxidation of Some Anthryl Phosphorus Compounds

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THE PHOTOOXIDATION OF SOME ANTHRYL PHOSPHORUS COMPOUNDS

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Abstract The photo-oxidation of anthryl phosphorus compounds occurs 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.

There have been many examples reported in the literature on the photo-oxidation of anthracene and its alkyl derivatives.[1-3] However, no work has been published on the photo-oxidation of anthryl phosphorus compounds. Such a study has now been carried out, and the preliminary results are reported herein. The work involved the direct (λ = 350nm radiation) and indirect (λ > 480nm radiation, Rose Bengal sensitized) photo-oxidation of an anthryl phosphate (1a), an anthrylmethylphosphonate (1b), and some anthrylmethylphosphonium salts (1c, 1d, & 1e), whilst paying particular attention to the fate of the phosphorus moiety.

As with anthracene and its alkyl derivatives, the photo-oxidation of these anthryl phosphorus compounds occurs via a Type II mechanism. This involves a 1,4-cycloaddition reaction between the anthracene nucleus and singlet oxygen ($^1O_2$) - singlet oxygen being photo-chemically generated in situ from ground state oxygen ($^3O_2$) - to give a 9,10-endoperoxide.

It is found that with compounds 1a-e, direct irradiation and the dye sensitized reactions of 1a, 1d, and 1e result in the fragmentation of the endoperoxide to give 9,10-anthraquinone (Tables I and II respectively). Anthraquinone is the only anthryl type photo-oxidation product observed. At the same time, cleavage of the

phosphorus moiety from the anthracene nucleus occurs (Scheme 1).

In the case of the phosphonium salts, trapping experiments have shown this cleaved phosphorus species to be an ylid, (Eq 1 and Table III). In the absence of any trapping agent, the ylid

$$^{-}CH_2\overset{+}{P}Ph_3 + CH_3(CH_2)_4CHO \longrightarrow Ph_3PO + CH_3(CH_2)_4CH{=}CH_2 \qquad \text{(Eq 1)}$$

will react with a further molecule of oxygen to form the phosphine oxide, 8, which is the only phosphorus bearing product observed from the photolysis. The formation of benzaldehyde, 10, and benzoic acid, 11, from the photolysis of 1e, is also indicative of a mechanism involving an ylid intermediate.

TABLE I Percentage yields of products obtained from the direct photo-oxidation of 1a-e.

% yields of / Substituent, R	Anthraquinone 3	$(EtO)_2$/ P(O)OH 4	$(EtO)_2$/ $P(O)CH_3$ 6	Ph_3PO 8	PhCHO 10	$PhCO_2H$ 11
1a, $OP(O)(OEt)_2$	46	84				
1b, $CH_2P(O)(OEt)_2$	76		75			
1c, $CH_2\overset{+}{P}Ph_3\ Br^-$	78			85		
1d, $CH_2\overset{+}{P}Ph_3\ ClO_4^-$	98			95		
1e, $PhCH\overset{+}{P}Ph_3\ Cl^-$	70			80	19	42

TABLE II Percentage yields of products obtained from the sensitized photo-oxidation of 1a-e.

% yields of / Substituent, R	Anthraquinone 3	$(EtO)_2$/ P(O)OH 4	$(EtO)_2$/ $P(O)CH_3$ 6	Ph_3PO 8	PhCHO 10	$PhCO_2H$ 11
1a, $OP(O)(OEt)_2$	95	87				
1b, $CH_2P(O)(OEt)_2$	0		0			
1c, $CH_2\overset{+}{P}Ph_3\ Br^-$	0			0		
1d, $CH_2\overset{+}{P}Ph_3\ ClO_4^-$	95			97		
1e, $PhCH\overset{+}{P}Ph_3\ Cl^-$	59			61	49	< 5

The phosphonate 1b, gives on direct irradiation the methylphosphonate, 6, and not diethyl phosphate, 4. This is consistent with the earlier observation that a methylene ylid, such as 5, does not undergo the Wadsworth-Emmons reaction with carbonyl

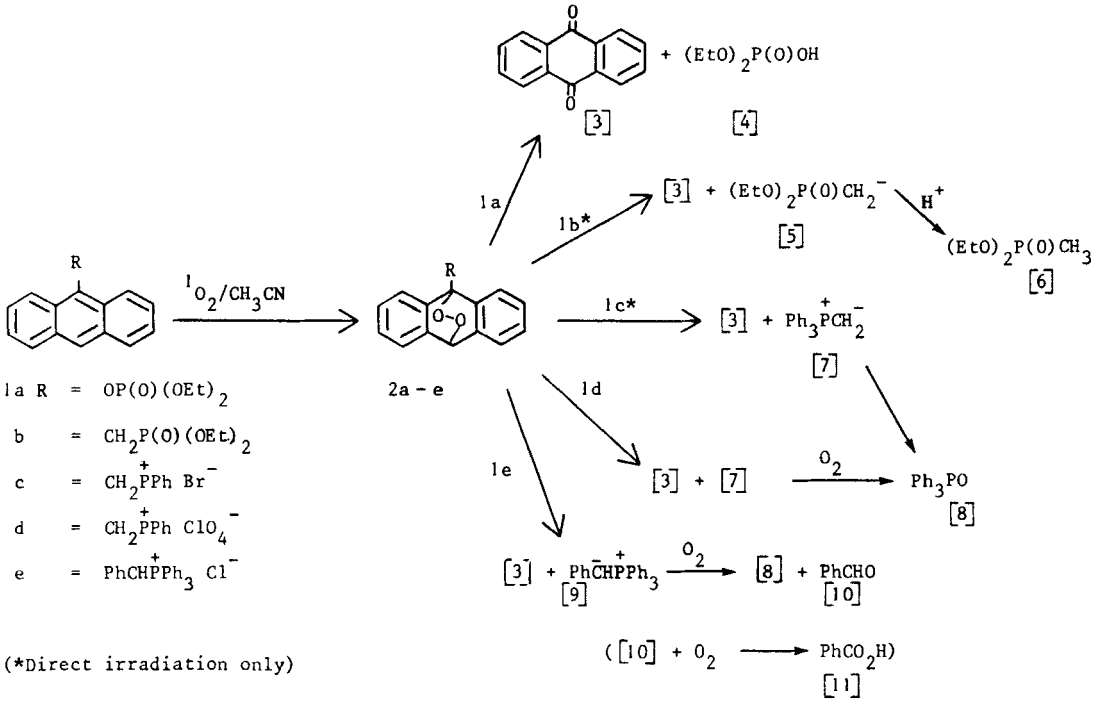
TABLE III Percentage yields of heptene obtained from the direct photo-oxidation of 1c and 1d when carried out in the presence of hexaldehyde.

Substituent, R	% yield of $CH_3(CH_2)_4CH{=}CH_2$
1c, $CH_2\overset{+}{P}Ph_3\ Br^-$	23
1d, $CH_2\overset{+}{P}Ph_3\ ClO_4^-$	35

compounds,[4] and hence would not be expected to react with oxygen. Its sensitized photolysis gives the endoperoxide, 2b, which is stable at room temperature and can be isolated in good yield (75%).

The direct irradiation of 2b under argon produces 3 and 6 in 90% and 76% yield respectively, giving further evidence for the participation of a similar endoperoxide intermediate under the two different photo-oxidation conditions.

SCHEME 1



The direct irradiation of 1c gives the expected products, 3 and 8, via 2c. Similarly, the sensitized photo-oxidation of 1c gives 2c, but in this case the endoperoxide does not fragment to 3 and 8. Instead, the endoperoxide, which is unstable at room temperature and cannot be isolated, reacts to give a complex mixture composed of at least five different phosphorus containing products. While the structures of these species have yet to be determined, it is clear that on sensitized irradiation, a different mechanism is involved for the reaction of the endoperoxide 2c to that given in Scheme 1.

In conclusion, it can be seen that the photo-oxidation of certain anthryl phosphorus compounds results in the cleavage of the phosphorus moiety from the anthracene nucleus. Therein exists the potential for the anthracene nucleus to be used as a protecting group at phosphorus, with subsequent deprotection being carried out photo-chemically.

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