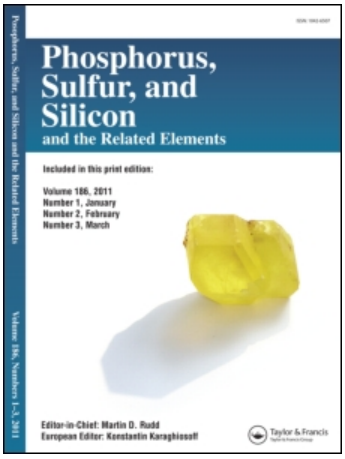

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PERACID AND ACYL PEROXY RADICAL MEDIATED OXIDATION AND REARRANGEMENT OF PHOSPHORAMIDES

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Abstract Acyl peroxy radicals can cause oxidation of sulphur at pentavalent phosphorus and can also affect the decomposition of phosphoramides. Peracids can also oxidise thiophosphorus compounds to their respective oxidised phosphorus analogues and oxidise phosphoramides via N-oxidation.

1. REACTION OF ORGANOPHOSPHORUS COMPOUNDS WITH PHOTOCHEMICALLY GENERATED ACYL PEROXY OR PEROXY RADICALS

It has previously been reported[1] that 1,2-dicarbonyl compounds, some quinones and benzoin can sensitise the photooxidation of sulphur at pentacovalent phosphorus. Results are shown with benzil as the photosensitiser.

By way of contrast, irradiation of solutions of diethyl,N,N-dialkyl thiophosphoramides containing sensitisers such as benzoin and 1,2-diketones led to little or no phosphoramide product, with only the diethyl,N,N-diisopropylthiophosphoramide giving a reasonable yield (8%) of phosphoramide.

This result indicates that the phosphoramides produced are themselves susceptible to oxidation. This was shown to be the case (Table I).

TABLE I Photolysis of phosphoramides using benzoin sensitiser(b)

Phosphoramide	No. equivs. benzoin added	Starting material remaining (%)
$(EtO)_2P(O)NMe_2$	2	0
$(EtO)_2P(O)NEt_2$	2	6
$(EtO)_2P(O)NHex_2$	2	17
$(EtO)_2P(O)N^iPr_2$	2	72

(b) irradiated in acetonitrile solution under oxygen using black light fluorescent lamps (λ_{max} = 350 nm) for 20 hours.

If the irradiation of the thiophosphoramides is carried out to low conversion, phosphoramides can be seen to be produced but they never accumulate in large quantities. It has under the conditions used in Table I, the complete decomposition of diethyl,N,N-dimethylthiophosphoramide takes about three and a half hours compared to about seven hours for the analogous phosphoramide. This leads to the proposed reaction scheme:

$$(EtO)_2P(S)NR_2 \xrightarrow{(a)} \text{products}$$
$$\downarrow (b)$$
$$(EtO)_2P(O)NR_2 \xrightarrow{(c)} \text{products}$$

Reaction (a) is normally the major reaction route and the rate of reaction of (a) is greater than the rate of reaction (c). However, for the sterically hindered diisopropylamino compound it is found that the rate of reactions of the thiophosphoramide and phosphoramide, i.e. steps (a) and (c), are relatively slow. In this case the oxidative desulphurisation step (i.e. (b)) becomes more important and much higher concentrations of phosphoramide can be observed during the reaction. The lower reactivity of the di-isopropylamine compound compared with the dimethylamino compound may be due to a combination of factors, e.g. the diisopropylamine compound contains two α-carbon-hydrogen bonds compared with six for the dimethylamino compound and tertiary amines are known to react with radicals via α-hydrogen abstraction;[4] also stabilisation of incipient radical by nitrogen would be less favourable in the di-isopropylamino compound due to steric inhibition of resonance. This rationalisation has been applied to many one electron oxidations of alkylamines.[5]

The photooxidation of the phosphoramides does not appear to follow the same course as the peracid mediated reactions of phosphoramides since no evidence could be found for the production of the phosphorus substituted hydroxylamines (see Section 2). These hydroxylamine products can be seen by ^1H n.m.r. if present. No trace of aldehydes or carboxylic acids derived from the N-alkyl groups were detected. A trace of diethylphosphonate was detected, after methylation of the photolysed mixture with diazomethane, indicating diethylphosphate may be a reaction product.

2. PERACID MEDIATED OXIDATION OF ORGANOPHOSPHOROUS COMPOUNDS

The oxidation of thiophosphorus compounds and phosphoramides by peracids has previously been reported.[6,7] Some of the results we have obtained using m-chloroperbenzoic acid (MCPBA) are shown in Tables II and III.

TABLE II Oxidation of thiophosphorus compounds by m-chloroperbenzoic acid(c)

Thiophosphorus compound $R_3P=S$	No equivs. MCPBA added	% s.m. remaining after 20 hours	% $R_3P=O$ product after 20 hours
$Ph_3P=S$	2	0	100
$(EtO)_3P=S$	2	0	100
$(EtO)_2P(S)NMe_2$	2	0	35
$(EtO)_2P(S)NEt_2$	2	0	43
$(EtO)_2P(S)NHex_2$	2	0	50
$(EtO)_2P(S)N^iPr_2$	2	6	90

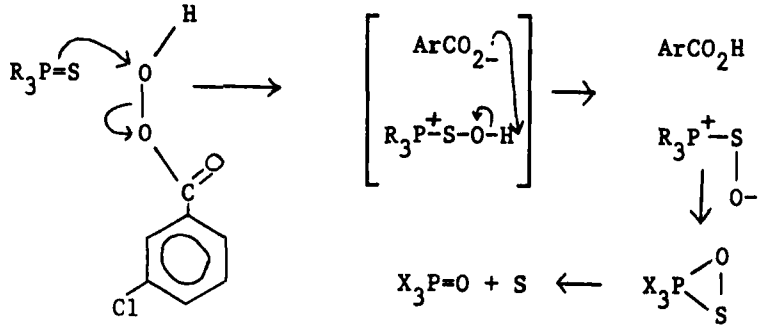
TABLE III Oxidation of phosphoramides by m-chloroperbenzoic acid(c)

Phosphoramides	No equivs. MCPBA added	% s.m. remaining after 20 hours
$(EtO)_2P(O)NMe_2$	2	45
$(EtO)_2P(O)NEt_2$	2	52
$(EtO)_2P(O)NHex_2$	2	61
$(EtO)_2P(O)NiPr_2$	2	90

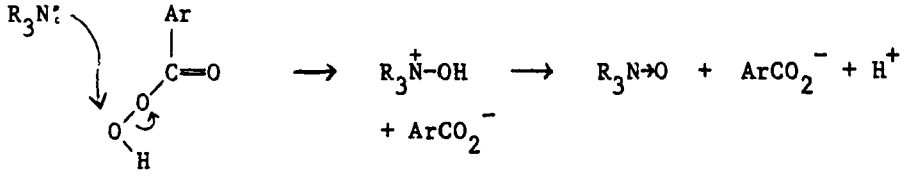
(c) 2 equivalents of MCPBA added to a stirred solution of phosphorus compounds in dichloromethane.

In the oxidation of the thiophosphorus compounds, the extruded sulphur was deposited as a yellow precipitate. Amongst the products detected by us and other workers[7] in the oxidation of the phosphoramides were the aldehydes and carboxylic acids derived from the alkyl group attached to the nitrogen. Diethylphosphate was detected as its methyl ester, after methylation with diazomethane followed by gas-liquid chromatograph analysis. When the diethyl,N,N-dimethylphosphoramide is used the formation of trans-nitrosomethane dimer was detected (by ^1H n.m.r.)

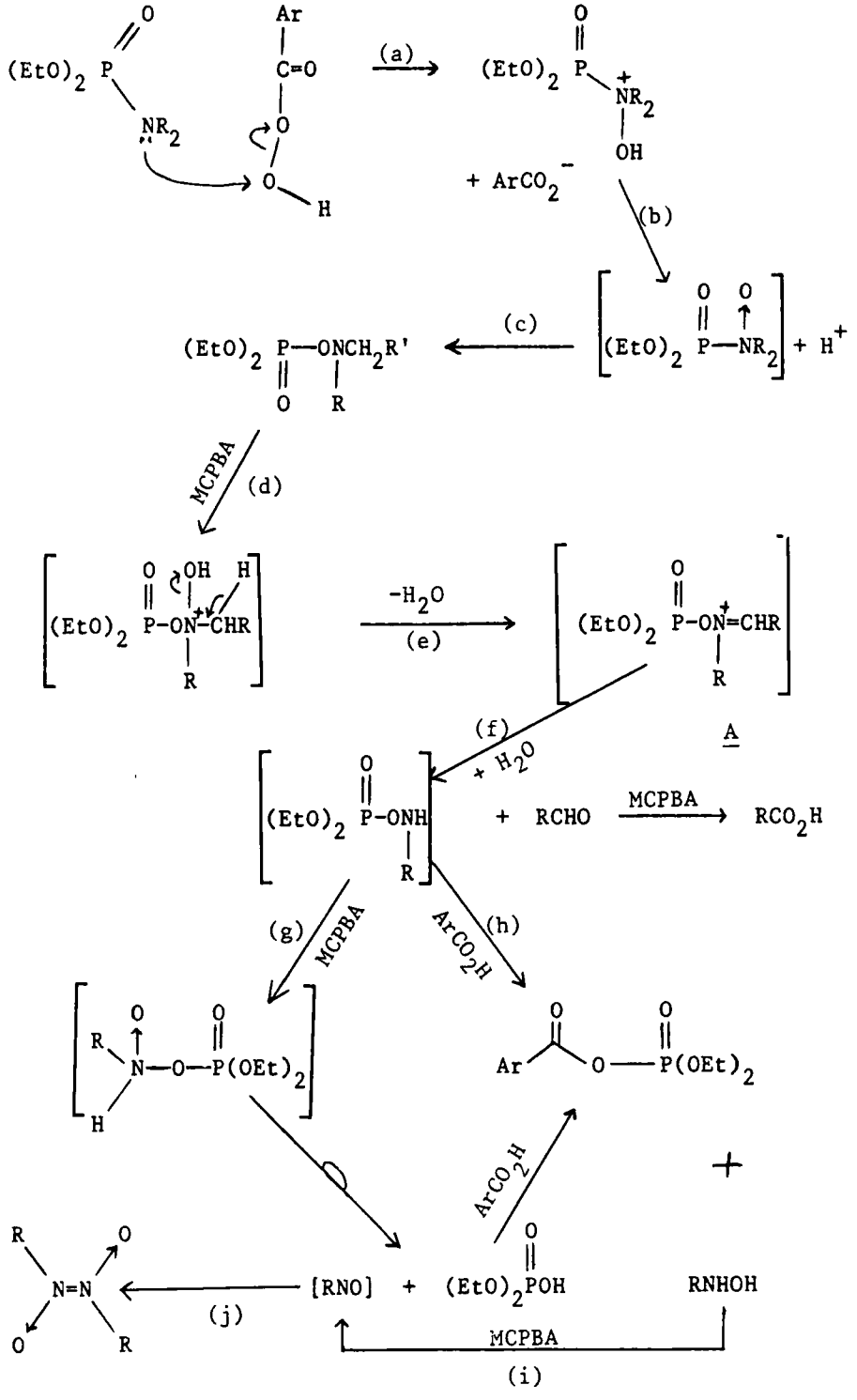
The mechanism of oxidative desulphurisation can be postulated as follows:



An alternative role for peracid is to oxidise the amino group as originally by Y. Segall and J. Casida[7]. This involves nucleophilic attack on a peroxy compound by the amino group, i.e. the mechanism analogous to that accepted for conversion of amines to N-oxides.



For this reaction to be successful the oxidising agent must possess a good leaving group like a carboxylate or an alkoxy anion. This mechanism also shows why it is necessary for the oxidant to possess an acidic hydrogen since collapse to the N-oxide requires proton removal from the $R_3\overset{+}{N}$-OH species. This explains why at low temperatures di-t-butylperoxide does not react. Of particular interest is the fact that the amino group of phosphoramides can act as a nucleophile, when this is not the case for the amino group of carboxamides. This is presumably due to the poor overlap of the non-bonding electrons on the nitrogen atom with the d_π-p_π orbitals of the P=O bond. Our results are best interpreted by the mechanism put forward by Y. Segal and J. Casida.



Steps (c), (g), (h), (i) and (j) have already been proposed for the oxidation of diethyl,N,N-dimethylphosphoramide by MCPBA[7]. Analogous steps to (d), (e) and (f) are known in the peroxidation of tertiary amines[10]. We found that the N-alkyl group is oxidised to the aldehyde and carboxylic acid suggesting the participation of iminium species (A).

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