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THE OXIDATION OF TRIVALENT PHOSPHORUS ESTERS BY DIMETHYLAMINO RADICALS

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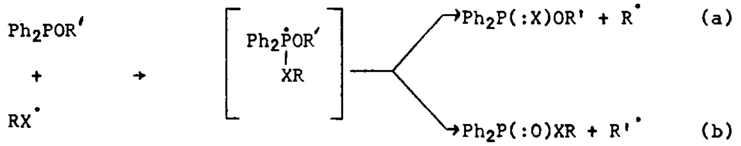
Alkoxy (1,2), peroxy (1,2) and thioalkyl (1,2,3) radicals are known to oxidise trivalent phosphorus esters.



(X = O or S)

Although in principle either reaction (a or b) can occur, the one leading to the radical R• (reaction a) is the most frequently encountered. It has been found that dimethylamino radicals oxidise trivalent phosphorus esters with the formation of alkyl radicals derived from the latter.

Irradiation (4) of a benzene solution of methyl diphenylphosphinite containing less than half a mole equivalent of tetramethyltetrazen (5) gave a high yield of methyldiphenylphosphine oxide as well as some of the expected product, NN-dimethyldiphenylphosphinic amide. A similar result was obtained with ethyl diphenylphosphinite (see Table).

An explanation for the formation of alkyldiphenylphosphine oxide is that the alkyl radical, initially produced by attack of a dimethylamino radical upon the phosphorus ester, reacts (6) with unreacted phosphorus ester giving another alkyl radical. In this manner a chain reaction is initiated

$$Me_2N^{\bullet} + Ph_2POMe \rightarrow Ph_2P(:O)NMe_2 + Me^{\bullet}$$

$$Me^{\bullet} + Ph_2POMe \rightarrow Ph_2P(:O)Me + Me^{\bullet}$$

TABLE

Products from Reaction of Alkyl Diphenylphosphinites with Dimethylamino Radicals

Phosphinite	No. of mole equivalents of tetrazen	No. of mole equivalents of Me_2NH added	Yield of NN-dimethyl-diphenylphosphinic amide	Alkyldiphenyl-phosphine oxide formed	(%)
Ph_2POMe	.34	-	32	$Ph_2P(:O)Me$	(68)
Ph_2POMe	2	-	40.5	$Ph_2P(:O)Me$	(59.5)
Ph_2POMe	2	16.5	65	$Ph_2P(:O)Me$	(35)
Ph_2POEt	.34	-	35	$Ph_2P(:O)Et$	(65)
Ph_2POEt	2	-	55	$Ph_2P(:O)Et$	(43)
Ph_2POEt	2	16.5	67	$Ph_2P(:O)Et$	(33)

The yields of products were determined by proton magnetic resonance spectroscopy and were calculated by taking into account the amount of unchanged phosphinite.

In order to suppress the chain reaction, the amount of tetrazen in the reaction mixture was increased. By this means, a higher concentration of dimethylamino radicals should be obtained, which was expected to facilitate attack upon the phosphorus by these radicals. Furthermore it was expected that dimethylamine, formed by disproportionation of the excess dimethylamino radicals, would act as an efficient scavenger for alkyl radicals and in so doing would act as another source of dimethylamino radicals.

$$Me^{\bullet} + Me_2NH \rightarrow MeH + Me_2N^{\bullet}$$

Secondary amines are known (7) to be particularly reactive towards alkyl radicals. Increased tetrazen concentration did result in a higher yield of the amide and lower yield of alkyldiphenylphosphine oxide. The addition of dimethylamine further increased the yield of amide.

The addition of dimethylamine to the reaction mixture is essential if good yields of the hydrocarbon derived from the phosphorus ester, are to be obtained. The yield of cyclohexane from cyclohexyldiphenylphosphinite plus 2 molar equivalents of tetramethyltetrazen in the presence (16.5 molar equivalents) and absence of dimethylamine was 68 and 21%. n-Octyl diphenylphosphinite gave, in the presence of dimethylamine, a 55% yield of n-octane. NN-dimethyldiphenylphosphinic amide was formed in the reactions with both these phosphinite esters and also in reactions with crotyl, cinnamyl and bornyl diphenylphosphinites.

The scope of the reaction as a means of accomplishing the conversion ROH to RH is being investigated.

REFERENCES AND FOOTNOTES

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