The Mechanism of Chlorination of Phosphorus Esters

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THE esters of quinquivalent phosphorus react with a variety of chlorinating agents such as thionyl chloride, phosphorus pentachloride, and carbonyl chloride, to give the corresponding phosphoryl chlorides. It has been suggested[1] that the reaction of phosphoryl esters with carbonyl chloride involves initial nucleophilic attack by the phosphoryl-oxygen atom at the electrophilic centre.

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[1] J. I. Cadogan, *J. Chem. Soc.*, 1961, 3067.

A detailed study[2] of the reaction of benzyl methylphenyl [^{18}O]phosphinate with carbonyl chloride showed this to be correct; the results also excluded the formation of intermediates in which the alkoxy- and phosphoryl-oxygens became equivalent. A more extensive study with the chlorinating agents oxalyl chloride, thionyl chloride, and phosphorus pentachloride and phosphorus esters of differing reactivity shows that this type of reaction can be mechanistically more complex.

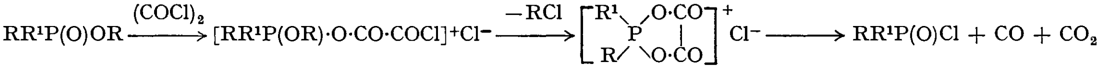
TABLE

Ester	*Chlorinating Agents* Phosphorus Pentachloride	Oxalyl chloride	Thionyl chloride
Benzyl methylphenyl [^{18}O]phosphinate	0·37	0·25	0·41
Benzyl neopentyl methyl [^{18}O]phosphonate	0·29	0·29	0·39
Benzyl diphenyl [^{18}O]phosphate	0·25	0·34	0·45

The esters benzyl methylphenyl [^{18}O]phosphinate, benzyl neopentyl methyl [^{18}O]phosphonate, and benzyl diphenyl [^{18}O]phosphate were prepared by reaction of the corresponding phosphoryl chlorides with benzyl [^{18}O]alcohol (0·90 atom % of ^{18}O) and a tertiary base. The chlorinating agents, oxalyl chloride, thionyl chloride, and phosphorus pentachloride, all reacted with these esters to give benzyl chloride and the corresponding phosphoryl chloride. The ^{18}O content of the phosphoryl chlorides was estimated[2,3] by hydrolysis to the acid, conversion to di-*p*-tolylurea and mass-spectroscopic estimation of the ^{18}O content of the carbon dioxide obtained on pyrolysis of the urea. These results are listed in the Table. Since one-half of the ^{18}O content of the phosphoryl chloride is lost on hydrolysis the maximum observable value for the ^{18}O content of the phosphorus acids assuming phosphoryl-oxygen attack on the chlorinating agents and no scrambling of the phosphoryl- and alkoxy-oxygens, is 0·45 atom % of ^{18}O.

The reactions with thionyl chloride clearly proceed *via* initial phosphoryl-oxygen attack without the intermediacy of symmetrical intermediates. It is of particular interest that although the reactivity of the phosphoryl-oxygen atom in esters decreases in the order phosphinate > phosphonate > phosphate, the phosphoryl-oxygen atom of the phosphate is still more nucleophilic than the alkoxy-oxygen atom.

The most satisfactory interpretation of the results obtained with oxalyl chloride and phosphorus pentachloride is that reaction paths involving symmetrical intermediates are important, *e.g.*,



(I)

$$RR^1P(O)OR \xrightarrow{PCl_5} [RR^1P(OR)O{\cdot}PCl_4]^+Cl^- \xrightarrow{-RCl} RR^1P(O)OPCl_4 \rightleftharpoons$$
$$RR^1P(O)O^-PCl_4^+ \longrightarrow RR^1P(O)Cl + POCl_3$$

(II)

The contrasting results obtained with oxalyl chloride and phosphorus pentachloride show that the same type of symmetrical intermediate cannot be involved in both reactions. It is suggested that a reaction path involving a five-membered cyclic intermediate (I) is of importance in the reaction with oxalyl chloride, whereas the ion-pair (II) is involved in the phosphorus pentachloride reactions. The formation of a cyclic intermediate would be assisted by electron release to the phosphorus atom, whereas ionisation of the oxygen-phosphorus bond in (II) would be enhanced by electron-withdrawing groups. These trends are in agreement with the experimental results.

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[2] M. Green and R. F. Hudson, *J. Chem. Soc.*, 1963, 1004.
[3] M. Halmann, *J. Chem. Soc.*, 1959, 305.