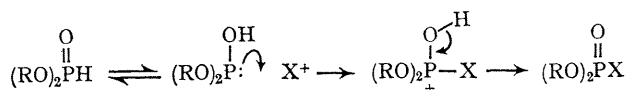


Electrophilic Substitution at Phosphorus: Dealkylation and Decarboxylation of Phosphinylformate Esters

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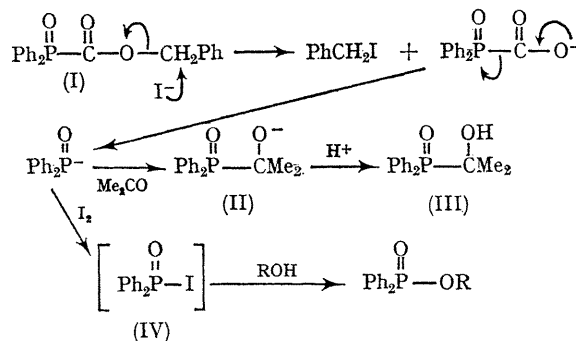
ELECTROPHILIC SUBSTITUTION at the tetra-co-ordinated phosphorus atom ($S_E P-4$) is a familiar reaction when the leaving group is a proton;¹ the base-catalysed addition reactions of dialkyl phosphite anions form a synthetically useful, if mechanistically straightforward, group of examples.² The proton is an unsatisfactory leaving group (or electrophile) even in the absence of base catalysis because the "tautomerism mechanism"¹ becomes important:



In fact, the proton is featured, either as leaving group or electrophile, in almost all $S_E P-4$ reactions except phosphorus 1,2-migrations.^{1,3} These *intramolecular* reactions might be used to establish structure-reactivity correlations (the object of our work) but they suffer from the complication of a three-membered cyclic transition state. We now report an *intermolecular* $S_E P-4$ reaction in which one C-P bond is replaced by another: both the electrophilic and the electrofugal centres are carbon atoms.

The reaction of iodide ion in acetone with the benzyl ester of diphenylphosphinylformate (I) gives the acetone adduct (III) of the debenzylated and decarboxylated ester in 75% yield. The reaction occurs with other carbonyl compounds (acetaldehyde, acetophenone). In the strict absence of protic solvents, the sodium salt of the product (II) can be isolated, but the reaction appears to be cleaner and faster if acetic acid (1 mol.) is added.

Iodine is also effective as the electrophile and then only a catalytic amount of sodium iodide is needed. A phosphinylating agent [presumably diphenylphosphinoiodate, (IV)] is formed, which reacts with water to give diphenyl phosphinic acid (70%) or with methanol to give methyl diphenyl phosphinate.



Three processes—debenzylation by iodide ion, decarboxylation, and attack by the electrophile on the phosphorus atom—must occur. We have represented them separately, but any or all of them may be concerted. We are investigating this point.

All compounds had satisfactory m.p.s and spectra; the mass spectra will be reported elsewhere.

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¹ S. G. Warren, *Angew. Chem. Internat. Edn.*, 1968, 7, 606, and references therein.

² R. F. Hudson, "Structure and Mechanism in Organo-Phosphorus Chemistry," Academic Press, London, 1965, pp. 131—203; A. J. Kirby and S. G. Warren, "The Organic Chemistry of Phosphorus," Elsevier, Amsterdam, 1967; K. Sasse, "Methoden der Organischen Chemie (Houben-Weyl)" vol. 12, Phosphororganische Verbindungen, part 2, pp. 39 *et seq.*

³ M. Sprecher and E. Nativ, *Tetrahedron Letters*, 1968, 4405.