

Direct Formation of Trialkyl Phosphites from Elemental Phosphorus

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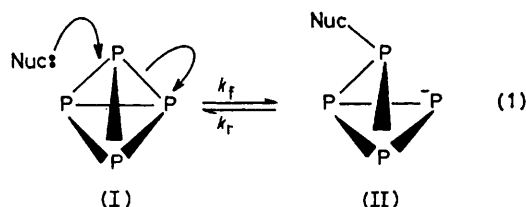
Summary Trialkyl phosphites can be prepared in high yield by direct reaction of alkoxide ion with elemental phosphorus in the presence of tetrachloromethane.

THE chemistry of elemental phosphorus has intrigued man for many years,¹ and the demand for organophosphorus compounds has prompted investigations² into the direct

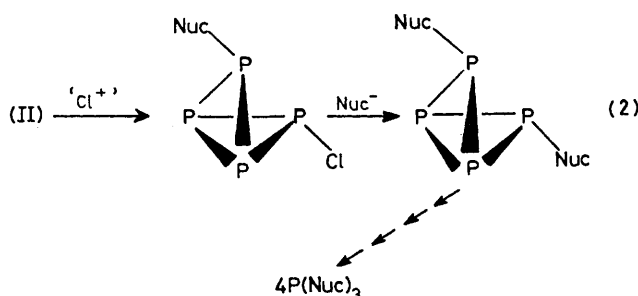
conversion of the element into useful derivatives as an alternative to the most widely used routes *via* the halides and oxides of phosphorus. In particular, the reactions of phosphorus with organometallic reagents³ and with alkyl halides⁴ have received considerable attention as a potentially useful route to compounds containing P-C bonds. Reactions leading to compounds with P-O-C bonds are less well understood,⁵ and are generally of little synthetic utility.†

† See, however, the work of M. L. Ernsberger and J. W. Hull, U.S.P. 2,661,364/1953 (*Chem. Abs.*, 1955, 49, 1774a).

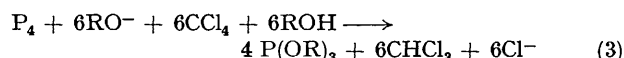
We report here a simple, high-yield conversion of elemental phosphorus into trialkyl phosphites using relatively mild conditions and readily available starting materials. The synthesis is based on two basic principles, both having their origin in the 'small-ring effect'.⁶ First, the phosphorus atoms in the white phosphorus P₄ tetrahedron are only very weakly nucleophilic, but the phosphorus atoms in partially opened structures become increasingly nucleophilic as ring-strain is reduced. Secondly, owing to ring-strain and to the weakness of the P-P bond, the P₄ phosphorus atoms are strongly *electrophilic*. However, nucleophilic attack on phosphorus produces phosphide anion, a very strong nucleophile. The back reaction (*k_r*) in equation (1) will therefore generally be fast relative to the forward reaction for all but the very strongest nucleophiles[†] (*e.g.* carbanions) unless the anion (II) can be intercepted in some way.



This has been achieved, for example, with $\alpha\beta$ -unsaturated compounds,⁷ again to give P-C bonds. However, if advantage were to be taken of the 'soft' nature of phosphorus nucleophiles,⁸ the anion (II) might be trapped by positive halogen, effectively converting a *nucleophilic* phosphorus centre into an *electrophilic* one. Replacement of the halogen atom by a second nucleophile and repetition of this sequence would convert (II) into (Nuc)₃P [equation (2)]

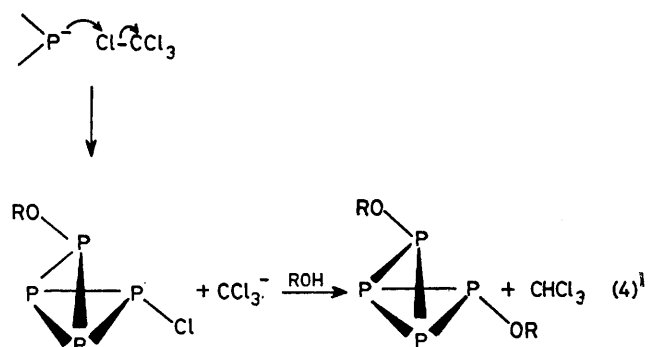


We have successfully applied this concept using tetrachloromethane as the positive chlorine source and finely divided phosphorus[§] in the presence of a two-fold excess of alkoxide [equation (3)]. Results are in the Table. Sodium

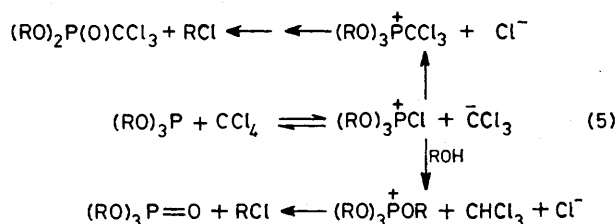


phenoxide failed to react under these conditions.

No intermediates were detected by ³¹P-¹H Fourier transform n.m.r. analysis, and hence the initial cleavage of the P-P bond [equation (1), Nuc=OR], appears to be rate determining. This is followed by rapid reaction between the phosphide ion and tetrachloromethane [equation (4)].



The production of chloroform (entries 1-4 in the Table) in excess of that given by equation (3) is explained by the reaction of trialkyl phosphite with tetrachloromethane [equation (5)].⁹ Lower yields of chloroform are produced



when the concentration of tetrachloromethane is considerably reduced (compare entries 5 and 6).

TABLE. Products of the reaction between sodium alkoxides (NaOR) and white phosphorus in alcohol-containing tetrachloromethane^a at room temperature

Entry	R	RO ⁻ /mol	ROH/mol	P ₄ /mol	Reaction time/h	CHCl ₃ ^c	Yields/% ^b		
							(RO) ₃ P	(RO) ₃ P(O)	(RO) ₂ P(O)H
1	Me	0.124	1.250	0.010	1	100	82	—	—
2	Me	0.124	1.250	0.010	3	116	74	7	11
3	Me	0.124	1.250	0.010	24	125	39	36	6
4	Et	0.120	1.250	0.008	1	104	76	7	—
5d	Bu ⁿ	0.120	1.00	0.009	3	48	58	0	0
6	Bu ⁿ	0.06	0.75	0.009	3	80	49	19	7

^a Unless otherwise stated, tetrachloromethane was in large excess (*ca.* 30-70 ml). ^b G.l.c. analysis using n-dodecane as internal standard. Confirmed by ³¹P and ³¹P-¹H n.m.r. spectroscopy. ^c Based on [P₄] using equation (3). ^d 0.084 mol of CCl₄ in BuⁿO (25 ml).

[†] These will normally be very poor leaving groups also.

[§] Prepared by rapidly chilling a vigorously stirred suspension of molten phosphorus.

Some decomposition to dialkylphosphonate is observed, but this is negligible for reactions carried out with an excess of alkoxide, except at long reaction times.

Initial results for other nucleophiles such as thiolate ions and amines indicate that the process may be a general one.

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¹ R. Boyle, 'New Experiments and Observations Made Upon the Icy Noctiluca,' London, 1681.

² M. M. Rauhut, 'Topics in Phosphorus Chemistry,' Eds. M. Grayson and E. J. Griffith, Interscience, New York, 1964; L. Maier, *Fortschr. Chem. Forsch.*, 1971, **19**, 1; H. Staendeke, *Chem.-Zt.*, 1972, **96**, 494.

³ M. M. Rauhut and A. M. Semsel, *J. Org. Chem.*, 1963, **28**, 471, 473.

⁴ L. Maier, *Helv. Chim. Acta*, 1966, **49**, 2458.

⁵ C. Walling, F. R. Stacey, S. E. Jamison, and E. S. Huyser, *J. Amer. Chem. Soc.*, 1958, **80**, 4543, 4546; R. W. Cummins, *Chem. and Ind.*, 1967, 918.

⁶ R. F. Hudson and C. Brown, *Accounts Chem. Res.*, 1972, **5**, 204.

⁷ M. M. Rauhut, R. Bernheimer, and A. M. Semsel, *J. Org. Chem.*, 1963, **28**, 478.

⁸ R. G. Pearson and J. Songstad, *J. Amer. Chem. Soc.*, 1967, **89**, 1827.

⁹ A. J. Burn and J. I. G. Cadogan, *J. Chem. Soc.*, 1963, 5788.