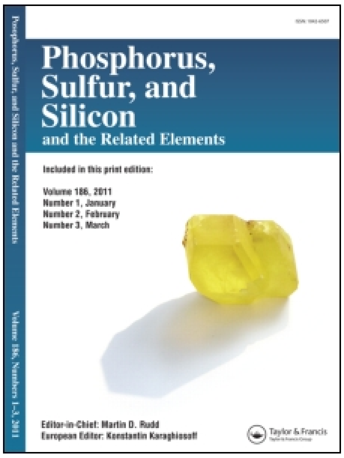

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SHORT COMMUNICATION

Protonation and Phosphorus–Oxygen Cleavage of Phosphorus(III) Esters by Hydrogen Chloride

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The formation of alkyl chlorides in the reactions of alcohols with phosphorus trichloride, dichlorophenylphosphine, or chlorodiphenylphosphine involves the dealkylation of an intermediate phosphorus(III) ester by hydrogen chloride (Scheme 1).[1-3] An analogous dealkylation occurs in the reactions of hydrogen chloride with triphenyl phosphite–alcohol mixtures (Scheme 2).[4]

Formation of a *P*-protonated intermediate, $(RO)_3\overset{+}{P}H\ X^-$ ($X = Cl$ or HCl_2) has been confirmed by ^{31}P n.m.r. spectroscopy in the reaction of hydrogen chloride with trineopentyl phosphite,[5] tri-*n*-butyl phosphite,[5] and triethyl phosphite[6,7] at temperatures of −40 to −70°C. Whereas the less hindered esters yield alkyl chloride rapidly on raising the temperature, the neopentyl ester is resistant to dealkylation by hydrogen chloride and a competing process of phosphorus–oxygen cleavage yields

$$n\ ROH + Ph_{3-n}PCl_n \longrightarrow (RO)_nPPh_{3-n} + nHCl$$

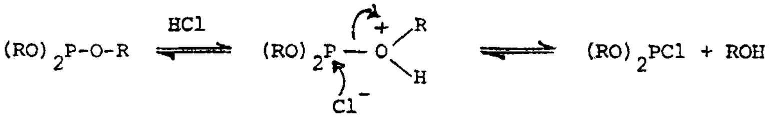
$$ROPXY + HCl \longrightarrow RCl + O{=}PHXY$$

$$[X = Ph \text{ or } RO;\quad Y = Ph \text{ or } RO]$$

SCHEME 1

$$(PhO)_3P \xrightarrow{ROH} (PhO)_2POR \xrightarrow{HCl} RCl + (PhO)_2P(O)H$$

SCHEME 2



$$(RO)_2P\text{-}O\text{-}R \overset{HCl}{\rightleftharpoons} (RO)_2P—\overset{+}{O}(R)(H)\ Cl^- \rightleftharpoons (RO)_2PCl + ROH$$

SCHEME 3

TABLE I

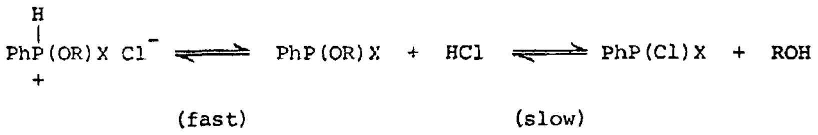
N.m.r. data for the reaction products from phosphorus(III) esters and hydrogen chloride[a]

			Reaction products				
			P^+—H species[c]			P—Cl species	
Ester[b]	HCl (mol. equiv.)	Temp. (°C)	mole %	δ_P	J_{PH}	mole %	δ_P
Ph_2POR (**1**)	9.6	25	75.8	51.5(s)	—	24.2	80.9[d]
		−20	97.1	50.9(s)	—	2.9	80.9[d]
		−80	98.9	50.4(d)	584	1.1	79.7[d]
$PhP(OR)_2$ (**2**)	7.9	25	96.8	52.6(s)	—	3.2	174.7[e]
		−20	100	51.7(s)	—	0	—
		−80	100	51.3(d)	684	0	—
$(PhO)_2POR$ (**3**)	7.2	27	0	—	—	100	159.6[f]
		−20	0	—	—	100	159.6[f]
		−80	0	—	—	100	159.0[f]
$PhOP(OR)_2$ (**4**)	7.8	27	24.6	28.2(s)	—	75.4	165.6[g]
		−20	21.2	23.9(s)	—	78.8	165.7[g]
		−80	7.5	24.0(d)	837	92.5	164.7[g]

[a] *ca.* 10% w/v in Et_2O–CD_2Cl_2 (9 : 1).
[b] R = Me_3CCH_2.
[c] In equilibrium with free ester. Time averaged signal above −40°C.
[d] Ph_2PCl.
[e] PhP(OR)Cl.
[f] (PhO)(RO)PCl (main product, *ca.* 78%) (t, J_{POCH_2} 6.1 Hz), plus 5–10% each of $(PhO)_2PCl$ (δ 155.3, s), $(RO)_2PCl$ (δ 164.9) and $ROPCl_2$ (δ 176.4).
[g] $(RO)_2PCl$ (main product, *ca.* 85%) (quintet, J_{POCH_2} 6.6 Hz), plus 5–10% each of (PhO)(RO)PCl (δ 159.2, t, J_{POCH_2} 6.1 Hz) and $ROPCl_2$ (δ 176.4 ppm).

an equilibrium concentration of the dialkyl phosphorochloridite, possibly *via* an *O*-protonated species (Scheme 3) although the latter is not detectable.[5] The displacement of chloride from phosphorus(III) by alcohol is thus reversible.

We now report the effects of phenyl and of phenoxy substituents at phosphorus on these processes at temperatures between 25° and −80°C (Table I). In the case of neopentyl diphenylphosphinite (**1**) and of dineopentyl phenylphosphonite (**2**), protonation at phosphorus is the principal reaction, although phosphorus-oxygen cleavage products are also obtained and are distinguishable at room temperature by ^{31}P n.m.r. Under these conditions the *P*-protonated species are in rapid equilibrium with the free esters (Scheme 4) so that time-averaged n.m.r. signals only are observed. The



$$\underset{+}{\overset{\overset{\mathrm{H}}{|}}{\mathrm{PhP(OR)X}}}\ \mathrm{Cl^-} \underset{\text{(fast)}}{\rightleftharpoons} \mathrm{PhP(OR)X} + \mathrm{HCl} \underset{\text{(slow)}}{\rightleftharpoons} \mathrm{PhP(Cl)X} + \mathrm{ROH}$$

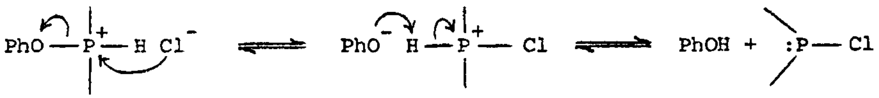
(X = Ph or RO)

SCHEME 4

$$\mathrm{ROP(OPh)X + HCl \rightleftharpoons ROPXCl + PhOH}$$

$$\mathrm{(X = PhO\ or\ RO)}$$

SCHEME 5



SCHEME 6

chemical shift in each case is, however, quite close to that of the protonated form if a large excess of hydrogen chloride is present.

Phosphorus–oxygen cleavage appears to be more favoured by the diphenylphosphinite although for both esters the equilibria move towards protonation of phosphorus as the temperature is lowered. At −80°C the protonated esters account for 99–100% of the phosphorus species present and are characterised by sharp doublets in the ^{31}P n.m.r. spectra with coupling constants (J_{PH} 584 Hz for **1** and 684 Hz for **2**) which reflect the increasing electron density at phosphorus as alkoxy groups are replaced by phenyl.[8]

Phosphorus–oxygen fission is predominant in the reactions of the phenyl esters (**3** and **4**) with hydrogen chloride (Scheme 5), the phosphorochloridite, plus minor amounts of products resulting from disproportionation and/or further cleavage, being the only detectable products from neopentyl diphenyl phosphite (**3**) at temperatures from 25 to −80°C. A protonated form of dineopentyl phenyl phosphite (**4**) was, however, detectable as a minor component (*ca.* 7.5 mole %) at −80°C. The preference for phosphorus–oxygen cleavage as opposed to *P*-protonation in these cases (and in the case of triphenyl phosphite[5]) may be correlated with lower electron density at phosphorus and with the leaving ability of the phenoxide group. Preferred cleavage of P—O also occurs in the case of tri-2-chloroethyl phosphite.[9] Triphenyl phosphite has been shown to give a *P*-protonated species in 100% sulphuric acid[8] and in super-acid media[10] in which effective nucleophiles are absent. Cleavage by hydrogen chloride could therefore occur by nucleophilic attack of chloride ion on the phosphonium intermediate with displacement of phenoxide (Scheme 6), as an alternative to *O*-protonation as suggested above for the alkyl esters.

EXPERIMENTAL

The esters were prepared as described previously.[11] A weighed quantity of each (0.7–0.8 g) was dissolved in sodium-dried ether (4–5 g) in a gas absorption apparatus and hydrogen chloride (Matheson Co., cylinder), dried successively by conc. H_2SO_4 and anhydrous $CaCl_2$, was passed in at room temperature to give the desired increase in weight (*ca.* 30 min.). A sample of each solution was transferred to a ^{31}P n.m.r. tube in a dry nitrogen atmosphere and CD_2Cl_2 was added as a deuterium lock. Variable temperature ^{31}P n.m.r. data were recorded on a Bruker HFX-90 spectrometer operating at 36.4 MHz. Chemical shifts are given relative to 85% H_3PO_4 (downfield positive).

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