The Unusual Course of the Reactions of Phosphorus Pentachloride with 1-Phosphorylated Alcohols and Acetals

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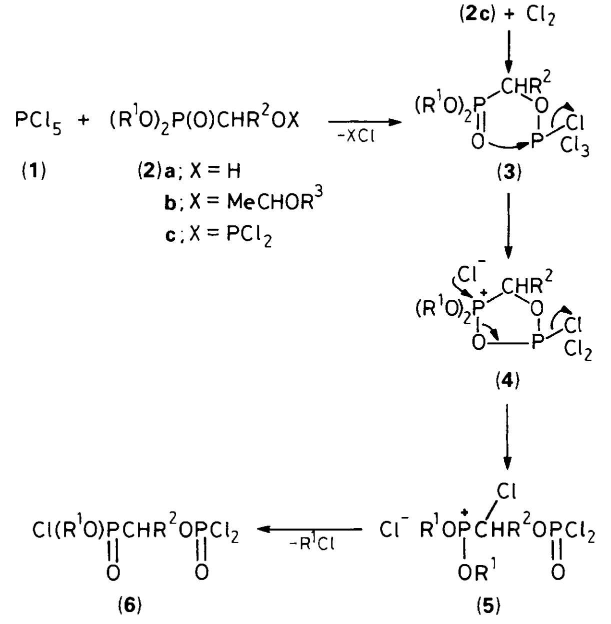
The unusual transformation of 1-phosphorylated alkoxyphosphoranes is discovered.

Phosphorus pentachloride (**1**) is well known to transform into phosphorus oxychloride in reactions with alcohols and acetals.[1,2] We have found an unusual course of these reactions when there is a phosphoryl group in position 1 of the alcohols (**2a**) or in alcohol fragments of acetals (**2b**): 1-phosphorylated alkyl phosphorodichloridates (**6**) are formed instead of phosphorus oxychloride.

The benzene solutions of the compounds (**1**) and (**2a**—**b**) were mixed at 10—20 °C and kept at 40—50 °C for 0.5—1.0 h; the compounds (**6**) were isolated by distillation.

The unusual course of the reactions can be explained by the nontrivial transformation of the intermediate phosphorane (**3**). Taking into consideration the fact that compound (**1**) in benzene solution exists in nonionic form,[1] we suggest Scheme



Scheme 1

1 for the reactions investigated. As a result of intermolecular nucleophilic substitution at P^V the phosphorane (**3**) is transformed into the new cyclic phosphorane (**4**) with the opening of a P=O group. The common tendency of (**4**) to generate the P=O group with high stability[3—5] promotes the completion of phosphorane–phosphate transformation (**3**) → (**4**) → (**5**). The phosphate (**6**) is formed due to dealkylation of the quasiphosphonium centre of (**5**).

Phosphorane (**3**) was also generated by two other independent procedures: by interaction of 1-phosphorylated alkyl phosphorodichloridates (**2c**)[6] with either chlorine or PCl_5. In the latter case, compound (**1**) is reduced to phosphorus trichloride, while phenyltetrachlorophosphorane is reduced to phenyldichlorophosphine.

We consider that the unusual transformation of phosphorane (**3**) is possible due to certain structural features. Firstly, a favourable arrangement of the electron donating P=O group and electrophilic phosphorane centre in the same molecule. Secondly, the presence of a labile P–Cl bond and sterically crowded 1-phosphorylated alkoxyl group at P^V. The reactions proceed in an ordinary way when compounds (**7a**—**c**) having the P=O group at position 2 and compounds (**7d**, **e**) having the ester group at position 1 are used. Phosphorus oxychloride and substituted alkyl chlorides (**8a**, **b**) are formed.

$Y(CH_2)_nOX$
(**7a**—**c**) $Y = (R^1O)_2P(O); n = 2$
$X = H, PCl_2, MeCH(OR^2)$
(**7d**—**e**) $Y = COR^1; n = 1$
$X = MeCHOR^2, PCl_2$
$Y(CH_2)_nCl$
(**8a**) $Y = (R^1O)_2P(O); n = 2$
(**8b**) $Y = CO_2R^1; n = 1$

Structures of phosphates (**6**) were confirmed by ^1H, ^{13}C, and ^{31}P n.m.r. spectra, which also allowed the detection of diastereoisomeric forms of (**6**) in the case of $R^1 = R^2 = Me$.†

Received, 6th June 1989; Com. 9/02478F

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† ^{31}P N.m.r. ($CDCl_3$); δ P_A 31.36, 30.63 and P_B 5.0 p.p.m. (d, J_{pp} 33 Hz); ^1H n.m.r. ($CDCl_3$); δ 1.76 (dd, *J* 21.0 and 6.5 Hz, Me), 3.98 (d, *J* 13.0 Hz, MeO), 5.33 (hept., *J* 6.5, 13.0, and 6.5 Hz, CH); ^1H {$^{31}P_A$} n.m.r. ($CDCl_3$): δ 1.76 (d, *J* 6.5 Hz, Me), 3.98 (s, OMe), 5.31 (secst., *J* 6.5 and 13.0 Hz, CH); ^1H {$^{31}P_B$} n.m.r. ($CDCl_3$); δ 1.76 (dd, *J* 21.0 and 6.5 Hz, Me), 3.98 (d, *J* 13.0 Hz, OMe), 5.33 (quin., *J* 6.5 Hz, CH); ^{13}C n.m.r. ($CDCl_3$): 14.93 (s, Me), 52.10 (d, *J* 5.5 Hz, OMe), 76.43, 75.64 (dd, *J* 155.4 and 10.0 Hz, CH).