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THE TRAPPING OF HYDROXYPHOSPHORANES

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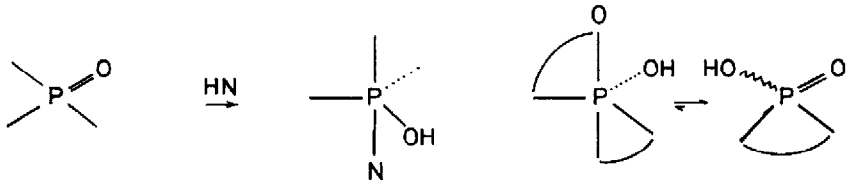
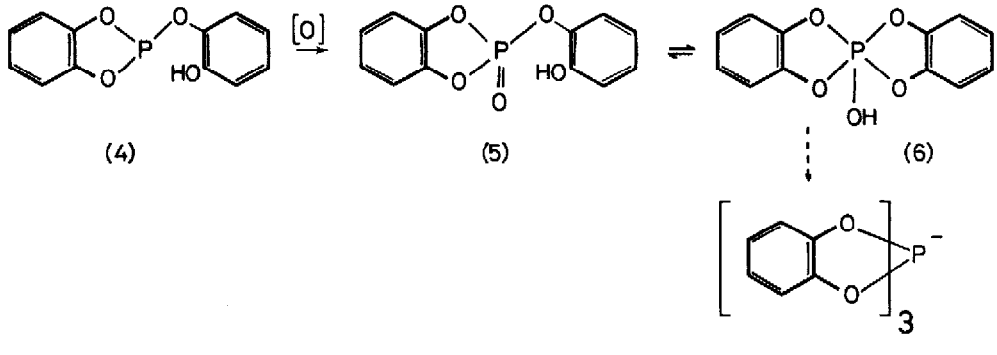
Hydroxyphosphoranes (1), or their conjugate bases, are intermediates in nucleophilic substitutions at phosphoryl centres.[1] However remarkably little is known about them and it is doubtful if an authentic hydroxyphosphorane has been described. When they might be expected to be stable, e.g. when there is no good leaving group attached to phosphorus or because of ring constraints as in (2), they prefer to exist as phosphonium hydroxides or as (hydroxy)phosphoryl species (3) respectively.



(1) (2) (3)

Equilibria analogous to (2)⇌(3) are of course involved in the migration of phosphate ester groups and hydroxyphosphoranes have often been postulated as intermediates in rearrangements.[2] Wolf[3] has recently interpreted the formation of the hexa-co-ordinate anion (7) in the oxidation of the phosphite (4) as evidence for the equilibrium (5)⇌(6).



(4) (5) (6)

(7)

In this note we present evidence for hydroxyphosphoranes as intermediates in the isomerisation of phosphinic esters of 3-methylcatechol and for their trapping as the corresponding methoxyphosphoranes.

The tetramethylphosphetinic chloride (8; R^1 = H) with 3-methylcatechol in the presence of base gave a crystalline phosphinate, m.p. 148-149°C, which in solution gave an equilibrium mixture of the isomeric esters (9) and (10; R^1 = H, R^2 = CH_3) in a ratio of 2.7:1.† In 1-bromonaphthalene the signals due to the aromatic methyls of the two isomers at δ 2.38 and 2.16 p.p.m. coalesced reversibly at 67-70°C, the associated ΔG^* being about 17.5 kcal mol^{-1}. The signals due to the two sets of phosphetan methyls (cis and trans to the phosphoryl oxygen) remained sharp at 180°C. The equilibrium between (9) and (10) presumably involves the hydroxyphosphoranes (11) and (12). When a solution of (9 + 10; R^1 = H, R^2 = CH_3) in ether at 0°C was treated with an excess of diazomethane some 5% of the methoxyphosphorane (13; R^1 = H, R^2 = CH_3), ^{31}P 2.9 p.p.m. to low field of external 85% H_3PO_4, $POCH_3$, δ 3.60 p.p.m., J_{PH} 12 Hz, was formed as well as the expected methylated phosphinates.

Similarly the trans-pentamethylphosphetinic chloride (8; R^1 = CH_3) with 3-methylcatechol gave a crystalline ester, m.p. 165-166°C, which in solution gave a 1.8:1† equilibrium of the isomers (9) and (10; R^1, R^2 = CH_3) [T_c (1-bromonaphthalene) 76-80°C, Δν 38 Hz, ΔG^* ~17.5 kcal mol^{-1}] which with diazomethane gave some 12% of the methoxyphosphorane (13; R^1, R^2 = CH_3), ^{31}P 4.7 p.p.m., J_{POCH_3} 12 Hz. The corresponding phenoxyphosphorane, m.p. 54-55°C, obtained from 2,2,3,4,4-pentamethyl-1-phenoxyphosphetan, 3-methylcatechol, and N-chlorodiisopropylamine,[4] had ^{31}P 6.2 p.p.m. The single ester, m.p. 123-4°C, obtained from the tetramethylphosphetinic chloride (8; R^1 = H) and catechol gave with diazomethane in ether about 10% of the methoxyphosphorane (13; R^1, R^2 = H), ^{31}P 3.5 p.p.m., J_{POCH_3} 12 Hz, whereas the ester, m.p. 114-5°C, from (8; R^1 = CH_3) and catechol gave <5% of the methoxyphosphorane (13; R^1 = CH_3, R^2 = H), ^{31}P 6.4 p.p.m., J_{POCH_3} 12 Hz, on the same treatment. This phosphorane was obtained pure by rapid t.l.c. on silica. The mass spectrum was consistent with the structure but was also similar to that of the isomeric o-methoxyphenyl phosphinate.

The barrier to interconversion of the isomeric diphenylphosphinates of 3-methylcatechol, (14) and (15), was sufficient to allow one of them (the major isomer at equilibrium) to be isolated essentially pure by slow crystallisation from CH_2Cl_2-light petroleum. The establishment of the equilibrium ratio of 1.83:1 could then be followed conveniently in $CDCl_3$ at 30°C by monitoring the aromatic methyl signals at δ 2.24 and 1.98 p.p.m., leading to a ΔG^* of 24.4 ± 0.2 kcal mol^{-1} for the conversion of one isomer into the other. No evidence was found for the formation of a methoxyphosphorane on treatment of the mixture of (14) and (15) with diazomethane.

The greater barrier to equilibration of the isomeric 2-hydroxy-3(6)-methylphenyl phosphinates in the acyclic as compared with the four-membered ester is largely due to relief of strain in the ring in the latter case on changing from tetrahedral to five-co-ordinate geometry round phosphorus and is in accord with rate differences of about 10^6 observed[5] in the alkaline hydrolyses of comparable phosphetanium and acyclic phosphonium salts where the rate-determining

steps involve addition of OH^- to the phosphonium centres to give hydroxyphosphoranes. This relief of strain also results in the hydroxyphosphoranes (11) and (12) being in a deeper energy well than are the acyclic hydroxyphosphoranes (16) and (17) and present in greater proportion relative to the respective phosphinates, so allowing the methoxyphosphoranes (13) to be detected after methylation with diazomethane. Because of the possibility of differential rates of methylation of the various species present in solution, the yields of methoxyphosphoranes do not necessarily reflect the equilibrium concentrations of the corresponding hydroxyphosphoranes. Indeed the F.T. $^{31}P[H]$ n.m.r. spectrum of the ester (9 + 10; R^1, R^2 = CH_3) at -50°C in CH_2Cl_2 showed the expected phosphinate peaks at 61.9 and 65.0 p.p.m. but no absorption ascribable to a hydroxyphosphorane.

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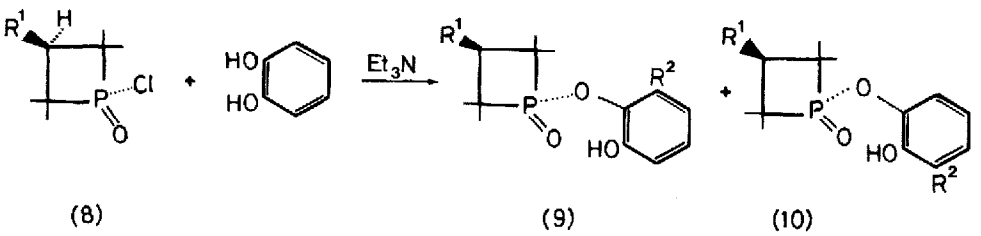

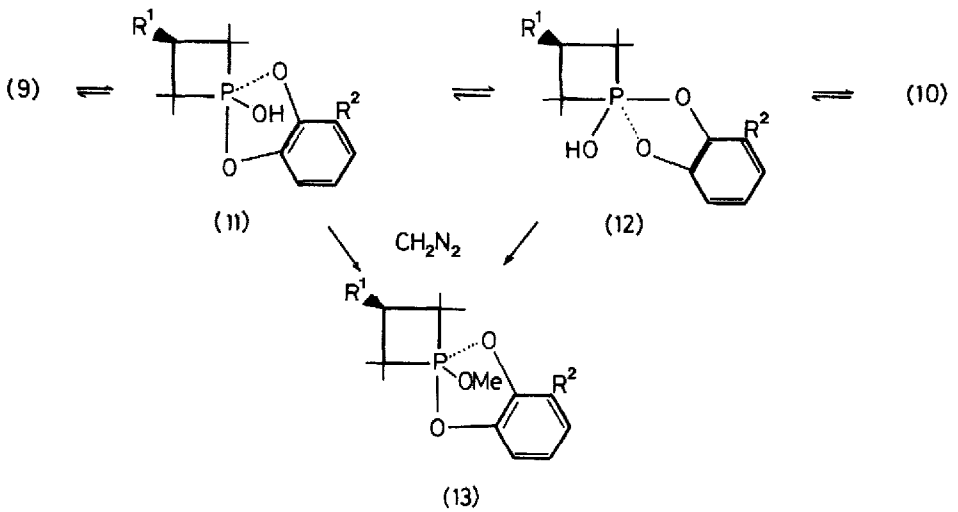

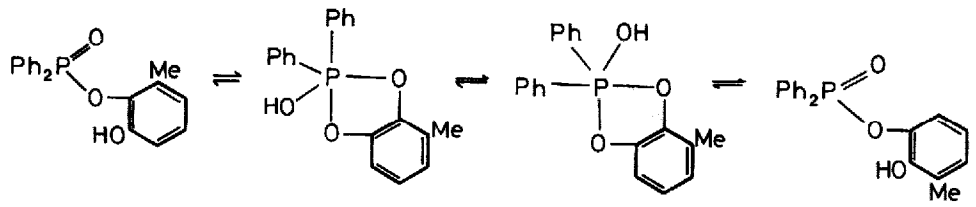

(14) (16) (17) (15)

Footnote

† It is not possible to identify the individual isomers and this ratio may be reversed.

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