Reversible Ring-opening in the Hydrolysis of Spirophosphoranes

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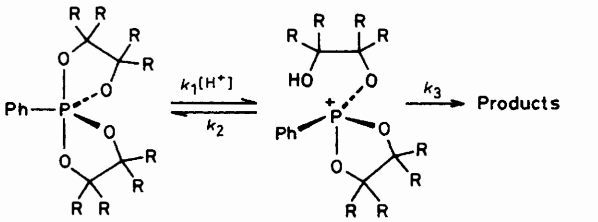
The spirophosphorane (**1b**) (5-phenyloctamethyl-1,4,6,9-tetraoxa-5-phosphaspiro[4.4]nonane) undergoes acid-catalysed ligand exchange 10^7 times faster than acid-catalysed hydrolysis; these two processes have a common phosphonium ion intermediate which has a large preference for reaction with its internal hydroxy group over capture by an external water molecule.

A previous study[1] has shown that the acid-catalysed hydrolysis of spirophosphorane (**1a**) is mechanistically analogous to that of acetals and ortho esters. With the latter the first reaction stage involving formation of an oxocarbocation is usually rate-limiting. For cyclic derivatives however, the possibility exists that the intermediate cation will recyclize faster than it can react with water, in which case cation hydration would be rate-limiting. Definitive evidence for reversibility is difficult to obtain, since this usually has no effect on the observed rate law.[2] Internal return has been shown to compete with cation hydrolysis in certain acetals[3,4] and ortho esters,[5,6] although not usually to an overwhelming extent. Reversibility is obviously also a possibility with a spirophosphorane. In this paper we employ a feature of pentavalent phosphorus compounds, namely their ability to undergo permutational isomerization, to demonstrate that the hydrolysis of the



(1)

(1) (2)

a; R = H
b; R = Me

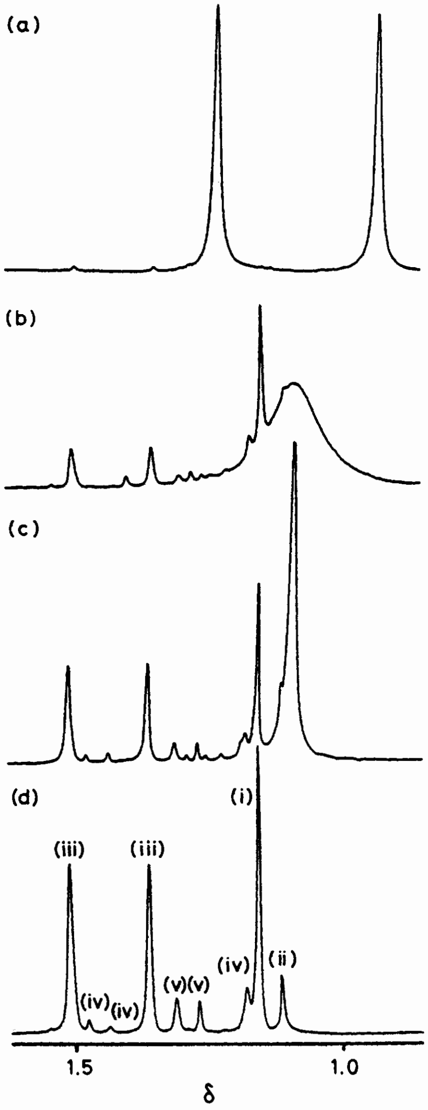


Figure 1. Partial 200 MHz ^1H n.m.r. spectra of the phosphorane (**1b**) in 1:1 CD_3CN–D_2O containing (a) 0, (b) 10^{-3}, and (c) 10^{-2} M DCl. Spectrum (d) was recorded after complete hydrolysis.

spirophosphorane (**1b**) proceeds with highly reversible ring opening.

In non-nucleophilic solvents, Lewis acids catalyse positional ligand exchange in the phosphorane (**1a**).[7] This presumably occurs by a mechanism that involves reversible formation of ring-opened phosphonium ions such as (**2a**). This ligand rearrangement is observed in the ^1H n.m.r. spectrum as a coalescence of the complex multiplet associated with the ring protons, while the remainder of the spectrum and the ^{13}C and ^{31}P n.m.r. spectra are unchanged.

The same phenomenon is observed with the phosphorane (**1b**)[8] during its hydrolysis in acidic 50% aqueous acetonitrile solutions. This phosphorane has two chemically non-equivalent methyl resonances [Figure 1(a)] which coalesce under acidic conditions [Figures 1(b) and 1(c)]. Hydrolysis does occur in these solutions and this gives rise to the additional peaks that are observed in Figures 1(b)—(d). Products have been identified[9] [see Figure 1(d) for assignments] as pinacol (i), pinacolone (ii), the cyclic ester 2-oxo-2-phenyltetramethyl-1,3,2-dioxaphospholane (iii), and the acyclic esters mono-(iv) and bis-(v) (2-hydroxytetramethylethyl)phenylphosphonate.

Although the coalescence is explained by the acid-catalysed equilibration of (**1b**) with the phosphonium ion (**2b**),[7] the concentration of (**2b**) must nevertheless be very small ($k_2 \gg k_1$). This is demonstrated by the fact that the average chemical shift of the methyl protons does not change appreciably with the acidity of the solution. The ^{31}P chemical shift (−35 p.p.m.) is similarly independent of pH. In contrast, acyclic phosphoranes or spirophosphoranes containing two six-membered rings give rise to spectroscopically detectable cations in acidic aqueous solutions.[10]

At acid concentrations above 10^{-2} M [Figure 1(c)], the linewidth of the fully coalesced signal does not differ from that observed for the individual methyl resonances in the absence of exchange [Figure 1(a)]. Line broadening at intermediate acid concentrations is therefore due solely to exchange and rate constants for this process can be calculated by conventional linewidth analysis.[11] Rate constants in 1, 2, 4, 6, and 8 × 10^{-3} M DCl were determined to be 2.7, 6.8, 13, 37, and 52 × 10^3 s^{-1} respectively. These values give a second order rate constant (k_{ex}) of 4.4(±2) × 10^6 mol^{-1} dm^3 s^{-1}. The second-order rate constant for hydrolysis (k_{hyd}) in the same solvent was obtained spectroscopically[1] and is 0.27(±0.014) mol^{-1} dm^3 s^{-1}. In terms of the individual rate constants of equation (1), $k_{ex} = k_1$ and $k_{hyd} = k_1/(1 + k_2/k_3)$, so that $k_{ex}/k_{hyd} = 1 + k_2/k_3$. From the experimental values of k_{ex} and k_{hyd}, k_2/k_3 is calculated to be 1.6(±0.85) × 10^7. This shows that the reaction of the phosphonium ion with the internal hydroxy group has an enormous preference over capture by a solvent water molecule and that the latter process must be rate-limiting in the hydrolysis reaction.

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