A Monocyclic Phosphorane Oxide Anion and the Extraordinary Reactivity of its Tautomeric Phosphine Oxide Alkoxide

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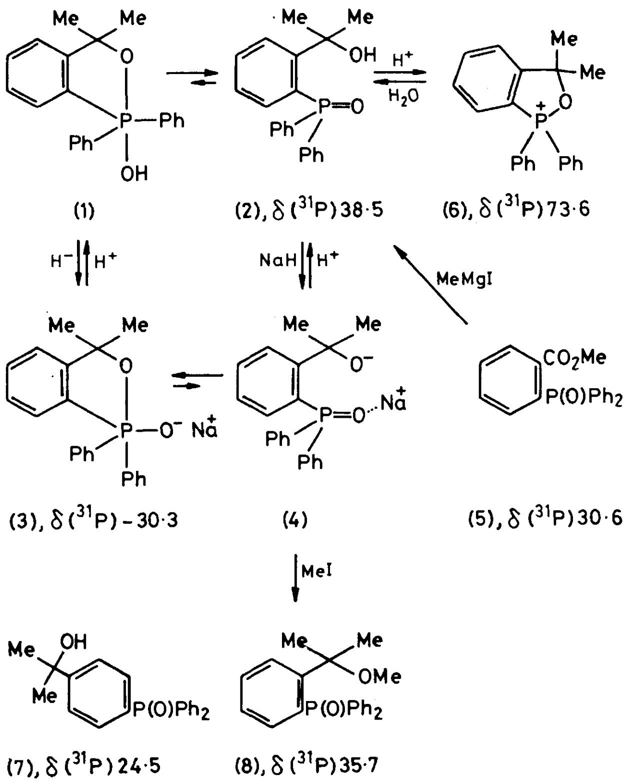
Summary Deprotonation of the alcohol (**2**) gives the phosphorane oxide anion (**3**) which equilibrates with its exceptionally reactive tautomeric phosphine oxide alkoxide (**4**).

Pentaco-ordinate trigonal bipyramidal (TBP) hydroxyphosphoranes, such as (**1**), and their conjugate bases, phosphorane oxide anions, are often thought to be intermediates or transition states in displacement reactions at tetraco-ordinate phosphorus, such as in (**2**).[1] Recently, stable hydroxyphosphoranes[2,3] and phosphorane oxide anions[4] have been isolated. Spectroscopic evidence[4,5] for equilibria between P=O bond-containing compounds and equatorial hydroxyphosphoranes has also been documented. However, all these phosphoranes, like other stable hypervalent molecules,[6] are stabilized primarily by their spirobicyclic nature.

We now report evidence for an equilibrium between an acyclic phosphine oxide alcohol (**2**) and its tautomer, the apical hydroxyphosphorane (**1**), direct observation of a monocyclic phosphorane oxide anion (**3**), and the extraordinary nucleophilic reactivity of its tautomeric phosphine oxide alkoxide (**4**).



Scheme. δ (^{31}P) values are in p.p.m. downfield from 85% H_3PO_4.

The ester (**5**), obtained from the parent acid,[7] and methylmagnesium iodide give the phosphine oxide alcohol (**2**). The ^{31}P n.m.r. chemical shift value of (**2**) is solvent-dependent and extremely dependent on pH: *e.g.* 42·7 p.p.m. (MeOH), 41·3 ($CDCl_3$), 39·3 (Me_2SO), 38·5 (tetrahydrofuran), and 73·6 (CF_3CO_2H) (positive shifts are downfield of 85% H_3PO_4). These values, expecially the latter which is assigned to (**6**), may indicate an equilibrium between the

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† The alcohol (**2**) had m.p. 147—149 °C, δ (^{1}H) ($CDCl_3$) 1·68 (6H, s, Me), 2·17 (1H, br s, HO), and 7·05—7·80 (14H, m, H-Ar); the ester (**5**) had m.p. 155 °C, δ (^{1}H) ($CDCl_3$) 3·47 (3H, s, Me) and 7·28—7·90 (14H, m, H-Ar); the ether (**8**) had m.p. 137—138 °C, δ (^{1}H) ($CDCl_3$) 1·57 (6H, s, MeC), 2·68 (3H, s, MeO), and 6·86—7·24 (14H, m, H-Ar); δ (^{13}C) ($CDCl_3$) (p.p.m. downfield from Me_4Si) 27·6 (s, *Me*C), 49·8 (s, MeO), and 81·6 (s, *C*Me_2).

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alcohol (**2**) and the hydroxyphosphorane (**1**). Such an equilibrium is also supported by the following observations. Incremental addition of sodium methoxide to a methanolic solution of (**2**) leads to broadening of the ^{31}P n.m.r. signal down to the noise level. This process is reversed by quenching the methoxide with methyl iodide. Deprotonation of (**2**) by sodium hydride in tetrahydrofuran (THF) at ambient temperature is much faster than that of the model alcohol (**7**). This deprotonation is accompanied by a broadening of the ^{31}P n.m.r. signal with a gradual shift upfield and eventually resharpening of the signal on reaching $-30{\cdot}3$ p.p.m. The latter signal is still somewhat broad ($w_{\frac{1}{2}}$ 35 Hz). We suggest that these phenomena result from the equilibria depicted in the Scheme. The ^{31}P n.m.r. chemical shift values reflect the increased stability of (**3**) as compared with (**1**). These observations may be accommodated within the frame of Musher's hypervalent bonding scheme.[8] Electronegative ligands would prefer apical positions in the TBP molecule which in turn would be further stabilized by an increased electronegativity difference between apical and equatorial ligands. Dehydration of protonated (**1**) gives (**6**), in analogy with and as a model for the suggested[1] mechanism of phosphate ester hydrolysis.

Most interesting is the reaction of methyl iodide with the equilibrium mixture of (**3**) and (**4**) in THF. In spite of the low concentration of (**4**), as shown by the high-field ^{31}P resonance at $-30{\cdot}3$ p.p.m., the only product of this surprisingly fast reaction is the ether (**8**).† Moreover, under the same conditions, the alkoxide obtained from (**7**) in THF does not react at all with methyl iodide. This extraordinary reactivity of the alkoxide (**4**) may result from intramolecular solvation of the sodium cation by the P=O group.

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