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 anions⁴ 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).

The ester (5), obtained from the parent acid,⁷ and methylmagnesium iodide give the phosphine oxide alcohol (2). The ³¹P n.m.r. chemical shift value of (2) is solventdependent and extremely dependent on pH: e.g. 42.7 p.p.m. (MeOH), 41.3 (CDCl₃), 39.3 (Me₂SO), 38.5 (tetrahydrofuran), and 73.6 (CF₃CO₂H) (positive shifts are downfield of 85%These values, expecially the latter which is H,PO). assigned to (6), may indicate an equilibrium between the



† The alcohol (2) had m.p. 147—149 °C, δ (¹H) (CDCl₃) 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 (¹H) (CDCl₃) 3.47 (3H, s, Me) and 7.28—7.90 (14H, m, H-Ar); the ether (8) had m.p. 137—138 °C, δ (¹H) (CDCl₃) 1.57 (6H, s, MeC), 2.68 (3H, s, MeO), and 6.86—7.24 (14H, m, H-Ar); δ (¹³C) (CDCl₃) (p.p.m. downfield from Me₄Si) 27.6 (s, MeC), 49.8 (s, MeO), and 81.6 (s, CMe_2). ‡ Deceased July 20th, 1981.

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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 ³¹P 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 ${}^{\mathbf{31}}\mathbf{P}$ n.m.r. signal with a gradual shift upfield and eventually resharpening of the signal on reaching -30.3 p.p.m. The latter signal is still somewhat broad $(w_{\pm} 35 \text{ Hz})$. We suggest that these phenomena result from the equilibria depicted in the Scheme. The ³¹P 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 suggested¹ 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 ³¹P resonance at -30.3 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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