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ALKALINE HYDROLYSIS OF PHOSPHINE OXIDES IN HOMOGENEOUS SOLUTION. THE NATURE OF THE PENTACOORDINATE PHOSPHORUS INTERMEDIATE[1]

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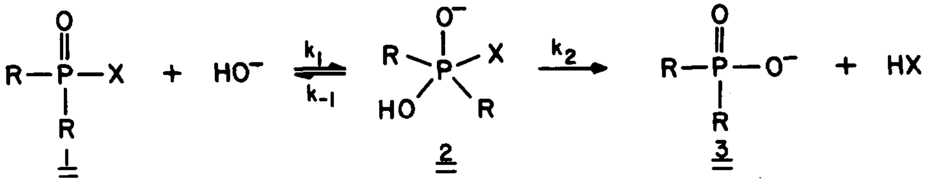
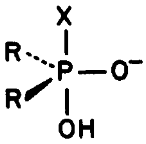
Much recent interest in phosphorus chemistry concerns the possibility of pentacoordinate, trigonal bipyramidal intermediates in substitution reactions (e.g., eq. 1) at tetrahedral phosphorus and the question of pseudorotation.[2] In cases previously reported, the lack of ^{18}O exchange into **1** during alkaline hydrolysis[3] can be rationalized by the preferred geometry of **2** in which OH and X occupy apical positions and O^- occupies a basal position, as in **4**, since the most electronegative atoms appear to occupy apical positions in phosphoranes.[2,4,5]



(1)

We have been able to study the alkaline hydrolysis of a phosphine oxide, **5**, in homogeneous solution and we can now report results which appear important to the general problem of the mechanism of displacement at phosphorus. Since in **5**, benzyl is the displaceable substituent, there are several important perturbations on the general problem shown schematically in eq. 1. First, since there are three P-C bonds, the preferred geometry of **2** might enable oxygen exchange. Recently consideration of the question of intermediates along the reaction pathway in the fusion of phospholane oxides with NaOH resulted in the conclusion that **6** would be the most probable.[6] Secondly, we have noted previously[7] that the known stability of many pentacoordinate phosphorus compounds indicates the probable existence of addition intermediates in displacements at tetracoordinate phosphorus. Benzyl anion should be sufficiently difficult to displace so that an intermediate (**2**) should certainly be involved and direct displacement can be rejected.



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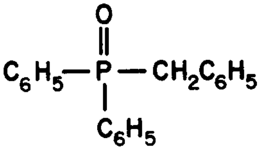
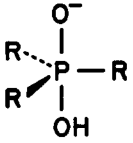


$$C_6H_5-\underset{C_6H_5}{\overset{O}{\overset{\|}{P}}}-CH_2C_6H_5$$

5



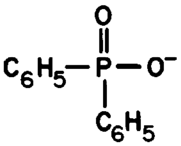
6

Previous experiments on cleavage of phosphine oxides by HO^- have been carried out by fusion with solid NaOH.[6,8] We have been able to study the kinetics of cleavage of 5 by ^-OH in homogeneous solution using 70.3 mole % DMSO in water and 0.1M KOH.[8] The presence of DMSO enables a sufficiently high activity of ^-OH to give reaction.[9] At 0.1M KOH and 0.03M 5, the reaction is first-order in phosphine oxide and first-order in ^-OH, with a second-order rate constant, $k = .030M.^{-1}sec^{-1}$ at 100°. This result contrasts with the second-order dependence on ^-OH in the hydrolysis of phosphonium salts.[10]

If an intermediate exists in the hydrolysis of 5, similar to 6, in which the oxygen atoms occupy equivalent apical positions,[6] rapid proton transfer should cause identity of the oxygens since the considerations above support the hypothesis that an intermediate of reasonable lifetime is involved. To determine if 5 undergoes ^{18}O exchange under conditions of alkaline hydrolysis, ^{18}O labeled H_2O was used.[11] The reaction was stopped at 50% hydrolysis and 5 and 7 were isolated and analyzed for ^{18}O content. The results shown in the table indicate incorporation of one solvent oxygen into 7 and negligible exchange of ^{18}O into 5. If a symmetrical intermediate does exist along the reaction pathway, such as 6, then it must collapse to products at least 200 times faster than to reactants.

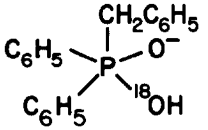
Atom% ^{18}O in Solvent	Compound Isolated	Atom% ^{18}O Found
0.198	5	0.20
1.709	5	0.20
0.198	7	0.20
1.709	7	0.95

a. Average of at least five determinations.



$$C_6H_5-\underset{C_6H_5}{\overset{O}{\overset{\|}{P}}}-O^-$$

7



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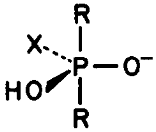

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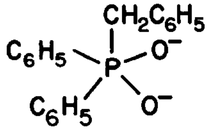

10

Does the lack of ^{18}O exchange in base, even in phosphine oxides, disprove the hypothesis that an intermediate is involved in displacement at phosphorus? How can there be 200 times faster loss of a benzyl group from 8 than the pseudorotation, proton transfer, and loss of hydroxide necessary for ^{18}O exchange? Two factors appear important. First, there have been some recent indications[4, 12] that in 8 there would be a strong preference for O^- to be the pivot atom[2] during pseudorotation. A simple way to understand this is in terms of electron repulsion theory[13] which has been useful in understanding the geometry of pentacoordinate compounds. An O^- group would be expected to be particularly repulsive and therefore should occupy a position where it interacts least with the other ligands and bonding electrons. Therefore, there should be a strong preference for the O^- atom to be basal in trigonal bipyramidal geometry (as in 4); and there should be a considerable barrier to pseudorotations unless O^- is the pivot group. If O^- must be the pivot atom and 4 is preferentially formed,[14] the only possible pseudorotation yields 9. This is clearly a high energy geometry with X = OR in the hydrolysis of esters, and with X = $CH_2C_6H_5$, as here, 9 may still be too energetic to be formed rapidly enough to allow ^{18}O exchange.[15] Alternatively, the presence of O^- may cause sufficient distortion in pentacoordinate geometry so that identity of OH and O^- is impossible. Secondly, with the strong activity of $^-$OH necessary to effect displacement on 5, the predominant state of ionization of the addition intermediate may be 10.[17] If so, loss of benzyl may be fast compared to reversal to 5 even if 10 is reasonably stable and the oxygens are equivalent. So long as 10 is predominant and addition of $^-$OH to 5 is rate-determining, the observed kinetics will be first order in $^-$OH.

These considerations suggested by the lack of ^{18}O exchange in phosphine oxides, may be of general importance in understanding displacements at phosphorus.[18]

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