Displacement at Phosphorus in a Four-membered Ring

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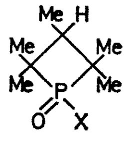
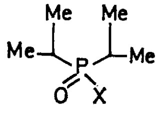
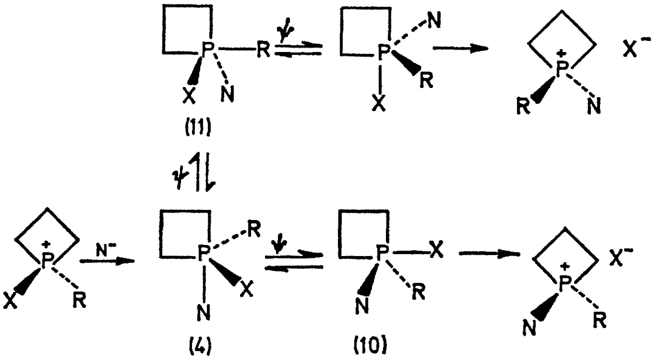
Summary It is suggested that all displacements at phosphorus in a four-membered ring proceed *via* trigonal-bipyramidal intermediates in which the ring spans an apical-equatorial position, the rate, relative to displacement at acyclic phosphorus, depending on the electronegativity of the displaced group.

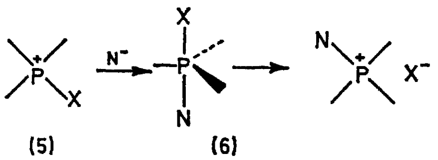
WHEREAS the phosphetan ethyl ester (**1**; X = OEt) undergoes alkaline hydrolysis more rapidly than the di-isopropylphosphinate (**2**; X = OEt),[1] Haake *et al.*[2] have recently shown that both the chloride (**1**; X = Cl) and the amide (**1**; X = NMe_2) hydrolyse much more slowly than the corresponding acyclic compounds (**2**; X = Cl and NMe_2). The more rapid hydrolysis of the phosphetan ester has been ascribed to the relief of ring strain in forming an intermediate (**4**) in which the four-membered ring spans an apical-equatorial position and the slower hydrolyses of the chloride and amide were ascribed to increased angle strain in intermediates or transition states involving direct displacement with the entering and leaving groups colinear with the phosphorus. The comparison of rates of reaction of (**1**) with those of (**2**) and/or (**3**) was suggested[2] as a criterion for mechanism of reaction at phosphorus.

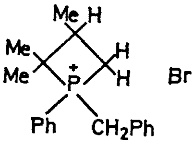

(**1**)

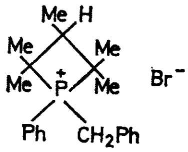

(**2**)

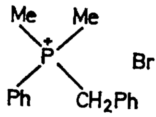
$Ph_2P(:O)X$
(**3**)



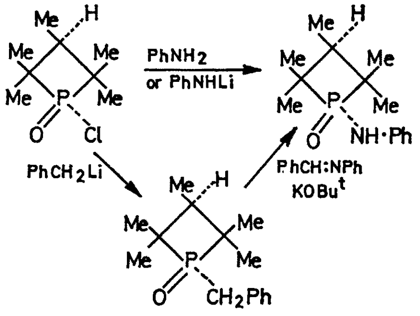



(**7**)


(**8**)


(**9**)

There are no data on the energy required to place a four-membered ring diequatorial in a trigonal bipyramid but it must be greater than the *ca.* 20 kcal mol^{-1} necessary in the case of a five-membered ring.[3] The choice of the di-isopropyl compounds (**2**) for comparison purposes is arguable; a true standard might include some di-t-butyl character and as derivatives of di-t-butylphosphinic acid are extremely inert[2] this might invalidate the criterion. We present an alternative explanation of substitution at the phosphorus of phosphetans which assumes that all such substitutions involve the formation of an intermediate (**4**) in which the four-membered ring is apical-equatorial. In comparison with the similar substitution of an acyclic compound (**5**) which involves an intermediate (**6**) in which entering and leaving groups are colinear with phosphorus, the phosphetan substitution is speeded up by relief of ring strain in (**4**) but is retarded[4] by the fact that, whereas (**6**) has two electronegative groups in apical positions, (**4**) has only one. The more electronegative is X, *i.e.*, in general, the better the leaving group, the greater will this retardation be and when X = Cl or $\overset{+}{N}HMe_2$ the net effect [when compared with (**2**)] is a retardation. With the less electronegative ethoxy-group the effects almost balance. The theory predicts that with a poor leaving group the net result should be an acceleration and this is indeed the case with benzylphosphetanium salts; the relative rates for the alkaline hydrolyses of (**7**),† (**8**), and (**9**) in 75% ethanol at 45° are $6 \times 10^7 : 2 \times 10^5 : 1$.



SCHEME

The colinear theory for substitutions of (**1**; X = Cl or NMe_2) predicts that such substitutions will involve inversion of configuration at phosphorus, in contrast to the retention observed with (**1**; X = OMe[5] or OEt[6]). However, the reaction of (**1**; X = Cl) with phenyl-lithium is known[6,7] to proceed with retention of configuration at phosphorus, and if one assumes that the corresponding reaction with benzyllithium has the same stereochemistry, then the cycle shown in the Scheme establishes that reactions of the chloride (**1**; X = Cl) with aniline and with *N*-lithioaniline also involve retention at phosphorus.

Substitutions *via* (**4**) will involve retention of configuration at phosphorus when X is a highly electronegative group as the preferred pseudorotation before loss of X from an apical position will be (**4**) → (**10**). However, if X and R have comparable electronegativities (*e.g.* X = CH_2Ph and R = Ph) the alternative pseudorotation (**4**) → (**11**) becomes important and leads to the observed[8] loss of stereospecificity in the substitution.

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† The faster rate of hydrolysis of (**7**) compared with that of (**8**) may be due to a steric and/or an electronegativity effect.

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