Tetrahedron Letters No. 2, pp 193 - 196.
© Pergamon Press Ltd. 1979. Printed in Great Britain.

0040-4039/79/0108-0193$02.00/0

THE STEREOCHEMISTRY OF NUCLEOPHILIC SUBSTITUTION AT PHOSPHORUS IN PENTACOVALENT PHOSPHORANES

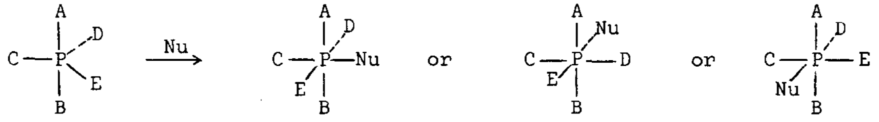
By Stuart Trippett* and Robin E.L. Waddling

Department of Chemistry, University of Leicester, Leicester LE1 7RH

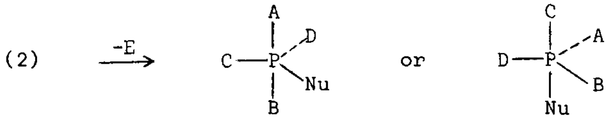
An increasing number of stable six-co-ordinate phosphorus species is known and there is a growing realisation that such molecules may play a more important role in organophosphorus chemistry than hitherto recognised.[1] They are readily formed from nucleophiles and neutral five-co-ordinate phosphoranes, e.g. for the equilibrium (1) Westheimer has shown[2] that $K > 10^3$ mol l^{-1}, and are presumably intermediates in nucleophilic substitution in such phosphoranes.

$$(PhO)_4PPh \ + \ PhO^- \rightleftharpoons (PhO)_5PPh^- \qquad (1)$$

Little is known of the mechanism of these substitutions. The assumption is usually made that attack of a nucleophile on a trigonal bipyramidal (tbp) phosphorane (1) will be in the equatorial plane to give three possible octahedral intermediates (2-4). The corollary of this is that loss of a group from an intermediate will give a tbp phosphorane having in the apical positions a pair of ligands originally trans to one another and syn to the leaving group, i.e. loss of E from (2) gives (5) or (6). The exchange of alkoxy groups in a tetraoxyphosphorane containing a 1,2-oxaphosphetan ring, described by Ramirez,[3] can be accounted for in these terms without postulating that nucleophilic attack must occur opposite to the leaving group.



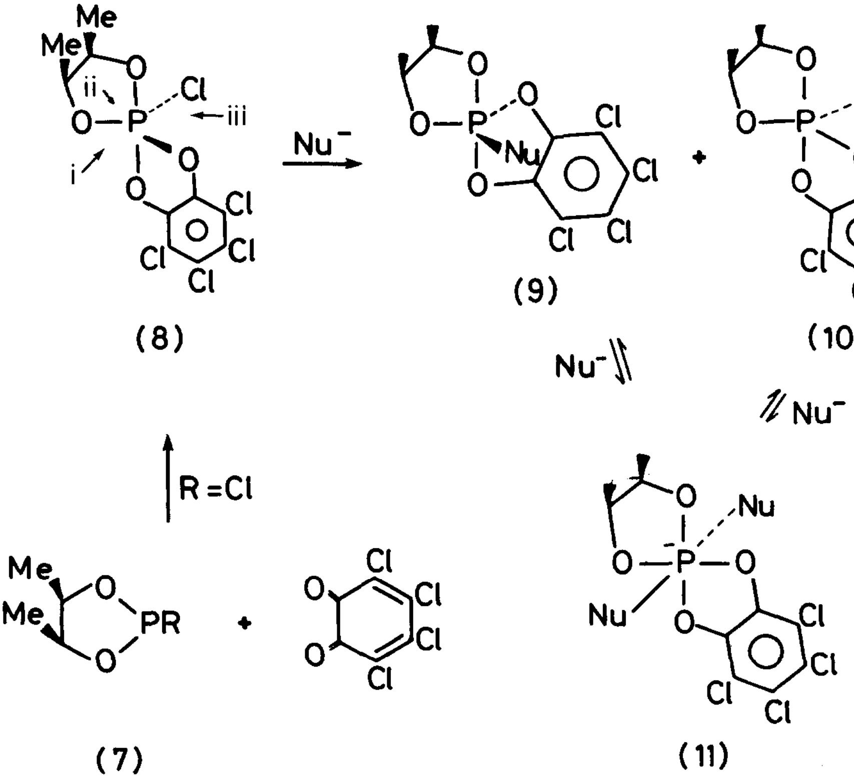
(1) (2) (3) (4)



(5) (6)

This communication is concerned with the stereochemistry of nucleophilic substitution of chlorine in the trans-chlorotetraoxyspirophosphorane (8) obtained by the addition of o-chloroanil to the trans-2-chloro-1,3,2-dioxaphospholan (7; R = Cl) derived from meso-butan-2,3-diol. Attack of the nucleophile trans to chlorine, i.e. in direction (i), will lead to inversion of configuration at phosphorus, whereas syn-attack [directions (ii) and (iii)] will give retention.[5]

(8) is a crystalline compound, ^{31}P +12.3 p.p.m. in $CDCl_3$;[6] there is no evidence for the presence in solution of the cis-isomer (9; Nu = Cl) although equilibration by pseudorotation would be rapid at room temperature ($\Delta G^* \sim 18$ kcal mol^{-1}).[7] We have followed, by F.T. ^{31}P n.m.r., the course of nucleophilic substitution in (8) at -78°C where equilibration of (8) with (9; Nu = Cl), and of the two possible products (9) and (10), by pseudorotation will be slow [e.g. for (8) $t_{\frac{1}{2}}$ at -78°C ≃ 4×10^5 h]. A possible complication is that equilibration of the isomeric products (9) and (10) can also occur, in the presence of a nucleophile, via the six-co-ordinate species (11).



With two equivalents of Me_2NH in THF at -78°C (8) gave the cis (9; Nu = NMe_2; +26.6 p.p.m.) and trans (10; Nu = NMe_2; +24.0 p.p.m.) dimethylaminophosphoranes in a ratio of 7.4:1 which did not change at room temperature (ΔG^{*} for pseudorotation ∿26 kcal mol^{-1}).[6] Equilibration at 100°C gave a ratio of 0.56:1. o-Chloranil and (7; R = NMe_2, 0.08:1::c:t) gave authentic dimethylaminophosphorane in a cis:trans ratio of 0.08:1; at 100°C this changed to 0.56:1. With Me_2NH, and with Me_2NLi which gave similar results, substitution of the chlorine in (8) therefore occurs with predominant inversion of configuration at phosphorus;with reference to (8), $k_i \approx 7\ (k_{ii} + k_{iii})$.

When (8) in THF at -78°C was treated with sodium phenoxide, the cis (9; Nu = OPh; +31.87 p.p.m.) and trans (10; Nu = OPh; + 30.76 p.p.m.) phenoxyphosphoranes were produced initially in a ratio of 0.94:1, but as the reaction proceeded at -78°C the ratio slowly changed to 0.66:1 over a 30 min period. Warming to room temperature, where equilibration of isomers by pseudorotation is rapid (ΔG^{*} ∿20 kcal mol^{-1}),[6] gave the equilibrium ratio of 0.64:1.[8] Similar results were obtained using $PhOH\text{-}Et_3N$. We interpret this to mean that the rates of formation of the cis- and trans- phenoxyphosphoranes are in a ratio of 0.94:1, i.e., with reference to (8), $k_i \approx k_{ii} + k_{iii}$, and that equilibration then occurs more slowly via (11; Nu = OPh). This interpretation is supported by results using sodium 2,6-dimethylphenoxide. Steric effects from the o-methyls would be expected to slow the initial substitution but to slow formation of the six-co-ordinate anion (11), containing two phenoxy ligands, even more. In fact the cis- and trans-2,6-dimethylphenoxyphosphoranes (+31.88 and +30.67 p.p.m. respectively) were formed at -78°C in a constant ratio of 0.95:1. Only on warming to room temperature was the equilibrium ratio of 0.39:1 established.

Other nucleophiles also substitute the chlorine of (8) with a mixture of inversion and retention of configuration at phosphorus, e.g. MeLi at -78°C gives cis- and trans-methylphosphoranes in about equal amounts. These results establish that nucleophilic substitution at five-co-ordinate phosphorus does not require attack of the nucleophile opposite to the leaving group. In order to understand more of the process it will be necessary to unravel those factors that determine the relative energies of isomeric six-co-ordinate phosphorus species.

We thank SRC for support.

References.

1. 'Organophosphorus Chemistry', ed. S. Trippett (Specialist Periodical Reports), The Chemical Society, London, Chapter 2.

2. C.L. Lerman and F.H. Westheimer, *J. Amer. Chem. Soc.*, 1976, 98, 179.

3. F. Ramirez, G.V. Loewengart, E.A. Tsolis, and K. Tasaka, *J. Amer. Chem. Soc.*, 1972, 94, 3531.

4. We thank Bayer AG for a generous supply of this diol.

5. A priori, nucleophilic substitution at five-co-ordinate phosphorus could also occur by a dissociative mechanism, i.e. via a phosphonium ion. This is very unlikely in the case of a spirophosphorane such as (8) because of strain in the corresponding four-co-ordinate ion.

6. Positive chemical shifts are upfield from external 85% H_3PO_4.

7. S. Bone, S. Trippett, and P.J. Whittle, *J.C.S. Perkin I*, 1974, 2125.

8. An authentic sample of the phenoxyphosphorane was produced from o-chloranil and (7; R = OPh). Although crystalline it was an equilibrium mixture of isomers.

(Received in UK 2 November 1978)