Kinetic Control in the Formation of Six-co-ordinate Phosphorus Anions

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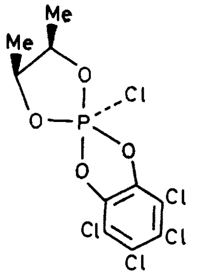
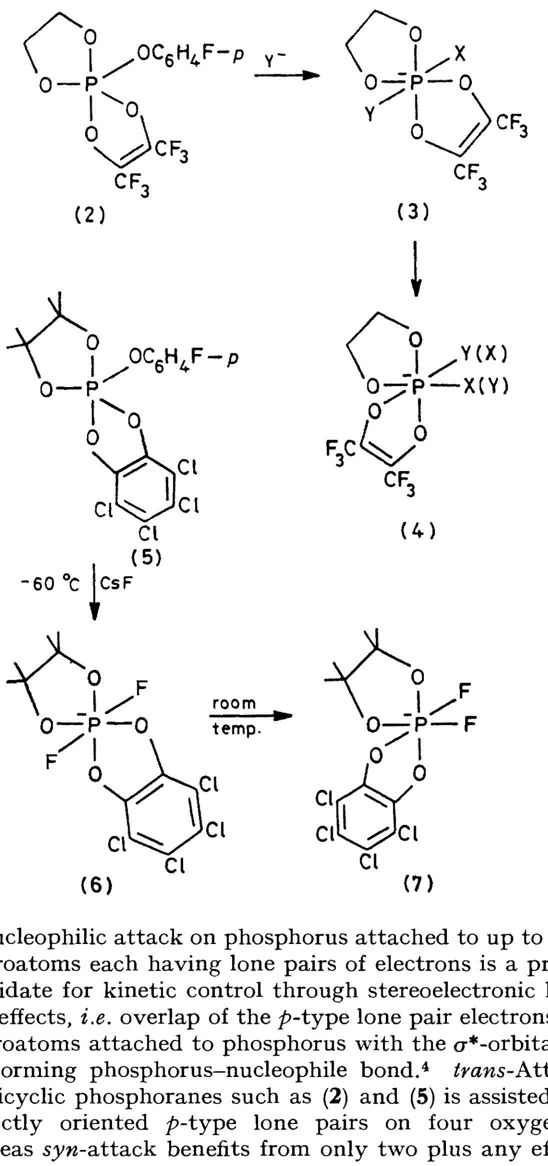
Summary The formation of six-co-ordinate anions from some spirophosphoranes and nucleophiles is kinetically controlled giving initially the less stable *trans*-isomers.

A GROWING number of stable six-co-ordinate organophosphorus molecules have been described and similar species may play a larger role in phosphorus chemistry than hitherto appreciated.[1] They are intermediates in associative nucleophilic substitutions at five-co-ordinate phosphorus which, in (**1**), proceed with inversion and/or retention of configuration at phosphorus.[2] Inversion here implies a *trans*-relationship of nucleophile to leaving group although the stable configuration of spirobicyclic six-co-ordinate phosphorus anions appears to be *cis* (ref. 3 and see below). In this communication we show that nucleophilic attack on some five-co-ordinate phosphoranes is under kinetic control giving initially the less stable isomers.


(1)

The ^{31}P and ^{19}F n.m.r. spectra of a solution of the spirophosphorane {(**2**), m.p. 24—25 °C, ^{31}P δ $-29{\cdot}0$ p.p.m. [d sept, $^{6}J_{PF}$ 4·1, $^{4}J_{PF}$ 1·0 Hz in tetrahydrofuran (THF)]} in THF, treated at -100 °C with sodium *p*-fluorophenoxide and maintained at -66 °C, showed the presence of (**2**) and the *trans*-six-co-ordinate anion (**3**; X, Y = p-FC_6H_4O), $\delta_P - 105{\cdot}1$ (t, $^{6}J_{PF}$ 3·6 Hz), $\delta_F - 1{\cdot}0$ (s, 6F) and $-60{\cdot}8$ (s, 2F) p.p.m.† On warming to room temperature this was replaced immediately by the *cis*-isomer (**4**; X,Y = p-FC_6H_4O), δ_P $-105{\cdot}5$ (t, $^{6}J_{PF}$ 3·6 Hz), δ_F $-$ 0·6 and $-1{\cdot}4$ (both 3F, q, $^{5}J_{FF}$ 10·5 Hz), and $-61{\cdot}3$ p.p.m. (2F, s). With CsF (2 mol. equiv.) in THF–MeCN (1 : 1) below -60 °C, (**2**) gave the *trans*-anions (**3**; X, Y = p-FC_6H_4O) and (**3**; X, Y = F), $\delta_P - 98{\cdot}8$ (t, $^{1}J_{PF}$ 756 ± 0·5 Hz), $\delta_F - 1{\cdot}2$ (6F, s) and $+22{\cdot}3$ p.p.m. (2F, d, $^{1}J_{PF}$ 746 ± 15 Hz). At room temperature these were replaced, over 48 h, by the *cis*-anion (**4**; X,Y = F), δ_P $-101{\cdot}0$ (dd, $^{1}J_{PF}$ 728 ± 5 and 738 ± 5 Hz), δ_F $-1{\cdot}2$ (6F, s), $+3{\cdot}2$ (1F, dd, $^{1}J_{PF}$ 726 ± 15 Hz, $^{2}J_{FF}$ 32 ± 1 Hz), and $+21{\cdot}5$ p.p.m. (1F, dd, $^{1}J_{PF}$ 717 ± 15 Hz, $^{2}J_{FF}$ 32 ± 1 Hz), with the transient appearance of the isomeric, probably *cis*, anions (**4**; X,Y = F and p-FC_6H_4O), δ_P $-102{\cdot}5$ (d, $^{1}J_{PF}$ 762 ± 5 Hz), δ_F $+23{\cdot}0$ (1F, d, $^{1}J_{PF}$ 748 ± 15 Hz), $-1{\cdot}2$ (6F, s), and $-60{\cdot}7$ (1F, s), and $\delta_P - 102{\cdot}7$ (d, $^{1}J_{PF}$ 767 ± 5 Hz), δ_F $+5{\cdot}7$ (1F, d, $^{1}J_{PF}$ 767 ± 15 Hz), $-1{\cdot}2$ (6F, s), and $-60{\cdot}7$ p.p.m. (1F, s), respectively.

Similar results were obtained with the phosphorane [(**5**); m.p. 132—133 °C, δ_P $-35{\cdot}0$ p.p.m. (d, $^{6}J_{PF}$ 3·9 Hz in THF)]; *e.g.* CsF in THF–MeCN (1 : 4) at -60 °C gave the *trans*-anion (**6**), δ_P $-99{\cdot}6$ (t, $^{1}J_{PF}$ 768·0 ± 0·5 Hz), δ_F $+33{\cdot}1$ p.p.m. (d, $^{1}J_{PF}$ 768 ± 15 Hz), replaced at room temperature by the *cis*-anion (**7**), δ_P $-102{\cdot}3$ (dd, $^{1}J_{PF}$ 735·5 ± 0·5 and 738·0 ± 0·5 Hz), δ_F $+12{\cdot}3$ (1F, dd, $^{1}J_{PF}$ 733 ± 15, $^{2}J_{FF}$ 33 Hz) and $+23{\cdot}0$ p.p.m. (1F, dd, $^{1}J_{PF}$ 738 ± 15, $^{2}J_{FF}$ 33 Hz).



(2) (3) (4) (5) (6) (7)

Nucleophilic attack on phosphorus attached to up to five heteroatoms each having lone pairs of electrons is a prime candidate for kinetic control through stereoelectronic lone pair effects, *i.e.* overlap of the *p*-type lone pair electrons on heteroatoms attached to phosphorus with the σ^*-orbital of the forming phosphorus–nucleophile bond.[4] *trans*-Attack on bicyclic phosphoranes such as (**2**) and (**5**) is assisted by correctly oriented *p*-type lone pairs on four oxygens‡ whereas *syn*-attack benefits from only two plus any effect from a lone pair on the fifth substituent.

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† Positive chemical shifts are to low fields of the standards, 85% H_3PO_4 and $PhCF_3$.

‡ The precise geometries of (**2**) and (**5**) will be somewhat between trigonal bipyramidal and square pyramidal; it is easier to look at the effect of lone pair orientations on the loss of nucleophile from the six-co-ordinate species.

Gorenstein[5] has proposed, on the basis of calculations, that attack of HO$^-$ on the dimethyl phosphate anion is kinetically controlled through stereoelectronic (antiperiplanar) lone pair effects. An increasing number of substitutions at four-co-ordinate phosphorus are now known which clearly do not proceed *via* the most stable of the possible five-co-ordinate intermediates[6] and kinetic control of this type is probably widespread in phosphorus chemistry.

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