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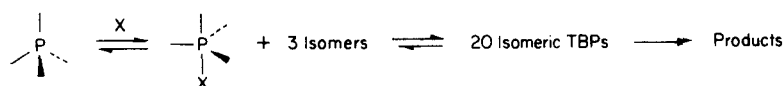
## APICOPHILICITY AND RING-STRAIN IN FIVE-COORDINATE PHOSPHORANES<sup>†</sup>

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In order to discuss mechanism in organophosphorus chemistry a number of assumptions have to be made. Among them are: (a) that substitutions at tetrahedral phosphorus proceed *via* five-coordinate intermediates; (b) these intermediates are trigonal bipyramidal; (c) they are formed by apical attack and decompose by apical loss; and (d) if sufficiently long-lived, they may undergo permutational isomerization, that is the ligands may alter their relative dispositions round the phosphorus, before going on to products or back to reactants.

In summary



Assuming that the course of a given substitution is dictated primarily by thermodynamic considerations, in order to understand the course of that substitution one needs to know how to assess the relative stabilities of the four isomeric tbps (trigonal bipyramids) that can be formed initially and of the others that could be formed by subsequent isomerization, the barriers to those isomerizations, and the relative rates of the various product-forming steps. We have concentrated on the first of these factors and this lecture describes our attempts to provide the necessary data.

The energy difference between two isomeric tbps can be analyzed in terms of changes in the relative apicophilicities<sup>1</sup> of the groups occupying apical positions, changes in ring-strain as small rings move between apical-equatorial and diequatorial positions, and changes in steric strain. I shall consider each of these in turn. Ligand subset symmetry may also have to be taken into account.<sup>1,2</sup>

### RELATIVE APICOPHILICITIES

The relative apicophilicity of two groups is the change in energy when these groups exchange apical and equatorial positions in a tbp. Calculations by several groups<sup>1,3</sup> suggest that apicophilicity should be a function of: (a) electronegativity, increase favoring occupation of an apical position; (b) the presence on the atom bonded to phosphorus of a lone-pair of electrons, this favoring occupation of an equatorial position; and (c) the presence on the atom or group of a vacant low-lying orbital, this favoring occupation of an apical position. With three factors to balance, it is not surprising that most experimental data can be satisfactorily rationalized. However what is not clear *a priori* is how far the relative apicophilicity of two groups will vary with the nature of the other groups attached to phosphorus. A wide variation could lead to data which would be extremely difficult to correlate.

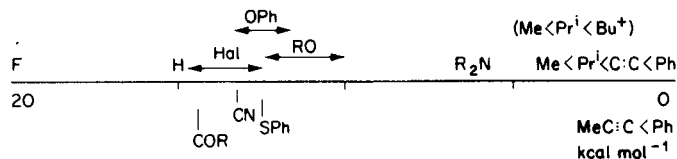
Most of our information on relative apicophilicities has been obtained from dynamic nmr studies on stable five-coordinate phosphoranes; the results being interpreted in terms of isomerizations that involve switching the two apical substituents for any two of the equatorial substituents, a condition imposed by the famous Whitesides and Mitchell experiment.<sup>4</sup> Whether these be Berry pseudorotations or turnstile rotations<sup>1,5</sup> is not of the first importance; out of habit I shall often refer to them as pseudorotations.

Typical of the systems studied are the hexafluorobiacetyl adducts 1.<sup>6</sup> When A is more apicophilic than B, the most stable conformer is 1 and equivalence of the CF<sub>3</sub> groups is achieved *via* the high-energy topomers 2 and 3. With a constant group B, the energy required for this process varies as the apicophilicity of A relative to B. The free energy of activation for a particular group A will overestimate the difference in apicophilicity between A and B. However pseudorotations between trigonal bipyramids of identical energies are thought to be very low-energy processes<sup>7</sup> and high-energy trigonal bipyramids are usually regarded as transition states rather than intermediates. The overestimate in this and similar systems will therefore probably be small.

Among other systems studied are the phosphetan-hexafluoroacetone adducts 4,<sup>8</sup> phosphoramidite-

<sup>†</sup> Plenary Lecture. Vth International Conference of Organic Phosphorus Chemistry, Gdansk, Poland, September 1974.

hexafluoroacetone adducts **5**,<sup>9</sup> spirophosphoranes such as **6** and **7** and others mentioned later in connection with ring strain,<sup>10</sup> and more recently dithietan **8** and 3,5-di-*t*-butyl-*o*-benzoquinone adducts **9**.<sup>11</sup> Where the barriers to permutational isomerization are sufficiently high, e.g. in equilibration of the geometrical isomers **10** and **11** (*R* = aryl, alkyl, vinyl, etc.), conventional kinetic methods can be employed.<sup>11</sup> From the accumulated data emerges a tentative scale of relative apicophilicity such as the one shown. It must be treated with caution but agrees with much experimental data in the literature.



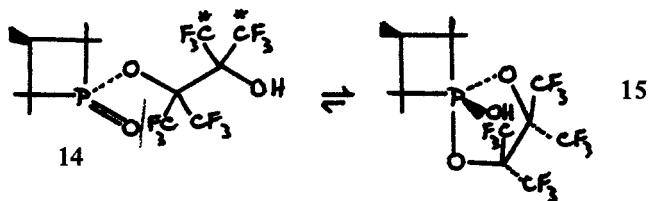
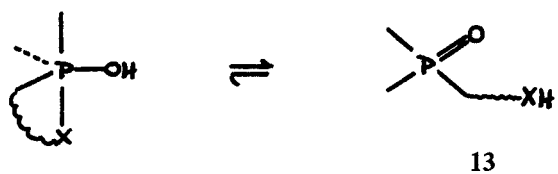
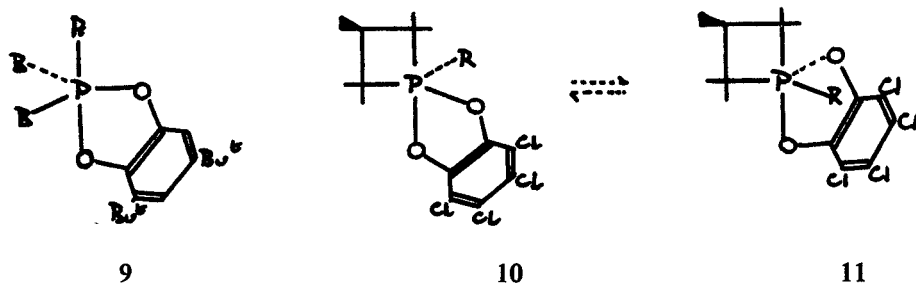
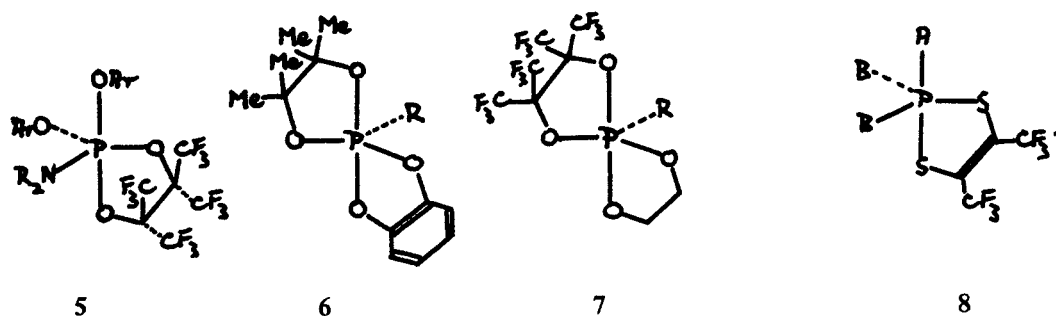
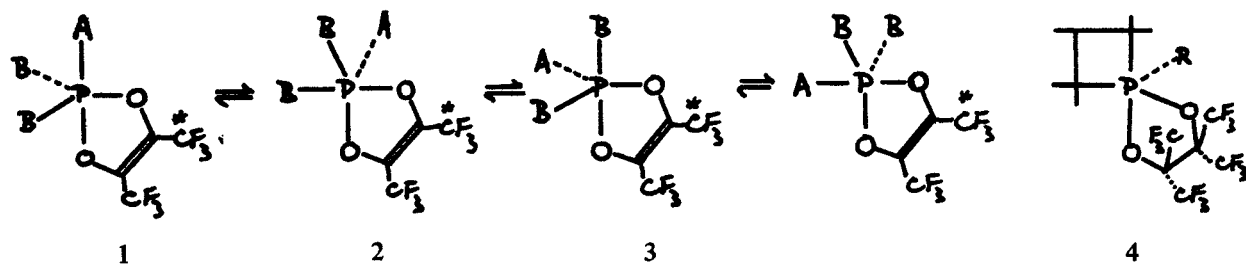
Among points of particular interest in this scale are the comparable apicophilicities of phenoxy- and phenylthio-groups,<sup>12</sup> the low apicophilicity of amino-groups, and the high apicophilicity of the hydrogen atom. The hydroxy-group is of considerable interest in this respect but we have been unable to obtain a genuine hydroxyphosphorane. The phosphoryl bond is so strong that equilibria of the type **12**  $\rightleftharpoons$  **13** lie on the right-hand side even in the case of the phosphinate **14** where the corresponding hydroxyphosphorane **15** would be stabilized by relief of strain in the four-membered ring. However the <sup>19</sup>F nmr spectrum of **14** at room temperature consists of a singlet which broadens at lower temperatures and splits into two multiplets of equal intensity below  $-87^{\circ}\text{C}$ . This may be associated with a slowing on the nmr time-scale of equilibration of the topomers **14** and **16** *via* the higher-energy phosphoranes **15** and **17**.<sup>11</sup>

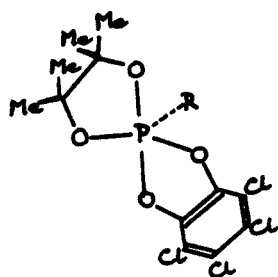
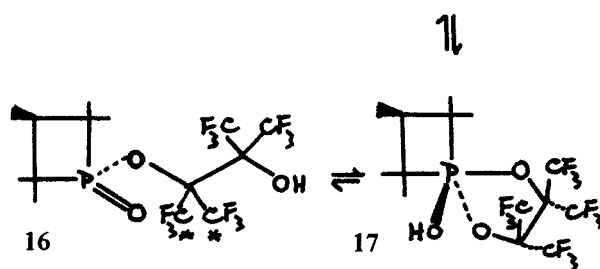
The interpretation of each individual dnmr experiment is always open to doubts which cannot be resolved entirely satisfactorily. Dissociation to betaines undoubtedly occurs in some cases<sup>1</sup> and cannot be eliminated completely in others. Adventitious nucleophiles may also lead to unexpectedly low energy barriers to permutational isomerization.<sup>13</sup> Evidence on the relative apicophilicities of chloro- and phenoxy-groups obtained from the phosphoranes **18** and **19**<sup>13</sup> is interesting in this connection. In the first case<sup>12</sup> chloro appears to be more apicophilic than phenoxy while in the second case<sup>6</sup> the position is reversed. Although both chloro-phosphoranes contain five-coordinate phosphorus, as shown by their positive <sup>31</sup>P chemical shifts and by their nmr spectra, the observed coalescence in either case could be due to an irregular process associated with the presence of nucleophilic impurities, e.g. chloride ions. If this were so the "true" coalescence temperature associated with the relevant pseudorotation would be higher than that actually observed, and the two experiments would be in better agreement, for an increased coalescence temperature in **18** (*R* = Cl) reduces the apicophilicity of chloro relative to phenoxy whereas an increased coalescence temperature for **19** (*R* = Cl) increases the apicophilicity of chloro relative to phenoxy.

## RING STRAIN

It is generally accepted<sup>14</sup> that small rings prefer to occupy apical-equatorial (*ae*) rather than diequatorial (*ee*) positions in trigonal bipyramidal phosphoranes but no quantitative data on these preferences have been reported. From the dynamic nmr spectra of a range of stable phosphoranes we have obtained data on the energies required to move various five-membered rings from *ae* to *ee* positions. Table I shows a selection of the relevant pseudorotations that can be slowed on the nmr time-scale and gives the free energies of activation for these processes. The signals (<sup>1</sup>H or <sup>19</sup>F) from the CH<sub>3</sub> or CF<sub>3</sub> substituents on the rings that remain *ae* were monitored. In each case the high-energy trigonal bipyramid **21** with a five-membered *ee* ring is regarded as equivalent to the transition state between **20** and **22**, two of the most stable topomeric conformers.

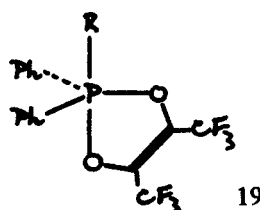
When a ring moves from an *ae* to an *ee* position (e.g. **23**  $\rightarrow$  **24**) of necessity some other group moves from an *e* to an *a* position. This may involve a change in apicophilicity of the apical substituents. Even if one allows for this, as in the penultimate column of the table, two facts are apparent: (a) the energy required to move five-membered rings containing heteroatoms bonded to phosphorus to an *ee* position is considerably greater than is needed in the case of a phospholan ring; and (b) the energy required depends not only on the nature of the heteroatom which moves from an *a* to an *e* position but also on the nature of the atom which remains equatorial.





R	$^{31}\text{P}$	$\Delta G^\ddagger$ (kcal mol $^{-1}$ )
Cl	13.6	17.8
PhO	38.9	20.5

18



R	$^{31}\text{P}$	$\Delta G^\ddagger$ (kcal mol $^{-1}$ )
Cl	4.9	12.0
PhO	18.8	12.6

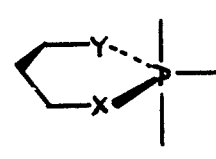
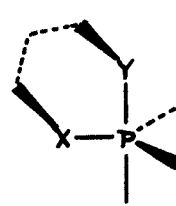
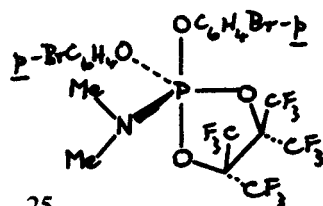
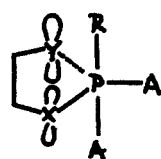
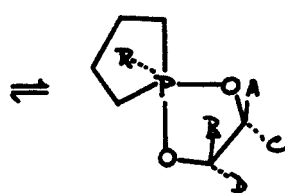
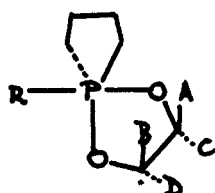
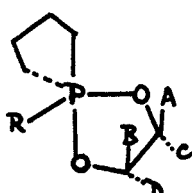
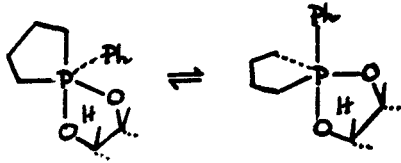
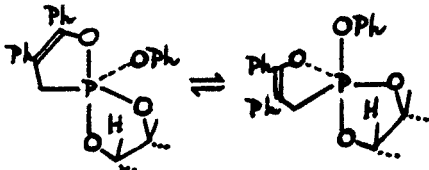
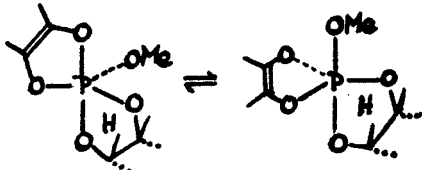
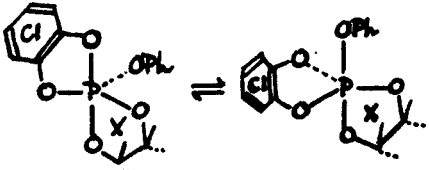
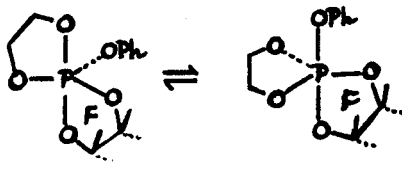
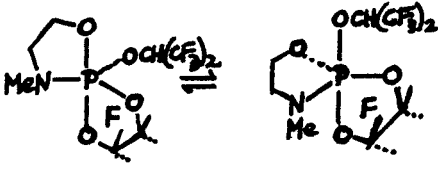
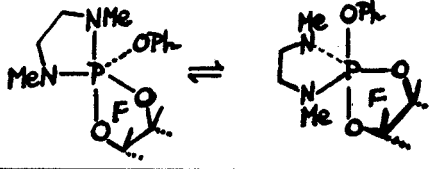


TABLE I

<u>Pseudorotation</u>	<u><math>\Delta G^\ddagger</math></u>	<u><math>\Delta G^\ddagger</math>-AA</u> (kcal mol <sup>-1</sup> )	<u><math>\Delta G^\ddagger</math> (Calc)</u>
	8.9	8	9
	14.1	15	14
	21.2	21	20
	X=F 21.8 X=H 20.5	22 21	20
	17.4	18	17
	21.0	22	22
	20.4	29	20

It is possible to rationalize these data<sup>10</sup> by taking into account the preferred orientation of lone-pairs on equatorially-bonded heteroatoms. This preference for the equatorial plane is well established both by calculation<sup>3</sup> and by experiment in the case of PN<sup>15</sup> and PS<sup>16</sup> (but not<sup>17</sup> PO) bonds and leads to a barrier to rotation round these bonds of 5-12 kcal mol<sup>-1</sup>. A recent x-ray analysis on the trigonal bipyramidal aminophosphoranes **25** shows the nitrogen to be planar with a 9° dihedral angle between the plane of the nitrogen and an apical plane.<sup>11</sup>

Note in particular that in a small *ee* ring, e.g. **24**, the lone-pairs occupying *p*-orbitals on equatorial heteroatoms are in an unfavourable apical plane. Therefore the total energy difference between **23** and **24** is composed of three basic terms: (a) an angle-strain factor due to increase in the bond angle at phosphorus; (b) the energy required to rotate the lone-pair on X from the *e* to an *a* plane; and (c) the difference in apicophilicity between R and Y, *when the lone-pair on equatorial Y is constrained to an apical plane*. The last is equivalent to the "normal" difference in apicophilicity between R and Y, as shown in acyclic systems in which the lone-pair on Y is free to take up the preferred equatorial orientation, plus the energy required to rotate the lone-pair on Y from the *e* to an *a* plane.

$$\text{i.e. } E^{24} - E^{23} = S + R^X + \Delta A(Y - R) + R^Y$$

The data in the last column of Table I were calculated on the following basis:

$$S^{\text{Phospholan}} = 8; \quad S^{\text{Phospholen}} = 10; \quad \Delta A(\text{PhO-AlkO}) = 1; \quad R^N = 10; \quad R^O = 5 \text{ kcal mol}^{-1}$$

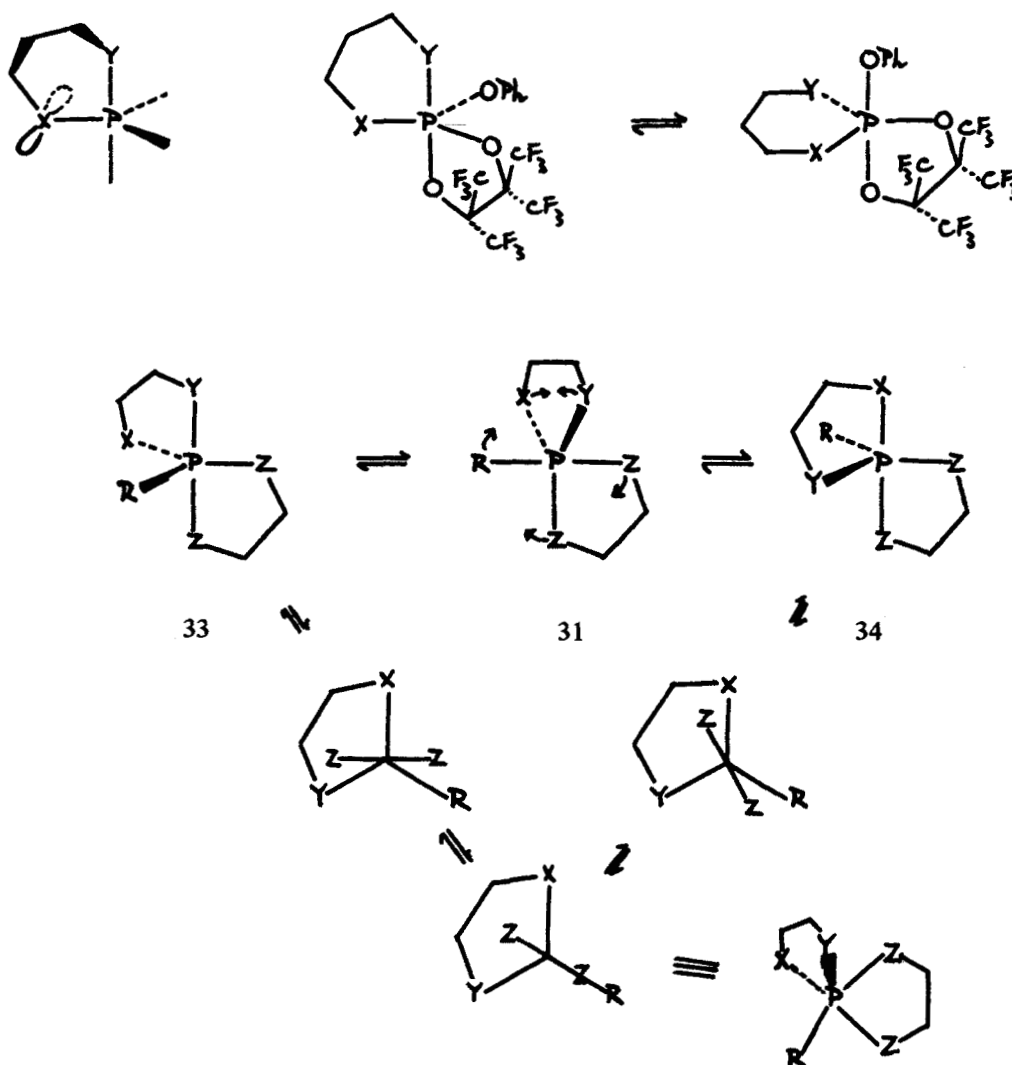
The only experimental evidence relating to  $R^O$  is<sup>17</sup> that it must be less than about 8 kcal mol<sup>-1</sup>. More information is required on this point but the general approach appears to be sound provided that steric effects are avoided.

The application of these ideas to six-membered rings is much more difficult. Models using  $sp^2$  hybridized heteroatoms suggest that with strain-free chair conformations occupying either *a-e* (**26**) or *e-e* (**27**) positions, the lone-pairs on equatorial heteroatoms are in *p*-orbitals nearer to an apical than to the favourable equatorial plane. However with an *a-e boat* conformation **28** the lone-pair on the equatorial substituent X can be in the equatorial plane. Certainly<sup>11</sup> there are considerably greater barriers to placing six-membered hetero-rings diequatorial (see Table II) than would be expected if these rings were most stable in the chair conformations **26** and once again the nature of the heteroatom that remains equatorial significantly affects the height of the barrier. An x-ray analysis on one of these compounds would be most interesting.

Table II  
Free energies of activation for the pseudorotations **29**  $\rightleftharpoons$  **30**

X	O	N	S	N
Y	0	0	0	N
$\Delta G^*$ (kcal mol <sup>-1</sup> )	6.1	9.5	9.2	<6

Although the permutational isomerizations of spiroposphoranes have been discussed in terms of bpr and ideal trigonal bipyramids, clearly this cannot be the case; the structures will distort to minimize destabilizing factors. In particular phosphoranes such as **31** with an *ee* small ring will try to reduce angle strain by distortion as shown towards the 0° [2+3] geometry **32** (shown in Newman projection), which is that of the highest-energy intermediate in the alternative TR<sup>2</sup> route from **33** to **34**.<sup>1,2</sup> Equally **32** will distort towards trigonal bipyramidal geometry in order to relieve the interaction between R and Z due to the small angle RPZ (*ca.* 80°). The "true" highest-energy intermediate between **33** and **34** will probably have a geometry somewhere between those of **31** and **32**. The justification in thinking about it as a trigonal bipyramid lies only in the fact that theoreticians have told us a great deal about bonding in trigonal bipyramidal phosphoranes and very little, so far, about [2+3] structures. To organic chemists, who are used to thinking of four-coordinate carbon as tetrahedral, this approximation may not be too absurd.



### STERIC FACTORS

It is often assumed that in a trigonal bipyramidal phosphorane the apical position is the more hindered, for the apical substituent has three nearest neighbors while the equatorial substituent has only two. However there is no clear experimental evidence on this point. We have looked for steric effects in the perfluorobiacyl adducts (35) of phenyl phosphinites where the pseudorotation that can be slowed on the nmr time-scale is  $35 \rightleftharpoons 36$  where  $R^1$  is less apicophilic than  $R^2$ . The results are in Table III.<sup>11</sup> The steadily increasing barrier to pseudorotation as both  $R^1$  and  $R^2$  change from Me to Bu<sup>t</sup> is due probably only in minor part to a change in the stereo-electronic component of apicophilicity as shown by the low barrier in the case of the *t*-butylmethylphosphinite adduct, and is consistent with increasing relative steric compression at the apical position as the alkyl groups remaining equatorial increase in size.

Another form of steric hindrance to pseudorotation is found in small-ring phosphoranes when there are substituents on an  $\alpha$ -carbon in the ring. A classical example, noted by Gorenstein,<sup>18</sup> occurs in benzylidene-



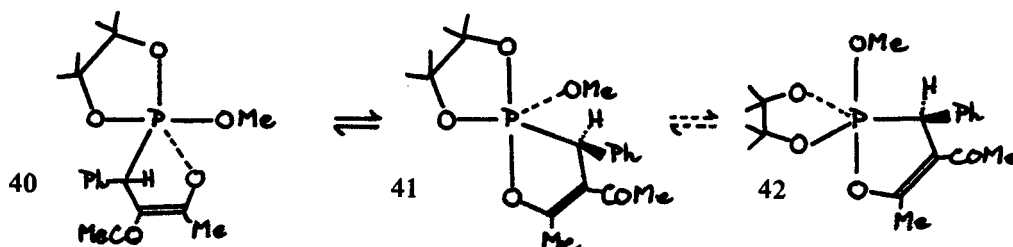
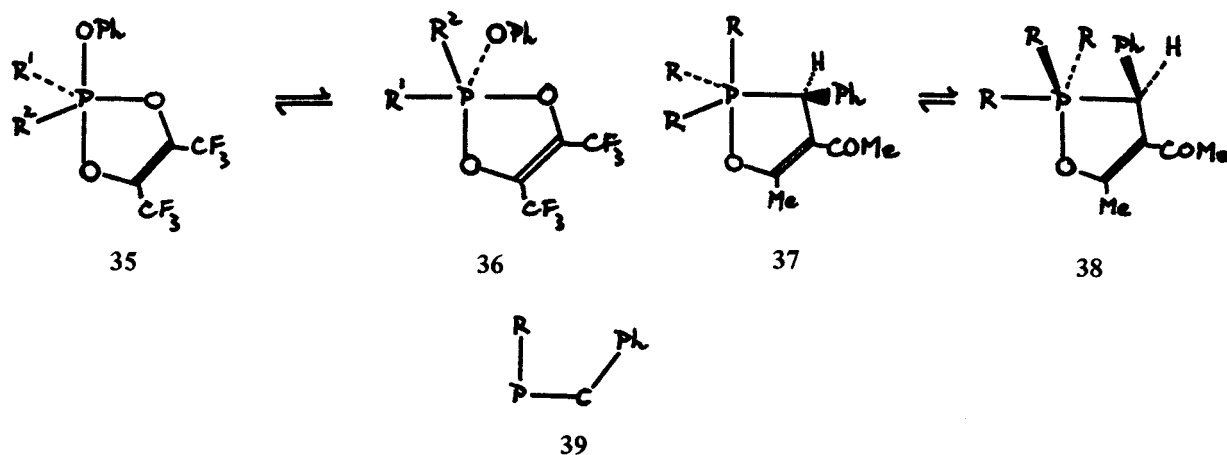
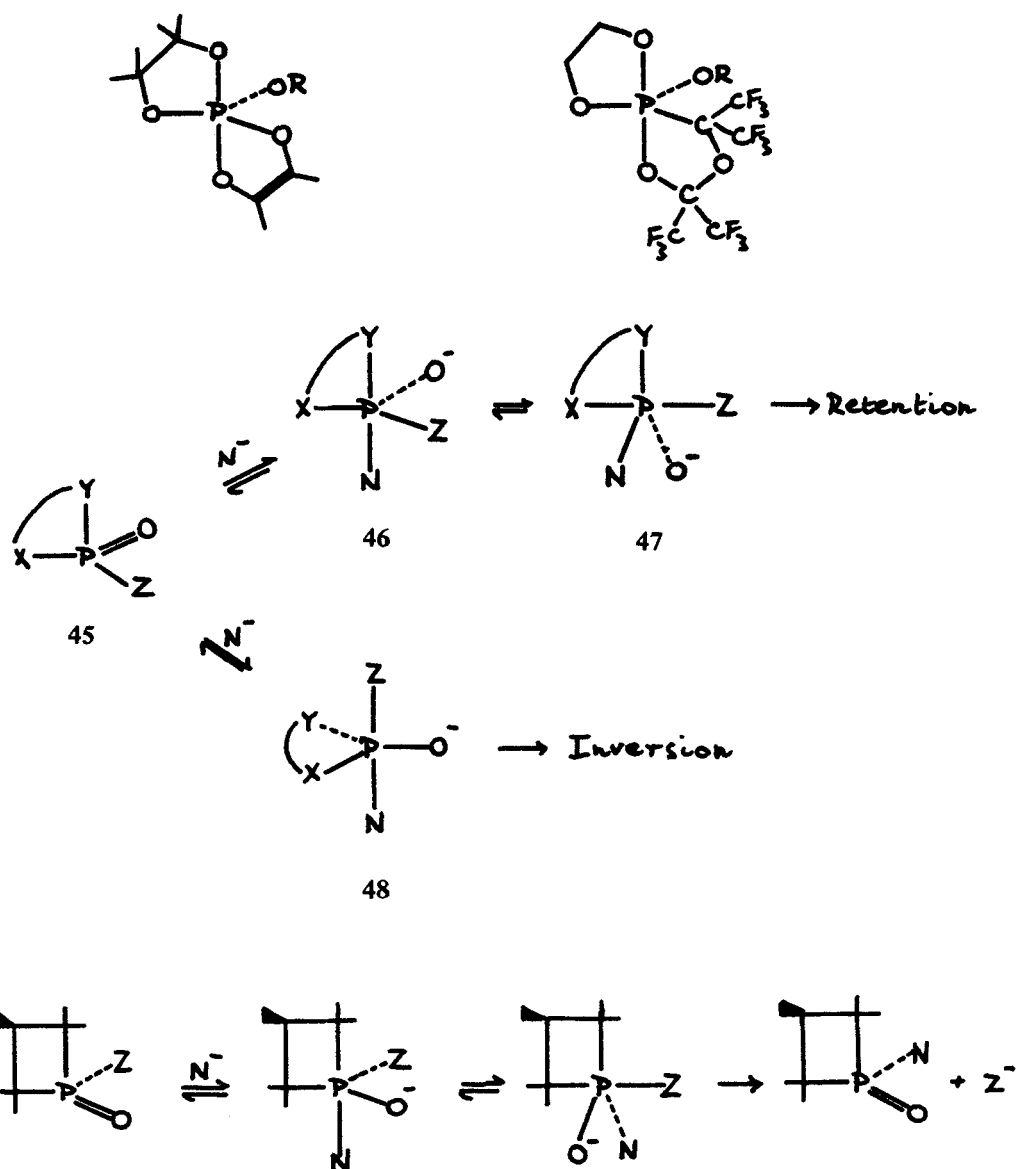


TABLE III  
Free energies of activation for the pseudorotations  $35 \rightleftharpoons 36$

$R^1$	Me	Et	$Pr^i$	$Bu^t$	Ph	$Bu^t$
$R^2$	Me	Et	$Pr^i$	$Bu^t$	Ph	Me
$\Delta G^*$ (kcal mol <sup>-1</sup> )	10.0	10.9	12.9	14.6	12.6	11.1

acetyl acetone adducts **37** where the barriers to pseudorotation are considerably higher than in the corresponding methyleneacetylacetone adducts. Note that when the carbon of the oxaphospholen ring is apical as in **38** there is complete eclipsing of the type shown in **39** of the substituents on that carbon and two equatorial substituents. Even in these adducts however the effect of the nature of the atom that remains equatorial when a ring takes up a diequatorial position is clearly shown. Thus in the spirophosphorane **41** the barrier to placing the oxaphospholen ring diequatorial as in **40** is 17.6 kcal mol<sup>-1</sup> while the pseudorotation of  $41 \rightleftharpoons 42$  is slow on the nmr time-scale at 170°, i.e.  $\Delta G^* > 23$  kcal mol<sup>-1</sup>.<sup>11,19</sup>

Such steric effects seem to be able to reverse small differences in apicophilicity. Thus in general and in for example the spirophosphoranes **43** methoxy is more apicophilic than *t*-butoxy. However in adducts analogous to **41** and in the 1,3,4-dioxaphospholans **44** the reverse is the case.<sup>11</sup>



## APPLICATIONS

Data on relative apicophilicities and strain factors are of considerable help in thinking about reactions at phosphorus, particularly when this atom is part of a ring. In general nucleophilic substitution at a cyclic phosphoryl centre 45 can proceed *via* 46 and 47 with retention of configuration at phosphorus or *via* 48 with inversion. The probably course can be assessed by comparing the energy of 48 with that of 46 or 47 whichever is the higher. The large energy required to place a five-membered hetero-ring diequatorial dictates that substitutions in these compounds will involve retention at phosphorus, but in similar six-membered rings the two competing paths could be more evenly balanced. As the apicophilicity of the

nucleophile increases there is the possibility that **47** will be of higher energy than **46** and a greater probability that the reaction will proceed with inversion at phosphorus. This approach is not always successful particularly in finely balanced systems, where other factors such as solvation may be important, and when the leaving group forms a particularly strong bond to phosphorus, e.g. fluorine.<sup>20</sup> Here the most important steps in deciding the course of the reaction are probably those involving loss of the leaving group.

Phosphetane chemistry, which is where our interest in five-coordinate intermediates began,<sup>21</sup> is readily understood in terms of ring-strain and relative apicophilicities. The 17-18 kcal mol<sup>-1</sup> required to place the four-membered ring diequatorial<sup>8</sup> is too large to be overcome by apicophilicity factors, and substitutions, e.g. in **49**, must involve retention at phosphorus as shown.<sup>22</sup>

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