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STRAIN FACTORS IN FIVE-MEMBERED PENTACOVALENT PHOSPHORANES

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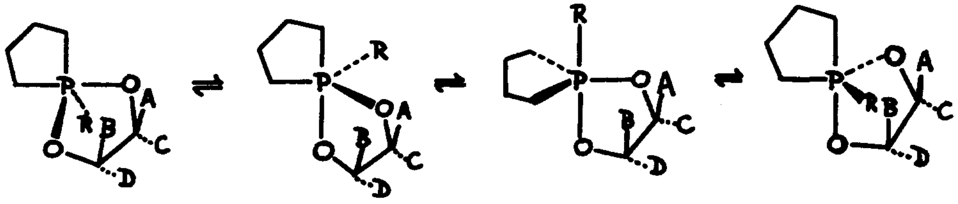
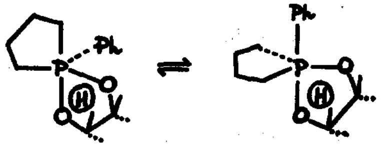
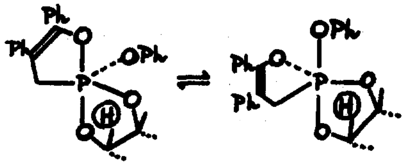
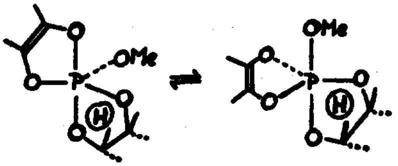
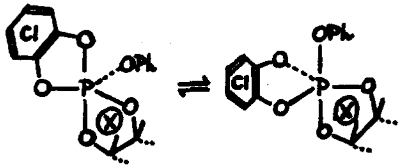
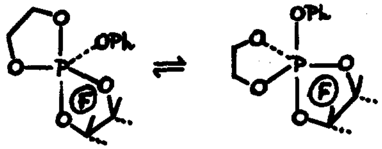
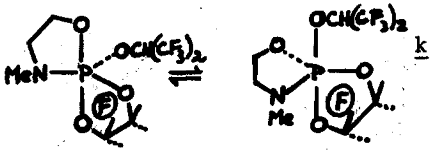
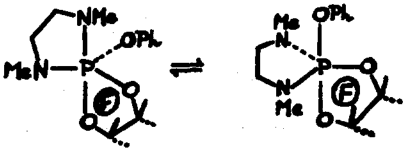
It is generally accepted[1] that small-membered rings prefer to occupy apical-equatorial (ae) rather than diequatorial (ee) positions in trigonal bipyramidal pentacovalent phosphoranes but no quantitative data on these preferences have been reported. From the dynamic n.m.r. spectra of a range of stable phosphoranes we have obtained data on the energies required to move various five-membered rings from ae to ee positions. The Table shows a selection of the relevant pseudorotations that can be studied on the n.m.r. time-scale and gives the free energies of activation for these processes. The signals (^1H or ^{19}F) from the CH_3 or CF_3 substituents on the rings that remain ae were monitored. In each case the high-energy trigonal bipyramid (3) with a five-membered ee ring is regarded as equivalent to the transition state between (1) and (4), two of the most stable topomeric conformers. At low temperatures, there is direct and rapid (on the n.m.r. time-scale) pseudorotation of (1) with (2) making A≡B and C≡D; A-D therefore appear in the n.m.r. spectrum as two equal signals. Equivalence of the four substituents A-D and coalescence of the two signals occurs when, with increasing temperature, the pseudorotation of (1) to (4) via (3) becomes rapid on the n.m.r. time-scale.



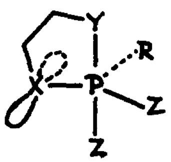
(2) (1) (3) (4)

When a ring moves from an ae to an ee position (e.g. 5 → 6), of necessity some other group moves from an e to and 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,

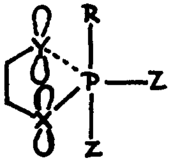
Table

Pseudorotation[a]		ΔG*[b]	ΔG*-ΔA[c] (kcal mol^{-1})	ΔG* (Calc)
	d	8.9	8[e]	9
	f	14.1	15	14
	g	21.2	21	20
	h	X=F 21.8 X=H 20.5	22 21	20
	j	17.4	18	17
	k	21.0	22	22
	j	20.4	29	20

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.



(5)



(6)

It is possible to rationalise these data 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[2] and by experiment in the case of PN[3] and PS[4] (but not[5] PO) bonds and leads to a barrier to rotation round these bonds of 5 - 12 kcal mol^{-1}. The point to note in particular is that in a small-membered *ee* ring the lone-pairs occupying *p*-orbitals on equatorial heteroatoms are in an unfavourable apical plane.

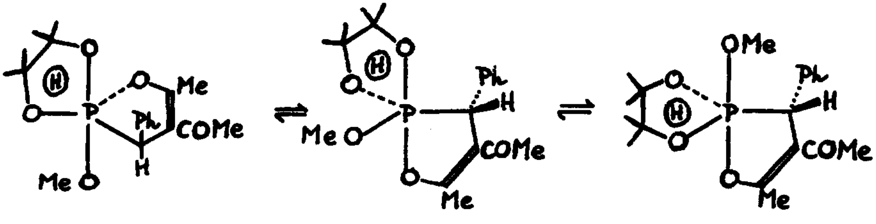
The total energy difference between (6) and (5) is therefore composed of three basic terms; (a) an angle-strain factor due to increase in the bond angle at phosphorus, (b) the energy required to rotate the lone-pair on X from the *e* to an *a* plane, and (c) the difference in apicophilicity between R 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 A 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.

i.e. $$E^6 - E^5 = S + R^X + \Delta A(Y\text{-}R) + R^Y$$

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

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

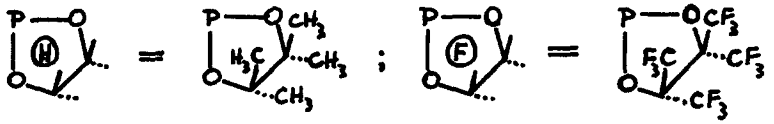
The only experimental evidence relating to R^O is[5] that it must be less than about 8 kcal mol^{-1}. More information is required on this point but the general approach appears to be sound provided that steric effects are avoided. These are found in phosphoranes with branching on atoms attached to phosphorus e.g. in the classical benzylideneacetylacetone adducts.[6] Even here the effect of the atom which remains equatorial is shown clearly; the pseudorotation (7)⇌(8) has $\Delta G^* = 17.6$ kcal mol^{-1} (calc.15) but the pseudorotation (8)⇌(9), which leads to equilibration of (8) with its *cis*-isomer, is slow on the n.m.r. time-scale at 170°C (i.e. $\Delta G^* > 23$ kcal mol^{-1}).[10]



(7) (8) (9)

Footnotes

a



b Calculated from the Gutowsky Holm equation. *c* Using data from acyclic systems.[7] *d* Obtained *via* the 'exchange' route.[8] *e* This agrees with data on $(CH_2)_4PF_3$.[9] *f* From methylenedeoxybenzoin. *g* From biacetyl. *h* From tetrachloro-*o*-benzoquinone. *j* From hexafluoroacetone. *k* From the corresponding dimethylamino compound and hexafluoroisopropanol. In this case four ^{19}F n.m.r. signals coalesce to two.

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