

INTRAMOLECULAR REARRANGEMENTS IN PHOSPHORANES VIA BIMOLECULAR INTERMEDIATES

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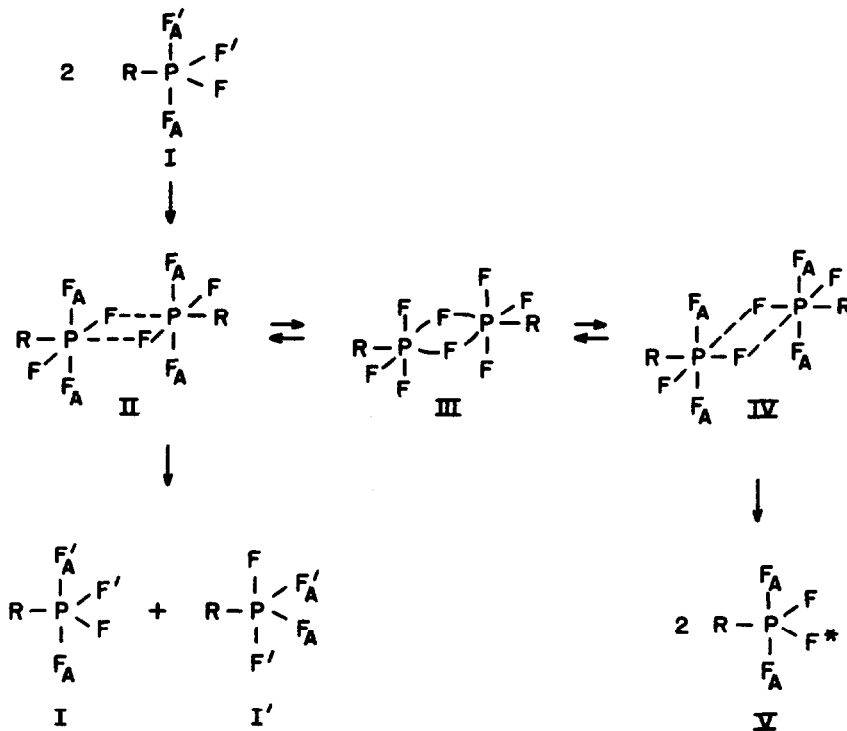
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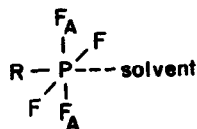
The intramolecular rearrangement of phosphoranes has been discussed by numerous authors¹⁻⁵ who invariably assume that the process is unimolecular. We suggest here that the process might actually be bimolecular, either involving a dimer of the phosphorane or involving a phosphorane-solvent complex, both of which could occur as transition states or more likely as metastable excited states. Experiment has not yet been able to distinguish⁵ between the favored BPR^{1,3} and TR² axax unimolecular mechanisms, and mechanisms associated with the axax mode. Proof of a bimolecular rearrangement would provide strong evidence in favor of the axax rearrangement. This would serve to essentially exclude an axax rearrangement and provide the first proof of the stereochemistry involved. We discuss explicitly a fluorophosphorane, RPF₄, although at least one of the arguments applies to all known phosphoranes.

It is well-known that phosphorus(V) is a strong Lewis acid and can form stable six-coordinate neutral complexes and negative ions. We suggest first that RPF₄, I, can form the non-symmetric dimeric intermediate II which can then decompose to I', the axax (e.g. Berry pseudorotation) product, or back to I itself. Only when more free energy is available does the dimer II go to IV, via the activated complex III, and then to V as postulated by Cowley.^{6,7} Recent CNDO/2 calculations⁸ have shown that the square pyramid lies 30kcal higher than the TBP. If each P...F bridge contributes a reasonable -12kcal the dimer would be excited by only 6kcal supporting our suggestion. We have not carried out further CNDO/2 calculations because of the known unreliability of the method away from equilibrium geometry. Notice that our discus-

sion is somewhat simplified in that there are actually several non-equivalent locations for the R-groups and that I and I' are not produced in equal concentration.



We further suggest that in the presence of appropriate solvents the phosphorane I can form the excited complex VI which can also decompose to either the rearranged I' or back to I. Since triethylamine and diethylether actually form stable such complexes,⁹ it is likely that many other solvents should at least form low-lying



VI

excited complexes. Unfortunately, the solubility of phosphoranes at low temperature is sufficiently low that it will be exceedingly difficult to do the necessary experiments with non-interacting solvents.

These mechanisms are attractive because:

(1) they provide one of the two possible stereospecific rearrangements consistent with experiment;⁵

(2) they utilize known octahedral phosphorus geometry rather than the speculative tetragonal pyramid of which there are no known examples; an example of the dimer has been proposed for the molecular structure of $(Cl_3CH)_2[(C_6H_5)_3PCl_2]_2$, and the related SbF_5 is polymeric even in solution. There should be no prejudice against non-symmetric dimers since other hypervalent molecules such as BrF_3 , ClF_3 , $(C_6H_5)_2ICl$ and probably SF_4 are well-known to have analogous structure.¹¹ Related examples in metals occur for hexacoordinate iron,¹² and tetracoordinate platinum.¹³

(3) they explain the wide range of activation energies obtained, since the barrier to dimer-formation will depend critically on the molecules involved as is generally the case in transitional metal complexes; the observed¹⁴ activation energies (ΔG^\ddagger) for RPF_4 molecules are $> 15kcal$ for $R=NH_2$,¹⁵ $9kcal$ for $R=N(CH_3)_2$, $\sim 4kcal$ for $R=Cl$, and $\lesssim 4kcal$ for $R=F$ and CH_3 .

We have assumed here that all phosphoranes are TBP's and rearrange according to the same mechanism. A non-TBP structure has been recently found,⁸ however, and a recent kinetic study has indicated the possibility of an ee process.¹⁶ Such assumptions are therefore not intended to be all-exclusive.¹⁷

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References and Footnotes

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$$\text{PF}_2(\text{NMe}_2) + \text{BrCN} \rightarrow \text{BrPF}(\text{NMe}_2) + \text{NCPF}_3(\text{NMe}_2)$$
 (J.E. Clone and K. Cohn, *Inorg. Chem.* **7**, 2067 (1968)) is likely to take place via a dimer of $\text{PF}_2(\text{NMe}_2)$ with $\text{NCPF}_2(\text{Br})(\text{NMe}_2)$.
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