

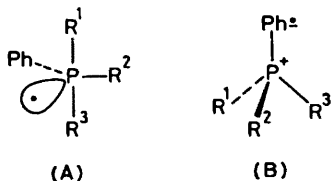
Evidence of Prevailing Strain Effects on the Valence State of the 5-Phenyl-4,6-dioxa-1-aza-5-phospha(v)bicyclo[3.3.0]octan-5-yl Radical

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Summary The valence state of phenylphosphoranyl radicals, which has been shown to depend on the electro- negativity of the other ligands, appears also to be influenced by incorporation of the phosphorus within

a rigid skeleton, which forces the unpaired electron of the bicyclic title compound to be centred on phosphorus in contrast to the behaviour of its acyclic analogue, in which the unpaired electron is preferentially located on the aromatic ring.

E.s.r. studies on a number of phosphoranyl radicals which possess an aryl ligand¹⁻³ reveal that two types can be distinguished, depending on the nature of the substituents R¹, R², and R³. If one of these ligands is highly electron-withdrawing (CF₃CH₂O, Cl, or MeS) a large a_P (600—1000 G) is observed, indicating a trigonal bipyramidal (TBP) configuration (type A).³ On the other hand, the presence of ligands with less P^v stabilizing capability (Me₂N or MeO) gives rise to only a small a_P (<40 G), which points to a



tetrahedral (T) structure with the unpaired electron located on the phenyl ring¹ (type B). In both cases the geometry of the phenylphosphoranyl radicals has been confirmed by van Dijk *et al.*⁴ using CNDO/2 and UHF calculations.

We now report that besides the electronic effects, there is another factor which exerts influence upon the structure of phenylphosphoranyl radicals, *i.e.*, the rigidity of the species. The e.s.r. spectrum of the 5-phenyl-4,6-dioxo-1-aza-5-phospha(v)bicyclo[3.3.0]octan-5-yl radical (**1**), generated by photolysis of (**2**) in the presence of di-*t*-butyl peroxide in toluene at 203 K, shows an a_P of 763 G.† This phosphorus-splitting value characterizes the structure of (**1**) as TBP (type A), in which the unpaired electron occupies an equatorial position.

† No further hyperfine splittings could be observed. Compound (**2**) was prepared according to the method of D. Houalla, T. Mouheich, M. Sanchez, and R. Wolf, *Phosphorus*, 1975, **5**, 229.

¹ G. Boekestein, E. H. J. M. Jansen, and H. M. Buck, *J.C.S. Chem. Comm.*, 1974, 118.

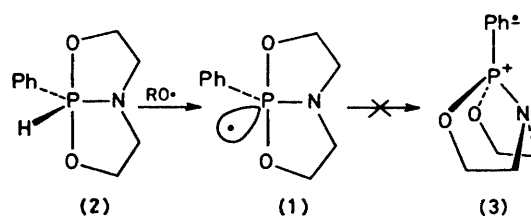
² P. Schipper, E. H. J. M. Jansen, and H. M. Buck, 'Topics in Phosphorus Chemistry,' vol. 9, eds. M. Grayson and E. J. Griffith, Wiley-Interscience, New York, 1977, pp. 407—503.

³ A. G. Davies, M. J. Parrott, and B. P. Roberts, *J.C.S. Chem. Comm.*, 1974, 974.

⁴ J. M. F. van Dijk, J. F. M. Pennings, and H. M. Buck, *J. Amer. Chem. Soc.*, 1975, **97**, 4836.

⁵ W. G. Bentrude, *Phosphorus and Sulfur*, 1977, **3**, 109.

⁶ R. F. Hudson and C. Brown, *Accounts Chem. Res.*, 1972, **5**, 204.



This is clearly not an electronic effect, since the hyperfine splittings of the acyclic analogous radical PhP(OEt)-(NEt₂)OBu[†] [a_P 10.9, $a(p-H)$ 14.4, $a(o-H)$ 5.9, and $a(m-H)$ 1.4 G] and the related radical PhP(NEt₂)₂OBu[†] [a_P 10.5, $a(p-H)$ 10.5, $a(o-H)$ 5.0, and $a(m-H)$ *ca.* 0 G] indicate a tetrahedral configuration (type B), as was earlier observed for PhP(OMe)₂OBu[†] (*vide supra*).¹ The radicals were generated by reaction of the corresponding phenylphosphonite with *t*-butoxyl radicals. Apparently the initially formed structure (A) underwent stereoisomerization to (B).⁵

The TBP structure of (**1**) is stabilized by the two five-membered rings, which bridge favourable apical-equatorial positions. Thus the energy of (**1**) is lowered with respect to its acyclic analogue. On the other hand, the rings will increase the energy of the phosphonium structure (**3**) by enhanced ring strain and crowding in comparison with the acyclic analogue.⁶ This results in the formation of a stable TBP structure. Apparently it is possible to impose the valence state v on phosphoranyl radicals by incorporation of the phosphorus within a rigid framework.

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