3,3,3′,3′-Tetramethyl-1,1′-spirobi[3*H*-2,1-benzoxaphosph(v)ole]-1-yl Radical: Evidence of a Correlation between Pseudorotation and Stereoisomerisation

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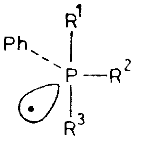
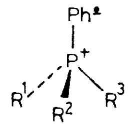
Summary It is shown that the factors which determine the stereoisomerisation of phenylphosphoranyl-radicals are similar to those determining the pseudorotation of P^V phosphoranes.

E.S.R. studies on phenylphosphoranyl-radicals show that the electronic nature of the other ligands prescribes the valence state of phosphorus in these radicals.[1-3] If one of these ligands is highly electron-withdrawing (CF_3CH_2O, Cl, MeS) large a_P values (600—1000 G) are observed indicating a P^V trigonal bipyramidal (TBP) structure with the unpaired electron mainly located on phosphorus as an equatorial fifth ligand, structure (A). In contrast, phenylphosphoranyl-radicals which do not possess ligands with a P^V stabilizing capability, *i.e.* Me$_2$N or MeO, do not favour the P^V TBP structure since the unpaired electron can be stored in the phenyl-ring, which results in a tetrahedral (T) configuration for phosphorus with low a_P values (< 40 G), structure (B).[1]



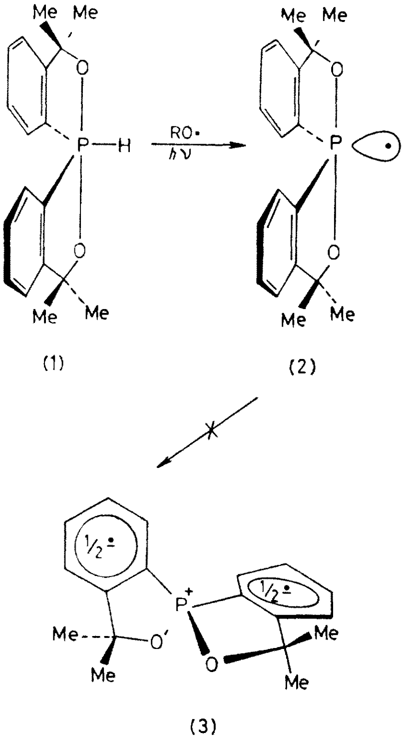
(A)



(B)

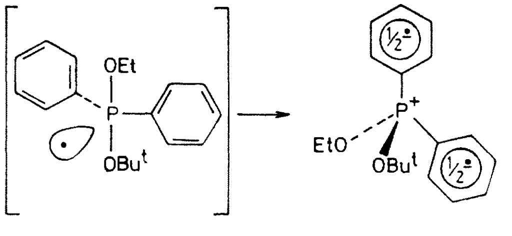
Recently it has been reported that the incorporation of rigidity into the phenylphosphoranyl-radical enables it to overcome the electronic effects, which accounts for the high a_P value observed in the 5-phenyl-4,6-dioxa-1-aza-5-phospha(V)bicyclo[3.3.0]octan-5-yl radical.[4]

We now report the behaviour of the spirocyclic phosphoranyl-radical (2) which indicates a correlation between pseudorotation and stereoisomerisation. The e.s.r. spectrum of the 3,3,3′,3′-tetramethyl-1,1′-spirobi[3*H*-2,1-benzoxaphosph(V)ole]-1-yl radical (2), generated by photolysis of (1) in the presence of di-t-butyl peroxide in toluene at 203 K (Scheme 1), shows an a_P of 652 G while no further hyperfine splittings could be observed.† This phosphorus-splitting value characterizes the structure of (2) as TBP (type A) in which the unpaired electron occupies an equatorial position. This is in sharp contrast with the behaviour of the analogous acyclic radical Ph$_2\dot{P}$(OEt)OBu^t possessing isoelectronic ligands which only shows a low a_P value of 23.0 G.[3] This a_P value indicates the occurrence of a T configuration (type B). Apparently, the initial TBP structure (4) isomerizes immediately to (5) (Scheme 2). The behaviour of (5) is consistent with other acyclic radicals such as Ph$\dot{P}$(OEt)$_2$OBu^t and Ph$_3\dot{P}$OBu^t which also occur in a T configuration (type B).[3]



(1) (2) (3)

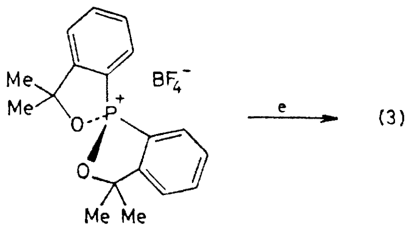
SCHEME 1



(4) (5)

SCHEME 2

Obviously, the different behaviour of (2) cannot be ascribed to electronic factors, but is correlated with the incorporation of its ligands into the five-membered rings. It is conceivable that the five-membered rings increase the energy of the tetrahedral phosphonium-structure (3), by both enhanced ring-strain and crowding in comparison with the acyclic analogous radical (5).[4] For structure (3) however, strain effects are probably not dominant since this radical could be generated by the cathodic reduction of the phosphonium salt (6) in acetonitrile at 228 K (Scheme 3).‡ The e.s.r. spectrum of (3) observed in this experiment shows a_P 8.4 G, $a_{p\,H}$ 5.6 G (2H), $a_{o\,H}$ 3.0 G (2H), and $a_{m\,H}$ *ca.* 0 G, indicating that the unpaired electron is located in both phenyl-rings, with phosphorus in a T configuration (type B).



(6)

SCHEME 3

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† Compound (1) was prepared according to the method of ref. 5.

‡ Compound (6) was prepared in a similar way to that described by I. Granoth and J. C. Martin, *J. Am. Chem. Soc.*, 1979, **101**, 4618 for the analogous phosphonium trifluoromethanesulphonate by using a 50% solution of fluoroboric acid in water instead of trifluoromethanesulphonic acid. ^{1}H n.m.r. (CD$_3$CN) δ 1.92 (6 H, s, Me), 1.97 (6 H, s, Me), and 7.62—8.18 (8 H, m, HAr), ^{31}P n.m.r. (CD$_3$CN) δ 82.2.

It is known that the stability of the P^V TBP structures is greatly enhanced by bridging apical and equatorial positions. Thus the precursor (**1**) is surprisingly stable[5] and furthermore shows no pseudorotation at room temperature, a behaviour which is in sharp contrast with that of the acyclic analogues. Similarly, the barrier to the stereoisomerisation of (**2**) to (**3**) is increased compared with that of the analogous acyclic phenylphosphoranyl-radical (**4**) to (**5**). Apparently, the factors which determine pseudorotation of the P^V phosphoranes (Muetterties' rules)[6] are similar to those determining the stereoisomerisation of the corresponding TBP phenylphosphoranyl-radicals (**2**) and (**4**). Moreover, this observation is consistent with the high a_P value (600—1000 G)[3] of acyclic phenylphosphoranyl-radicals on the introduction of highly electron-withdrawing ligands (Cl, MeS, CF_3CH_2O). These ligands preferentially occupy apical sites of the TBP P^V structure, thus suppressing pseudorotation and consequently stereoisomerisation.

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[1] G. Boekestein, E. H. J. M. Jansen, and H. M. Buck, *J. Chem. Soc., Chem. Commun.*, 1974, 118.

[2] P. Schipper, E. H. J. M. Jansen, and H. M. Buck in '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. Chem. Soc., Chem. Commun.*, 1974, 974.

[4] J. H. H. Hamerlinck, P. Schipper, and H. M. Buck, *J. Chem. Soc., Chem. Commun.*, 1979, 350.

[5] I. Granoth and J. C. Martin, *J. Am. Chem. Soc.*, 1979, **101**, 4623.

[6] R. F. Hudson and C. Brown, *Acc. Chem. Res.*, 1972, **5**, 204.