Reduction of Nitro- and Nitroso-compounds by Tervalent Phosphorus Reagents. Part XIII.[1] ^{1}H Nuclear Magnetic Resonance Studies of 3-Aryl-2,3-dihydro-1,3,2-benzoxazaphosph(v)oles and their 2-Oxo-analogues

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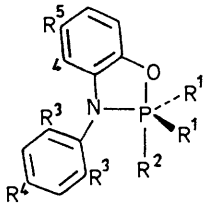
^{1}H N.m.r. spectra of two new series of phosphorus compounds are described, namely the tetraco-ordinate 3-aryl-2,3-dihydro-2-oxo-1,3,2-benzoxazaphospholes (2) and the pentaco-ordinate trigonal bipyramidal 3-aryl-2,3-dihydro-1,3,2-benzoxazaphosph(v)oles (1). Both types of compound generally exhibit a marked shielding of one of the aromatic protons by the second aromatic ring, the extent of which points to significant sterically induced antiplanarity between the two aromatic systems. The spectra of compounds (1) are temperature-dependent, indicating ligand reorganisation in the trigonal bipyramid. Measurements of coalescence temperatures and hence of ΔG^* for these processes indicate that the steric barriers already mentioned markedly influence the ease of ligand reorganisation.

THE preceding paper [1] describes reductions of aryl 2-nitroaryl ethers by tervalent phosphorus compounds leading to pentaco-ordinate phosphorus derivatives formulated as 3-aryl-2,3-dihydro-1,3,2-benzoxazaphosph(v)oles (1), which on hydrolysis gave various 3-aryl-2-oxo-1,3,2-benzoxazaphosph(v)oles (2; R^2 = alkoxy, HO, alkyl, or aryl). This paper describes ^{1}H n.m.r. evidence



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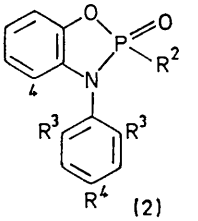


(2)

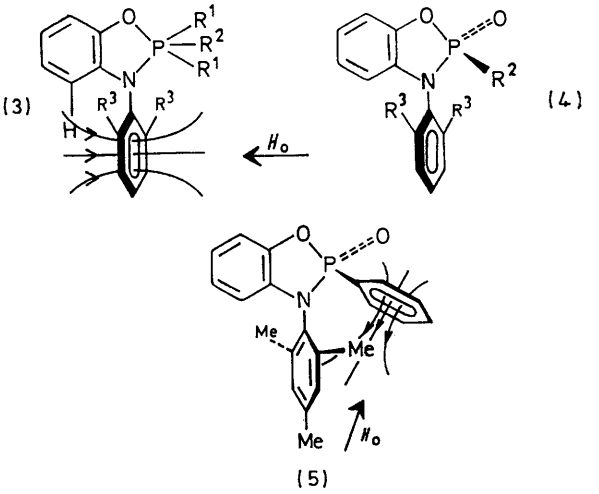
in favour of these formulations and includes the results of variable-temperature studies of permutational isomerisation (PI) of the trigonal bipyramidal oxazaphospholes (1).

Structures of the 3-*Aryl*-2,3-*dihydro*-1,3,2-*benzoxazaphospholes* (1).—The essential features of the ^{1}H n.m.r. spectra are recorded in Table 1. As an example, 3-(2,6-dimethylphenyl)-2,2,2-triethoxy-2,3-dihydro-1,3,2-benzoxazaphosphole (1; $R^1 = R^2 = EtO$, $R^3 = Me$, $R^4 = R^5 = H$) exhibited the expected phosphorus splitting of the methylene groups of P·O·CH_2·CH_3 (J_{HH} 7, J_{PH} 8.8 Hz) and also of the β-methyl group (J_{HH} 7, J_{PH} 1.6 Hz). The three aromatic protons of the 2,6-dimethylphenyl group are assigned to the signal at τ 2.98, and the high-field complex doublet or multiplet (1 H) at τ 4.14, which implies considerable shielding, is assigned to the aromatic proton at position 4 of the 1,3,2-benzoxazaphosphole system. This shielding effect is seen in each of the twenty-three compounds in Table 1, even in those cases where the phenyl *ortho*-positions are unsubstituted.

In these cases where the *ortho*-positions are unsubstituted [compounds (K), (L), (M), (P), (Q), (R), and (V)], the 4-proton resonates at a lower field (3.82—3.97), indicating that shielding, though still significant, is reduced. These results point to restricted rotation of the pendant *N*-aryl group in all cases; when the *ortho*-positions are blocked this results in the *N*-aryl group spending more of its time in an orthogonal or near orthogonal relation to the second aryl group [see (3)]. This suggestion of orthogonality is given substance by the variable-temperature studies described below and by the results of a related *X*-ray crystallographic investigation.[2]

Further support for the positional assignment of the high-field proton is provided by compound (1; $R^1 = R^2 = EtO$, $R^3 = R^5 = Me$, $R^4 = H$): the presence of a 5-methyl group leads to the appearance of the 4-proton signal as a broad singlet, rather than the usual multiplet.

Structures of the 3-*Aryl*-2,3-*dihydro*-2-*oxo*-1,3,2-*benzoxazaphospholes* (2).—The ^{1}H n.m.r. spectra are recorded



(3) (4) (5)

in Table 2. Again the 4-protons in those derivatives which contain *ortho*-blocking groups [compounds (AA)—(II)] exhibit a high field signal (τ *ca.* 3.8) indicating significant shielding by the second aromatic ring, and hence considerable sterically induced orthogonality. The shielding effect is not as great as in the corresponding pentaco-ordinate oxazaphospholes (τ *ca.* 4.1; Table 1),

[1] Part XII, J. I. G. Cadogan, D. S. B. Grace, P. K. K. Lim, and B. S. Tait, preceding paper.

[2] J. I. G. Cadogan, R. O. Gould, S. E. B. Gould, P. A. Sadler, S. J. Swire, and B. S. Tait, following paper.

which are more crowded. Further, in the tetracoordinate oxazaphospholes (2) which do not have blocked *ortho*-positions [compounds (JJ)—(LL)] the *N*-aryl ring has sufficient freedom of rotation to make the 4-proton signal indistinguishable from those of the remaining aromatic protons. In those compounds (2) the 2,4,6-trimethylphenyl groups of other oxazaphospholes resonate as a broad singlet, those of (5) resonate as two one-proton singlets, separated by 0.22 p.p.m.

When the remaining ligand on phosphorus is OH as in (4; R^2 = HO) [compounds (EE) and (FF) in Table 2], hydrogen bonding in the PO_2H group leads to equivalent

TABLE 1

^{1}H N.m.r. characteristics of 3-aryl-2,3-dihydro-1,3,2-benzoxazaphospholes (1) [a] at 28 °C

					τ Values				
					R^1 (J_{PH}/Hz)				
Compd.	R^1	R^2	R^3	R^4			H-4 [b]	Other ArH	Other Me
(A)	OEt	OEt	Me	H	9.0 (1.6)	6.10 (8.8)	4.14	3.0—3.6	7.88
(B)	OMe	OMe	Me	H		6.44 (13)	4.15	2.9—3.5	7.85
(C)	OPr^i	OPr^i	Me	H	8.92	5.2—5.7	4.1	2.9—3.5	7.88
(D)	OEt	Me	Me	H	9.08	6.26	4.17	2.9—3.6	7.85, 8.15 (17)
(E)	OEt	OEt	Me	H	9.0 (1.5)	6.08 (8.5)	4.28	3.0—3.7	7.86, 7.92
(F)	OEt	OEt	Me	Me	8.98 (1.5)	6.10 (8.5)	4.13	3.1—3.6	7.70, 7.92
(G)	OMe	OMe	Me	Me		6.47 (13)	4.12	3.0—3.6	7.70, 8.02
(H)	OPr^i	OPr^i	Me	Me	8.93	5.4	4.1	3.0—3.4	7.70, 7.94
(I)	OEt	Me	Me	Me	9.08	6.30	4.16	3.1—3.6	7.70, 7.90, 8.18 (17)
(J)	OEt	OEt	OMe	H	9.0 (1.5)	6.17 (9)	4.02	2.6—3.5	6.28
(K)	OMe	Ph	H	OMe		6.64 (12)	3.82	2.2—3.5	6.22
(L)	OMe	Ph	H	H		6.64 (12)	3.86	2.2—3.6	
(M)	OEt	Me	H	H	9.14	6.30	3.94	2.5—3.6	8.12 (18)
(N)	OMe	Ph	Me	Me		6.60 (12)	4.06	2.1—3.6	7.70, 7.89
(O)	Ph	OMe	Me	Me		7.51 (1)	4.03	1.9—3.6	7.73, 8.01
(P)	OMe	OMe	H	Me		6.50 (13)	3.97	2.7—3.7	7.60
(Q)	OMe	Ph	H	Me		6.63 (12)	3.81	2.2—3.28	7.63
(R)	Ph	OMe	H	Me		7.56 (10)	3.90	1.9—3.6	7.64
(S)	OMe	Ph	Me	H		6.62 (12.5)	4.09	2.2—3.6	7.86
(T)	OMe	OMe	Me	CO_2Me		6.44 (13)	4.16	2.19, 3.0—3.6	6.10, 7.83
(U)	[c]	Ph	Me	Me		5.7—6.5	4.08	1.96—3.5	7.70, 7.88, 8.14
(V)	OEt	OEt	H	OMe	8.98 (1.5)	5.9—6.3 (9)	3.90	2.9—3.5	6.20
(W)	OMe	Ph	OMe	H		6.65	3.95	2.2—3.6	6.36

[a] Correct ^{1}H integrals and multiplicities were obtained in each case. All compounds except (E) (R^5 = Me) had R^5 = H. [b] Except for compound (E), which gave a broad singlet, the signal was a multiplet centred at the τ value shown. [c] R^1R^1 = O·$[CH_2]_2$·O.

TABLE 2

^{1}H N.m.r. characteristics of 3-aryl-2,3-dihydro-2-oxo-1,3,2-benzoxazaphospholes (2) at 28 °C

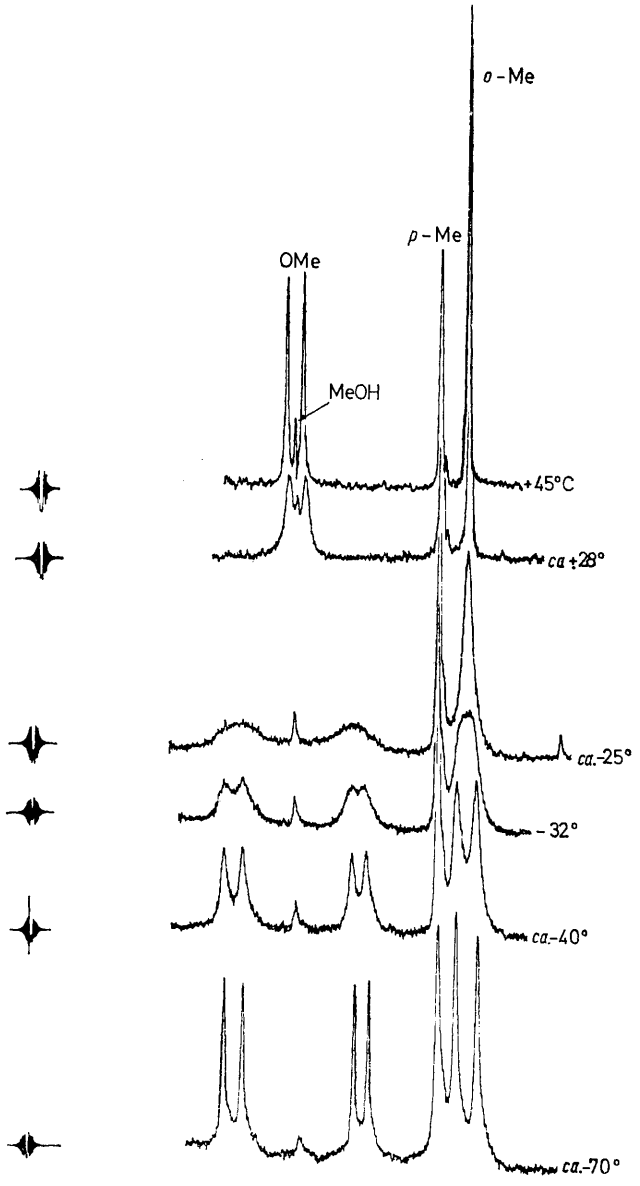
				τ Values			
Compd.	R^2	R^3	R^4	R^3	H-4	Other ArH	R^2 (J_{PH}/Hz)
(AA)	OMe	Me	H	7.69, 7.63	3.8	2.7—3.2	6.15 (12)
(BB)	OPr^i	Me	H	7.83, 7.71	3.88	2.8—3.2	8.88, 8.62, 5.18
(CC)	OMe	OMe	H	6.28, 6.19	3.70	2.64—3.35	6.20 (12)
(DD)	Me	OMe	H	6.25, 6.22	3.75	2.5—3.4	8.10 (17)
(EE)	OH	Me	H	7.80	3.80	2.7—3.2	
(FF)	OH	Me	Me	7.84 (7.65; R^4)	3.80	2.65—3.2	
(GG)	Ph	Me	Me	8.56, 7.63 (7.75; R^4)	3.78	2.1—2.9, 3.0—3.24	
(HH)	Ph	Me	H	8.50, 7.56	3.85	2.0—3.3	
(II)	Ph	OMe	H	6.86, 6.24		2.0—3.8	
(JJ)	Ph	H	Me	(7.72; R^4)		2.1—3.3	
(KK)	Ph	H	H			2.10—3.25	
(LL)	Me	H	OMe			2.5—3.5	8.20 (18)

which contain *o*-Me or *o*-MeO groups, the spectra exhibit separate signals for each group. This confirms that free rotation about the *N*-aryl bond is restricted, leading to different environments [*e.g.* (4)] for the blocking groups, which are then *syn* or *anti* to the phosphorus ligand [R^2 in (4)]. The difference in chemical shift is small (<0.2 p.p.m.) except when R^2 is phenyl, in which case the ring current effect on one of the *ortho*-groups, *e.g.* (5), leads to a larger chemical shift difference of 0.62—0.94 p.p.m. Furthermore, whereas the *meta*-protons of environments for the *ortho*-groups and a single signal is observed.

Permutational Isomerisation (PI) as Shown by Variable-temperature Studies of the ^{1}H *N.m.r. Spectra of* 3-*Aryl*-2,3-*dihydro*-1,3,2-*benzoxazaphospholes*.—The ^{1}H n.m.r. spectra of 2,2,2-trimethoxy-derivatives [(G) and (T); Table 3], at 28 °C, display sharp signals and do not distinguish between ligands which would be apical and equatorial in a 'frozen' trigonal bipyramid (TBP), indicating that PI is fast on the n.m.r. time scale. Slight

broadening of signals was apparent even at 28 °C in the corresponding 2-methyl- or 2-phenyl-2,2-dialkoxy-derivatives, however, indicating a retardation of the PI process.

Thus, the *PP*-dimethoxy-*P*-phenyl derivative (N) (Table 3) (Figure) showed a sharp doublet at +45 °C



Variable-temperature ^{1}H n.m.r. study of compound (6; Ar = 2,4,6-$Me_3C_6H_2$)

(J_{POMe} 12.3 Hz) due to the magnetically equivalent methoxy-ligands (τ 6.60). The signal broadened progressively as the temperature was lowered, being replaced by two doublets at *ca.* −32 °C, and giving at −60 °C two sharp three-proton doublets, the high-field doublet (J_{POMe} 10.8 Hz) being assigned to the apical methoxy-ligand in accord with its lower coupling constant as compared with the low-field doublet (J_{POMe} 14 Hz), assigned to the equatorial OMe. The coalescence temperature (T_c) (−5 °C) corresponds to a free energy of activation, for the two site-exchange process outlined

TABLE 3

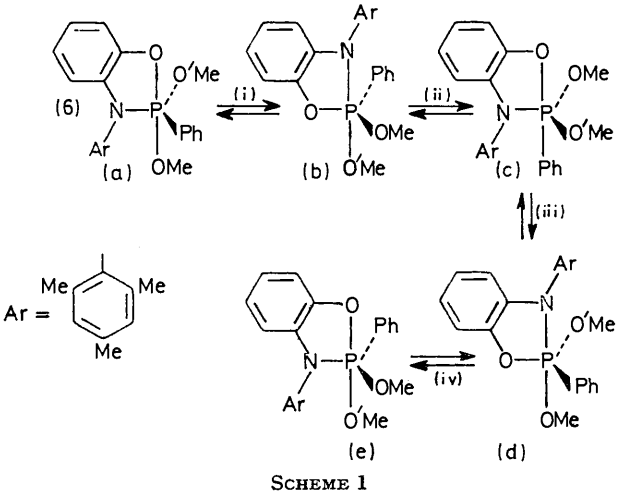
Variable-temperature ^{1}H n.m.r. studies on 3-aryl-2,3-dihydro-1,3,2-benzoxazaphospholes (1) †

Compd.	Phenyl subst.	$R^1_2R^2P$	T_c (°C)	ΔG^*/ kJ mol^{-1}
(M)	None	$(EtO)_2PMe$	−56	41.6
(L)	None	$(MeO)_2PPh$	−59	40.9
(Q)	4-Me	$(MeO)_2PPh$	−50	43
(K)	4-MeO	$(MeO)_2PPh$	−58	41.2
(N)	2,4,6-Me_3	$(MeO)_2PPh$	−5	52
(I)	2,4,6-Me_3	$(EtO)_2PMe$	−26	48.5
(O)	2,4,6-Me_3	Ph_2POMe	>200	v. high
(R)	4-Me	Ph_2POMe	>200	v. high
(U)	2,4,6-Me_3	PhP(−O−)(−O−)	+175 ‡ +175 ‡	23
(G)	2,4,6-Me_3	$(MeO)_3P$	−71	
(T)	2,6-Me_2-4-CO_2Me	$(MeO)_3P$	−75	

† In compounds (M) and (I) signals due to P·O·CH_2·CH_3 were observed. In all other cases PO·CH_3 signals were observed. ‡ T_c refers to *o*-Me coalescence.

in Scheme 1, of 52 kJ mol^{-1}. The most stable form, the ' frozen ' form, is (6a) or (6e), on the assumption that the ring oxygen prefers to be apical, in accord with its higher electronegativity and with its structure as determined by *X*-ray crystallography.[2] The high energy TBP may be that either with the phenyl group (6c) or, more likely, the amino group (6b) or (6d) apical, the TBP with both phenyl and amino-groups apical being considered very unlikely.

In order to probe the effect of the *ortho*-methyl groups in (6) on the PI process, the corresponding *N*-*p*-tolyl derivative (6; Ar = *p*-MeC_6H_4) was investigated. The overall behaviour was identical with that observed for the *N*-mesityl analogue (6; Ar = 2,4,6-$Me_3C_6H_4$), but, in contrast, the methoxy-resonance was a sharp doublet at +28 °C and the coalescence temperature was much lower (−50 °C; ΔG^* 43.0 kJ mol^{-1}). This energy difference



SCHEME 1

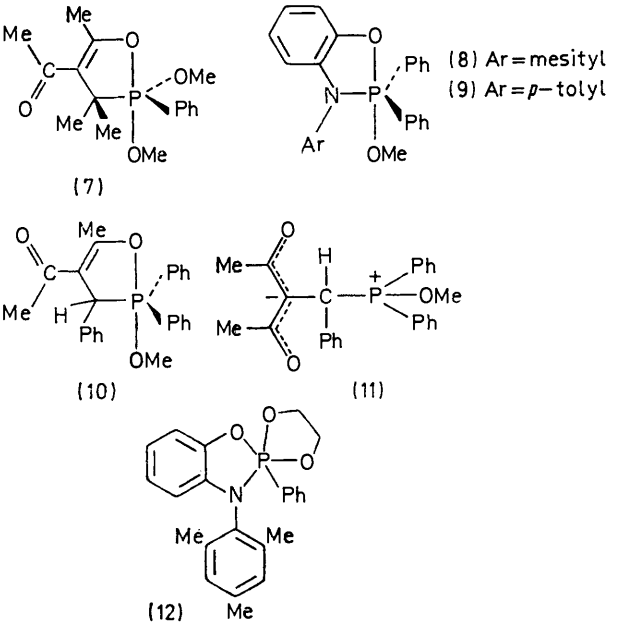
could be due merely to the difference in steric interactions between the exocyclic ligands and the *N*-aryl

function during the interconversion of the isomeric TBPs. An alternative explanation lies in the possibility of more freedom of rotation of the *N*-aryl group about the C–N bond, when *ortho*-methyl substituents are lacking. Interaction between the nitrogen p_z orbitals and the exocyclic aryl system (possible if the amino- and *N*-aryl functions were coplanar) would result in decreased availability of electrons for back-bonding to phosphorus. Thus, the ' apicophobicity ' of the amino-function would fall. The dimethyl phenylphosphonite derivatives, having relatively high T_c, are eminently suited to probe this and other effects.

An additional spectral change was observed in the ^{1}H n.m.r. spectrum of 2,3-dihydro-3-mesityl-2,2-dimethoxy-2-phenyl-1,3,2-benzoxazaphosphole (6) when the temperature was reduced (Figure). The *ortho*-methyl resonance (a sharp singlet at +45 °C) of the mesityl ring broadened and split into two three-proton singlets at *ca.* −60 °C. The coalescence temperature for this process was −32 °C (whereas the *P*-methoxy coalescence temperature was −5 °C). This could arise by the rapid rotation of the mesityl group about the C–N bond being decelerated on the n.m.r. time-scale by steric interaction with the phosphorus exocyclic ligands when fast exchange of the latter groups was inhibited. But, as Gorenstein and Westheimer [3] pointed out when they observed a similar difference in coalescence temperatures of the *gem*-dimethyl and *P*-methoxy-signals in the spectrum of compound (7), the coalescence temperature of a given process depends on the frequency separation of the signals due to the exchanging groups. In the present case the close similarity of free energy barriers for the equivalence of the mesityl *ortho*-methyl groups (ΔG^* 52 kJ mol^{-1}) and of the *P*-methoxy groups (ΔG^* 50) suggests that these processes are linked, *i.e.* the *N*-aryl ring is restricted in its rotation, the apparent equivalence of the *ortho*-methyl groups at high temperature being a result of rapid positional exchange of the *P*-methoxy-ligands, which also averages the *ortho*-methyl environment.

When the *P*-phenyl ligand in (6) is replaced by the smaller *P*-methyl ligand [compound (I); Table 3], no corresponding signal coalescence was observed, in accord with the weaker effect of P–Me on the environment of the *N*-aryl ring. This is in contrast to the corresponding tetraco-ordinate oxazaphosphole (4; $R^2 = R^3 = Me$) where steric factors are more important.

This study was pursued to its logical conclusion with the synthesis of 2,3-dihydro-3-mesityl-2-methoxy-2,2-diphenyl-1,3,2-benzoxazaphosphole (8). The methoxy-ligand resonated as a sharp doublet (J_{POMe} 11.0 Hz) between +28 and +200 °C without observable change. The temperature invariance and low coupling constant suggest a frozen structure, with the methoxy-ligand apical, as shown. The *p*-tolyl analogue (9) exhibited identical behaviour, despite the reduction in steric effects. If the methoxy-group was to move into an equatorial position, both a phenyl group and the amino-function would have to be placed unfavourably apical. It is probable that there is no contribution from this



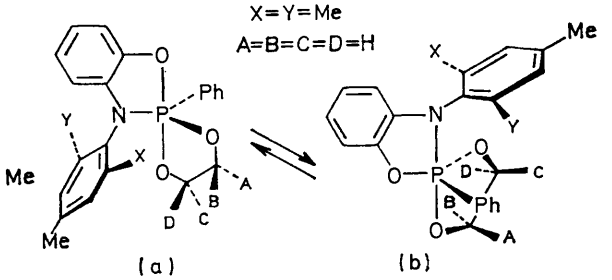
high-energy form at all, even at +200 °C. A similar observation has been made by Ramirez *et al.*[4] for the dioxyphosphorane (10) in chlorobenzene. In this case, however, the endocyclic P–O bond was broken reversibly (with T_c +127 °C), to give the open dipolar species (11). This process would presumably cause a change in the chemical shift and J_{POMe} of the methoxy-ligand. Such a process was not observed in our investigations. Evidently, the 2,3-dihydro-1,3,2-benzoxazaphosph(v)ole system is considerably more stable than the 1,2-oxaphosph(v)olen analogue

Although the importance of electronic factors [5,6] should not be discounted, these results and those of related compounds summarised in Table 3 indicate that the PI process in the oxazaphospholes (1) is very sensitive to steric effects,[7] particularly those originating in the *N*-aryl group.

Finally, we describe the behaviour of 2,2-ethylenedioxy-2,3-dihydro-3-mesityl-2-phenyl-1,3,2-benzoxazaphosphole (12) in the ^{1}H n.m.r. probe at high and low temperatures. The dioxaphospholidine ring protons resonate as a complex multiplet at +28 °C. The *N*-mesityl *ortho*-methyl groups resonate as two separate three-proton singlets, indicating different environments for these groups. The ethylenedioxy splitting pattern is complex and phosphorus spin-tickling provided no

[3] D. Gorenstein and F. H. Westheimer, *J. Amer. Chem. Soc.*, 1970, **92**, 634.
[4] F. Ramirez, J. F. Pilot, O. P. Madan, and C. P. Smith, *J. Amer. Chem. Soc.*, 1968, **90**, 1275.
[5] R. K. Oram and S. Trippett, *J.C.S. Chem. Comm.*, 1972, 554; S. Bone, S. Trippett, and P. J. White, *J.C.S. Perkin I*, 1974, 2125.
[6] R. G. Cavell, D. D. Poulin, K. I. The, and A. J. Tomlinson, *J.C.S. Chem. Comm.*, 1974, 19.
[7] *Cf.* D. Gorenstein, *J. Amer. Chem. Soc.*, 1970, **92**, 644.

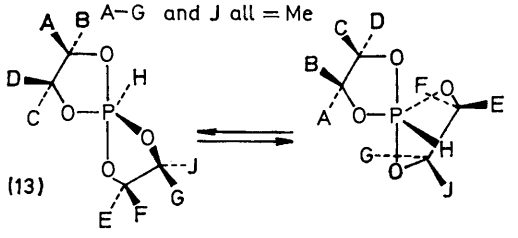
elucidation of the structure. That some interchange of the apical and equatorial ring-termini may be occurring was indicated by broadening into a single, broad doublet at *ca.* −60 °C ($CDCl_3$). Some broadening due to



SCHEME 2

increased viscosity was apparent in the rest of the spectrum, but this was not as extensive. It is tentatively suggested that a rapid interchange of the ring termini between apical and equatorial positions occurs above −60 °C as in Scheme 2; below this temperature the process is inhibited chiefly owing to steric interaction between the *P*-phenyl ligand and the *N*-mesityl group. This process should supply partial equivalence within the pairs of ethylenedioxy-protons A,C and B,D, since these groups are in respectively similar positions in isomers (a) and (b). Total equivalence of these pairs is not possible as an apical amino-group in (b) is dissimilar to an apical ring oxygen in (a). This same process maintains the *N*-mesityl *ortho*-methyl protons in different environments, the methyl group Y remaining *syn* to the phenyl group in both (a) and (b). Hence, two separate resonances are observed for these groups at both low and normal temperatures.

Similar low-energy processes have been observed.[8,9] In these cases, however, complete equivalence of pairs of substituents in both rings was possible, the ring termini being symmetrical about their C–C bonds. Houalla *et al.*[9] reported that the spectrum of the spiro-phosphorane (13) was invariant down to −70 °C and suggested the process in Scheme 3. Steric and stereoelectronic barriers should be considerably lower for the exchange in Scheme 3 than for that in Scheme 2; hence, lack of

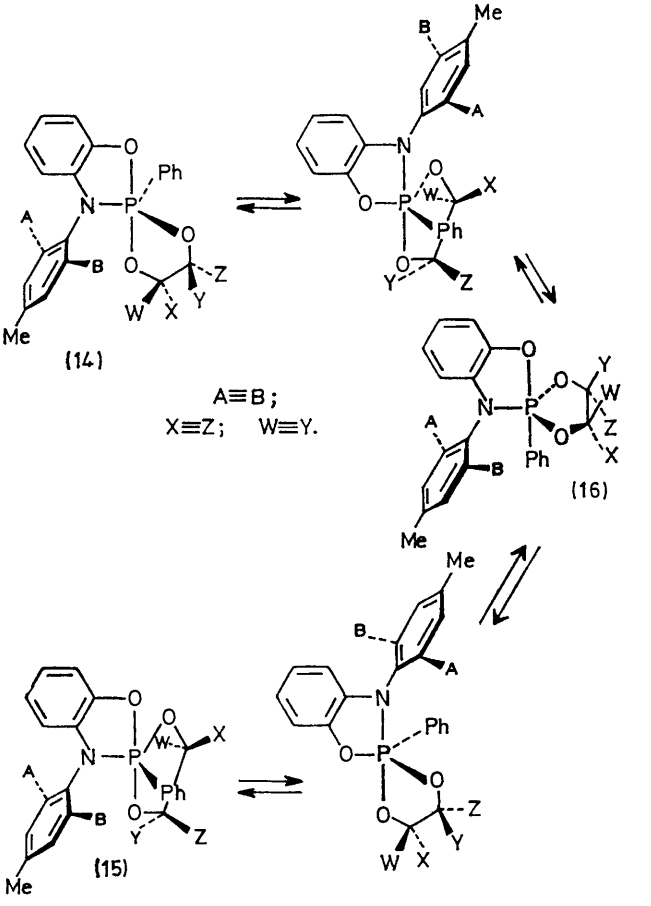


SCHEME 3

evidence for a low-temperature slow exchange in the latter case is as expected.

At +150 °C the mesityl *ortho*-methyl singlets of (12) started to coalesce and the ethylenedioxy-multiplet broadened. Coalescence of the *ortho*-methyl singlets occurred at +175 °C [ΔG^* 96 kJ mol^{-1} (23 kcal mol^{-1})] and the ethylenedioxy-resonance coalesced to a symmetrical 'mound' at +192 °C. These effects were reversible.

Three possible explanations must be considered. (i) The steric inhibition towards rotation of the *N*-mesityl ring could be overcome at high temperature, thus giving equivalence to the *ortho*-methyl groups. However, this fails to explain the accompanying change in the ethylenedioxy-resonance. (ii) One of the spiro-linked rings could undergo reversible cleavage to give



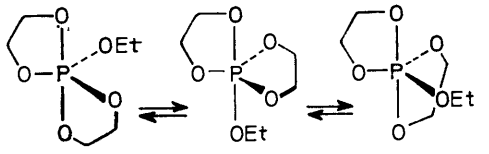
SCHEME 4

phosphonium species related to (11), thus interchanging the position of the *P*-phenyl group with respect to the mesityl *ortho*-methyl groups and making *cis*-pairs of ethylenedioxy-protons equivalent (compare the low-temperature process in Scheme 2, above, which only partially interchanged the environments of these protons). We discount this because we observed no ring opening of the oxazaphospholes (8) and (9) even at +200 °C in diphenyl ether. It seems unlikely that thermal ring opening should be so much easier in

[8] B. C. Chang, W. E. Conrad, D. B. Denney, D. Z. Denney, R. Edelman, R. L. Powell, and D. W. White, *J. Amer. Chem. Soc.*, 1971, **93**, 4004.

[9] D. Houalla, R. Wolf, D. Gagnaire, and J. B. Robert, *Chem. Comm.*, 1969, 443.

the spiro-oxyphosphorane (12) than in (8) or (9), especially since a zwitterionic form of (12) should be disfavoured by the small-ring effect.[10] (iii) The preferable explanation invokes a high-temperature, regular PI process in which the enantiomers (14) and (15) interchange *via* the TBP (16), in which the ethylenedioxy-group is placed diequatorially (Scheme 4).



SCHEME 5

This Scheme allows the equivalence of both the *ortho*-methyl substituents (A and B) and the *cis*-ethylenedioxy-protons W,Y and X,Z. The free-energy barrier of 23 kcal mol^{-1} is, however, rather low for a process which places the ethylenedioxy-group in a diequatorial position. Denney *et al.*[8] observed a coalescence temperature of 172 °C for the process in Scheme 5, which approximates to a free-energy barrier of *ca.* 22 kcal mol^{-1}.[11] In the latter case, the energy required to place the ethylenedioxy-group diequatorially is not increased by also having to place a less electronegative (*e.g.* phenyl) ligand in an apical position.

EXPERIMENTAL

The benzoxazaphospholes (1) and (2) were obtained as described in Part XII.[1]

^1H N.m.r. spectra were recorded on a Varian HA-100 instrument operating at 100 MHz normally at 28 °C, with $CDCl_3$ as solvent unless otherwise stated and tetramethylsilane as internal standard.

Variable-temperature Studies.—These were carried out as follows. The phosphorane (*ca.* 40 mg) was dissolved in an appropriate solvent (0.3 ml; dry methylene chloride for low temperatures, diphenyl ether for elevated temperatures), in a 5 mm n.m.r. tube. The sample temperature was adjusted in the probe in 5 or 10 °C intervals by using a Varian temperature-control unit. The temperature was allowed to stabilise for 5 min before spectra were recorded on a Varian HA-100 instrument (250 Hz sweep-width). Where separation of a single peak (or doublet) into several peaks (or doublets) was observed, the coalescence temperature (T_c) refers to that temperature at which the separate peaks (or doublets) merged to become just indistinguishable. The exact temperature was then found in the usual way fro calibration obtained based on the chemical shift difference between alkyl and hydroxy-protons of methanol (or ethanediol at higher temperatures). Coalescence temperatures could not be located to better than within ± 1 °C. Other temperatures are corrected by ΔT, where $\Delta T = T_c$ (instrument) $- T_c$ (tube); experience indicated that such a correction was valid over the 0—100 °C temperature range to an accuracy of $\pm 3°$.

Determinations of ΔG^* for three-site exchange processes were not carried out because these would have required complete line-shape analyses. ΔG^* Values for two-site exchange processes were calculated by a combination of a simplified Cutowsky–Holm equation[12] for the situation at the coalescence temperature ($2\pi\tau\Delta\nu = \sqrt{2}$, where τ is half the lifetime of either site and $\Delta\nu$ is the frequency separation of the site-occupant resonance at slow-exchange) and the Eyring equation[13] [$k' = (\sigma kT/h) \exp(-\Delta G^*/RT)$, where σ is the transmission coefficient (0.5), k' is the rate constant for the exchange process, and other symbols are conventional]. Thus $k' = \pi\Delta\nu/\sqrt{2}$, and hence $\Delta G^* = RT \ln(\sigma kT\sqrt{2}/\pi\Delta\nu h)$. The error in the determinations of ΔG^* was ± 0.5 kJ mol^{-1}.

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