Direct Observations of Diastereoisomers in Chiral Oxazaphosphoranes [3-Aryl-2,3-dihydro-1,3,2-benzoxazaphosph(v)oles] by ^{1}H and ^{31}P Nuclear Magnetic Resonance Spectroscopy

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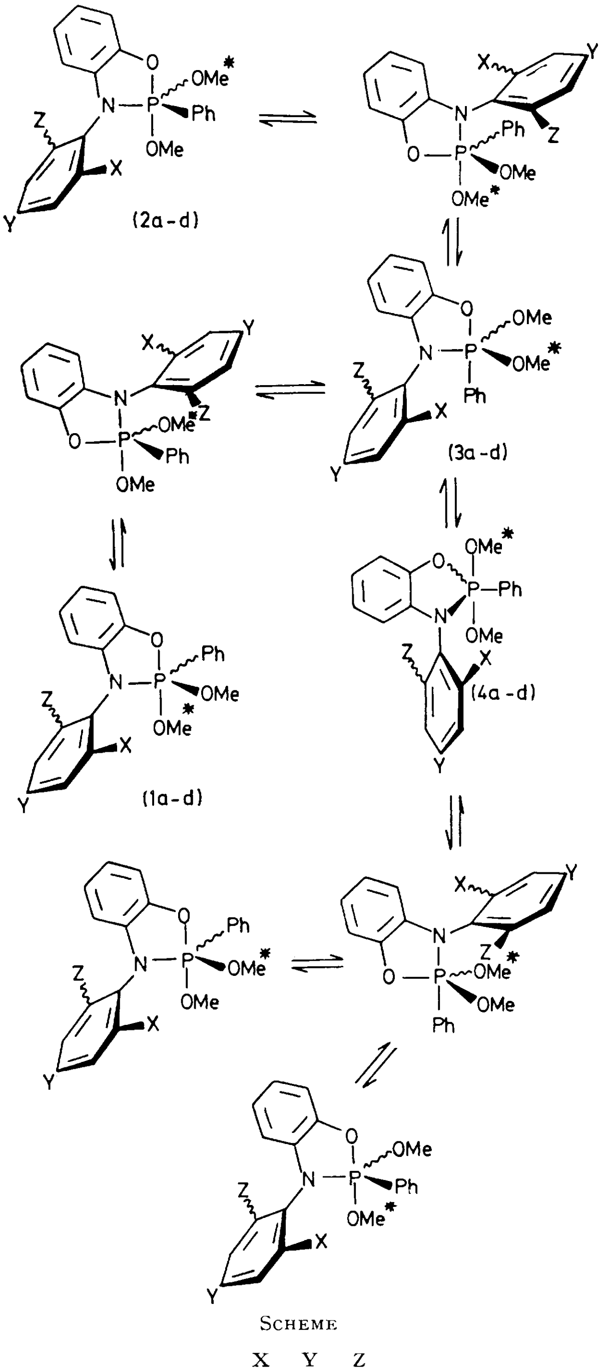
Summary Low- and variable-temperature studies of the ^{1}H and ^{31}P n.m.r. spectra of 3-(2-substituted-phenyl)-2,3-dihydro-1,3,2-benzoxazaphosph(v)oles (**1**) show the presence of unequally populated diastereoisomeric forms (**1**) and (**2**) corresponding to two possible orientations of the *N*-aryl ring, interconversion of isomers occurring solely *via* ligand reorganisation (pseudorotation) about the phosphorus atom and not by rotation about the *N*-aryl bond, leading, in principle, to a resolvable phosphorane system.

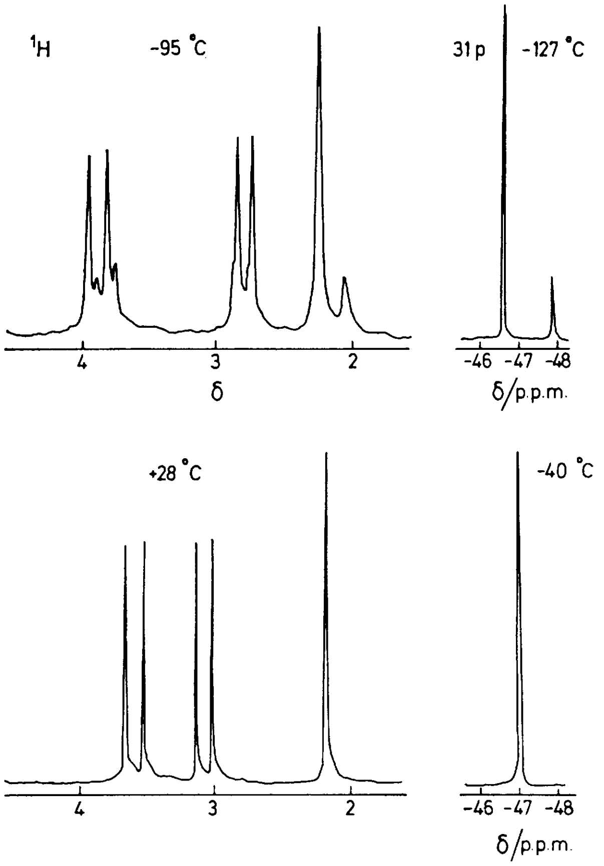
In principle, many classes of phosphoranes carrying unlike ligands are chiral, but in practice this is usually impossible to demonstrate because such species racemise too easily by ligand reorganisation, *e.g.* by pseudorotation. Exceptions are bicyclic spirophosphoranes derived from chiral aminoalcohols.[1] We now report a demonstration of chirality in monocyclic phosphoranes *via* the direct observation of diastereoisomers, achieved by imposition of an asymmetric steric restraint in a phosphorane nevertheless still able to undergo pseudorotation.



Scheme

	X	Y	Z
a;	Me	Me	Me
b;	Me	H	H
c;	Me	Me	H
d;	MeO	H	H

This demonstration follows from the case of 3-mesityl-2,2-dimethoxy-2-phenyl-2,3-dihydro-1,3,2-oxazaphosph-(v)ole (**1a**) in which rotation about the *N*-mesityl bond is severely restricted[2,3] but in which ligand reorganisation (and hence racemisation) involving the enantiomers (**1a**) and (**2a**) occurs readily, the observed equivalence of the *o*-methyl groups at high temperature being a result of rapid positional exchange of the *P*-methoxy ligands which also averages the *o*-methyl environment. Replacement of *one* of the *o*-methyl groups in (**1a**) by hydrogen would be expected still to present a high steric barrier to *N*-aryl rotation,[2,3] but would now impose an asymmetry on the phosphorane system which could not be averaged by pseudorotation involving the *P*-ligands, thus leading to unequally populated diastereoisomeric forms, *e.g.* (**1c**) and (**2c**). We now present direct evidence of this obtained from the temperature dependence of ^1H and ^{31}P spectra.



Figure

At −127 °C the proton decoupled ^{31}P n.m.r. spectrum of the racemic mixture represented by (**1b**) and (**2b**) and their enantiomers consists of two unequal singlets at δ −46·75 and −47·88 in the ratio of 5·5 : 1. On warming, these signals coalesce and at −40 °C a single sharp line at δ −46·90 is observed; the ^1H n.m.r. spectrum of (**1b**) and (**2b**) at −95 °C similarly exhibits P–OMe and Ar–Me signals due to major and minor isomers in the ratio of 5·4 : 1, while at +28 °C a sharp averaged spectrum is obtained (Figure). Since the *P*-phenyl group of (**1b**) and (**2b**) is expected to be orthogonal to the equatorial plane,[3b] the minor isomer is assigned as (**2b**) on the basis of the shielding of the arylmethyl group of the minor isomer relative to that of the major isomer.

From the positions of the low field equatorial- and high field apical-P–OMe doublets in the averaged ^{1}H n.m.r. spectrum (Figure)† it is apparent that coalescence of the *major* equatorial P–OMe doublet with the *minor* apical P–OMe doublet (and of the *major* apical P–OMe doublet with the *minor* equatorial P–OMe doublet) has occurred.

This observation confirms that rotation about the *N*-aryl link is inhibited because rotation would cause the major and minor equatorial P–OMe doublets to coalesce with each other (and similarly the major and minor apical P–OMe doublets). It therefore follows that the observed coalescences arise from interconversion of (**1b**) and (**2b**) *via* pseudorotation involving the high energy intermediate (**3b**). The introduction of the further element of asymmetry in the form of a single *o*-aryl substituent therefore leads to a pseudorotation which links, not a pair of enantiomers , but a pair of diastereoisomers. Further, there is no pseudorotation process which could cause equilibration of enantiomeric configurations in this chiral system, which in principle is now resolvable, the energy barrier for racemisation being at least 88 kJ mol^{-1} (Table).

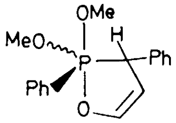
The *N*-2,4-dimethylphenyl- and the *N*-2-methoxyphenyl-analogues (**1c**) and (**2c**) and (**1d**) and (**2d**) behave similarly and it is noteworthy that free energies of activation for the pseudorotation (**1**)→(**2**) (Table) are similar to those observed for analogous systems, *e.g.* (**1a**) and (**2a**).[2]

Complete averaging of the environments of the P–OMe groups in the above phosphoranes is only observed in the cases of (**1d**) and (**2d**) for which process a free energy of activation of 94·9 ± 2·6 kJ mol^{-1} obtains. This value is similar to those obtained[2,4] for pseudorotations proceeding *via* high energy intermediates with a five-membered ring in a diequatorial position, and suggests that complete equilibration of the P–OMe groups of (**1d**) and (**2d**) occurs *via* the intermediate (**4d**) rather than by a combination of pseudorotation *via* (**3d**) and simple rotation of the *N*-aryl group.

TABLE[a]

	$\Delta G_1^{\ddagger}$/kJ mol^{-1} [b]			$\Delta G_2^{\ddagger}$/kJ mol^{-1} [b]
	o-subst.[c]	P–OMe[c]	^{31}P[d]	P–OMe[e]
(**1b**)–(**2b**)	47·1 ± 1·9	46·5 ± 2·8	44·9 ± 2·9	>88
(**1c**)–(**2c**)	48·2 ± 2·0	47·9 ± 3·9	45·8 ± 2·2	>93
(**1d**)–(**2d**)	46·6 ± 2·2	46·8 ± 1·1	44·9 ± 1·1	94·9 ± 2·6

[a] $\Delta G^{\ddagger}$ calculated as in reference 5 from coalescences of *o*-aryl-substituent, P–OMe, and ^{1}H decoupled ^{31}P signals. [b] $\Delta G_1^{\ddagger}$: isomerization (**1**)→(**2**). $\Delta G_2^{\ddagger}$: complete equilibration of P–OMe groups. [c] In CH_2Cl_2. [d] In CH_2Cl_2 + 20% $(CD_3)_2C{=}O$. [e] In Ph_2O.



(5)

Similar arguments account for the previously reported variable temperature ^{1}H n.m.r. phenomena exhibited by the cyclic phosphorane (**5**), which observations were not then discussed in terms of chirality.[6]

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† Complete averaging of the environments of the P–OMe groups does not occur at this temperature.

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