predominate for **4b**.[17] However, **4a** can assume the conformation **9** in which p_π–d_π stabilization is maximal. Thus, normal vicinal interactions which give rise to the axial preference for other substituents[1,2] may be outweighed by the conjugative effects available in **9**. We recognize that p_π–d_π bonding is likely to be considerably reduced in a molecule such as **4**, which is more similar to $(MeO)_2PNMe_2$ than to Me_2NPF_2. It seems likely nonetheless that the conformational preference peculiar to the Me_2N is in some way related to the presence of the lone pair on nitrogen and its interaction with the orbitals, occupied or empty, on phosphorus.[18]

That lone-pair orientation at phosphorus may affect $^3J_{H_{eq}P}$ was suggested[19] earlier. Our results appear to be the first to substantiate the idea that $^3J_{HCOP}$ depends on both the HCOP dihedral angle (Karplus-like relation) *and* the phosphorus lone-pair orientation. This approach may in fact turn out to be a very powerful one indeed for assignment of substituent configuration at trivalent phosphorus in 1,3,2-dioxaphosphorinanes.

Acknowledgment. This work was supported by a grant from the National Science Foundation (GP-22885).

[17] 1,3-Interactions in **8** may be relieved to some degree by ring reversal to the alternate chain with Me_2N equatorial or the analogous boat or twist form with Me_2N pseudoequatorial in which p_π–d_π bonding would be available.

[18] *E.g.*, a referee has suggested that the Me_2N in **7** and **9** may be pyramidal and that a stabilizing lone pair–lone pair gauche effect available to **9** is responsible for its lower energy.

[19] D. Gagnaire and J. B. Robert, *Bull. Soc. Chim. Fr.*, 2240 (1967).

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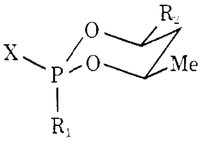
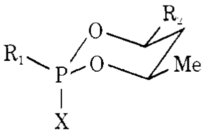
Phosphorus Stereochemistries in Isomeric 2-Dimethylamino-1,3,2-dioxaphosphorinanes

Sir:

The factors governing the relative stabilities of the two possible configurations a and b at phosphorus in cyclic six-membered ring systems have received significant attention in a number of laboratories recently. In trivalent phosphorus systems (X = lone pair (lp)) strong evidence has been reported for the greater thermodynamic stability of configuration a compared to b for I and II.[1–3] While the bulk of the reported evidence supports the same phosphorus stereochemistry for several analogous systems, there have been reports contending for the greater stability of equatorial alkoxy substituents.[4] Although IIIa and b closely resemble Ia and b, we present in this communication evidence that the b isomer of the latter compound is the more thermodynamically stable as is also very probably the case for IVa and b.[5]





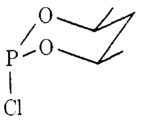
	X	R_1	R_2		X	R_1	R_2
Ia	lp	OMe	Me	Ib	lp	OMe	Me
IIa	lp	OMe	H	IIb	lp	OMe	H
IIIa	lp	NMe_2	Me	IIIb	lp	NMe_2	Me
IVa	lp	NMe_2	H	IVb	lp	NMe_2	H
Va	O	H	Me	Vb	O	H	Me
VIa	O	H	H	VIb	O	H	H
VIIa	O	NMe_2	Me	VIIb	O	NMe_2	Me
VIIIa	O	NMe_2	H	VIIIb	O	NMe_2	H
IXa	O	OMe	Me	IXb	O	OMe	Me
Xa	O	OMe	H	Xb	O	OMe	H

Pentavalent phosphorus a and b isomers where X = O are also known and the stereochemistry at phosphorus has been deduced from nmr results in solution and X-ray diffraction experiments in the solid state.[6] In the vast majority of cases where R = aryl, alkyl, or alkoxy, the P=O group prefers the equatorial position although chair–chair and chair–boat equilibria in solution can occur to varying degrees.[6,7] The preference of the P=O group to be equatorially disposed has also recently been shown when R_1 is H in Va,b and VIa,b.[2] In this communication we report the isolation and the phosphorus stereochemical assignments of the a and b isomers of VII and VIII.

The first steps in reactions 1 and 2 each produce a 10:1 ratio of IIIb to IIIa in overall yields exceeding 60% as shown by their pmr spectra, details of which will be published in due course. Pmr spectra also show that this ratio is preserved in the stereospecific and nearly quantitative oxidation to VIIb and VIIa. Reaction scheme 3 produces the indicated pentavalent phosphorus systems in greater than 60% yield although the b to a ratio is now 2:1 as revealed from integration of the pmr spectra. The isomers of VII and VIII can

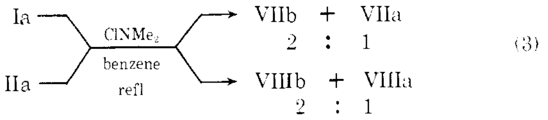
$$P(NMe_2)_3 + \textit{meso}\text{-}(HOCHMe)_2CH_2 \xrightarrow[-2HNMe_2]{85^\circ}$$

$$\underset{1}{\text{IIIa}} + \underset{10}{\text{IIIb}} \xrightarrow[\substack{CCl_4\\0^\circ}]{NO_2} \underset{1}{\text{VIIa}} + \underset{10}{\text{VIIb}} \qquad (1)$$



$$+ \quad \text{xsMe}_2\text{NH} \xrightarrow[Et_2O]{-20^\circ}$$

$$\underset{1}{\text{IIIa}} + \underset{10}{\text{IIIb}} + \xrightarrow[\substack{CCl_4\\0^\circ}]{NO_2} \underset{1}{\text{VIIa}} + \underset{10}{\text{VIIb}} \qquad (2)$$



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[1] J. Rodgers, D. W. White, and J. G. Verkade, *J. Chem. Soc. A*, 77 (1971).

[2] J. A. Mosbo and J. G. Verkade, *J. Amer. Chem. Soc.*, in press.

[3] M. G. B. Drew, J. Rodgers, D. W. White, and J. G. Verkade, *J. Chem. Soc. D*, 227 (1971).

[4] See D. W. White, R. D. Bertrand, G. K. McEwen, and J. G. Verkade, *J. Amer. Chem. Soc.*, 92, 7125 (1970), for a recent summary of this controversy.

[5] W. G. Bentrude and H. W. Tan, *ibid.*, **94**, 8222 (1972), reach the same conclusion for the isomeric pair of 2-dimethylamino-5-*tert*-butyl-1,3,2-dioxaphosphorinanes.

[6] See D. W. White, G. K. McEwen, R. D. Bertrand, and J. G. Verkade, *J. Chem. Soc. B*, 1454 (1971), for a recent summary of these results.

[7] (a) W. G. Bentrude and K. C. Yee, *Tetrahedron Lett.*, 3999 (1970); (b) W. G. Bentrude, K. C. Yee, R. D. Bertrand, and D. M. Grant, *J. Amer. Chem. Soc.*, **93**, 797 (1971).

be separated and purified by vacuum distillation and they do not appear to isomerize on heating.

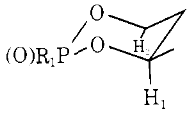
Dipole moment measurements form the main basis of our structural assignments of the isomers of VII. The locking of the ring by equatorial methyl groups in these compounds offers the advantage that dipole moment contributions from other conformers are negligible. Furthermore, since the P=O moment exceeds by a factor of at least two that of a $PNMe_2$ or POMe group,[8] the overall moments of VIIa and IXa should be comparable but larger than those of VIIb and IXb and this is confirmed in Table I. That the stereochemistries of the comparison compounds IXa and b are as shown is fixed by the established[1,2] configurations of Ia and Ib and the conclusion that oxidation of cyclic phosphorus systems proceeds with retention of configuration.[9,10] Since the same oxidation procedure produced Xa and Xb from IIa and IIb, their stereochemistries at phosphorus are also established with considerable firmness. If the reasonable assumption can be made that IIIa,b oxidized with retention of configuration at phosphorus, then VIIb (and by implication VIIIb) is thermodynamically more stable than the a isomer. This conclusion arises from the observation of a 10:1 IIIb to IIIa ratio in the first step of the equilibrium process represented in reaction 1. That the 1:10 ratio of IIIa to IIIb is very likely the equilibrium ratio is indicated by the production of this ratio in two different reactions (1 and 2) carried out at rather different temperatures. Moreover, the ratio did not change upon heating to 120° for 18 hr nor on vacuum distillation on a spinning band column.

Table I. Dipole Moments[a] and ^{31}P Chemical Shifts[b] of Cyclic Phosphorus Compounds

Compd	μ, D	$\delta\,^{31}$P
IXa	6.11 ± 0.05	$+7.06$
IXb	4.69 ± 0.05	$+4.98$
VIIa	5.80 ± 0.1	-3.49
VIIb	4.05 ± 0.1	-6.58

[a] Measured at 25° in benzene using the apparatus and procedure described in A. C. Vandenbroucke, R. W. King, and J. G. Verkade, *Rev. Sci. Instrum.*, **39**, 558 (1968). [b] Measured in benzene relative to 85% H_3PO_4.

Additional strong support for the above configurational assignments of VIIa,b and IXa,b comes from the lanthanide-induced pmr shifts of H_1 and H_2 in the isomers of VIII and X. Because these particular protons apparently experience greater downfield shifts when the P=O group is axial,[2,11] such deshielding



should be more pronounced in VIIIb and Xb than in their a counterparts and the data in Table II confirm this.

Table II. Lanthanide[a] Shift Behavior of Selected Protons in Cyclic Phosphorus Compounds[b]

Compd	$\Delta\delta H_1$[c]	$\Delta\delta H_2$[c]
VIIIa	2.3	2.3
VIIIb	5.3	4.6
Xa	3.3	3.0
Xb	5.1	4.5

[a] Tris(1,1,1,2,2,3,3-heptafluoro-4,6-octanedione)europium(III) ($Eu(fod)_3$). [b] The downfield increments were obtained by comparing spectra of $CDCl_3$ solutions of these compounds with $CDCl_3$ solutions 0.2 *M* in compound and 0.1 *M* in $Eu(fod)_3$. [c] Relative to TMS.

The ^{31}P chemical-shift progression to lower applied fields from IXa and VIIa to their respective b isomers (Table I) seems to parallel the change in configuration at phosphorus.

In contrast to pentavalent phosphorus a and b isomers where X = oxygen and R = aryl, alkyl, or alkoxy, the P=O group prefers the axial position when R = NMe_2. In preliminary acid-catalyzed hydrolysis experiments on VIIa and VIIb, for instance, VIIb is observed by pnmr spectroscopy to convert to VIIa while VIIa hydrolyzes without apparent isomerization. Pnmr and stereospecific reaction studies have led to the conclusion that the equatorial NR_2 axial P=O stereochemistry is also preferred for relatively nonrigid 1,3,2-dioxaphosphorinanes in solution[5,12,13] and preliminary X-ray work indicates that the same is true in the solid state.[14]

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Biogenetic-Type Total Synthesis. 24,25-Dihydrolanosterol, 24,25-Dihydro-$\Delta^{13(17)}$-protosterol, Isoeuphenol, (−)-Isotirucallol, and Parkeol

Sir:

In the biogenesis of the euphol and lanosterol classes, it is assumed that enzyme-controlled all-chair folding of squalene 2,3-oxide (**1**)[1] prefigures generation of the former type, while the chair–boat–chair conformation determines production of the latter category.[2] In order to pursue total synthesis in this area and also realize the closest simulation so far of the biological cyclization process, we have sought to employ the parallel, abiological reaction of a selected oxide **1** variant.[3] We now report the nonenzymic transforma-

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