Eu(fod)$_3$ Induced $^3J_{HP}$ Variation and Conformational Changes in Seven-membered-ring Phosphates

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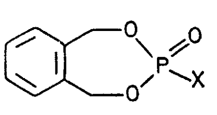
Summary A conformational equilibrium between the two chair forms, (**2a**) and (**2b**), has been established for the 3-substituted 1,5-dihydro-2,4,3-benzodioxaphosphepin 3-oxides (**1**) with the aid of Eu(fod)$_3$, which caused a large variation of $^3J_{HP}$ attributable to the increase of the axial phosphoryl conformer.

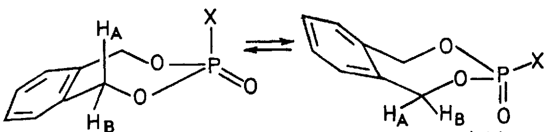
Many studies of six-membered-ring phosphorus heterocycles have been reported, but larger homologues have received little attention. While carrying out a conformational analysis of the 3-substituted 1,5-dihydro-2,4,3-benzodioxaphosphepin 3-oxides (**1**)† we observed a variation of $^3J_{HP}$ on addition of the lanthanide shift reagent, from which conformational aspects of this mobile system were deduced.

^{1}H N.m.r. data are shown in the Table. Coupling constants were determined from the AB part of an ABX (X=P) pattern. Spectra are simplified to an AMX type with the Eu or Pr reagent which co-ordinates at the phosphoryl oxygen. Plots of chemical shifts *vs.* [shift reagent]/[**1**] are linear.



(1)

X
a; Cl
b; OMe
c; OPh



(2a) (2b)

While the geminal coupling constant, J_{AB}, remains constant, the two sets of $^3J_{HP}$ vary greatly and in a comple-

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† 3-Chloro-1,5-dihydro-2,4,3-benzodioxaphosphorepin 3-oxide (**1a**), m.p. 135—139°, was prepared from phthalyl alcohol and phosphorus oxychloride. Treatment of (**1a**) with methanol or phenol gave methyl (**1b**), m.p. 126·5—128°, and phenyl phosphates (**1c**), m.p. 96—97°. Satisfactory analytical and spectral data were obtained for these compounds.

mentary manner. This is not expected from a consideration of substituent effects[1] and suggests perturbation to the conformational equilibrium.[2]

The stable conformation of the cycloheptenes and their benzologues is the chair form.[3] Our results (Table) show an equilibrium between the two chair forms, (**2a**) and (**2b**), following from a Karplus-like correlation[4] between ^3J (POCH) and the dihedral angles ($\angle$ POCH$_{ax}$ 30°, $\angle$ POCH$_{eq}$ 150°).

Compound (**1c**) exists predominantly in the chair form (**2a**; X=OPh). This is supported by $\nu_{P=O}$ (1320 cm^{-1} in CCl$_4$, *eq*-P=O) and the constancy of the $^3J_{HP}$ values even at −60°. Eu(fod)$_3$ addition shifts the equilibrium to the (**2b**; X = OPh) side.‡ Increase of (**2b**) should result in an averaging of $^3J_{HP}$ and a greater downfield shift of the axial proton H$_B$ than for H$_A$. This is found to be the case. Equatorial co-ordination would not be expected to show such a large $\Delta\delta_{AB}$.

General trends are followed with (**1a**, $\nu_{P=O}$ 1306 cm^{-1}) but the equilibrium appears not to be seriously perturbed, possibly reflecting a greater stability of the conformer (**2a**) and a decreased basicity of the phosphoryl oxygen due to the electronegative chlorine atom.

The methyl ester (**1b**) shows $\nu_{P=O}$ at 1285 cm^{-1} as a broad peak, indicating conformational mixtures. Without the shift reagent, the $^3J_{HP}$ values are similar. That this is not due to other conformers such as twist-boat, but is caused by the presence of two chair forms in nearly equal amounts, can be proved by Eu(fod)$_3$ addition. The shifted spectrum shows the presence of a greater proportion of (**2b**; X = OMe).§

TABLE. *Chemical shifts and coupling constants in* CDCl$_3$

Compound	[Eu(fod)$_3$]/[substrate]	J_{AB}	J_{AP}	J_{BP}	δ_A	δ_B	$\delta_B - \delta_A$
(**1a**)	0	13·3	10·6	29·6	5·45	5·07	−22·4
	0·2	13·4	10·2	28·9			−24·2
	0·4	13·3	11·2	28·7			−16·3
	0·6	—[a]	—[a]	—[a]			−11
(**1b**	0[b]	13·7	15·0	16·7	5·15		0
	0·2	13·6	15·8	16·3			42·1
	0·4	13·8	17·1	15·6			81·5
	0·8	13·8	18·5	13·8			151·5
(**1c**)	0	13·2	10·0	23·3	5·31	5·20	−6·6
	0·2	13·3	14·7	17·7			39·1
	0·45	13·7	16·3	16·0			103·5
	0·66	13·7[a,c]	—[a]	14·6[d]			143
	0·83	13·7[a,c]	—[a]	13·7[d]			182

[a] Obscured by phenyl protons. [b] A small amount of Eu(fod)$_3$ was added to determine *J*'s. [c] Estimated. [d] J_{AB} was assumed to be 13·7 Hz.

Saturated seven-membered-ring phosphates undergo pseudo-rotation between twist-boat forms, as indicated by the time-averaged coupling constants found for 2-methoxy- (b.p. 92—93·5°/0·5 mm, J_{AB} 12·0, J_{AP} 16·8, J_{BP} 16·2 Hz) and 2-phenoxy-1,3,2-dioxaphosphepan 2-oxides (b.p. 146—148°/0·2 mm, J_{AB} 11·9, J_{AP} 16·5, J_{BP} 16·8 Hz).

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‡ An equilibrium point is determined by the equatorial preference of the P=O group and the steric effects of a substituent on phosphorus. The geometrical preference of P=O appears to be lost by complexation with the Eu reagent, which modifies the nature of P=O bonding.

§ In support of the axial phosphoryl preference on Eu(fod)$_3$ addition, a constant value for $^3J_{HP}$ was reported for a six-membered-ring phosphonate in which the phosphoryl group is axially oriented in the stable form (K.C. Yee and W. G. Bentrude, *Tetrahedron Letters*, 1971, 2775).

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