
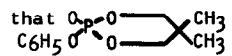
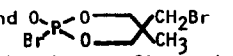


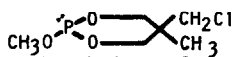

STEREOCHEMISTRY AT PHOSPHORUS IN A
SIX-MEMBERED RING PHOSPHITE

D. W. White, G. K. McEwen and J. G. Verkade

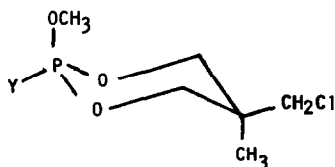
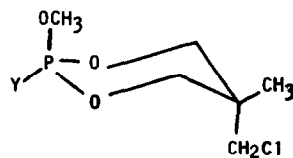
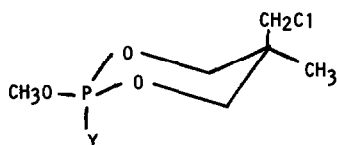
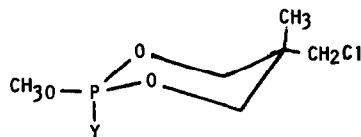
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Considerable progress has been made toward the understanding of the stereochemistry of six-membered ring phosphorus systems of the type  where Y=O or S, Z=OR (1-4); Y=O, Z=R (1,5); Y=O, Z=halogen (1); Y=electron pair, Z=halogen (2,4,6); and Y=electron pair, Z=OR (2,4,6,7) especially by the use of nmr spectroscopy. This technique, however, does not permit an unambiguous assignment of the stereochemistry at phosphorus and in only two cases have the configurations been determined by x-ray studies. These structure determinations showed that  (8) and  (9) contain an axial phenoxy and bromo group, respectively, although some flattening of the phosphorus portion of the ring was noted. Because six-membered ring phosphites are liquids at room temperature, x-ray techniques are difficult to apply. Moreover, the possibility of atomic inversion at phosphorus further complicates the problem of ascertaining the configuration around phosphorus by solution spectroscopic methods.

On the basis of preliminary dipole moment and nmr measurements herein described, we propose that the methoxy group in the phosphites  and  and their BH₃ adducts are axial in the chair conformation of the rings.

Trimethyl phosphite reacts with 2-chloromethyl-2methyl-1,3-propanediol in a 1:1 molar ratio at 90° to give a mixture of two phosphites. Two isomers each having two conformers are possible:

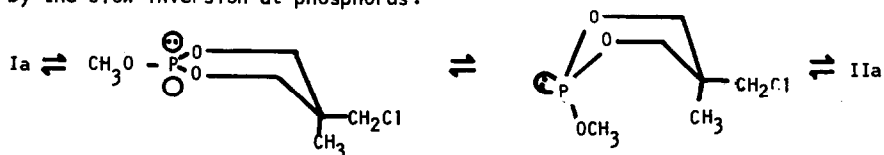
Ia (Y=electron pair), Ib (Y=BH₃)IIa (Y=electron pair), IIb (Y=BH₃)IIIa (Y=electron pair), IIIb (Y=BH₃)IVa (Y=electron pair), IVb (Y=BH₃)

The ¹H nmr spectrum of the neat mixture referenced to TMS exhibits in addition to complicated methylene absorptions, two CH₃ peaks at 0.75 and 1.28 ppm and two CH₂Cl resonances at 3.26 and 3.80 ppm. Only one OCH₃ doublet at 3.55 ppm (J_{POCH}=12.0 Hz) was noted. Slight downfield shifts were observed in dilute CDCl₃ solution. The downfield CH₃ peak is broader than the upfield one and can be resolved into a triplet (J=0.7 Hz) in CDCl₃. Since axial CH₃ protons have been found in similar systems to couple more strongly to the axial ring methylene protons than do equatorial CH₃ hydrogens (1), the downfield methyl resonance corresponds to Ia and/or IVa and the upfield to IIa and/or IIIa. The relative areas under the CH₃ absorptions vary with temperature (CH₃_{ax}:CH₃_{eq} is 1.0:3.3 at 21° and 1.0:6.9 at -80°) and establishment of an equilibrium ratio at a new temperature requires as much as several days. The presence of distinct CH₃ resonances which do not broaden from -60 to 156° and the presence of only one OCH₃ doublet suggests that only two species are present to any appreciable extent and that these differ at the carbon opposite the phosphorus in the ring. Although no conclusion can be drawn as to the rapidity of ring flipping, it appears certain that only one conformer of each isomer is present within the limits of detection.

Reaction of the 1.0:3.3 mixture of the phosphites with B₂H₆ at -40° using standard

vacuum procedures produced two borane adducts formed in a 1.0:3.0 ratio as determined by integration of the $\text{CH}_{3\text{ax}}$ and $\text{CH}_{3\text{eq}}$ proton resonances observed in CDCl_3 (1.30 and 0.91 ppm, respectively). The $\text{CH}_2\text{Cl}_{\text{ax}}$ and $\text{CH}_2\text{Cl}_{\text{eq}}$ proton peaks appear at 3.78 and 3.44 ppm, respectively, and the OCH_3 resonance is at 3.76 ppm ($J_{\text{POCH}}=10.8$ Hz). The B-H stretching bands in the infrared spectrum taken in CCl_4 were observed at 2412 (asym) and 2365 (sym) cm^{-1} . Calculation of the dipole moments* of the BH_3 adducts Ib, IIb, IIIb, and IVb, gave values of 4.8, 5.6, 3.05, and 2.6D, respectively. The measured value in benzene of 5.9 D strongly suggests that the OCH_3 group is axial (Ib and IIb) in the adduct mixture. Since the ratio of BH_3 adducts is quite similar to the ratio of the phosphites and if the reasonable assumptions are made that adduct formation is not accompanied by inversion and is very rapid compared to inversion, these experiments imply that the phosphite mixture also contains axial OCH_3 (Ia and IIa).

Finally, the sluggish change in isomer ratio (Ia:IIa) with temperature can be explained by the slow inversion at phosphorus:



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* Details of this method and its efficacy in predicting the conformation of many other six-membered ring pentavalent phosphorus compounds will be described in a forthcoming paper. The present unreliability of the method for trivalent phosphorus systems will also be discussed.

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