Configurations and Conformations of the Geometrical Isomers of 2-Ethoxy-4-methyl-1,3,2-dioxaphosphorinane

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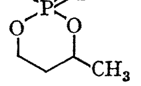
Summary The more stable stereoisomer of 2-ethoxy-4-methyl-1,3,2-dioxaphosphorinane has the *trans*-configuration and assumes a chair conformation with equatorial methyl and axial ethoxy-group, whilst the less stable isomer has the *cis*-configuration and, at room temperature, adopts a rapidly flipping chair conformation.

INTEREST in the stereochemistry of heterocyclic phosphorus esters, particularly 1,3,2-dioxaphosphorinanes,[1] is growing. So far, however, the only such compound of tervalent phosphorus to be separated into two pure, stable stereoisomers, dependent for their separate existence upon the configurational stability of tervalent phosphorus, is 2-ethoxy-4-methyl-1,3,2-dioxaphosphorinane (1; X = EtO, Y = lone pair). Aksnes[1b] isolated *cis*- and *trans*-isomers of this phosphite, but did not recognise which isomer was which.

We have studied the ^{1}H n.m.r. spectra, using homo- and hetero-nuclear decoupling techniques, of these two geometrical isomers, their sulphides (1; X = EtO, Y = S), and the corresponding phosphorochloridite (1; X = Cl, Y = lone pair) from which the phosphites are prepared. In the case of the more stable phosphite isomer, the phosphorochloridite (of which only one isomer is known) and the sulphide derived by addition of sulphur to the less stable phosphite isomer (sulphide A), the n.m.r. spectra clearly indicate that the ring adopts a chair conformation with the ring methyl equatorial.† The spectrum of the sulphide derived from the more stable phosphite isomer (sulphide B), by addition of sulphur, suggests that the ring methyl is probably also equatorial in this compound. The less stable phosphite isomer has a comparatively simple spectrum at room temperature but this becomes more complex at −30° ($CDCl_3$ solution) when, although less well resolved, it resembles that of the other compounds. This suggests that the ring is flipping rapidly at room temperature. In the low temperature spectrum the three protons in the 4- and the 6-positions give rise to a multiplet, corresponding to two protons, at lower field than the signal due to the third proton. Principally on the basis of their chemical shifts we believe that the two lower-field protons are axial, the higher-field proton is equatorial, and the ring methyl therefore equatorial. Available data on 1,3,2-dioxaphosphorinanes containing tervalent phosphorus[1c,d,e,2] (and quinquevalent phosphorus[2,3]) indicate that an equatorial proton absorbs at higher field than does the corresponding axial proton.



(1)

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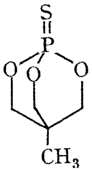
† Ring protons had J_{gauche} *ca.* 2—5 c./sec. and J_{anti} *ca.* 10 c./sec. The 4- and 6-protons were coupled to phosphorus with J_{gauche} *ca.* 3—6 c./sec. and J_{anti} *ca.* 10 c./sec. (P^{III} compounds) or *ca.* 20—25 c./sec. (sulphides). Absence of cross-ring coupling to the equatorial 6-methylene proton[1d] and absence of coupling between the ring methyl protons and the axial 5-methylene proton,[1f,3] together with chemical shift data for the 4- and 6-protons (see discussion of less stable phosphite), support this assignment.

Prediction of dipole moments of tervalent phosphorus compounds is difficult and has been referred to by Verkade.[1f] Using values of 0·40 and 0·71 for the bond moments of $\overleftarrow{\mathrm{C{-}H}}$ and $\overrightarrow{\mathrm{C{-}O}}$ respectively,[4] and obtaining a value of 3·44 for the group moment of $S{=}PO_3$ from the reported dipole moment of the cage sulphide (2),[5] we predicted a dipole moment for a sulphide (1; X = EtO, Y = S) with equatorial ethoxy-group of 3·31 D and for a sulphide with axial ethoxy-group of 5·78 D. In the absence of precise bond-angle data we assumed a tetrahedral angle at each ring atom. Free rotation about exocyclic P–O bonds was also assumed although this may not be valid for an axial ethoxy-group. Nevertheless, restriction of rotation about an axial P–O does not alter our conclusion that a chair-shaped ring with equatorial ethoxy-group will have a smaller dipole moment than a ring with axial ethoxy-group. The observed dipole moments (measured in benzene, the solvent employed in the n.m.r. studies of the sulphides) for the sulphides are 3·19 D for (A) and 5·36 D for (B) and we therefore conclude that in (A) the ethoxy-group is equatorial and in (B) it is axial. As (A) and (B) have opposite configurations, it follows that, as suggested by the n.m.r. spectra, the ring methyl is equatorial in both, and that (A) is the *cis*- and (B) the *trans*-isomer. As the addition of sulphur to tervalent phosphorus is accepted to proceed with retention of configuration at phosphorus,[6] it therefore follows that the less stable phosphite has the *cis*-configuration and the more stable phosphite the *trans*.



(2)

At room temperature the less stable, *cis*-phosphite is rapidly flipping, although at −30° the flipping is retarded, or stopped, and the conformation principally populated is, we believe, that with equatorial methyl and ethoxy-groups. The more stable *trans*-phosphite has equatorial methyl and axial ethoxy-group. As suggested by Hargis and Bentrude,[1e] an effect analogous to the 'anomeric effect' does appear to be operative in this ring system. On purely steric grounds the *cis*-diequatorial isomer would be expected to be the more stable. The chloridite has equatorial methyl and, on these (and other) grounds, probably axial chlorine.

These isomers offer interesting possibilities for the investigation of phosphite reaction mechanisms.

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