Dynamic Stereochemistry of Five-co-ordinate Arsenic Compounds

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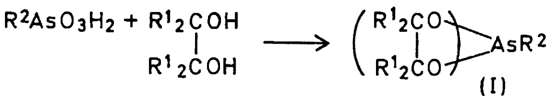
Summary Rapid ligand exchange has been observed in a number of five-co-ordinate arsenic compounds, and is accounted for by a pseudorotation hypothesis.

THE dynamic stereochemistry of a wide range of five-co-ordinate phosphorus compounds has been recently rationalized[1] by the application of a hypothesis of rapid intramolecular ligand exchange (pseudorotation) which is subject to a number of constraints dependent on inter-ligand angles, ligand bulk, electronegativity, *etc.* However, apart from a brief comment on the dynamic stereochemistry of arsenic pentafluoride,[2] the ligand exchange hypothesis has not so far been applied to five-co-ordinate arsenic compounds. This Communication reports an interpretation of the ^{1}H n.m.r. spectra of a number of five-co-ordinate arsenic compounds using a pseudorotation hypothesis.

Reaction between arsenic acid or arsonic acids and glycols was long ago reported to lead to five-co-ordinate arsenic compounds,[3] as shown in reaction (1). These molecular structures were reported on the basis of empirical analyses and, in a few cases, cryoscopic molecular weight determinations. Repetition of these reactions has led to the compounds described earlier,[3] and their molecular constitutions have now been confirmed by mass spectrometry. For example, compound (Ia) shows a weak molecular ion, and major ions from the loss of the fragments CH_3, $(CH_3)_4C_2 + CH_3$, $(CH_3)_4C_2O_2$, $(CH_3)_4C_2O_2 + CH_3$; and from the appearance of the ions AsO^+, $AsOH^+$, $AsOC(CH_3)(CH_2)^+$, and $HOAsOC(CH_3)_2^+$. Analogous ions are observed from the other compounds studied. In addition, treatment of compounds (Ia) and (Ib) with ethereal diazomethane gives the corresponding methoxy-compounds (Id) and (Ie). The formulae of these new compounds were confirmed by elemental analysis and mass spectrometry.



$$R^2AsO_3H_2 + \begin{matrix} R^1{}_2COH \\ | \\ R^1{}_2COH \end{matrix} \longrightarrow \left(\begin{matrix} R^1{}_2CO \\ | \\ R^1{}_2CO \end{matrix}\right) AsR^2 \qquad (1)$$

(I)

	R^1	R^2
a	Me	OH
b	H	OH
c	Me	Ph
d	Me	OMe
e	H	OMe

The ^{1}H n.m.r. spectra of these five-co-ordinate arsenic compounds show clearly that ligand exchange is occurring rapidly. For instance, compound (Ic) in carbon disulphide or tetrachloroethylene solution shows only two peaks (δ 1·03, 1·32 p.p.m.) for the *C*-methyl groups over the temperature range +100 to −75°. Suitable control experiments, *e.g.* with a mixture of compounds (Ia) and (Ic), show that intermolecular ligand exchange, if it occurs at all, is slow on the n.m.r. time-scale. A plausible static model for compound (Ic), assuming a trigonal-bipyramidal structure in which the phenyl group is equatorial, and the AsO_2C_2 rings span axial and equatorial positions, predicts four environments for the *C*-methyl groups. However, pseudorotation using the phenyl group as a pivot, interchanges the *C*-methyl groups attached to axial and equatorial oxygen atoms while preserving the *syn*- and *anti*-relationships to the phenyl group (Figure 1). Thus four different C-methyl environments may, by this process, be time-averaged into two on the n.m.r. time-scale.

The results for compounds where all ligands are bonded to arsenic *via* oxygen are equally indicative of rapid ligand exchange processes. For example, (Ia) and (Id) show only one C-methyl environment in $CFCl_3$ solution from room temperature down to −110°. Thus a very rapid interchange of ligands must be occurring since, in these compounds also, a plausible static trigonal-bipyramidal structure would lead to four different C-methyl environments (Figure 1).† The mechanism of this interchange is probably also a pseudorotation, though it is clear that to average the positions of all the C-methyl groups, must involve an intermediate which has one AsO_2C_2 ring spanning equatorial positions, and presumably with an enlarged (120°) ring angle (Figure 2).

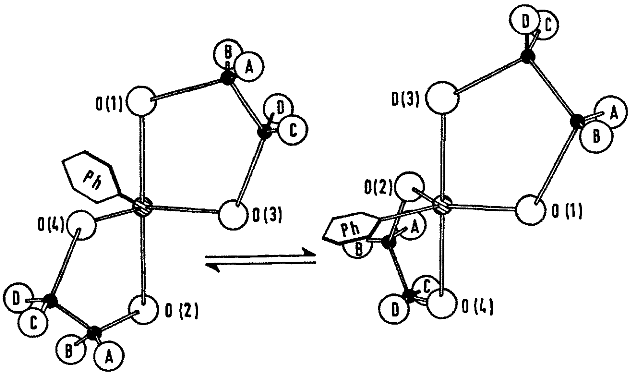


FIGURE 1

Some analogous five-co-ordinate phosphorus compounds have been shown to undergo similar pseudorotational processes above room temperature,[4,5] and the free energy of activation for forming a diequatorial ring intermediate in these compounds has been estimated as about 20 kcal/mole.[5] The present observations suggest that the process is much more ready in these five-co-ordinate arsenic compounds, where pseudorotation is fast even at −110°.

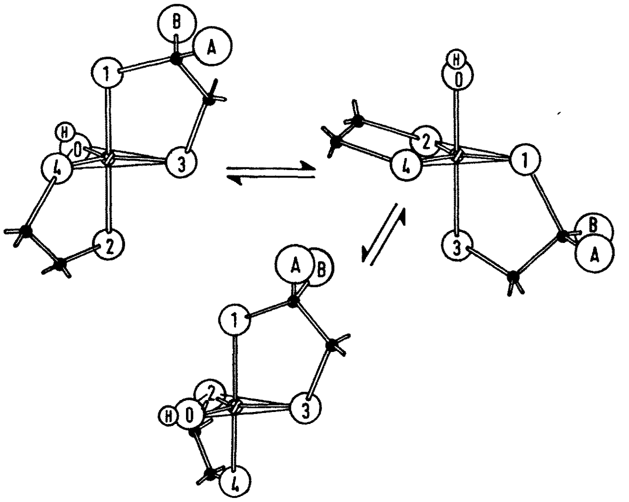


FIGURE 2

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† Even the less-plausible static square-pyramidal structure (*cf.* A. C. Skapski, *Chem. Comm.*, 1966, 11) would lead to at least two C-methyl environments for these compounds.

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