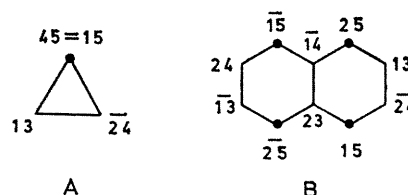# Barriers to Pseudorotation in Spiroarsoranes

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Summary Barriers to pseudorotation in As^V species, in which a five-membered ring is constrained to span the equatorial positions in the trigonal bipyramidal intermediates, are in the range of 20—23 kcal mol⁻¹, and thus are comparable with the corresponding barriers in P^V systems with similar structures.
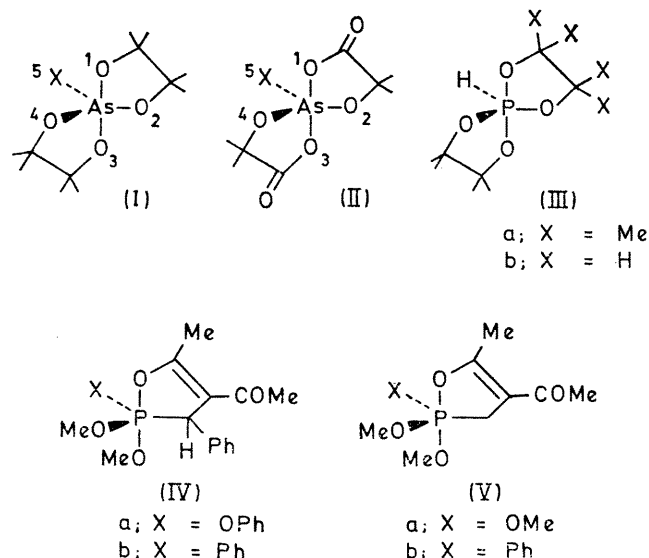
In a recent report[1] it was suggested that ligand reorganization by the Berry mechanism is much more rapid in five-membered ring spiroarsoranes than in spirophosphoranes. Our concurrent dynamic n.m.r. studies on the former class of compounds have led us to conclusions which are at variance with this suggestion.

(I)   (II)   (III)

a; X = Me
b; X = H

(IV)
a; X = OPh
b; X = Ph

(V)
a; X = OMe
b; X = Ph

The 5-alkyl- and 5-aryl-1,4,6,9-tetraoxa-5-arsaspiro[4,4]-nonanes (I) and (II) described in the Table† were synthesized by condensation of pinacol or α-hydroxyisobutyric acid with the appropriate arsonic acid in benzene under reflux.[2] For each entry in the Table two methyl proton signals of equal intensity were seen to broaden, coalesce, and finally sharpen at elevated temperatures.‡ Each

phenomenon was demonstrably reversible and in no case was there any evidence for decomposition of the solute.

A   B

As an aid to discussion of these results we use topological representations in which vertices of a graph represent stereoisomers and edges pseudorotational pathways. The numbering convention is that previously used.[3] For (I), the Desargues–Levi graph[4] reduces to (A), wherein $13 \rightleftarrows \overline{24}$ represents interconversion between (I) and its enantiomer using X (ligand index 5) as pivot. This process has been previously discussed for (I)[1] and (III)[5] and, if rapid on the n.m.r. time scale, reduces the four methyl signals expected for the C_2 structure to two, since the cis vicinal groups of each ring, syn and anti to X, become enantiotopic and thus isochronous. This step, which does not require placement of the ring into the di-equatorial positions and therefore has a low activation energy,[6] has not been observed in (I) or in (III), but has been characterized for bis-biphenylyl penta-co-ordinate systems.[7,8].

A second pathway which is available for the interconversion between (I) and its enantiomer involves pseudorotation to an intermediate with a plane of symmetry in which one of the rings is constrained to span the equatorial positions and the X group is apical [solid circle in (A)], followed by a second pseudorotation to give the enantiomer of the starting isomer. This pathway, if rapid on the n.m.r. time scale, renders enantiotopic the gem methyl groups of the apical-equatorial ring and, separately, the cis vicinal groups of the di-equatorial ring in the trigonal bipyramidal intermediate. Because of the necessity of placing a ring in the equatorial positions, the activation energy for this process is higher than for the one described above. Interconversion of 13 and $\overline{24}$ by this pathway ($13 \rightleftarrows 45 \rightleftarrows \overline{24}$ $\rightleftarrows 15 \rightleftarrows 13$) reduces the four methyl signals to one on the

n.m.r. time scale. The coalescence of two methyl proton signals to one is therefore associated with the high barrier.

The topological representation of pseudorotation in (II) is shown in (B). N.m.r. spectra of (IIa) and (IIb) reveal only a single pair of methyl signals from ambient temperatures up to the coalescence point. This observation is consistent with one of the following alternatives: the predominance of one racemic pair, $13/\overline{13}$ or $24/\overline{24}$, to the virtual exclusion of other diastereomers; predominance and rapid interconversion of 13 and $\overline{24}$ (and $\overline{13}$ and 24); predominance and rapid interconversion of the enantiomeric pair $\overline{14}$ and 23; accidental isochrony of the methyl doublets for these stereoisomers. As in (I), pseudorotation passing through high energy (solid circle) intermediates must be rapid to render the *gem* methyl groups isochronous, *i.e.*, the interconversion of 13 or 24 to their enantiomers, $\overline{13}$ and $\overline{24}$, necessitates pseudorotations through the intermediates 25 and $\overline{15}$ (or their enantiomers) which possess a di-equatorial five-membered ring.

Analogous processes in which a five-membered ring is placed di-equatorially in phosphoranes have been observed for (IIIa),[5] $\Delta G_{95}^{\ddagger} = 18 \cdot 4$ kcal mol^{-1}, (IIIb),[5] $\Delta G_{87}^{\ddagger} = 15 \cdot 4$ kcal mol^{-1}, and, in a case where a single ring is bound to P by one carbon and one oxygen, (IVa),[9] $\Delta G_{141}^{\ddagger} = 21 \cdot 8$ kcal mol^{-1}. When OPh in (IVa) is replaced by Ph (IVb), the high barrier increases to >24 kcal mol^{-1} and the lower barrier observed for these phosphoranes from *ca.* 12—13 to 15·8 kcal mol^{-1}. Similarly, a change from (Va) to (Vb) increases the low barrier to pseudorotation from 14·4 to *ca.* 17 kcal mol^{-1}.[9] The increase in the barrier height may be considered to result from a placement of the more electropositive Ph group into the apical position in intermediate phosphoranes in (IV) and (V).[6,9]

Evidence that the observed coalescence in the arsorane system (I) is also associated with passage through an intermediate in which X occupies an apical position (solid circle)

is afforded by the observation that the barrier of (Ie) is substantially less than that of (Ic); in the former, the substituent X is more electronegative than in the latter. If one assumes that the effect of replacing X = Ph with X = OR is similar in the two systems, it follows that the high barrier in (I), X = OR should have a value of *ca.* 15—20 kcal mol^{-1}. This process should be observable by d.n.m.r. above 0°, even with a limiting $\Delta\nu$ of only 1·0 Hz. The

Pseudorotation barriers of spiroarsoranes[a]

	Substituent X	Limiting $\Delta\nu$ (Hz)[b]	T_c (°)	$\Delta G_T^{\ddagger}$ (kcal mol^{-1})
(Ia)	Me	7·6[d]	155	21·8
(Ib)	PhCH$_2$	16·6	154	21·1
(Ic)	p-MeO·C$_6$H$_4$	14·8	187	22·9
(Id)	Ph	17·8	178	22·2
(Ie)	p-NO$_2$·C$_6$H$_4$	20·6	141	20·2
(IIa)	Me	3·1[e]	140	21·7
(IIb)	Ph	11·4	168	22·1

[a] *Ca.* 20% solute in α-bromonaphthalene; hexamethyldisiloxane used as internal reference and homogeneity standard.
[b] Measured in the range 60—95°.
[c] Calculated assuming transmission coefficient of $\frac{1}{4}$.[5]
[d] $\Delta\nu = 2 \cdot 8$ Hz in CS$_2$ at *ca.* 40° (ambient temperature of probe).
[e] $\Delta\nu = 0 \cdot 0$ Hz, $\omega_{\frac{1}{2}} = 0 \cdot 8$ Hz in CDCl$_3$ at *ca.* 40°.

earlier observation[1] of singlets in the n.m.r. spectra of (I), X = OH and X = OMe, at $-110°$ may have been due to accidental isochrony of the ring substituents, a difficulty noted in the present work (Table, footnote e) and in other reports concerning the interpretation of trivalent arsenic n.m.r. spectra.[10]

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