

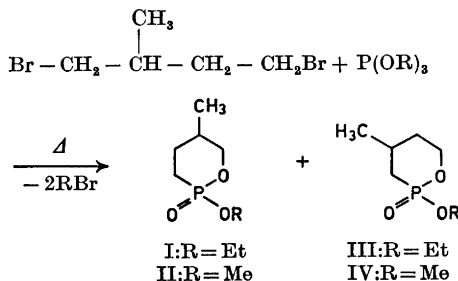
The Conformation of 5-Methyl-2-alkoxy-2-oxo-1,2-oxaphosphorinanes

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During the last few years considerable progress has been made toward the understanding of the stereochemistry of six-membered rings with phosphorus and oxygen as heteroatoms. Rings substituted 2-chloro-1,3,2-dioxaphosphorinanes¹⁻³ have been determined by PMR analysis. The stable isomers of 4- and 5-substituted phosphites exist in a chair conformation with equatorial substituent in 4 and 5 positions. There is also evidence that the P-Cl group occupies an axial position in the compounds studied. Shook and Quin⁴ demonstrated the existence of geometric isomers of 4-alkyl-1-methyl-phosphorinols. The appearance of the two P-CH₃ doublets in the PMR spectrum indicated that the difference in the two isomers occurs at the phosphorus atom, *i.e.* either axial or equatorial methyl substituent. The purpose of this work is to discuss the spectral properties and conformational equilibria of the *cis* and *trans* isomers of 5-methyl-2-alkoxy-2-oxo-1,2-oxaphosphorinanes.

In an earlier paper⁵ the GLC preparation of the *cis* and *trans* isomers of 5-methyl-2-ethoxy-2-oxo-1,2-oxaphosphorinane (I) was reported. The geometric isomers of 5-methyl-2-methoxy-2-oxo-1,2-oxaphosphorinane (II) were prepared in the same way. In the preparation, 20% of the geometric isomers of 4-methyl-2-alkoxy-2-oxo-1,2-oxaphosphorinanes (III and IV) were also found. The conformation of these isomers will be discussed in a later paper.



The *cis* isomer was believed to be the isomer with shortest retention time on GLC.

The PMR spectra of the isomers in dichloromethane showed no change over the temperature range -60 to $+120^\circ\text{C}$, but below -65°C the isomers crystallize. This observation can be explained by ring rigidity, an equilibrium greatly favouring one conformer and rapid equilibration over the whole temperature range. The chemical shift of methyl groups of the isomers was different, Table 1, indicating different

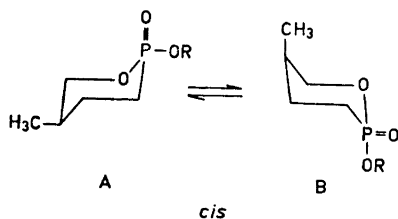
Table 1. Physical data and chemical shifts for the *cis* and *trans* isomers of I and II.

Com- pound	Isomer	Retention time (min), 185°C	n_D^{20}	P=O cm^{-1}	CH ₃ Chemical shift, ppm
I	<i>cis</i>	31.5	1.4597	1240 1245	1.02
	<i>trans</i>	42.5	1.4541	1250	0.90
II	<i>cis</i>	29.0	1.4545	1242 1248	1.10
	<i>trans</i>	38.5	1.4503	1253	0.96

orientation of the substituent at carbon 5. A similar observation has been made by Denney and Denney⁶ on 5-methyl-2-methoxy-1,3,2-dioxaphosphorinane. The methyl group experiences different shielding when situated in axial position as compared to equatorial position in the ring.

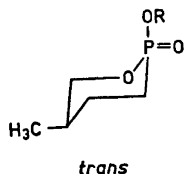
The infrared spectra of *cis* and *trans* isomers of dialkylcyclohexanes⁷ reveal characteristic frequencies in the region $585-650\text{ cm}^{-1}$ only for those forms having one *axial* substituent. An axial position for a methyl group has also been found for the *cis* isomer of 3-methyl-2-ethoxy-2-oxo-1,2-oxaphosphorinane⁸ and the *cis* and *trans* isomers of 4,5-dimethyl-2-ethoxy-2-oxo-1,2-oxaphosphorinane.⁹ The infrared spectra of the *cis* isomer of I and II showed strong bands at 594 and 663 cm^{-1} , and the *trans* isomer one band at 590 cm^{-1} . The appearance of the band at 663 cm^{-1} in the *cis* isomer is assigned to an axial substituted methyl group at carbon 5, and the lack of this band in the *trans* isomer indicates an equatorial methyl group. Since any ring inversion will be registered on the infrared time scale, the *cis* isomer is

believed to be in an rapid equilibration between the two conformers A and B,



while the *trans* isomer exist in a rigid chair conformation.

The phosphoryl absorption band for the *cis* isomer of I is found to give a doublet at 1240 and 1245 cm^{-1} , while the *trans* isomer is found to give a singlet at 1250 cm^{-1} . Since atoms linked to six-membered rings usually give higher infrared stretching frequencies in equatorial position than in



axial, the phosphoryl absorptions at 1240 and 1245 cm^{-1} for the *cis* isomer are assigned to an equilibrium between an axial and an equatorial position of the P=O group. The frequency at 1250 cm^{-1} in the

Table 2. Equilibrium data for the *cis* and *trans* isomers of 5-methyl-2-ethoxy-2-oxo-1,2-oxaphosphorinane (*cis* \rightleftharpoons *trans*).

Temp. $^{\circ}\text{C}$	Equilibrium constant, K	ΔG° kcal/mol	$-\Delta H^{\circ}$ kcal/mol
200.8	1.13	0.12	
219.0	1.09	0.08	
239.8	1.05	0.05	
259.9	1.02	0.02	0.9 ± 0.2
279.0	1.00	0.00	
299.0	0.97	-0.03	

trans isomer is assigned to an equatorial position of the P=O group.

The conformational equilibria of the *cis* and *trans* isomers of I have been studied at six different temperatures over a range of approx. 100 $^{\circ}\text{C}$ (Table 2). The equilibrations for the isomers were carried out in sealed tubes catalyzed by trifluoroacetic acid, and each sample was analyzed by GLC. The equilibrium was approached from both sides of the isomers. The equilibration of the isomers shows that the *trans* isomer with an axial ethoxy group attached to the phosphorus atom is 0.9 kcal/mol more stable than the *cis* isomer.

Further detailed studies and analysis of proton magnetic resonance of these isomers are in progress in this laboratory.

Experimental. The synthesis and physical data for the mixed isomers of 5-methyl-2-ethoxy-2-oxo-1,2-oxaphosphorinane (I) have been reported earlier.⁵

5-Methyl-2-methoxy-2-oxo-1,2-oxaphosphorinane (II), b.p.₁₀ 133 $^{\circ}\text{C}$, n_{D}^{20} : 1.4550. The isomers were separated by means of an Aerograph Autoprep A-700 gaschromatograph. GLC shows that the purity of these isomers was above 99%. The PMR spectra were measured at 60 MHz, JEOL C-60H, in 20% solution of the compounds in CDCl_3 at 25 $^{\circ}\text{C}$. The infrared spectra were recorded on Unicam SP 100, from samples prepared as films between KBr-windows.

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