

Conformational Analysis of 6-Methyl-2-oxo-2-alkoxy-1,2-oxaphosphorinanes

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Proton magnetic resonance and infrared spectra of the *cis* and *trans* isomers of 6-methyl-2-oxo-2-alkoxy-1,2-oxaphosphorinanes indicate difference in the configuration around the phosphorus atom. The 6-methyl group is found to occupy the equatorial position.

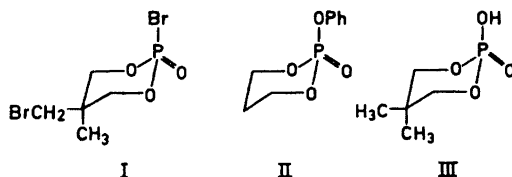
Some years ago Denny and Denny¹ found evidence from proton magnetic resonance (PMR) spectra for the presence of geometric isomers in 2-methoxy-5-methyl-1,3,2-dioxaphosphorinane and 2-methoxy-2-oxo-5-methyl-1,3,2-dioxaphosphorinane. The isomers of the former showed two doublets for C-CH₃ absorption at 0.69 and 1.28 ppm, indicating different environments around the methyl groups in position 5 of the two isomers. The C-CH₃ absorption of the corresponding phosphate isomers seemed to indicate similar position of the 5-methyl substituent. Shook and Quin² have shown the existence of geometric isomers in 4-alkyl-1-methyl-phosphorinanol, and from PMR spectra the presence of two P-CH₃ doublets indicated differences in the configuration around phosphorus. During the last years considerable progress has been made toward the understanding of the stereochemistry of 6-membered rings with phosphorus as heteroatom.³⁻²⁰ The purpose of this work is to discuss the spectral properties of the isomers of 6-methyl-2-alkoxy-2-oxo-1,2-oxaphosphorinanes.

EXPERIMENTAL

The syntheses and physical data of the isomers of 6-methyl-2-oxo-2-ethoxy-1,2-oxaphosphorinane (IV) have been reported.³ Physical data, P=O and P-CH₃ frequencies for IV, V, and VII are given in Table 2. The PMR spectra were measured at 60 Mc (JEOL C-60 H) in 20 % solution of the compounds in CDCl₃ at 25°C. The infrared spectra were recorded on Unicam SP100, from samples prepared as films between KBr windows.

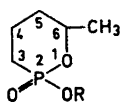
RESULT AND DISCUSSION

In analogy with cyclohexanes it was assumed that six-membered ring phosphites, phosphonate, and phosphates exist only in chair configuration. The X-ray diffraction method has been applied to three compounds¹⁰⁻¹² (I, II, III).



It has been confirmed that these compounds have chair-like structures where the phosphoryl oxygen atom occupies the equatorial position. From PMR studies in solution, it has been postulated that the 1,3,2-dioxaphosphorinane ring exists in a chair-like structure with either an axial or an equatorial phosphoryl oxygen group.¹³ However, dipole moment determination of 2,2-disubstituted-1,3,2-dioxaphosphorinanes¹⁴ in benzene solution, suggested that the isomers with the phosphoryl oxygen group in equatorial position are favoured.

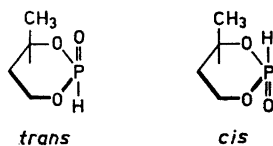
In a previous paper the gas liquid chromatographic (GLC) preparation of *cis* and *trans* isomers of 6-methyl-2-oxo-2-ethoxy-1,2-oxaphosphorinane (IV) was reported.³ The *cis* isomer was believed to be the isomer with the shortest retention time on GLC. The geometric isomers of 6-methyl-2-oxo-2-methyl-1,2-oxaphosphorinane (V) were prepared in the same way.



IV: R = C₂H₅

V: R = CH₃

The PMR signal of the 6-methyl group in the isomers IV and V consists of two doublets due to the coupling to the methine proton and to the phosphorus atom. The chemical shifts for the 6-methyl group of the *cis* and *trans* isomers were slightly different (compound IV 1.25 and 1.27, and compound V 1.34 and 1.35 ppm) (Table 1), indicating that the methyl group at carbon 6 is in the same position in both pairs of isomers. A similar observation has also been done for the 4-methyl group in the geometric isomers of 2-hydrogen-2-oxo-4-methyl-1,3,2-dioxaphosphorinane¹⁵ (VI), where the hydrogen atom attached



VI

$\delta_{\text{CH}_3} = 1.45 \text{ ppm}$

$\delta_{\text{CH}_3} = 1.43 \text{ ppm}$

to phosphorus is *trans*, respectively *cis*, to the ring substituent. In accordance with this, Aksnes *et al.*⁶ showed that reaction of the cyclic chlorophosphite, 3-chloro-4-methyl-1,3,2-dioxaphosphorinane, with ethanol gives the less stable form of the corresponding ester with inversion of configuration at phosphorus.

Infrared spectral characteristics of *cis-trans* isomers of dialkylcyclohexanes²³ reveal characteristic frequencies in the region 585–650 cm^{-1} only for those forms having one axial substituent. (For the 1,3 series the rather narrow frequency ranges were 623–633 cm^{-1} .) No characteristic frequency was observed for the equatorial substituted isomers in the region 560–770 cm^{-1} . Similar effects are shown in the stereoisomers of 1,3,5-trimethylcyclohexane, where, in the spectrum of the *trans* isomer, one of the methyl groups in the axial position has an IR band at 630 cm^{-1} . In the spectrum of the *cis* isomer, in which all methyl groups are in equatorial position, no such frequency occurs. The infrared spectra of the *cis* and *trans* isomers of IV and V show no bands in the region 570–770 cm^{-1} indicating an equatorial methyl group in position 6. Consequently, the isomers must have the methine proton at the 6-carbon in axial position. Atoms linked to six-membered rings usually give higher infrared stretching frequencies in equatorial positions compared with axial positions.²⁴ According to this, the equatorial C–D stretching

Table 1. Chemical shifts and coupling constants for the 6-methyl group of the isomers of IV, V, and VII.

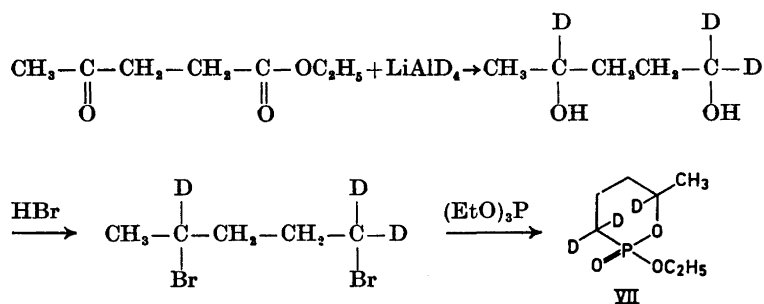
Compound	Chemical shifts	Coupling constants Hz. ^a	
IV	<i>cis</i>	1.25	$J_{\text{H-CH}_3} = 6.2$, $J_{\text{P-O-CH-CH}_3} = 1.8$
	<i>trans</i>	1.27	$J_{\text{H-CH}_3} = 6.0$, $J_{\text{P-O-CH-CH}_3} = 2.1$
V	<i>cis</i>	1.34	$J_{\text{H-CH}_3} = 6.0$, $J_{\text{P-O-CH-CH}_3} = 1.8$
	<i>trans</i>	1.35	$J_{\text{H-CH}_3} = 6.2$, $J_{\text{P-O-CH-CH}_3} = 2.0$
VII	<i>cis</i>	1.24	$J_{\text{P-O-CH-CH}_3} = 1.9$
	<i>trans</i>	1.25	$J_{\text{P-O-CH-CH}_3} = 2.1$

^a From first order analysis. The accuracy is probably ± 0.1 Hz.

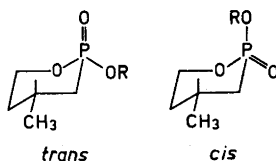
Table 2. Physical data of the IV, V, and VII isomers.

Compound	Isomer	Retention time (min) 185°C	n_D^{20}	P=O cm^{-1}	P-CH ₂ cm^{-1}
IV	<i>cis</i>	27.5	1.4492	1255 1240	1290
	<i>trans</i>	46.0	1.4525	1250	1300
V	<i>cis</i>	25.0	1.4460	1255 1240	1290
	<i>trans</i>	43.5	1.4480	1245	1300
VII	<i>cis</i>	28.5	1.4490	1255 1230 1215	No
	<i>trans</i>	45.5	1.4510	1265 1240	No

should occur at higher frequency than the axial. The infrared spectra of the isomers of 6-methyl-2-ethoxy-2-oxo-3,3,6-trideutero-1,2-oxaphosphorinane (VII) would reveal if the two isomers have different or similar configuration of the deuterio-atom in position 6. The isomers of VII were prepared by reducing the ethyl ester of levulinic acid with LiAlD_4 to the deuterio dialcohol. Bromination of this with HBr and heating the formed deuteriodibromide with triethylphosphite gave a mixture of both isomers. These were separated by GLC.



The infrared C-D stretching frequency bands in the *cis* and *trans* isomers of VII are similar, and show medium absorption bands at 2140, 2165, and 2225 cm^{-1} . The bands at 2225 and 2165 cm^{-1} are due to the asymmetric and symmetric C-D stretching frequency of the CD_2 group, while the band at 2140 is assigned to the C-D axial stretching frequency.²⁴ According to this observation the following structures for the *cis* and *trans* isomers of IV, V, and VII are reasonable to expect:



The infrared spectra of the isomers show differences between the phosphoryl absorption band, which also indicate different configurations around the phosphorus atom in the isomers. Computer analysis of 60 MHz proton magnetic resonance spectra of the isomers is in progress in this laboratory.

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