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## Phosphorus, Sulfur, and Silicon and the Related Elements

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### Pseudorotation and Conformational Transmission in Pentacoordinated Phosphorus Compounds

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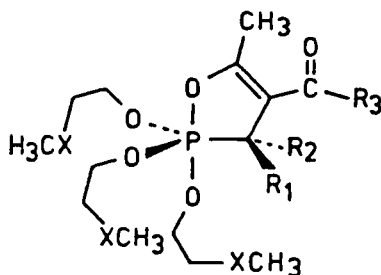
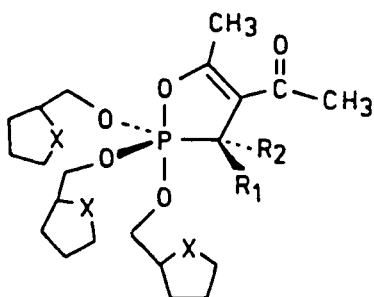
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## PSEUDOROTATION AND CONFORMATIONAL TRANSMISSION IN PENTACOORDINATED PHOSPHORUS COMPOUNDS

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This poster reviews our recent work on conformational transmission and pseudorotation in the pentacoordinated phosphorus ( $P^V$ ) compounds **1a-d** and **2a-d** (1,2).



**1a:** X=O, R<sub>1</sub>=H, R<sub>2</sub>=C<sub>6</sub>H<sub>5</sub>

**1b:** X=CH<sub>2</sub>, R<sub>1</sub>=H, R<sub>2</sub>=C<sub>6</sub>H<sub>5</sub>

**1c:** X=O, R<sub>1</sub>=R<sub>2</sub>=CH<sub>3</sub>

**1d:** X=CH<sub>2</sub>, R<sub>1</sub>=R<sub>2</sub>=CH<sub>3</sub>

**2a:** X=O, R<sub>1</sub>=H, R<sub>2</sub>=C<sub>6</sub>H<sub>5</sub>, R<sub>3</sub>=CH<sub>3</sub>

**2b:** X=CH<sub>2</sub>, R<sub>1</sub>=H, R<sub>2</sub>=C<sub>6</sub>H<sub>5</sub>, R<sub>3</sub>=CH<sub>3</sub>

**2c:** X=O, R<sub>1</sub>=R<sub>2</sub>=CH<sub>3</sub>, R<sub>3</sub>=OC<sub>2</sub>H<sub>5</sub>

**2d:** X=CH<sub>2</sub>, R<sub>1</sub>=R<sub>2</sub>=CH<sub>3</sub>, R<sub>3</sub>=OC<sub>2</sub>H<sub>5</sub>

It is demonstrated that the pseudorotation rate of **1a,c** and **2a,c** (X = O) exhibiting conformational transmission is 2-4 times faster than in **1b,d** and **2b,d** (X = CH<sub>2</sub>) in which conformational transmission is absent. A conformational change in the basal ligands ( $g^+$ ,  $g^1 \rightarrow g^-$ ) of the intermediate square pyramidal structure is responsible for the observed lowering of the pseudorotation energy barrier by 2-3 kJ/mol. Furthermore we have studied the solvolysis of a set of 5'-tetrahydrofurfuryl (thff) and 5'-cyclopentanemethyl (cp) diphenylphosphinates. A remarkable acceleration (20 times) is encountered for the thff system in comparison with the cp compound (3). This is due to the fact that conformational transmission in the thff system facilitates the build-up of a  $P^V$  trigonal bipyramid as reaction intermediate.

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