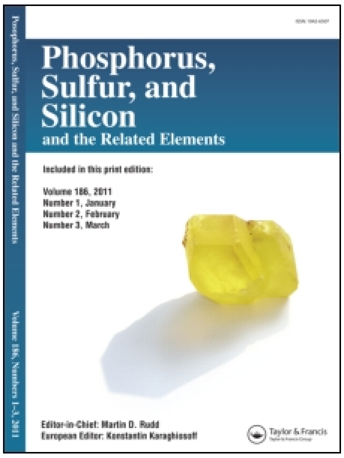

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The Effect of Substituents at the Phosphorus Atom on the Equilibrium Position in the Tautomeric Phosphoryl-Hydroxy-Ylide Triad Systems

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The Effect of Substituents at the Phosphorus Atom on the Equilibrium Position in the Tautomeric Phosphoryl-Hydroxy-Ylide Triad Systems

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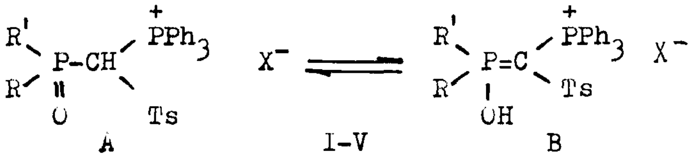
By means of NMR and IR spectroscopy there has been established that the equilibrium position in the phosphoryl-hydroxy-ylide prototropic systems /I-V/ depends on the nature of substituents at the phosphorus atom.



I: R = R' = PhO; II: R = R' = EtO; III: R = R' = Bu;

IV: R = Et, R' = Ph; V: R = R' = Ph; X: X = Cl, Br, ClO_4

Thus, for compounds I and II the equilibrium is completely shifted to the phosphoryl form /A/. For III and IV both tautomeric forms /A/ and /B/ are observed, the ratio of the forms being effected by temperature, solvent and the nature of anion X. Compound V in solution, independent of the above mentioned conditions, exists only in the hydroxy-ylide form /B/.

For the first time there have been isolated stable acyclic ylides with OH group at the phosphorus atom. The structure of hydroxy-ylide VB /X = Br/ was confirmed by X-ray analysis.

Dissociation constants pK_a of the synthesized substances were measured by potentiometric titration in nitromethane.