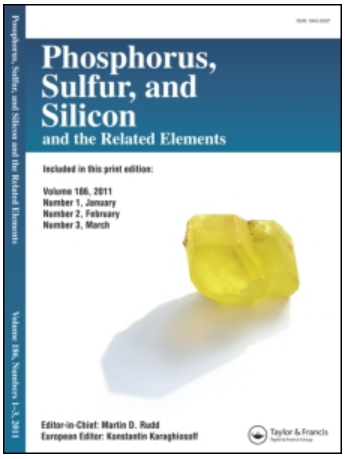

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The Effect of Swstituents at the Carbon and Phosphorus on the Tautomeric Equilibrium in the Phosphoryl-Hydroxyylide Systems

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THE EFFECT OF SUBSTITUENTS AT THE CARBON AND PHOSPHORUS ON THE TAUTOMERIC EQUILIBRIUM IN THE PHOSPHORYL-HYDROXYYLIDE SYSTEMS

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It has been established that in the phosphoryl-hydroxyylide systems (I-VIII) the increasing acidity of the carbon atom depending on substituent Y (which is characterized by σ^-_{CH} value) shifts the equilibrium to the hydroxy--ylide form (B).

$$RR'P(O)CH(Y)\overset{+}{P}Ph_3\ X^- \ (A) \rightleftharpoons RR'P(OH)=C(Y)\overset{+}{P}Ph_3\ X^- \ (B)$$

Y: $CONEt_2$ (I), $P(O)Ph_2$ (II), COOEt (III), $COCH_3$ (IV), Ts (V), CN (VI), COPh (VII), $\overset{+}{P}Ph_3X$ (VIII); R=R' = Bu, Ph, BuO, PhO, EtO; R=Ph, R'=Et; R=EtO, R'=Bu; X = Cl, Br, ClO_4, BF_4.

On the contrary, the content of form (B) decreases with the increase of the acidity of the phosphorus atom; for the quantitative estimation of this effect σ^Φ constants are used. Compounds with one or two phenyl groups at the phosphorus atom are an exception.

In the case of the acyl substituted compounds (IV, VII) the enol form $RR'P(O)C(^+PPh_3)=C(OH)R''\ X^-$ (C) (R" = Me, Ph) along with forms (A) and (B) are observed in the solution.

The equilibrium of tautomeric systems (I-VIII) is also affected by the nature of the anion X, used solvent and temperature.

In the crystalline state compounds (I-VIII) exist in one of the three tautomeric forms (A, B or C) depending on the nature of the substituents Y, R, R' and anion.