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

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

I. M. Aladzheva<sup>a</sup>; O. V. Sykhovsizaya<sup>a</sup>; I. V. Leontieva<sup>a</sup>; P. V. Petrovskii<sup>a</sup>; T. A. Mastryukova<sup>a</sup>; M. I. Kabachnik<sup>a</sup>; A. N. Nesmeyanov<sup>a</sup>

<sup>a</sup> Institute of Organo-Element Compounds, Academy of Sciences of the USSR, Moscow, USSR

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

I.M.ALADZHEVA, O.V.BYKHOVSKAYA, I.V.LEONTIEVA,  
 P.V.PETROVSKII, T.A.MASTRYUKOVA, and M.I.KABACHNIK  
 A.N.Nesmeyanov Institute of Organo-Element Compounds,  
 Academy of Sciences of the USSR, Vavilov Str. 28,  
 Moscow 117813, USSR

It has been established that in the phosphoryl-hydroxylyde systems (I-VIII) the increasing acidity of the carbon atom depending on substituent Y (which is characterized by  $\sigma_{CH}^-$  value) shifts the equilibrium to the hydroxylyde 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<sub>2</sub> (I), P(O)Ph<sub>2</sub> (II), COOEt (III), COCH<sub>3</sub> (IV),  
 Ts (V), CN (VI), CPh (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<sub>4</sub>, BF<sub>4</sub>.

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  $\sigma^{\Phi}$  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  $RR'P(O)C(\overset{+}{P}Ph_3)=C(OH)R'' X^- (C)$  (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.