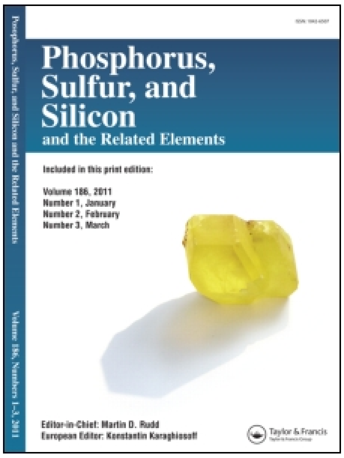

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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M. I. Kabachnik[a]; T. A. Mastryukova[a]; I. M. Aladzheva[a]
[a] A. N. Nesmeyanov Institute of Organo-Element Compounds, USSR Academy of Sciences, Moscow

To cite this Article Kabachnik, M. I. , Mastryukova, T. A. and Aladzheva, I. M.(1983) 'Prototropic Tautomerism in Phosphoryl-Hydroxyylide and Thiophosphoryl-Mercaptoylide Systems', Phosphorus, Sulfur, and Silicon and the Related Elements, 18: 1, 249 — 252

To link to this Article: DOI: 10.1080/03086648308076013

URL: http://dx.doi.org/10.1080/03086648308076013

Phosphorus and Sulfur, 1983, Vol. 18 pp. 249-252
0308-664X/83/1801-0249/$18.50/0

PROTOTROPIC TAUTOMERISM IN PHOSPHORYL-HYDROXYYLIDE AND THIOPHOSPHORYL-MERCAPTOYLIDE SYSTEMS

M.I. KABACHNIK, T.A. MASTRYUKOVA, I.M. ALADZHEVA
A.N.Nesmeyanov Institute of Organo-Element
Compounds, USSR Academy of Sciences, Moscow

Abstract Two new types of tautomerism are discussed: phosphoryl-hydroxyylide and thiophosphoryl-mercaptoylide tautomerism.

The possibility of phosphoryl-hydroxyylide tautomerism

$$>P(O)-CH< \rightleftharpoons >P(OH)=C<$$

phosphorus analogue of keto-enol tautomerism was first discussed by A.Ye. Arbuzov and A.I.Razumov in 1929.[1]

The position of equilibrium in prototropic tautomeric systems is known to be determined by the relationship between the acid properties of the forms and to be always shifted towards the less acid form. In all the previously known alkylphosphoryl compounds - $R_2P(O)CHR'R''$, $R(RO)P(O)CHR'R''$ or $(RO)_2P(O)CHR'R''$ - the acidities of CH forms are so small that OH forms are not observed at all. For the appearance of hydroxyylide structures it was, therefore, necessary to introduce into the CH group strongly acidifying electron-acceptor groups R' and R". Indeed, the introduction of two SO_2Ph groups made it possible for O.I.Kolodiazhnyi[2] to observe, along with a stable CH form, the formation of an unstable hydroxyylide. We observed[3] in solution only the hydroxyylide form after protonating dimethylphosphoryl-substituted phosphoranphosphonium salt by means of HSO_3F

$$Me_2P(O)C(=PPh_3)^+PPh_3.X^- \longrightarrow Me_2P(OH)=C(^+PPh_3)_2.2X^-$$

To estimate the electron effect of different groups on CH acidity by means of an equation of Hammett's type we developed a system of σ_C^- constants having the same meaning as Hammett's σ^- constants but differing for each X group depending on whether it was attached to a primary, secondary or tertiary carbon atom (constants $\sigma_{CH_3}^-$, $\sigma_{CH_2}^-$ and σ_{CH}^-, respectively).[4] Good results were obtained when using these constants to correlate the pK_a of CH acids with $\Sigma\sigma_C^-$. Application of these constants to the above examples showed that for $R_2P(O)CHXY$ structures the region of phosphoryl-hydroxyylide tautomery should be sought within the interval of $\Sigma\sigma_{CH}^-$ values for two phenylsulphonyl and two triphenylphosphonium groups, i.e. from 1.42 to 2.16.

Logically, the first compound investigated in this interval at $\Sigma\sigma_{CH}^- = 1.78$ was $Ph_2P(O)CH(Ts)^+PPh_3 \cdot Br^-$. This crystalline substance proved to have an undoubtedly hydroxyylide structure. To identify an ylide OH structure or a phosphoryl CH structure we worked out (partially based on literature data) a system of criteria in ^{31}P NMR, PMR, IR and other spectra. The structure of the above crystalline salt was studied by X-ray analysis. For the central carbon atom a planar trigonal configuration was found with the angles sum of 358.6°, which unambigously confirms the OH structure. A strong OH...Br hydrogen bond ($l = 3.078$ Å) is observed. In solution this salt also has OH structure. Only in CF_3COOH the structure of the salt changes into a CH structure, and in CH_2Cl_2 solution in the presence of one or two mol CF_3COOH both forms are observed.[5] The $\Sigma\sigma_C^-$ interval to detect among the $Ph_2P(O)CHXY$ structures has thus been narrowed to 1.42 - 1.78. And, indeed, we found a system with pronounced tautomeric equilibrium

$Ph_2P(O)CH(COOEt)^{+}PPh_3Cl^{-} \rightleftharpoons Ph_2P(OH){=}C(COOEt)^{+}PPh_3Cl^{-}$

with the corresponding $\Sigma\sigma^{-}_{CH} = 1.68$. In crystalline state this salt is an hydroxyylide. In solution the equilibrium of CH and OH forms of this salt depends on temperature. With an increase in temperature the content of the CH form increases; and the OH form is thus more stable ($-\Delta H = 1.66$ kcal/mol). The tautomeric equilibrium constant also depends on the nature of solvent. By their "enolyzing" ability the solvents can be arranged in a series: EtOH > CH_2Cl_2 > (CH_2Cl_2+MeCN, 4:1) > $MeNO_2$ > MeOH > $CHCl_3$ > CF_3COOH.[6]

A large excess of HCl or HBr converts both tautomers into dication

$Ph_2{}^{+}P(OH)\text{-}CH(COOEt)^{+}PPh_3$

Thiophosphoryl-mercaptoylide tautomerism

$R_2P(S)\text{-}CHXY \rightleftharpoons R_2P(SH){=}CXY$

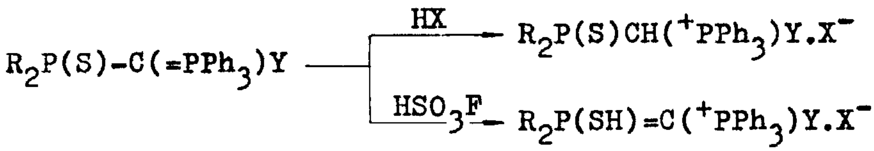
has previously been completely unknown. Basicity of the P=S-group is essentially lower than that of P=O and acidity of the P-SH fragment, accordingly, - higher than that of P-OH. The region of thiophosphoryl-mercaptoylide tautomerism could be expected to shift in the $\Sigma\sigma^{-}_{CH}$ scale towards higher values which corresponds to a higher CH acidity of the thiophosphoryl form. The first mercaptoylide observed by us[3] has the structure of $Me_2P(SH){=}C(^{+}PPh_3)_2.2SO_3F^{-}$ and was obtained by protonating the conjugated base, $Me_2P(S)C({=}PPh_3)\text{-}{}^{+}PPh_3.X^{-}$, with fluorosulphonic acid.

We synthesized a number of α-substituted thiophosphorylphosphinomethylenes

$R_2P\text{-}C({=}PPh_3)Y + S \longrightarrow R_2P(S)\text{-}C({=}PPh_3)Y$

R = Me, Bu, Ph, EtO, PhO; Y = COOEt, Ts, $^{+}PPh_3X^{-}$

and investigated their protonation in different conditions[7]



$$R_2P(S)\text{-}C(\text{=}PPh_3)Y \xrightarrow{HX} R_2P(S)CH(^{+}PPh_3)Y.X^{-}$$

$$R_2P(S)\text{-}C(\text{=}PPh_3)Y \xrightarrow{HSO_3F} R_2P(SH)\text{=}C(^{+}PPh_3)Y.X^{-}$$

Protonation of all the ylides with Y = COOEt or Ts, irrespective of the nature of R, yields CH forms. But ylides with two triphenylphosphonium groups are bases so weak that in usual conditions they are not protonated at all. However, at a low temperature under the action of the excess of acid or under the action of HSO_3F they are protonated on sulphur with the formation of SH ylide. Not in a single case did we observe the formation of a mixture of tautomeric forms. The region of thiophosphoryl-mercaptoylide tautomerism may well lie within the interval of $\sum \sigma^{-}_{CH}$ values between 1.78 and 2.16 that has not been studied yet.

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