Translated from *Uspekhi Khimii* **60** 2167–2188 (1991) U.D.C. 547.341 + 547.544.3

Enolisation of the phosphoryl group

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ABSTRACT. The potential ability of the phosphoryl group to undergo enolisation is demonstrated. The conditions for enolisation of phosphoryl and thiophosphoryl groups are examined. In order to determine the acidifying capacity of groups attached to the α-carbon atom, constants that depend on the number of substituents on this atom have been used. The limiting values of the totals of the constants that are responsible for enolisation of the phosphoryl group have been calculated. It is shown that enolisation of the phosphoryl group obeys the laws comprising the theory of prototropic tautomeric acid–base equilibrium.

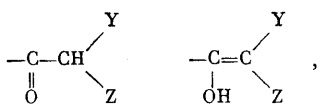
The bibliography includes 71 references.

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I. Introduction

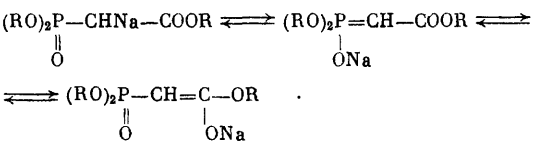
The ability of the carbonyl group to undergo enolisation is well known. It manifests itself most clearly in β-dicarbonyl compounds and in other cases where another electronegative group is situated at the β-position relative to the carbonyl group



(I)

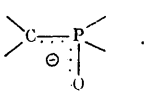
where Y and Z = COR, COOR, CN, SO_2R, etc., while Y can be H, Alk, or Ar. It is also known that simple ketones are only slightly enolised. It was established some time ago that a strong acidifying effect is needed from substituents Y and Z for enolisation to occur. This question was examined at one time by Arndt[1–4] and also Schwarzenbach et al.[5–7] in a series of studies on enolisation and acidity.

In the chemistry of organophosphorus compounds the phosphoryl group P=O is the analogue of the carbonyl group C=O. However, until the end of the 1970s not a single case of enolisation of the phosphoryl group was recorded in the literature. It may merely be mentioned that A E Arbuzov and A I Razumov in 1929 and 1934 proposed that the sodium derivative of phosphonoacetic ester undergoes tautomerism:[8,9]



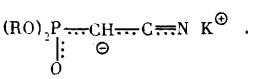
If it is borne in mind that at that time the concept of mesomeric ambident anions had not been widely developed, this report may be regarded as the first suggestion that the phosphoryl group can enolise. It was, of course, purely speculative in nature.

Subsequently lithium derivatives of di- and tri-phosphoryl-methanes were used more than once in organic synthesis.[10–13] In these Li derivatives the negative charge of the anion of the phosphorylated CH acid is undoubtedly delocalised on to the oxygen atoms of the phosphoryl groups in (II):



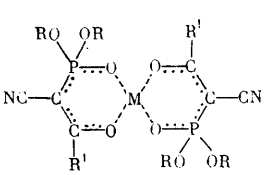
(II)

The same can be said of the metal-containing intermediates of the widely used Horner olefination that is activated by P=O.[14–16] Many examples of the alkylation and acylation of metal derivatives of β-ketophosphonates and other compounds have been reported.[7–29] However, in these cases the authors were dealing with conventional metal enolates on the carbonyl group. Nevertheless, the structure of these metal derivatives has not been studied in detail. In the studies of Kirilov and Petrov[20,22] the potassium derivative of phosphorylacetonitrile was thought to contain the ambident anion (III), whose charge is concentrated to a considerable degree on the phosphoryl oxygen atom:



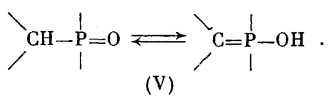
(III)

Finally, mention should be made of the crystalline magnesium and copper complexes of acylated phosphorylacetonitriles whose structure is described by Petrov and Kirilov.[30] These are *cis*-chelates with a P–O–M (IV) bond



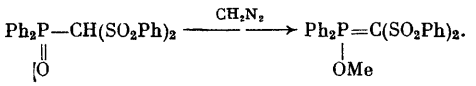
(IV)

Thus, in anions of phosphorylated CH acids the oxygen atoms of the phosphoryl group can carry, if only partially, the anion charge with a corresponding reduction in multiplicity of the P=O bond and in certain cases can form a bond with a metal cation. However, there has been no single recorded case of the tautomerism of phosphoryl and phosphaenol structures (V):



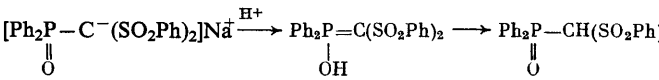
(V)

The enolisation of β-phosphorylated carbonyl compounds has been studied in great detail, but in all cases only the normal enol forms ($=\overset{|}{C}-OH$) rather than phosphaenol forms ($=\overset{|}{P}-OH$) have been observed.[20,22,26–28,31–38] The same occurs for thiophosphoryl compounds.[39] The above does not apply, of course, to the ambident reactivity of phosphoryl compounds, or more accurately their carbanions, towards electrophilic reagents. An example is the reactivity towards methylation of phosphoryl oxygen atom on treatment of diphenylphosphinylbis(phenylsulphonyl)methane with diazomethane:[40]



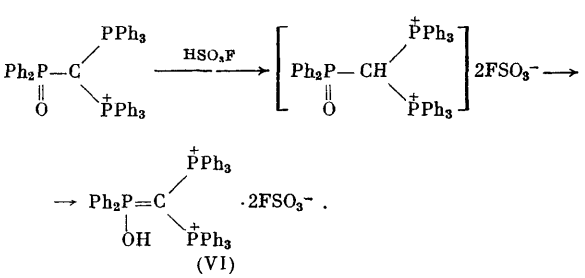
But this is a methylation reaction, rather than the addition of a proton which is needed to produce the phosphaenol form.

The first reports on enolisation of the phosphoryl group appeared in the latter half of the 1970s. Kolodyazhnyi[41] reported the formation of the unstable phosphaenol form of diphenylphosphinylbis(phenylsulphonyl)methane on acidification of a solution of its sodium derivative:



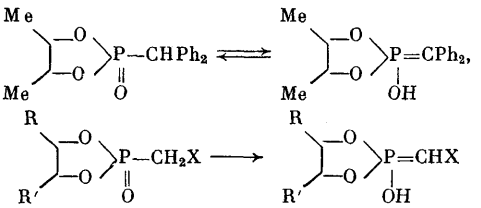
This phosphaenol form is rapidly and irreversibly converted to the CH form.

Mastryukova et al.[42] observed the formation of the stable phosphaenol form of diphenylphosphinylbis(triphenylphosphonio)-methane (VI) on protonation of the corresponding phosphorane-phosphonium salt with fluorosulphonic acid:



(VI)

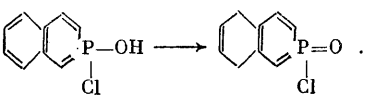
There are two reports by Ovchinnikov et al.[43,44] on the phosphaenolisation of cyclic phosphates:



R=Me, R′=H, Me; X=COOMe, CN.

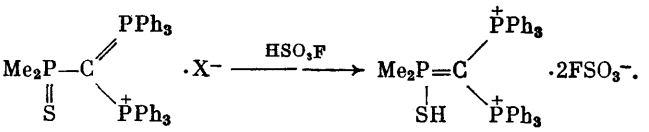
However, the phosphaenol structure of these compounds was later disputed.[45]

Finally, in 1979 Bickelbaupt et al.[46] synthesised the cyclic phosphaenol (VII), which readily and irreversibly "ketonised":



(VII)

With regard to enolisation of the thiophosphoryl group, the only example of this type (VIII) was found by Mastryukova et al.[47] It fully resembles the enolisation of the corresponding phosphoryl compound:



(VIII)

Thus, up to the beginning of the 1980s there were only isolated reports concerning phosphaenol forms in the literature and information about phosphoryl–phosphaenol (phosphoryl–hydroxy-ylide) tautomerism was absent altogether.

II. Possible enolisation of the phosphoryl group

It has been established that the position of a prototropic tautomeric equilibrium is determined by the ratio of the acidity constants of the forms in the given medium:

$$K_T = K_1/K_2. \qquad (1)$$

Here K_T is the tautomeric equilibrium constant, and K_1 and K_2 are the acidity constants of the tautomeric forms.[48] On enolisation of carbonyl groups, enol OH acids are formed, which, depending on their structure and stereochemical configuration, have an acidity that varies over a wide range—from pK_a = 10–12 for simple ketones and the least acidic β-dicarbonyl compounds to pK_a = 5–9 for normal β-dicarbonyl compounds† (data for aqueous solution).[49] Therefore, in order for enolisation to occur, it is necessary that the CH acidity of the ketone forms are similar to that of enols, i.e., pK_a = 5–10 (in water). In the case of enolisation of phosphoryl groups, the OH acidity of phosphaenols is substantially higher than

† Only when there are certain structural features of a β-dicarbonyl compound (fluorinated β-diketones, *trans*-configured cyclic enols with small rings, etc.) is an OH acidity with pK_a = 2–4 attained.[50]

that for their carbon analogues. Unfortunately, there are no comparative data for aqueous solutions. However, the acidity in water of other OH acids of phosphorus, and carbon (phosphoric and carbonic acid, methylphosphonic and acetic acids, etc.) can be compared. In this case there is very convincing evidence that phosphorus OH acids are stronger by a factor of 10^2-10^4. Therefore, for enolisation of the phosphoryl group to occur, phosphoryl CH acids must have $pK_a = 3-5$. This can only be achieved when there are strongly acidifying electron-withdrawing groups, stronger than in the chemistry of β-dicarbonyl compounds, at the β-position relative to the phosphoryl group.

Because of the need to make an objective determination of the acidifying effect of groups on CH acidity, we have developed a method of σρ correlation analysis of CH acidity based on the familiar Hammett equation:[51] $pK = pK^0 - \rho\sigma$. It was natural to use σ^- constants, which take into account directly polar conjugation of the substituent with the nucleophilic reaction site. However, difficulties related to the existence of the so-called "saturation effect" arose.[52] This means that the effect of an acidifying group attached to the central carbon atom is variable. It depends on the number of those groups that are already attached and decreases as these groups accumulate. This circumstance required the calculation of three σ^- values for each substituent — $\sigma_{CH_3}^-$, $\sigma_{CH_2}^-$, and σ_{CH}^- — depending on whether the substituent is located on a primary, secondary, or tertiary carbon atom. In developing this method of σρ correlation, the values of the $\sigma_{CH_n}^-$ constants were refined from the large quantity of experimental data in the literature on the CH acidity of different compounds and also from our own data on the CH acidity of organophosphorus compounds. Some of the derived values of the $\sigma_{CH_2}^-$ and σ_{CH}^- constants are given in Tables 1 and 2.[53-55] When these constants were used, good and excellent correlations between the pK of a large number of CH acids and the $\sigma_{CH_n}^-$ constants were obtained in different media and under different experimental conditions.

Table 1. $\sigma_{CH_2}^-$ and σ_{CH}^- constants for certain groups X.[53,54]

X	$\sigma_{CH_2}^-$	σ_{CH}^-	X	$\sigma_{CH_2}^-$	σ_{CH}^-
Me	0.12	0.13	$PhSO_2$	0.77	0.71
Ph	0.365	0.26	n-$MeC_6H_4SO_2$	0.75	0.70
MeCO	0.88	0.66	NO_2	1.26	1.12
PhCO	0.98	0.78	COOEt	0.725	0.60
CN	0.80	0.75	$CONEt_2$	0.58*	0.42

* See study of Matveeva et al.[54]

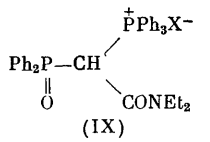
By using the new $\sigma_{CH_n}^-$ constants it proved possible to correlate the CH acidity of β-dicarbonyl compounds with their enolising capacity. Thus, for the completely enolised triacetylmethane, $\Sigma\sigma_{CH}^- = 1.98$; for the strongly enolised benzoylacetone, $\Sigma\sigma_{CH_2}^- = 1.86$; for the slightly less enolising acetylacetone, $\Sigma\sigma_{CH_2}^- = 1.76$; for the weakly enolising acetoacetic ester, $\Sigma\sigma_{CH_2}^- = 1.60$; and for malonic ester, which has a very low tendency to undergo enolisation, $\Sigma\sigma_{CH_2}^- = 1.44$. Thus, a range of values of $\Sigma\sigma_{CH_n}^-$ approximately from 1.6 to 2.0 in β-dicarbonyl compounds governs the strength of CH acidity that assists enolisation. It is of course necessary to take into account the OH acidity of the enol forms [cf. Eqn. (1)]. The acidifying effect of the substituents influences the OH acidity of enols, although to a lesser extent, but to a first approximation we can confine ourselves to the treatment of $\Sigma\sigma_{CH_n}^-$.

Table 2. $\sigma_{CH_2}^-$ and σ_{CH}^- constants for certain phosphorus groups X.[55]

X	$\sigma_{CH_2}^-$	σ_{CH}^-	X	$\sigma_{CH_2}^-$	σ_{CH}^-
$Ph_3\overset{+}{P}$	1.22	1.08	$Ph_2P(O)$	0.57	0.44
$(PhO)_2P(O)$	0.60	0.47	$Et_2P(O)$	0.47	0.36
$(EtO)_2P(O)$	0.56	0.44	$Me_2P(O)$	0.47	(0.35)*
$(BuO)_2P(O)$	0.55	(0.43)*	PhEtP(O)	0.51	(0.39)*
Bu(EtO)P(O)	0.50	(0.38)*	$Ph_2P(S)$	0.60	0.46
$Bu_2P(O)$	0.45	0.34	$(EtO)_2P(S)$	0.59	0.50

* Figures in brackets are values obtained by interpolation.

The OH acidity of phosphaenol forms is higher than in β-dicarbonyl compounds. Therefore, their CH acidity must also be substantially higher. We recently discovered that compound (IX) with $\Sigma\sigma_{CH}^- = 1.94$ does not enolise under any conditions,[56] whereas it was found previously that the corresponding diphosphonium derivative (VI) with $\Sigma\sigma_{CH}^- = 2.60$ is completely enolised.[42] Consequently, a value of $\Sigma\sigma_{CH}^-$ ranging from 2.0 to 2.6 is most favourable for enolisation of the phosphoryl group and phosphoryl–hydroxyl-ylide tautomerism:

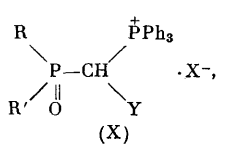


(IX)

Since it is difficult to achieve such high values of $\Sigma\sigma_{CH_n}^-$ without the use of phosphonium substituents, studies were subsequently made on compounds in which a triphenylphosphonium group was located on the central carbon atom together with the phosphoryl group. In this case by varying substituent Y it was possible to obtained cases of $\Sigma\sigma_{CH_n}^-$ ranging from 2.0 to 2.6.

III. Synthesis of phosphoryl compounds

Phosphoryl(triphenylphosphonio)methanes substitueed on the central carbon atom with the general formula (X)



(X)

where Y = $^{+}PPh_3X^{-}$, CN, Ts, COOEt, $CONEt_2$; R and R′ = Et, Bu, Ph, EtO, BuO, PhO in different combinations: X = Cl^{-}, Br^{-}, ClO_4^{-}, BF_4^{-} were synthesised.[57–60] The starting materials used were the respective phosphine-substituted phosphoranes (XII) obtained in accordance with literature data[61,62] from the corresponding monosubstituted triphenylmethylenephosphoranes (XI) and halophosphines or halophosphites in the presence of triethylamine:

$$Ph_3P{=}CHY + RR'PX \xrightarrow{Et_3N} RR'P{-}C(PPh_3)(Y)$$

(XI) (XII)

The phosphinophosphoranes (XII) were then oxidised to the phosphorylphosphoranes (XIII) on treatment with $KMnO_4$ in acetone or H_2O_2 in t-butanol:

$$(XII) \xrightarrow{KMnO_4 \text{ or } H_2O_2} R'P(O)(R)-C(PPh_3)(Y)$$

(XIII)

In many cases, instead of starting from monosubstituted triphenylmethylenephosphoranes (XI), it proved more advantageous to use the corresponding phosphonium salts (XIV), i.e., to treat them with dialkyl- or diaryl-halophosphines (RR′PX) or phosphorohalidites [$(RO)_2PX$] and triethylamine in a solution of dichloromethane under mild conditions (atmosphere of argon, temperature 0–20 °C):

$$\underset{(XIV)}{Ph_3P{-}CH_2{-}Y} + RR'PX + 2Et_3N \rightarrow (XII) + 2Et_3N{\cdot}HX.$$

It subsequently proved possible to carry out the oxidation stage of (XII) → (XIII) without isolation of (XII) from the reaction mixture but to treat it directly with H_2O_2 in t-butanol at 0 °C.

Phosphoranephosphonium salts (XIII), where Y = $^{+}PPh_3X^{-}$, were obtained by addition of diphenyl- or dialkyl-halophosphines to hexaphenylcarbodiphosphorane (XV) with isolation of the intermediate crystalline phosphino derivative (XII), Y = $^{+}PPh_3Cl^{-}$:

$$\underset{(XV)}{Ph_3P{=}C{=}PPh_3} + R_2PCl \longrightarrow (XII) \xrightarrow{KMnO_4} (XIII).$$

Oxidation of (XII) to (XIII), Y = $^{+}PPh_3Cl^{-}$, was carried out with $KMnO_4$ in acetonitrile. Protonation of phosphoranes (XIII) was carried out in benzene or dichloromethane at 20 °C by treatment with an ethereal solution of halogen halides:

$$(XIII) \xrightarrow{HX} (X).$$

Crystalline phosphonium salts (X) were generally obtained; their melting points are given below in Table 3.

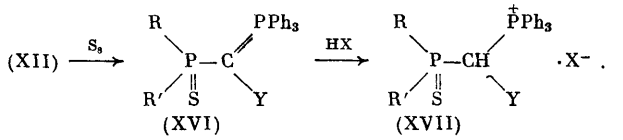
Table 3. Melting points and IR spectra of phosphorylphosphonium salts in the crystalline state.[57–60,65]

$R_2P(O)-CH(Y)-{}^{+}PPh_3X^{-}$ (A) or $R_2P(OH)=C(Y)-{}^{+}PPh_3X^{-}$ (B)

No.	Y	R	X	m.p.	IR spectrum, KBr pellets, ν, cm^{-1}			Other frequencies	Form of compound
					P=O	P–OH	OH...X		
1	COOEt	Ph	Cl	123–125 (decomp.)	–	970 2*	1500–2200	1600(CO), 3440(EtOH)	B
2	COOEt	Ph	ClO_4	164–166 (decomp.)	1160, 1180 (shld.)	–	–	1730(CO), 2900(CH)	A
3	COOEt	PhO	ClO_4	113 (decomp.)	1290	–	–	1740(CO), 2880(CH)	A
4	COOEt	Ph	BF_4	117–119 decomp.)	–	–	600–1800	1670(CO)	BHB+
5	$CONEt_2$	Ph	Cl	167–168	1150	–	–	1630(CO), 2500–2800 (CH...Cl)	A
6	CN	Bu	Br	144–146	–	975	1500–3000	2170(CN)	B
7	CN	Ph	Br	160.5–162	–	965	1500–3000	2175(CN)	B
8	CN	Bu	ClO_4	144–145	–	910	1960–3000	2170(CN)	B
8[a]	After crystallisation in air			116–118	–	–	1640–1900	3100–3600(H_2O)	$BHOH_2^{+}$
9	CN	Ph	ClO_4	149–151	–	–	700–1700(OH...O)	2170(CN)	BHB+
10	Ts	Bu	Br	149–150	–	960	1800–2000	1130, 1280 3*	B
11	Ts	Ph, Et	Br	179–181	–	940	1700–2800	1125, 1285 3*	B
12	Ts	Ph	Br	123–125	–	945	2000–2700	1135, 1280 3*	B
13	Ts	BuO	Br	100–102	–	970	2000–3000	1140, 1290 3*	B
14	Ts	Bu	ClO_4	154–155	see 4*	–	–	1150, 1330 3*	A
15	Ts	Ph, Et	ClO_4	181–184	1195	–	–	1150, 1330 3*	A
16	Ts	Ph	ClO_4	173–178	–	–	600–1800	1135, 1282 3*	BHB+
17	Ts	Bu, EtO	ClO_4	167–168	1245	–	–	1159, 1330 3*	A
18	Ts	BuO	ClO_4	162–163	1275	–	–	1150, 1340 3*	A
19	Ts	EtO	ClO_4	184–185	1272	–	–	1155, 1330 3*	A
20	+ Ts	BuO	ClO_4	220–222	1290	–	–	1165, 1330 3*	A
21	PPh_3Br^{-}	Ph	Br	261–264	–	940 (br.) 980 (br.)	1600–3000	–	B 5*

*With 1/2 M of crystalline EtOH; 2*in petrolatum 960, 980 cm^{-1}; 3*first figure for symmetric SO_2 vibrations, second figure for antisymmetric SO_2 vibrations; 4*PO vibration region masked by ClO_4 band; 5*B...H...OH_3^{+} is possible.

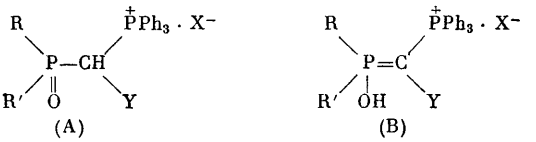
The thiophosphoryl derivatives (XVI) were obtained by addition of sulphur to phosphinophosphoranes (XII) in benzene, acetonitrile, or mixtures of them in the cold for 6–24 h or by boiling for 10–15 min.[63,64]



(XII) (XVI) (XVII)

IV. Phosphaenols (hydroxyl-ylides) in the crystalline state

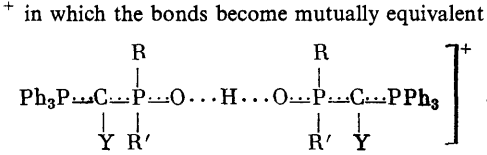
The crystalline phosphorylphosphonium salts that were studied are listed in Table 3. They are stable compounds that can be recrystallised in air without any special precautions. The conclusion about their phosphoryl CH structure (A) or phosphaenol structure (B) is based on an examination of their IR spectra, and in a number of cases X-ray diffraction analysis was used:



(A) (B)

The IR spectra of the compounds with structure (A) contain a very characteristic band due to P=O in the region 1150–1195 cm^{-1} when alkyl or aryl groups are attached to phosphorus and at 1270–1290 cm^{-1} when RO groups are attached. When structure (B) is formed this band disappears and in its place a band appears at 910–975 cm^{-1} that is typical of the protonated P=O group.[66] At the same time very broad absorption bands appear in these spectra at 1500–3000 cm^{-1} which suggest that OH groups with strong hydrogen bonds OH...X^- are present. As far as the vibrations of groups Y are concerned, these groups are attached to an sp^3-hybridised carbon atom in structures (A) and to an sp^2-hybridised carbon atom in structures (B). As a consequence the frequencies in the first case are higher. Thus, the CO vibration of the carbethoxy group for structure (A) is 1730–1740 cm^{-1} while for structure (B) it occurs at 1660 cm^{-1}. The symmetric SO_2 vibrations in structure (A) are at 1150–1165 cm^{-1} while in structure (B) they occur at 1125–1140 cm^{-1}, the antisymmetric vibrations occur at 1330–1340 cm^{-1} (A) and 1280–1290 cm^{-1} (B) respectively. All of these changes are very uniform, which provides sufficient reliability in the assignment of structures to (A) and (B).

In addition to structures of the type (B) with an OH...X^- hydrogen bond, "dimeric" structures in which the conjugate base acts as an H-bond acceptor were detected. A complex of the type BHB^+ in which the bonds become mutually equivalent is formed:



The IR spectra of the BHB^+ structures are characterised by the absence of bands due to P=O and P–OH and the presence of a broad complex band at 600–1800 cm^{-1}. In this case the vibrations of Y conform to structure (B). Such "dimeric" complexes have been confirmed by X-ray diffraction data.

It should be noted that the X-ray diffraction data very clearly characterise both the phosphaenol forms and BHB^+ structures. Thus, in the structure of the tosyl derivative with form (B) (No. 12, Table 3) (Fig. 1), the central carbon atom [C(1)] has only a slightly distorted planar trigonal coordination with a projection of 0.118 Å from the P(1)P(2)S plane. The C(1)–PPh_2OH and C(1)–PPh_3 have virtually the same length—1.751(4) and 1.764(4) Å—and a multiplicity of one and a half.[67] The phosphaenol form is stabilised in the crystalline state by an OH–Br hydrogen bond of length 3.078 Å.

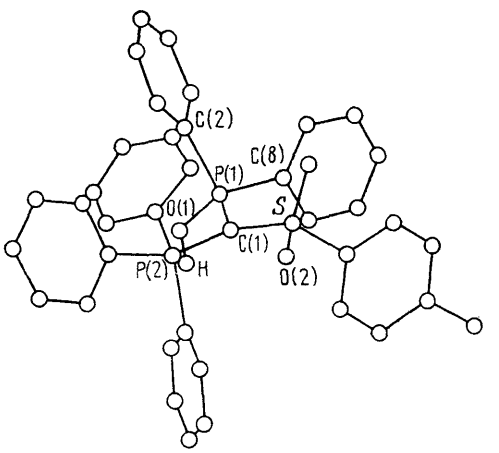


Figure 1. Crystalline structure of the cation component of the bromide salt of (hydroxydiphenylphosphoranylidene)tosyl(triphenylphosphonio)methane $Ph_3P^+C(Ts)=P(Ph_2)O-H...(Br^-)$.[65]

Stabilisation of the phosphaenol structure can, however, be achieved with the assistance of another protophilic species. Thus, in the case of crystals of (dibutylhydroxyphosphoranylidene)cyano-(triphenylphosphonio)methane perchlorate (No. 8, Table 3), structure (B) is unstable, and on recrystallisation from an acetone–ether mixture when air is admitted, it is stabilised by absorption of a single water molecule to form a salt of the type $(BHB')^+$, where B' is the water molecule. In this novel structure the crystal is composed of two crystallographically independent cations. In each of them (Fig. 2) the central carbon atom C(1) is also planar trigonal, the projections from the plane are 0.072 and 0.054 Å, and the sum of the angles about C(1) is 359.4°. The C(1)–PBu_2OH and C(1)–PPh_3 bonds are virtually the same and on average have a length of 1.745(9) Å, which corresponds to a multiplicity of approximately one and a half. The oxygen atoms of the water molecule O(11) act as acceptors of protons from the P–OH group. The O...H...O distances are equal to 2.501(6) and 2.482(7) Å, which corresponds to hydrogen bonds of increased strength.[68] It is interesting to note that in turn the H_2O molecules also participate through their H atoms in the formation of O–H...N bonds with the cyano groups of the neighbouring cations.

The structure of (diphenylhydroxyphosphoranylidene)carbethoxy (triphenylphosphinio)methane borofluoride (No. 4, Table 3) is shown in Fig. 3 as an example of a symmetric BHB^+ complex. The

structure is centrosymmetric. Its two "halves" are identical and joined by a hydrogen bridge. The central C(1) carbon atom is planar trigonal, the sum of the angles is 359.3° and the lengths of the C(1)—PPh_2OH and C(1)—PPh_3 bonds are virtually the same—1.725(8) and 1.735(8) Å—with a multiplicity of about one and a half. The length of the O...H...O hydrogen bond is 2.422(8) Å. The lengths of all the bonds of the "dimer" are mutually equivalent, which suggests that the cation charge is delocalised over both "halves".

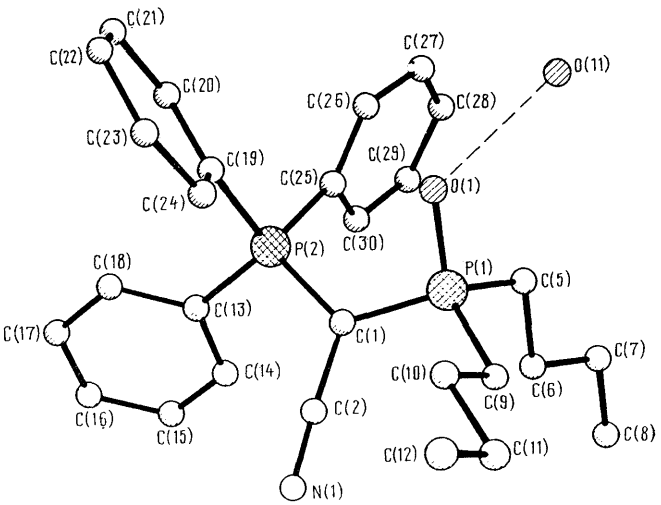


Figure 2. Structure of one of the two crystallographically independent cations of (hydroxydibutylphosphoranylidene)cyano-(triphenylphosphonio)methane perchlorate—a $(BHB')^+$ complex with a molecule of H_2O [the O(11) oxygen atom is shown]; $PH_3P^+C(CN)=(Bu_2)O-H...OH_2(ClO_4^-)$.

It may be concluded from an examination of the data in Table 3 that there are two principal factors that govern the alternative structure. The first is the nature of Y. The phosphaenolising capacity of the Y groups is given by a series that corresponds to the following variation in σ_{CH}^- values:

	$Ph_3\overset{+}{P}$	>CN	>Ts	>COOEt	>$CONEt_2$
σ_{CH}^-	1.08	0.75	0.70	0.60	0.42

The $^+PPh_3$ group has the highest phosphaenolising capacity while $CONEt_2$ has the lowest capacity. The second factor is the nature of the counterion X^-. The OH...X^- hydrogen bond undoubtedly stabilises the phosphaenol. The anions also form the following series of ability to form an H bond: $Cl^- > Br^- > ClO_4^- \approx BF_4^-$. Therefore, with the exception of the compound with a $CONEt_2$ group, all the chlorides and bromides are phosphaenols. The ClO_4^- anion, which has a low tendency to form H bonds, gives rise to the formation of structures (A) or BHB^+ (Table 3). The results can be understood if the combined effect of these two factors is taken into account.

Two phosphonium groups (compound No. 21, Table 3) have such a strong acidifying effect that the proton is not retained on the central carbon atom but is located on the PO group. When Y = CN (bromides Nos. 6 and 7, Table 3), the phosphaenol structure is governed by the fairly strong acidifying effect from the CN group and the stabilising effect from a strong OH...Br hydrogen bond. For the perchlorate this stabilisation is achieved either with a molecule of the conjugate base (No. 9, Table 3) or with a water molecule (No. 8, Table 3)—BHB^+ or $BH-OH_2^+$ complexes are formed. The pattern is quite clear when Y = Ts; the bromides have structure (B) and the perchlorates have structure (A) or BHB^+. As for compounds with the relatively weakly acidifying group Y = COOEt—, although the chloride (No. 1, Table 3) in this case has structure (B), the perchlorates (Nos. 2 and 3, Table 3) have structure (A), and the borofluoride has a BHB^+ structure. Finally, the carbamoyl group (Y = $CONEt_2$, compound No. 5, Table 3) with the weakest effect causes the chloride to have structure (A).

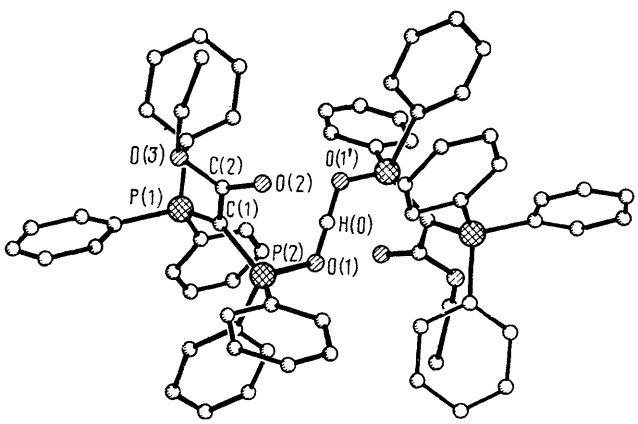


Figure 3. BHB^+ structure of (hydroxydiphenylphosphoranylidene)-carbethoxy(triphenylphosphonio)methane:

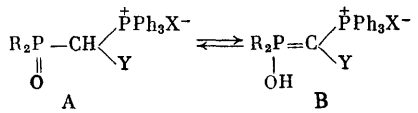
$$Ph_3P^+-C(COOEt)=P(Ph_2)O\cdots H\cdots O=$$
$$=P(Ph_2)P-C(COOEt)=PPh_3(BF_4^-)\ .$$

The relative stability of the phosphaenol forms in the crystalline state naturally depends on the many factors that determine the crystal lattice energy, but it may be assumed that the acidifying effect of groups Y and the strength of the OH...X^- hydrogen bonds are amongst the most important ones.

V. Phosphoryl—phosphaenol tautomerism

Phosphoryl—phosphaenol tautomerism, otherwise known as Phosphoryl—hydroxy-ylide tautomerism, as in (V), is the phosphorus analogue of keto—enol tautomerism, as in (I). Therefore the methods used to study keto—enol systems can be applied to it also.

Table 4. $^{31}P-\{^1H\}$ NMR of phosphorylphosphonium salts (X), CH_2Cl_2.[61,62]

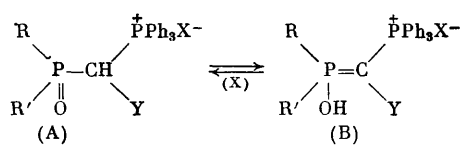


A B

Y	R	X	T, °C	Form	δ_{PO}, ppm	δ_{PPh_3}, ppm	J_{PP}, Hz
$^+PPh_3X^-$	Ph	Br	30	B	40.9 (trip.)	23.5	20
$^+PPh_3X^-$	Ph	ClO_4	20	B	38.3 (trip.)	24.8	21*
$^+PPh_3X^-$	Ph	CF_3COOH	30	B	49.2 (trip.)	22.7	20 [2*]
CN	Ph	Br	30	B	51.5 (br. s.)	22.7	27
CN	Ph	CF_3COOH	−20	A	33.4 (br. s.)	24.3	см [2*]
CN	Ph	ClO_4	30	BHB^+	43.6	23.9	26
CN	Bu	Br	30	B	74.8	23.4	20
CN	Bu	ClO_4	30	B	76.9	23.2	20
				A	51.5 (br. s.)	26.0	–
CN	PhO	Cl	−80	A	6.9 (br. s.)	23.7 (br. s.)	–
CN	EtO	Cl	−80	A	0.1 (br. s.)	24.6 (br. s.)	–
COOEt	Bu	Cl	−70	B	79.2; 78.0	19.2; 20.3	24 [3*]
				A	48.8	23.1	7
COOEt	Ph	Cl	−80	B	43.8; 40.6	19.0; 20.0	40, 42 [3*]
				A	28.6	23.8	7
COOEt	Ph	ClO_4	30	A	25.2	24.3	7
COOEt	PhO	Cl	30	A	4.1	22.0	–
COOEt	PhO	ClO_4	30	A	2.6	23.0	5 [4*]
$CONEt_2$	Ph	Cl	30	A	29.4	27.0	10

In $MeNO_2$; [2] in CF_3COOH; [3*] two conformers; [4*] in $CHCl_3$.

In the $^{31}P-\{^1H\}$ NMR spectra in solutions of tautomeric phosphonium salts (X) two pairs of doublet signals are generally observed.



(A) (B)

In this case forms (A) display two doublet signals with chemical shifts that are not very different from the initial phosphorylphosphoranes (XIII) but with much smaller spin-spin coupling constants J_{PP} (from 0 to 10 Hz). For forms (B) the chemical shifts of the phosphorus nucleus in the PPh_3 group hardly differ from the above, but the signals due to the nuclei in the P−OH groups are displaced downfield by 20−30 ppm. On the other hand the values of J_{PP} are similar to those of the initial phosphoranes. We should note that the number of signals from forms (B) can double, especially at low temperatures, because of the presence of two conformers in solution or of two diastereoisomers in other cases. On increasing the temperature a number of changes occur in the ^{31}P NMR spectra. There is a redistribution of intensities of the signals due to a change in position of the tautomeric equilibrium and the signals change because of an acceleration of both conformational transitions and proton exchange between the forms. At first the conformational doublets coalesce—a single pair of doublets remains in the spectrum—and these are then converted to broad singlets or even merge into the background noise.[56−60,63−65]

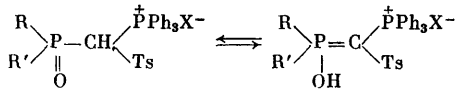
In the PMR spectra, triplet or doublet-doublet signals due to the methine protons of forms (A) with J_{PCH} constants of the order of 13−17 Hz, singlet signals due to the P−OH protons of form (B), and also signals from other groups occur. However, because of rapid proton exchange the signals from CH and OH frequently combine to give a broad singlet. The protons of other groups, such as those from COOEt or $SO_2C_6H_4Me$, on the other hand, appear as separate signals from the tautomeric forms, and they can be used to determine the tautomeric equilibrium constants. However, this is also more suitable to observe at a low temperature.

The tautomeric equilibria are established rapidly and do not change with time. They do not depend on the method of preparing the solution—by dissolving salt (X) or by treatment of phosphorane (XIII) with acid. The results obtained by various methods of studying the tautomeric equilibria are in good agreement. The $^{31}P-\{^1H\}$ NMR data recorded in CH_2Cl_2, the most significant for all of the compounds studied, are given in Table 4 and 5.

It was found that the bis(triphenylphosphonium) salt (X), $Y = {}^+PPh_3$, R and R′ = Ph, exists in solution solely as form (B) (Table 4).[61,62] This applies both to the bromide and perchlorate. Moreover, in trifluoroacetic acid, in which only the (A) forms occur in all other cases, only form (B) occurs in the case of the bis(phosphonium) salt. Evidently because of the strong acidifying capacity of the triphenylphosphonium groups ($\sigma_{CH}^- = 1.08$), the CH acidity of the diphosphonium salt is so high that formation of the CH structure [form (A)] is impossible even in CF_3COOH.

CN-Substituted compounds (X), Y = CN (bromides) with R and R′ = Ph or Bu are in the form of phosphaenols (B), while when R

Table 5. $^{31}P-\{^1H\}$ NMR of phosphorylphosphonium salts (X), Y = Ts, CH_2Cl_2.[58,60,64]



(A) (B)

R	R′	X	T, °C	Form	δ_{PO}, ppm	δ_{PPh_3}, ppm	J_{PP}, Hz
Ph	Ph	Br	30	B	46.4	18.2	29.0 *
Ph	Ph	ClO_4	30	B	45.9	17.5	26.0 *
Ph	Et	Br	30	B	58.1	18.2	24.0
Ph	Et	ClO_4	30	B	60.7	18.3	26.0
				A	44.4 (s.), 43.0 (s.)	20.1 (s.), 21.0 (s.)	см 2*
Bu	Bu	Br	30	B	75.3	16.7	23.0
				A	55.6 (s.)	19.6 (s.)	–
Bu	Bu	ClO_4	30	B	78.0	17.0	23.0
				A	58.4	19.0	–
Bu	EtO	Br	−80	B	72.0	17.0	24.5
				A	45.8 (c)	18.2	–
Bu	EtO	ClO_4	30	B	70.2	17.5	27.0 3*
				A	45.9; 43.6 (s.)	19.5 (s.); 19.7 (s.)	6.0 2*
BuO	BuO	Br	−80	B	22.0	17.7	39.0
				A	7.3 (s.)	20.4 (s.)	–
BuO	BuO	ClO_4	30	A	6.7 (s.)	21.3 (s.)	–
EtO	EtO	Br	−80	B	25.5	17.9	41.5
				A	6.8 (s.)	20.4 (s.)	–
EtO	EtO	ClO_4	30	A	6.5 (s.)	21.2 (s.)	–
PhO	PhO	Br	−80	A	−0.2 (s.)	20.7 (s.)	–
PhO	PhO	ClO_4	30		−0.9 (s.)	22.0 (s.)	–

(98% B); 2 two diastereoisomers; 3* in $CHCl_3$.

and R′ = EtO or PhO (chlorides) at low temperature, they exist as (A). As for perchlorates, both forms occur in solution when R and R′ = Bu, while when R and R′ = Ph a complex of the type BHB^+, in effect form (B), is formed. In contrast to the bis(phosphonium) salt, only for (A) occurs in CF_3COOH.

In the tosyl derivatives (X), Y = Ts (Table 5) when R and R′ = Ph only form (B) occurs in a solution of the bromide and perchlorate. When R = Ph and R′ = ET a tautomeric equilibrium occurs for the perchlorate.‡ There is also a tautomeric equilibrium when R and R′ = Bu (bromide and perchlorate) and when R = Bu and R′ = EtO (X = Br^- and ClO_4^- also), as well as when R and R′ = AlkO (in the bromides). But in solutions of the perchlorates when alkoxy groups are attached to phosphorus, only the (A) forms occur. This also applies, of course, when R and R′ are phenoxy groups.

The carbethoxy derivatives (X), Y = COOEt (Table 4), exhibit a tautomeric equilibrium only when R and R′ = Ph or Bu with X = Cl. In the remaining cases only the (A) forms are present. Finally, if Y = $CONEt_2$, the group that has the lowest acidifying capacity (σ_{CH}^- = 0.42), only form (A) occurs (Table 4). Thus, a decrease in the electron-withdrawing capacity of groups Y leads to a predominance of form (A) and vice versa.

The R and R′ groups attached to phosphorus have a considerable effect on the position of tautomeric equilibrium, as was to be expected. Data on the effect of these groups on the tautomeric equilibrium constants in the series of tosyl derivatives are given in Table 6. These results are correlated with σ^Φ constants, which characterise the effect of the substituents attached to phosphorus on the acidity of phosphorus acids.[69] It can be seen that the content of form (B) increases with a decrease in electronegativity of R and R′. This is quite natural—highly electronegative groups R and R′ increase the strength of P−OH acids, which assists transfer of the proton to carbon.§ A special position is occupied, however, by aromatic derivatives. A phenyl group attached to phosphorus markedly assists phosphaenolisation. The cause of this phenomenon has been discussed more than once in other cases of the "phenyl anomaly". It has been suggested that OH...Ph hydrogen bonds are formed,[70] that there is steric destabilisation of the CH form,[60] that the hydrophoby and rigidity of the benzene rings have an effect, etc. Unfortunately, the origin of this phenomenon is still not clear.

The nature of the anion has a considerable effect on the position of the tautomeric equilibrium (A) ⇄ (B), varying in accordance with its ability to form an H bond that stabilises the phosphaenol: $Cl^- > Br^- < BF_4^- \geqslant ClO_4^-$. The effect of the solvent is also considerable. In aprotic media the percentage content of form (B) decreases with an increase in dielectric constant ε of the solvent.

‡ In this case the signals due to form (A) are split because of diastereomeric anisochronism.

§ This explanation implies that the substituents attached to phosphorus have a greater on effect on the strength of P−OH acids than on P−CH acids, which is very probable.

As an example we can illustrate the effect of solvents on the content of form (B) in $PPh_2(O)CH(\overset{+}{P}Ph_3Cl^-)COOEt$ at −60 °C:

	CH_2Cl_2	CH_2Cl_2+MeCN (4 : 1)	$MeNO_2$
ε	9.14	14.6	38.57
% B	77.0	60.0	<45

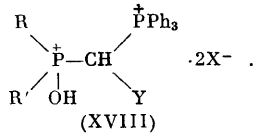
The proton-donating solvent chloroform effectively solvates the P=O group and hence shifts the equilibrium towards from (A). In alcohols, which effectively solvate the OH forms, the equilibrium is shifted towards form (B).

Table 6. Effect of substituents R and R′ on the position of the tautomeric equilibrium A ⇄ B of phosphonium salts (X), Y = Ts, CH_2Cl_2.[58,60,64]

R	R′	$\sum\sigma^{\Phi}$	X=Br⁻ (−80° C)		X=ClO_4 (30° C)	
			% B	K_T	% B	K_T
Bu	Bu	−2.44	75	3.00	29	0.39
Bu	EtO	−1.43	50	1.00	12	0.14
BuO	BuO	−0.82	45	0.82	<2	<0.02
EtO	EtO	−0.42	25	0.33	<2	<0.02
PhO	PhO	−0.12	<2	<0.02	<2	<0.02
Ph	Et	−1.58	95	19.0	60	1.5
Ph	Ph	−1.18	>98	>49	>98	>49

As for the effect of temperature, it depends on the nature of the solvent. In the aprotic solvent CH_2Cl_2 an increase in temperature shifts the equilibrium in favour of the (B) forms, which characterises the (A) forms as more stable. In an alcoholic medium the opposite occurs. The thermodynamic parameters for tautomerism of (X), when Y = COOEt, were calculated from the temperature dependence of the tautomeric equilibrium constants. The tautomers proved to have very similar enthalpies ($\Delta H°$ ranging from −1.5 to +2.5 kcal mol^{-1}). The entropy differences were found to be higher (ΔS ranging from −3.6 to 10.6 E. U.).[59]

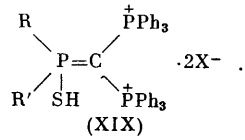
The effect of the acidity of the medium on the position of the equilibrium (A) ⇄ (B) is interesting. An increase in acidity of the medium shifts the equilibrium towards form (A). It would appear that protons from the acid compete with the protons of the P−OH group for hydrogen bonding with the anions and thus decrease the stabilising effect of the latter. With a large increase in acid concentration doubly protonated products (XVIII) are formed:



(XVIII)

In the ^{31}P NMR spectra of these acid salts the chemical shifts of the phosphoryl P nucleus occur at lower field. Thus, when Y = COOEt, X = Cl, and R and R′ = Ph, δ_{PO} = 50.1 ppm (as opposed to 28.6 ppm in the monoprotonated (A) form], while when R and R′ = Bu, δ_{PO} = 82.7 ppm [48.8 ppm in the (A) form].

Enethiolisation of the thiophosphoryl group is markedly different from its oxygen analogue.[63] All the phosphonium salts (XVII) have a CH structure in the crystalline state. The salt with two phosphonium groups (XVII), Y = $\overset{+}{P}Ph_3X^-$, cannot be obtained in the crystalline state because of the extremely low basicity of the corresponding phosphorane (XVI), but in solution of CH_2Cl_2 or FSO_3H it has the mercapto-ylide structure (XIX), which is established with certainty from its ^{31}P-{^1H} NMR spectrum:



(XIX)

All of the remaining (XVII) salts, regardless of the nature of Y, R, R′, and X, have a thiophosphoryl structure and do not exist as tautomers. Only in diphosphonium salt does a low value of J_{PP} occur—from 1 to 8 Hz. In all of the remaining salts the value of J_{PP} is in line with that of the thiophosphorylphosphoranes.

Thus, enethiolisation of the thiophosphoryl group only occurs when Y = $\overset{+}{P}Ph_3$. Even the CN group has an insufficient acidifying effect for the enethiol form to occur, and all derivatives with CN and other groups with lower σ_{CH}^- values have the thiosphosphoryl structure (XVII) and do not exist as tautomers. It may be assumed that the region of thiophosphoryl−mercapto-ylide tautomerism must occur when the $\Sigma\sigma_{CH}^-$ values approximately vary from 2.5 to 2.7. Unfortunately, this region remains inaccessible for the time being (cf. Tables 1 and 2).

VI. Enolisation of the phosphoryl group and acidity

It has been known for a long time that the acidic properties of prototropic tautomeric compounds are related in a complex manner to the position of the tautomeric equilibrium. The latter, as is evident from Eqn. (1), is determined by the ratio of the acidity constants but not by the degree of acidity of both forms. Experimentally the given apparent dissociation constant K_{app} of the equilibrium mixture, which is related to the dissociation constants of the individual forms, is determined by ratio (2):[48]

$$K_{app} = K_1.K_2/(K_1 + K_2), \quad (2)$$

where K_1 and K_2 are the dissociation constants of the forms. By measuring the apparent dissociation constant K_{app} and the tautomeric equilibrium constant K_T, it is possible to calculate the dissociation constants of the individual forms:

$$pK_1 = pK_{app} - \lg (K_T + 1), \quad (3)$$

$$pK_2 = pK_1 + \lg K_T. \quad (4)$$

It was of considerable interest to elucidate the acidic properties of phosphoryl CH acids [(A) forms] and phosphaenols [(B) forms] and their structural dependences. It was also suitable to make use of σρ correlation analysis for this purpose. In addition to that it was necessary to test the applicability of the latter for a quantitative representation of the acidity of compounds with these structures on products that were of the same type but not tautomeric. The

thiophosphorylphosphonium salts (XVII) were used as such compounds. The dissociation constants of these compounds in nitromethane and absolute ethanol were determined potentiometrically with a glass electrode.[71] The results of the measurements are given in Table 7.

Table 7. Acid dissociation constants of thiophosphorylphosphonium salts (XVII) $R_2P(S)CH(Y)\overset{+}{P}Ph_3\cdot X^-$ in $MeNO_2$ and absolute EtOH at 25 °C.

No.	R	Y	$\Sigma\sigma_{CH}^-$	pK_{app}, $MeNO_2$,	pK_{app}, EtOH
1	Bu	COOEt	2.06	9.60	4.56
2	Ph	COOEt	2.14	7.63	4.08
3	Bu	Ts	2.16	6.05	4.05
4	Bu	CN	2.21	4.71	–
5	Ph	Ts	2.24	4.03	3.63
6	EtO	Ts	2.28	3.86	3.61
7	Ph	CN	2.29	3.50	3.36
8	PhO	Ts	2.30	2.55	3.31

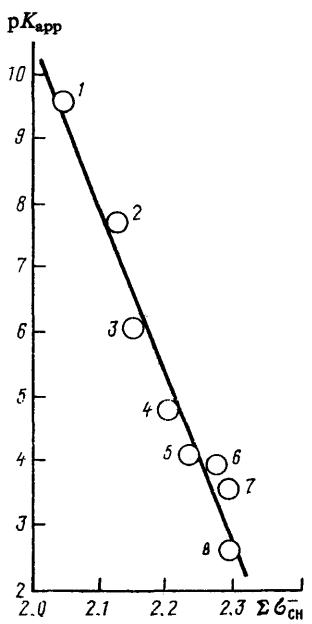


Figure 4. Correlation of pK_{app} with $\Sigma\sigma_{CH}^-$ for $RR'P(S)CH(Y)\overset{+}{P}Ph_3X^-$ in $MeNO_2$; the numbers of the points correspond to the numbers of the compounds in Table 7.

These acids can evidently be classed as fairly strong. We can show for comparison that in $MeNO_2$, pK = 7.05 for CF_3COOH, pK = 11.62 for $ClCH_2COOH$, and pK = 14.41 for CH_3COOH.

On Hammett coordinates with σ_{CH}^- constants they give a good correlation (even an excellent one in absolute ethanol) (Figs. 4 and 5) with the following parameters

In $MeNO_2$: $pK_{app} = 65.82 - 27.410\ \Sigma\sigma_{CH}^-$;

n=8; r=0.980; s=0.52; s_ρ=2.32.

In EtOH: $pK_{app} = 14.94 - 5.052\ \Sigma\sigma_H^-$;

n=7; r=0.998; s=0.03; s_ρ=0.13.

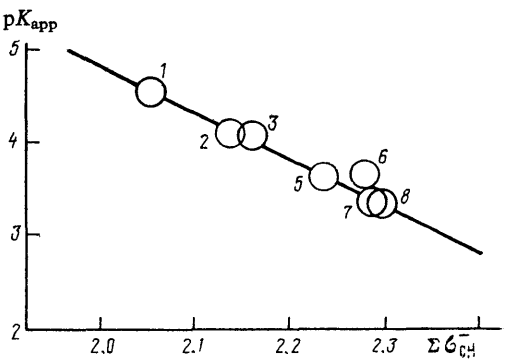


Figure 5. Correlation of pK_{app} with $\Sigma\sigma_{CH}^-$ for $RR'P(S)CH(Y)\overset{+}{P}Ph_3X^-$ in EtOH; the numbers of the points correspond to the numbers of the compounds in Table 7.

In the correlation in $MeNO_2$ two details attract attention. Firstly, the straight line has a very high gradient (ρ = 27.410). This results from the well-known strong differentiating effect of $MeNO_2$; the difference between the strengths of the acids in this case is as high as a factor of 10^7. Secondly, there is a very high value of pK^0 (almost 66). Theoretically this should correspond to the pK of methane in $MeNO_2$. Measurement of this constant is, of course, experimentally impracticable. Ethanol, on the other hand, is a solvent that causes a levelling out; in this case the difference in pK_{app} values does not exceed a factor of $10^{1.25}$. A linear Brønsted relationship occurs between the pK in the two solvents.

$$pK_{MeNO_2} = -15.72 + 5.535 pK_{EtOH},$$

r=0.978; s=0.58; s_ρ=0.52.

The high gradient, which differs markedly from unity, suggests that there are considerable differences in the differentiating capacity of nitromethane and ethanol.

The acid dissociation constants of the tautomeric phosphorylphosphonium salts (X) were determined in a similar manner. The results are listed in Table 8, where the equilibrium content of the phosphaenol forms (B) determined ^{31}P NMR is given for comparison. It can be seen that all the compounds can also be classed as comparatively strong acids. In nitromethane their strength is on average about 0.7 pK units lower than the thiophosphoryl acids (XVII) examined above; in ethanol they are virtually of equal strength. The strong differentiating action of nitromethane occurs here in the same way. The dissociation

constants vary by a factor of 10^{11} in accordance with the substituents attached to phosphorus and carbon, while they vary by a factor of only 10^3 in ethanol, which levels out the differences. With the same substituents on phosphorus the acid strength decreases on changing from Y = CN via compounds with Y = Ts to the carbethoxy and then carbamoyl derivative. These results vary in the same way as the σ_{CH}^- constants of the Y groups. Marked variations in the content of the phosphaenol forms occur on changing the substituents in both solvents, and phosphaenolisation does not vary in the same way as acidity. For example, the more acidic compound 2 (Table 8) is only slightly enolised while the less acidic compounds 1 and 4 (Table 8) are almost completely enolised. Relationships of this type are known in the classical chemistry of tautomeric compounds. For example, the more acidic cyclopentanonecarboxylic ester is enolised less than the less acidic cyclohexanonecarboxylic ester. As has already been mentioned, enolisation depends on the acidity ratio of the forms rather than the overall degree of acidity.

Table 8. Dissociation constants of tautomeric phosphorylphosphonium salts

$$\underset{(A)}{RR'P(O)CH(Y)\overset{+}{P}Ph_3X^-} \rightleftarrows \underset{(B)}{RR'P(OH)=C(Y)\overset{+}{P}Ph_3X^-}$$

in $MeNO_2$ and absolute EtOH at 25 °C.

№ п/п	R, R'	Y	$\Sigma\sigma_{CH}^-$	$MeNO_2$				EtOH			
				pK_{app}	% B	pK_{CH}	pK_{OH}	pK_{app}	% B	pK_{CH}	pK_{OH}
1	Ph	CN	2.27	4.27	~98	2.57	4.26	3.86	>99	–	~3.86
2	PhO	Ts	2.25	2.44	~2	2.43	0.73	–	–	–	–
3	EtO	Ts	2.22	3.38	~2	3.37	1.68	3.63	>99	–	~3.63
4	Ph	Ts	2.22	6.00	~98	4.30	5.99	3.14	>99	–	~3.14
5	BuO	Ts	2.21	–	–	–	→	3.70	>99	–	~3.70
6	Ph, Et	Ts	2.18	5.27	50	4.97	4.97	–	–	–	–
7	Bu	CN	2.17	5.79	~98	4.09	5.78	3.88	>99	–	~3.88
8	PhO	COOEt	2.15	6.60	~2	6.59	4.90	–	–	–	–
9	Bu	Ts	2.12	6.70	16	6.62	5.90	4.58	97	3.06	4.57
10	Ph	COOEt	2.12	8.82	16	8.74	8.02	3.54	70	3.02	3.39
11	Bu	COOEt	2.02	10.59	33	10.42	10.11	4.73	36	4.54	4.29
12	Ph	$CONEt_2$	1.94	13.84	~1	13.84	11.84	6.22	~2	6.21	4.51

The dissociation constants of the (A) forms (pK_{CH}) and the dissociation constants of the (B) forms (pK_{OH}) were calculated using Eqns. (2)–(4). The results are included in Table 8. It can be seen that the value of pK_{CH} increases as $\Sigma\sigma_{CH}^-$ decreases. At the same time the Hammett correlation is perfectly satisfactory in nitromethane and good in ethanol (Fig. 6):

In $MeNO_2$: $pK_{CH} = 81.99 - 35.246\ \Sigma\sigma_{CH}^-$;

$n=11$, $r=0.977$, $s=0.80$, $s_\rho=2.55$.

With regard to the pK_{CH} in ethanol, only the last four figures in Table 8 are reliable. There is a good correlation between them and $\Sigma\sigma_{CH}^-$.

In EtOH: $pK_{CH} = 39.61 - 17.268\ \Sigma\sigma_{CH}^-$;

$n=4$; $r=0.996$; $s=0.16$, $s_\rho=1.06$.

In these correlations also there is an unusually high value of pK^0, especially in nitromethane.

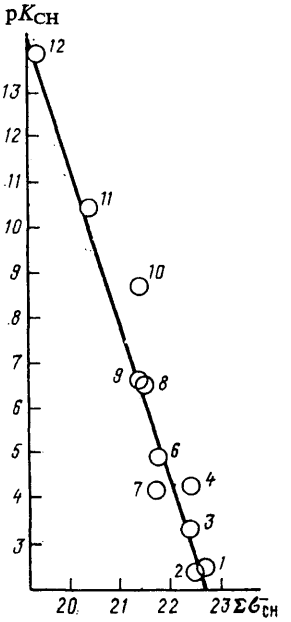


Figure 6. Correlation of pK_{CH} with $\Sigma\sigma_{CH}^-$ for $RR'P(O)CH(Y)\overset{+}{P}Ph_3X^-$ in $MeNO_2$; the numbers of the points correspond to the numbers of the compounds in Table 8.

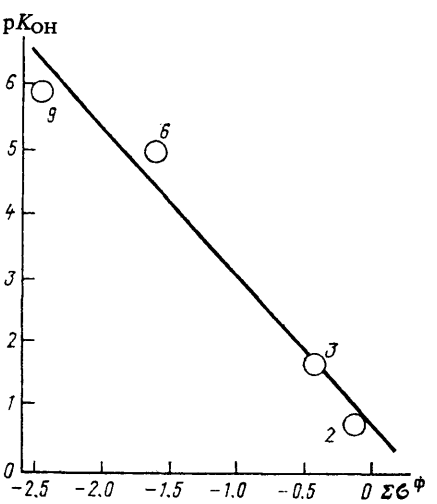


Figure 7. Correlation of pK_{OH} with $\Sigma\sigma^*$ for $RR'P(OH)=C(\overset{+}{P}Ph_3X^-)CH(Ts)$ in $MeNO_2$; the numbers of the points correspond to the numbers of the compounds in Table 8.

The dependence of pK_{OH} on structure proves to be quite complex, since in the (B) forms it is not only the substituents on the phosphorus atom that vary but also the nature of the $=C(^{+}PPh_3X)(Y)$ group.

group, which mimics the oxygen atom of the P=O group. When Y is constant, for example, Y = Ts, the pK_{OH} values provide a linear correlation with the σ^{Φ} constants[69] (Fig. 7)

In $MeNO_2$: $pK_{OH} = 0.70 - 2.296\ \Sigma\sigma^{f}$;

$n=4$; $r=0.983$; $s=0.56$; $s_{\rho}=0.30$.

Admittedly in this case the point corresponding to two benzene rings was excluded (see above). With regard to the pK_{OH} values in ethanol, they are virtually equal to pK_{app}, as more than 99% of the (B) form is present in solution. The relationship between pK_{OH} and the nature of the substituents is complex.

Thus, the pK_{app} acidity measurements and calculation of pK_{CH} and pK_{OH} provide a clear definition of the relationship between enolisation of the P=O group and the acidity of phosphoryl compounds.

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The main conclusion to be drawn from the above material is that the phosphoryl group *can* undergo enolisation. A high acidity of the phosphoryl CH form (A) is a necessary condition for this to occur. This condition is of course necessary, but it is not sufficient. It is also necessary that the corresponding enol form (B) has a similar acidity to that of the phosphoryl form; this is readily achieved, however, with sufficiently acidic CH forms. The conditions for enolisation of the thiophosphoryl group are more rigorous. The reason for this is the higher acidity of phosphorus thio acids compared to their oxygen analogues. It can be demonstrated that up to the present time it was not possible to observe enolisation of the P=O group because the $\Sigma\sigma^{-}_{CH}$ values of the groups attached to the central carbon atom did not exceed 2, which was naturally a consequence of the fact that the attached groups had an insufficient acidifying effect. Thus, for example, for the "phosphonoacetic ester" of Arbuzov and Razumov[1-9]—$(EtO)_2P(O)CH_2COOEt$—the $\Sigma\sigma^{-}_{CH_2}$ value is 1.28, which is quite insufficient for phosphaenolisation to occur, while the compound used by Kolodyazhnyi[40,41]—$Ph_2P(O)CH(SO_2C_6H_5)_2$—has $\Sigma\sigma^{-}_{CH}$ = 1.97, which is at the limit of enolisability. On introduction of electronegative substituents into the benzene ring, this limit is exceeded and enolisation becomes quite appreciable.

All in all, enolisation of the phosphoryl group fully obeys the laws comprising the theory of prototropic tautomeric acid–base equilibrium.

References

1. F Arndt, C Martius *Liebigs Ann. Chem.*, 1932, **490** 228
2. F Arndt, B Eistert *Ber. Bunsenges. Phys. Chem.*, 1941, **74** 423
3. F Arndt, L Loewe, R Ginkök *Rev. Faculte Sci. Univ. Istanbul*, 1946, **A-11** 147
4. B Eistert, F Arndt, L Loewe, A Ayca *Ber. Deutsch. Chem. Ges.*, 1951, **84** 156
5. G Schwarzenbach, K Lutz *Helv. Chim. Acta*, 1940, **23** 1147, 1162
6. G Schwarzenbach, E Felder *Helv. Chim. Acta*, 1944, **27** 1044, 1701
7. G Schwarzenbach, Ch Wittwer *Helv. Chim. Acta*, 1947, **30** 669
8. A E Arbuzov, A I Razumov *Zh. Russ. Fiz.-Khim. Obshch.*, 1929, **61** 623
9. A E Arbuzov, A I Razumov *Zh. Obshch. Khim.*, 1934, **4** 834
10. K Issleib, H P Abicht *J. Prakt. Chem.*, 1970, **312** 456
11. I-J Colquhoun, W McFarlane, J M Bassett, S O Grim *J. Chem. Soc., Dalton Trans.*, 1981, 1645
12. S O Grim, L C Satek, J D Mitchell *Z. Naturforsch.*, 1980, **35** 832
13. H H Karsh *Z. Naturforsch.*, 1979, **34** 1171
14. L Horner, H Hoffmann, H G Wippel *Chem. Ber.*, 1958, **91** 61
15. A V Dombrovskii, V A Dombrovskii *Usp. Khim.*, 1966, **35** 000 [English translation in *Russ. Chem. Rev.*, 1966(0)]
16. J Boutagg, R Thomas *Chem. Rev.*, 1974, **74** 87
17. H Kreutzkamp *Chem. Ber.*, 1955, **88** 195
18. C T D Gough, S Trippett *J. Chem. Soc.*, 1962, 2333
19. J E Tompson *J. Org. Chem.*, 1965, **30** 4276
20. M Kirilov, D Petrov *Dokl. Bulg. Akad. Nauk*, 1965, (4) 331
21. M Kirilov, D Petrov *Chem. Ber.*, 1967, **100** 3139
22. M Kirilov, G Petrov *Monatsh. Chem.*, 1968, **99** 166
23. R K Izmailov, R L Yafarova, A I Razumov *Zh. Obshch. Khim.*, 1972, **42** 2113
24. M Kirilov, G Petrov *Monatsh. Chem.*, 1972, **103** 1651
25. G Petrov, M Kirilov *Monatsh. Chem.*, 1973, **104** 1301
26. B A Arbuzov, V G Sakhibullina, N A Polezhaeva *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1975, 2763
27. B A Arbuzov, V G Sakhibullina, N A Polezhaeva *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1976, 2139
28. V G Sakhibullina, N A Polezhaeva, B A Arbuzov *Zh. Obshch. Khim.*, 1982, **52** 1265
29. V G Sakhibullina, N A Polezhaeva, B A Arbuzov *Zh. Obshch. Khim.*, 1984, **54** 1016
30. G Petrov, M Kirilov *Monatsh. Chem.*, 1968, **99** 1923
31. A N Pudovik, R D Gareev, S E Shtil'man *Zh. Obshch. Khim.*, 1973, **43** 1646
32. A N Pudovik, R D Gareev *Zh. Obshch. Khim.*, 1976, **46** 458
33. B A Arbuzov, A M Polozov, N A Polezhaeva *Zh. Obshch. Khim.*, 1984, **54** 1517
34. B A Arbuzov, A M Polozov, N A Polezhaeva *Dokl. Akad. Nauk SSSR*, 1986, **287** 849
35. J F Allen, O H Johnson *J. Am. Chem. Soc.*, 1955, **77** 2871
36. S T Ioffe, K V Vachuro, P V Petrovskii *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1970, 1504
37. S T Ioffe, K V Vachuro, P V Petrovskii *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1971, 731
38. S T Ioffe, E I Goryunov, T V Ershova *Zh. Obshch. Khim.*, 1971, **41** 2664
39. A M Polozov, N A Polezhaeva, B A Arbuzov *Zh. Obshch. Khim.*, 1987, **57** 2200
40. O I Kolodyazhnyi *Tetrahedron Lett.*, 1982, **23** 499
41. O I Kolodyazhnyi *Zh. Obshch. Khim.*, 1976, **46** 2386
42. T A Mastryukova, I M Aladzheva, I V Leont'eva *Zh. Obshch. Khim.*, 1977, **47** 2454
43. V V Ovchinnikov, V I Galkin, E G Yarkova, et al. *Dokl. Akad. Nauk SSSR*, 1977, **235** 118
44. V V Ovchinnikov, V M Valitova, R A Cherkasov, et al. *Zh. Obshch. Khim.*, 1979, **49** 2434
45. T Bottin-Strzhalko, J Seyden-Penne, M J Ponet, et al. *J. Chem. Soc., Perkin Trans. 2*, 1985, 1801
46. Th Klebach, C Jongsma, F Bickelbaupt *Recl. Trav. Chim. Pays-Bas*, 1979, **98** 14
47. T A Mastryukova *Phosphorus, Sulfur, Silicon*, 1990, **49/50** 65
48. M I Kabachnik *Dokl. Akad. Nauk SSSR*, 1952, **83** 407
49. M I Kabachnik *Dokl. Akad. Nauk SSSR*, 1952, **83** 859

50. O J Neuland *Structure and Tautomeric Conversions of β-Dicarbonyl Compounds* (Translated into Russian), Zinatne, Riga, 1977, p. 77
51. L P Hammett *Physical Organic Chemistry*, McGraw-Hill, New York, 1940, Ch. 7
52. P W Taft, Jr. *Steric Effects in Organic Chemistry* (Edited by M S Newman), John Wiley, New York, Chapman and Hall, London, 1956, Ch. 13, Pt. 7
53. M I Kabachnik, T A Mastryukova *Dokl. Akad. Nauk SSSR*, 1981, **260** 893
54. A G Matveeva, M I Terekhova, N P Nesterova, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1988, 2067
55. M I Kabachnik, T A Mastryukova *Zh. Obshch. Khim.*, 1984, **54** 2161
56. T A Mastryukova, I M Aladzheva, O V Bykhovskaya, et al. *Zh. Obshch. Khim.* (in the Press)
57. I M Aladzheva, I V Leont'eva, P V Petrovskii, et al. *Zh. Obshch. Khim.*, 1982, **52** 2358
58. O V Bykhovskaya, I M Aladzheva, P V Petrovskii, et al. *Zh. Obshch. Khim.*, 1988, **58** 1980
59. L V Leont'eva, I M Aladzheva, T A Mastrykova, et al. *Zh. Obshch. Khim.*, 1988, **58** 1987
60. O V Bykhovskaya, I V Leont'eva, I A Aladzheva, et al. *Zh. Obshch. Khim.*, 1988, **58** 1998
61. K Issleib, R Lindner *Liebigs Ann. Chem.*, 1966, **699** 40
62. G H Birum, C D Matthews *J. Am. Chem. Soc.*, 1966, **88** 4188
63. T A Mastryukova, I M Aladzheva, O V Bykhovskaya, et al. *Zh. Obshch. Khim.*, 1984, **54** 36
64. O V Bykhovskaya, Candidate's Thesis in Chemical Sciences, Institute of Organoelemental Compounds, USSR Academy of Sciences, 1990
65. T A Mastryukova, I M Aladzheva, O V Bykhovskaya, et al. *Dokl. Akad. Nauk SSSR*, 1982, **264** 1396
66. D Hadzi *J. Chem. Soc.*, 1962, 5128
67. G Märkl *Phosphorus Sulfur*, 1977, **3** 77
68. A Nowak *Struct. Bonding (Berlin)*, 1974, **18** 177
69. T A Mastryukova, M I Kabachnik *J. Org. Chem.*, 1971, **36** 1261
70. H S Aaron *Topics in Stereochemistry* (Edited by N L Allinger, E L Eliel), Interscience, New York, 1970, Vol. 11, p. 1
71. T A Mastryukova, A A Grigor'eva, E I Matrosov, et al. *Zh. Obshch. Khim.*, 1990, **60** 2215