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Enolization of the Phosphoryl Group

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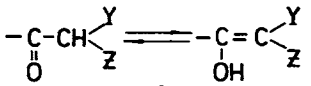
ABSTRACT

Enolization of the phosphoryl group $RR'P(O)CH(Y)\overset{+}{P}Ph_3X^-$ *has been studied where* $Y = PPh_3$, *CN, Ts, COOEt,* $CONEt_2$; *R and R' = Et, Bu, Ph, EtO, BuO, PhO; and X = Cl, Br,* ClO_4, BF_4. *It has been established that substances with* $Y = \overset{+}{P}h_3X^-$ *are phosphaenols, but in substances with* $Y = CONEt_2$ *the phosphoryl group cannot be enolized under any conditions. Phosphaenolization is favored by a high acidifying ability of the Y group, the ability of the X anion to stabilize the phosphaenolic form due to formation of a hydrogen bond OH· · ·X with the anion, and a low electronegativity of R and R' groups. To evaluate the acidifying ability of Y, this article defines specific* σ^- *constants dependent on the number of substituents at the α-carbon atom:* $\sigma^-_{CH_3}$, $\sigma^-_{CH_2}$ *and* σ^-_{CH}. *Their sums characterize the enolization ability of the phosphoryl group. The enolic structure in the solid state is possible if* $\Sigma\sigma^-_{CH_n} > 2$. *If this sum lies in the range of* $2 < \Sigma\sigma^-_{CH_n} < 2.6$ *the phosphoryl–phosphaenol tautomerism can be expected in appropriate solutions. Acidic properties of the investigated compounds in* $MeNO_2$ *and EtOH (absolute) have been determined. Calculations of the acidity of the phosphoryl CH forms (A) and of the phosphaenol OH forms (B) have been carried out.*

INTRODUCTION

The capability of the carbonyl group to be enolized is well known (**1**).



1

A strong acidifying effect of substituents Y and Z was found to be necessary for enolization. Some time ago, this problem was thoroughly studied by F. Arndt et al. and G. Schwarzenbach et al. [1].

In organophosphorus chemistry, the phosphoryl group P=O is analogous to the carbonyl group, C=O. However, no communication on enolization of the phosphoryl group appeared in the literature until the late 1970s, with the exception of tautomerism of a derivative of phosphonacetic ester [2] postulated by A. E. Arbuzov and A. I. Razumov as early as 1929 and 1934, which was of a purely speculative character.

Later, lithium derivatives of di- and triphosphorylmethanes were repeatedly used in organic syntheses [3–6]. The same can also be said about metal-containing intermediates in the widespread P=O activated olefination reported by L. Horner [7]. Many examples of alkylation and acetylation reactions of β-ketophosphonate metal derivatives and other compounds were described [8, 9].

However, tautomerism of phosphoryl and phosphaenolic structures **2** has never been observed.

2

Enolization of β-phosphorylated carbonyl compounds was studied in detail, yet only conventional enolic forms (=C—OH) and not phosphaenolic ones (=P—OH) were always found [8(d, f, g · k, l), 10, 11, 12], with the exception of methylation of the phosphoryl group by the action of diazomethane [13].

In the second half of the 1970s O. I. Kolodyazh-

Dedicated to Professor Dr. Rolf Appel on the occasion of his seventieth birthday.

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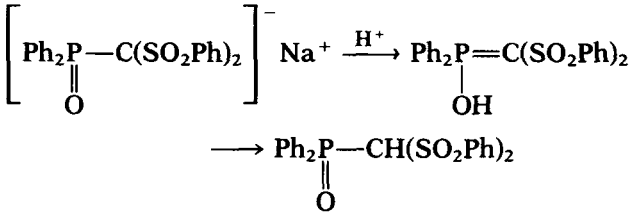
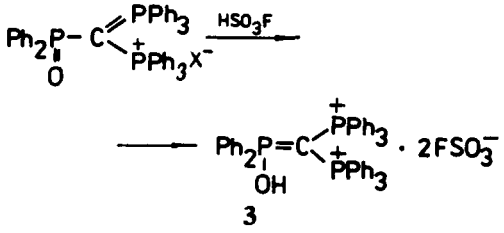
nyi [14] reported formation of an unstable phosphaenolic form of diphenylphosphoryl-bis(phenylsulfonyl)methane upon acidifying a solution of its sodium derivative:

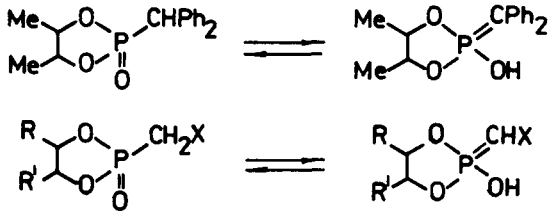


This phosphaenolic form was readily and irreversibly converted into its CH form. We [15] observed formation of a stable phosphaenolic form of diphenylphosphinyl-bis(triphenylphosphonio)methane **3** upon protonation of the corresponding phosphorane–phosphonium salt by fluorosulfonic acid:



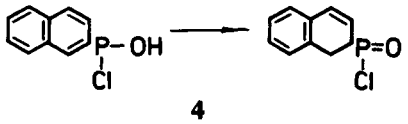
3

There are two communications by Kazan chemists [16, 17] on phosphaenolization of cyclic phosphonates:



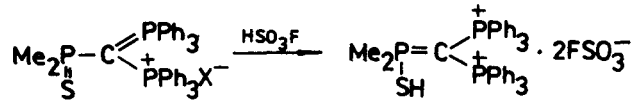
R = Me; R′ = H, Me; X = COOMe, CN

Nevertheless, the phosphaenolic structure of these compounds was refuted later [18]. Eventually, F. Bickelhaupt et al. [19] reported the synthesis of the cyclic phosphaenol **4** that they claimed was easily and irreversibly "ketonized."



4

As for enolization of the thiophosphoryl group, the only example of such type **5** was found by us and our co-workers [15]. It is entirely analogous to enolization of the corresponding phosphoryl compound.



5

Thus, until the early 1980s no information on the phosphoryl–phosphaenolic (phosphoryl–oxyylidic) tautomerism was available [20].

CAPABILITY OF THE PHOSPHORYL GROUP FOR ENOLIZATION

The prototropic tautomeric equilibrium position is known to be determined by the acidity constant ratio of both forms in a given medium [21]:

$$K_T = \frac{K_1}{K_2} \qquad (1)$$

Here K_T is the tautomeric equilibrium constant, and K_1 and K_2 are the acidity constants of the respective tautomeric forms. In the process of enolization of carbonyl groups, OH–enolic acids are formed. These possess acidities changing over a wide range; from pK_a = 10–12 for simple ketones and less acidic β-dicarbonyl compounds to pK_a = 5–9 for conventional β-dicarbonyl compounds (data for water solutions [22]). The OH acidity of pK_a = 2–4 [23] is attained only with β-dicarbonyl compounds of specific structure (fluorinated β-diketones, transfixed cyclic enols with small rings, etc.). Therefore, to observe enolization it is necessary that the CH acidity of the keto-forms be close to that of the corresponding enols; i.e., they must have the same pK_a = 5–10 (in water). If the phosphoryl groups are enolized, the OH acidities of the corresponding phosphaenols are essentially higher than those of their carbon prototypes.

One can consider that phosphorus OH acids are by 2–4 orders of magnitude stronger acids. Therefore, to observe enolization of the phosphoryl group, it is necessary for CH–phosphoryl acids to have pK_a = 3–5. This can be attained only if strongly acidifying groups are in the β-position to the phosphoryl group.

In connection with the necessity of an objective assessment of the effects of acidifying groups on the CH acidities, we developed a modification of the σρ-correlation analysis based on the known Hammett equation [24]: $pK = pK^\circ - \rho\sigma$. Naturally, σ^- constants were used, allowing for the direct polar conjugation of the substituent with the nucleophilic reaction center. However, in carrying out σρ–CH acidity correlations, we faced difficulties associated with the so-called saturation effect [25]. The point is that the effect of an acidifying group bonded to the central carbon atom is variable. It depends on the number of the still bonded groups and decreases with an increasing number of such groups. It is required that three σ-values, $-\sigma_{CH_3}^-$, $\sigma_{CH_2}^-$ and

TABLE 1 Substituent Constants $\sigma_{\bar{C}H_2}$ and $\sigma_{\bar{C}H}$ of Some X Groups[a]

X	$\sigma_{\bar{C}H_2}$	$\sigma_{\bar{C}H}$	X	$\sigma_{\bar{C}H_2}$	$\sigma_{\bar{C}H}$
Me	0.12	0.13	$PhSO_2$	0.77	0.71
Ph	0.365	0.26	p-$MeC_6H_4SO_2$	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[b]	0.42

[a] Ref. [26].
[b] See [26(b)].

TABLE 2 Substituent Constants $\sigma_{\bar{C}H_2}$ and $\sigma_{\bar{C}H}$ of Some Organophosphorus X Groups[a]

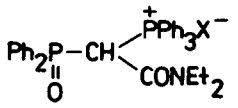
X	$\sigma_{\bar{C}H_2}$	$\sigma_{\bar{C}H}$[b]	X	$\sigma_{\bar{C}H_2}$	$\sigma_{\bar{C}H}$[b]
$Ph_3\overset{+}{P}$	1.22	1.08	$Ph_2P(O)$	0.57	0.44
$(PhO)_2P(O)$	0.60	0.47	$Et_2P(O)$	0.47	0.36
$(EtO)_2P(O)$	0.56	0.44	$Me_2P(O)$	0.47	(0.35)
$(BuO)_2P(O)$	0.55	(0.43)	PhEtP(O)	0.51	(0.39)
Bu(EtO)P(O)	0.50	(0.38)	$Ph_2P(S)$	0.60	0.46
$Bu_2P(O)$	0.45	0.34	$(EtO)_2P(S)$	0.59	0.50

[a] Ref. [27].
[b] Numbers in parentheses refer to an interpolated value.

$\sigma_{\bar{C}H}$, be calculated for each substituent, depending on its position at the primary, secondary, or tertiary carbon atom. In the development of this modification of the $\sigma\rho$ correlations, $\sigma_{\bar{C}H_n}$ constants were refined using numerous literature experimental data on CH acidities of versatile compounds as well as our own data on CH acidities of organophosphorus compounds. Some of the obtained values of $\sigma_{\bar{C}H_2}$ and $\sigma_{\bar{C}H}$ constants are listed in Tables 1 and 2 [26, 27].

With the help of new $\sigma_{\bar{C}H_n}$ constants, we could compare the CH acidities of β-dicarbonyl compounds and their enolizabilities. Thus, for fully enolized triacetylmethane $\Sigma\sigma_{\bar{C}H} = 1.98$; for strongly enolized benzoylacetone $\Sigma\sigma_{\bar{C}H_2} = 1.86$; for less enolized acetylacetone, -1.76; for weakly enolized acetoacetic ester, -1.60; and for very slightly enolized malonic ester, -1.44. Thus, the CH acidity power of a β-dicarbonyl compound necessary for enolization is determined by its $\Sigma\sigma_{\bar{C}H_2}$ area, ranging from approximately 1.6 to 2.0. Naturally, one must also take into account the OH acidity of the enolic forms (cf. Equation 1). The substituents' acidifying effect also affects, though in a lesser degree, the enols' OH acidity, but, as a first approximation, one can be limited to $\Sigma\sigma_{\bar{C}H_n}$.

The OH acidities of phosphaenolic forms are higher than those of β-dicarbonyl compounds. Therefore, their CH acidities must be essentially higher. Recently we have found that compound **6** with $\Sigma\sigma_{\bar{C}H} = 1.94$ is not enolized [28], while, as reported earlier [15], the corresponding diphosphonium derivative **3** with $\Sigma\sigma_{\bar{C}H} = 2.60$ is fully enolized. Hence the $\Sigma\sigma_{\bar{C}H}$ range from 2.0 to 2.6 is the most favorable for observing the phosphoryl group enolization.

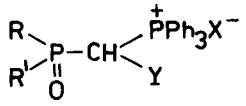


6

Since it is hard to obtain such high $\Sigma\sigma_{\bar{C}H}$ values without phosphonium substituents, later on only those compounds were investigated in which, together with the phosphoryl group, the triphenylphosphonium group was linked to the central carbon atom. Then, variations in substituent Y made it possible to produce $\Sigma\sigma_{\bar{C}H}$ values ranging from 2.0 to 2.6.

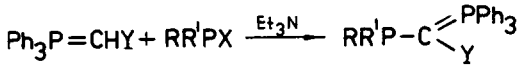
SYNTHESIS OF PHOSPHORYL COMPOUNDS [29–32]

Synthesis was accomplished with phosphoryl (triphenylphosphonio)methanes of general formula **7** substituted at the central carbon atom by Y = $\overset{+}{P}Ph_3X^-$, CN, Ts, COOEt, $CONEt_2$; R and R′ = Et, Bu, Ph, BuO, PhO in various combinations; and X^- = Cl^-, Br^-, ClO_4^-, BF_4^-.



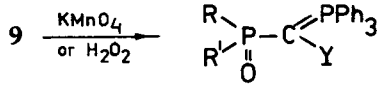
7

Appropriate phosphino-substituted phosphoranes **9**, prepared according to literature data [33, 34] from monosubstituted triphenylmethylenephosphoranes **8** and halogenphosphines or halogenphosphites, served as starting compounds:



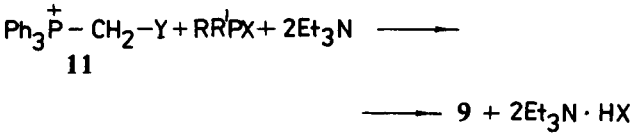
8 **9**

They were then oxidized to phosphorylphosphoranes **10**:



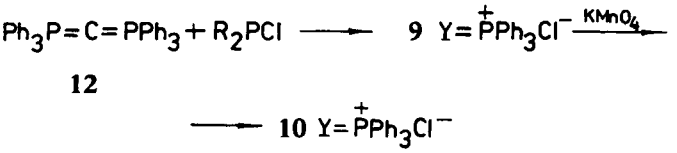
10

Often it appeared more reasonable to start from the corresponding phosphonium salt **11**. Moreover, we could cary out the oxidation stage **9** → **10** without isolating **9** from the reaction mixture by treating it immediately with H_2O_2 in *tert*-butyl alcohol at 0°C.



11

Phosphoranephosphonium salts **10**, Y = $\overset{+}{P}Ph_3X^-$ were prepared by addition of diphenyl- or dialkylhalogenphosphines to hexaphenylcarbodiphosphorane **12** with isolation of the crystalline phosphine derivative, **9**, Y = $\overset{+}{P}Ph_3X^-$, as an intermediate.



12

The protonation of phosphoranes **10** was carried out in benzene or methylene chloride solutions at 20°C by treatment with ether solutions of hydrogen halides:

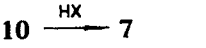


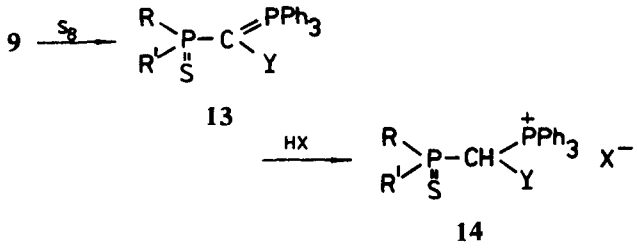
TABLE 3 Yields, MP, IR, and NMR Data for Phosphorylphosphoranes (**10**)[a]

RR'P(O)—C(Y)=PPh_3

Y	R	R'	Yield (%)	MP (°C)	IR, $\nu_{cm^{-1}}$, KBr Pellet			NMR ^{31}P-{^1H}, CH_2Cl_2, 30°		
					ν_{PO}, ν_{CO},	ν_{CN}, ν_{SO_2} (s.),	ν_{SO_2} (as.)	δ_{PO}(d)	δ_{PPh_3}(d)	J_{PP}, Hz
COOEt	Bu	Bu	83	106–108	1170	1635(CO)		47.0[b]	21.2[b]	27.0
COOEt	Ph	Ph	82	158.5–160.5	1180	1630(CO)		28.9[c]	21.3[c]	34.0
COOEt	PhO	PhO	64	171–172.5	1250	1660(CO)		18.4	22.1	59.0
$CONEt_2$	Ph	Ph	80	195–197	1175	1535(CO)		21.6	18.0	43.0
CN	Bu	Bu	50	113–114	1155	2150(CN)		45.6	25.6	21.0
CN	Ph	Ph	39	196–198	1170	2155(CN)		28.7	25.7	24.0
CN	EtO	EtO	31	141.5–143	1230	2170(CN)		26.0; 24.4[d]		
CN	PhO	PhO	51	173–174.5	1255	2170(CN)		20.5; 24.9[d]		
Ts	Bu	Bu	83	203–205	1152	1127(SO_2 s.)	1270(SO_2 as.)	48.7	17.0	22.0
Ts	Ph	Et	85	238–240	1175	1130(SO_2 s.)	1273(SO_2 as.)	38.1	17.9	23.0
Ts	Bu	EtO	60	168–170	1230	1135(SO_2 s.)	1280(SO_2 as.)	46.9	17.5	27.0
Ts	Ph	Ph	86	230–232	1165	1135(SO_2 s.)	1280(SO_2 as.)	30.2	16.8	18.0
Ts	BuO	BuO	63	159–161	1235	1130(SO_2 s.)	1280(SO_2 as.)	19.3; 18.2[d]		
Ts	EtO	EtO	54	186–187	1235	1140(SO_2 s.)	1280(SO_2 as.)	19.3; 17.9[d]		
Ts	PhO	PhO	62	203–205	1250	1138(SO_2 s.)	1283(SO_2 as.)	12.5	18.5	42.0
$\overset{+}{P}Ph_3 \cdot Br^-$	Ph	Ph	quant.	262–264	1170			30.2 (tripl.)	23.0	19.0
$\overset{+}{P}Ph_3 \cdot BF_4^-$	Ph	Ph	71	236–240	1165			—		—

[a] Refs. [29–32].
[b] At −80° two conformers: δ_{PO} 48.4 and 46.5; δ_{PPh_3} 20.1 and 21.3; J_{PP} 27 Hz.
[c] At −90° two conformers: δ_{PO} 23.4 and 27.3; δ_{PPh_3} 20.6 and 19.9; J_{PP} 38, 37 Hz.
[d] AB-system; the assignment of signals is difficult.

As a rule, crystalline phosphonium salts **7** were obtained. Thiophosphoryl derivatives **13** were prepared by the addition of sulfur to phosphinophosphoranes **9** [35, 36]:

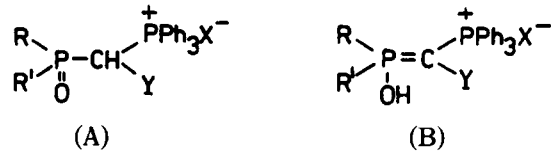


Sulfur addition can be carried out without isolation of phosphinophosphoranes **9** from the reaction mixture.

The composition and structures of all the obtained compounds were confirmed by elemental analyses, IR, and NMR spectra. Data for phosphoranes **10** and **13** are listed in Tables 3 and 4.

CRYSTALLINE PHOSPHAENOLS (OXYYLIDS)

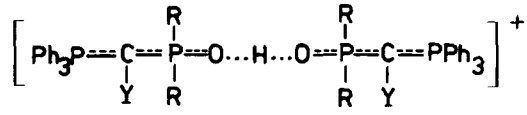
All investigated crystalline phosphorylphosphonium salts are listed in Table 5. They are stable compounds that can be recrystallized in air without special precautions.



(A) (B)

Characteristic frequency regions for forms (A) and (B) allow for an easy identification of the compounds by IR spectroscopy (see Tables 3, 4, and 5).

In addition to structures (B) with the hydrogen bond OH···X$^-$, "doubled" structures, in which a conjugate base served as an H-acceptor, were found; a complex of the BHB$^+$ type with pairwise equalized bonds was formed.



Such "doubled" structures were confirmed by X-ray structure analysis.

Phosphaenol structures are distinctly characterized by X-ray structure analysis. Thus, in the structure of the tosyl derivative (B) (Y = Ts, R = Ph, X = Br, No. 12 in Table 5) (Figure 1) the central carbon atom (C_1) has a slightly distorted planar trigonal coordination. Bonds C_1–PPh_2OH 1.751(4) Å

TABLE 4 Yields, MP, IR, and NMR Data for Thiophosphorylphosphoranes (**13**)[a]

$R_2P(S)—C(Y)=PPh_3$

Y	R	Yield %	MP (°C)	IR ν_{cm}^{-1} KBr Pellet	Temp. (°C)	NMR ^{31}P-{^1H}, CH_2Cl_2 $\delta_{PS(d)}$	$\delta_{PPh_3(d)}$	J_{PP}, Hz
COOEt	Ph	81	186–188	1660(CO)	−95	41.0	19.8	42
						42.9[b]	20.3	42
COOEt	Bu	65	111–114	1640(CO)	−85	47.3	21.2	30
						44.6[b]		
$CONEt_2$	Ph	60	208–210	1540(CO)	+30	38.1	20.5	46
CN	Ph	84	260–261	2170(CN)	+30	39.8	25.8	34
CN	Bu	73	105–106	2175(CN)	−80	45.7	25.0	29
Ts	Ph	87	253.5–255	1130(SO_2 s.) 1280(SO_2 as.)	−80	39.8	17.7	39
Ts	Bu	62	185–186	1130(SO_2 s.) 1265(SO_2 as.)	+30	49.3	15.4	32
Ts	EtO	53	201–202	1135(SO_2 s.) 1280(SO_2 as.)	+30	83.0	18.1	31
Ts	PhO	80	261.5–263	1140(SO_2 s.) 1285(SO_2 as.)	−80	79.1	17.8	35
$Ph_3\overset{+}{P}Cl^-$	Ph				−85	43[c]	23.8	21
$Ph_3\overset{+}{P}Cl^-$	Bu	96	263–264.5 (dec.)		−85	51.1[c]	23.2	14
$Ph_3\overset{+}{P}Br^-$	Bu	97	261.5–263 (dec.)		+30	51.7[c]	23.8	13.5

[a] Refs. [35, 36].
[b] Two conformers.
[c] Triplet.

TABLE 5 MP and IR Data for Phosphorylphosphonium Salts 7 in Crystalline State[a]

$R_2P(O)CH(Y)—\overset{+}{P}Ph_3X^-$ or $R_2P(OH)=C(Y)—\overset{+}{P}Ph_3X^-$
Form (A) Form (B)

No.	Y	R	X	MP (°C)	IR, ν_{cm}^{-1}, KBr Pellet				Form
					P=O	P—OH	OH···X⁻	Others	
1	2	3	4	5	6	7	8	9	10
1	COOEt	Ph	Cl	123–125 (dec.)[b]	—	970[c]	1500–2200	1660(CO) 3440(EtOH)	B
2	COOEt	Ph	ClO_4	164–166 (dec.)	1160 1180	— —		1730(CO), 2900(CH)	A
3	COOEt	PhO	ClO_4	113 (dec.)	1290	—		1740(CO), 2880(CH)	A
4	COOEt	Ph	BF_4	117–119 (dec.)	—	—	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	After crystallization on 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	149–150.5	—	960	1800–2000	1130(SO_2 s.), 1280(SO_2 as.)	B
11	Ts	Ph, Et	Br	179–181	—	940	1700–2800	1125(SO_2 s.), 1285(SO_2 as.)	B
12	Ts	Ph	Br	123–125	—	945	2000–2700	1135(SO_2 s.), 1280(SO_2 as.)	B
13	Ts	BuO	Br	100–102	—	970	2000–3000	1140(SO_2 s.), 1290(SO_2 as.)	B
14	Ts	Bu	ClO_4	154–155	[d]	—	—	1150(SO_2 s.), 1330(SO_2 as.)	A
15	Ts	Ph, Et	ClO_4	181–184	1195	—	—	1150(SO_2 s.), 1330(SO_2 as.)	A
16	Ts	Ph	ClO_4	173–178	—	—	600–1800	1135(SO_2 s.), 1282(SO_2 as.)	BHB^+
17	Ts	Bu, EtO	ClO_4	167–168	1245	—	—	1159(SO_2 s.), 1330(SO_2 as.)	A
18	Ts	BuO	ClO_4	162–163	1275	—	—	1150(SO_2 s.), 1340(SO_2 as.)	A
19	Ts	EtO	ClO_4	184–185	1272	—	—	1155(SO_2 s.), 1330(SO_2 as.)	A
20	Ts	PhO	ClO_4	220–222	1290	—	—	1165(SO_2 s.), 1330(SO_2 as.)	A
21	$\overset{+}{P}Ph_3Br^-$	Ph	Br	261–264	—	940 980	1600–3000		B[e]

[a] Refs. [28–32, 37].
[b] With 1/2 EtOH.
[c] In liquid paraffin.
[d] PO band is masked by ClO_4 band.
[e] Possibly B–H···OH_2^+.

and C_1–PPh_3 1.764(4) Å have almost equal lengths and correspond to a bond order of nearly 1.5 [39]. The phosphaenol structure in the crystal is stabilized by a strong hydrogen bond OH···Br (3.078Å).

Stabilization of the phosphaenol structure might be realized, however, by means of another particle. Thus, in the case of Y = CN, R,R′ = Bu, X = ClO_4 (N8 in Table 5 after crystallization in an atmosphere of air) the structure is of the BHB'^+ type, where B′ is H_2O. The crystal contains two crystallographically independent cations. In each of them (Figure 2), the central carbon atom is planar trigonal; out of plane deviations are 0.072 and 0.054 Å; the angles sum at C_1 is 359.4°. The C_1PBu_2OH and C_1–PPh_3 bonds are almost equal; their average length is 1.745(9) Å, which approximately corresponds to the bond order of 1.5. Oxygen atoms of water molecules O(II) serve as proton acceptors for the P–OH group. Distances O–H···O are 2.501(6) and 2.482(7) Å, which correspond to hydrogen bonds of increased stability [40].

As an example of a symmetric BHB^+ complex, the structure of (diphenyloxyphosphoranylidene)-carbethoxy(triphenylphosphonio)methane boron tetrafluoride is shown in Figure 3 (Y = COOEt, R,R′ = Ph, X = BF_4, No. 4 in Table 5). The structure is centrosymmetric; the two equal moieties are united by an H-bridge. The central carbon atom C_1 is planar trigonal; the angles sum at C_1 is 359.3°; bond lengths C_1–PPh_2OH and C_1–PPh_3 are almost equal, 1.725(8) and 1.735(8) Å; their bond order is close to 1.5; the O···H···O bond length is 2.422(8) Å. All bond

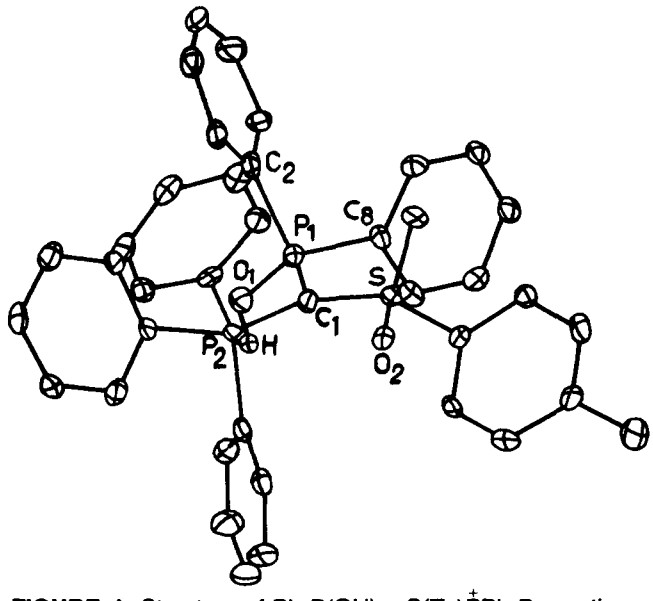


FIGURE 1 Structure of $Ph_2P(OH)=C(Ts)\overset{+}{P}Ph_3Br^-$ cation.

lengths of the dimer are pairwise equal, which is evidence for cation charge delocalization in both moieties.

As seen in Table 5, the alternative structure is determined by two main factors. The first factor is the nature of Y. In accordance with their phosphaenolizing ability, Y groups form a sequence corresponding to changes in their σ_{CH}^- values.

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

PPh_3 groups have the greatest enolizing ability, $CONEt_2$, the smallest. The second factor is the nature of counterion X^-. No doubt the hydrogen bond $OH\cdots X^-$ stabilizes the phosphaenol. The results obtained are understandable by considering the cooperative effect of these two factors.

Both these main factors determine the position of tautomeric equilibrium in solution (see below). It is understandable that the stability of phosphaenolic forms in the crystal depends on a variety of factors contributing to the crystal lattice energy. However, the acidifying effect of Y groups and the strength of $OH\cdots X$ hydrogen bonds might be the most important considerations.

PHOSPHORYL–PHOSPHAENOLIC TAUTOMERISM

The phosphoryl–phosphaenolic or phosphoryl–oxyylidic tautomerism **2** is a phosphorus analogue of the ketoenolic one **1**. Therefore, methods of investigation applied to ketoenolic systems can also be used for the study of the analogous phosphorus systems. The most effective methods proved to be ^{31}P, ^1H, ^{13}C, NMR, and IR spectroscopy.

In general, $^{31}P\{^1H\}$ NMR spectra of solutions of tautomeric phosphonium salts **7** consist of two pairs of doublets. The number of signals might be doubled, especially at low temperatures, because of the presence of both conformers or both diastereomers in solution.

Triplet or doublet–doublet signals of protons of the (A) form with J_{PCH} of the order of 13–17 Hz; singlets of P–OH protons of the (B) form; and signals of other groups can be observed in the NMR

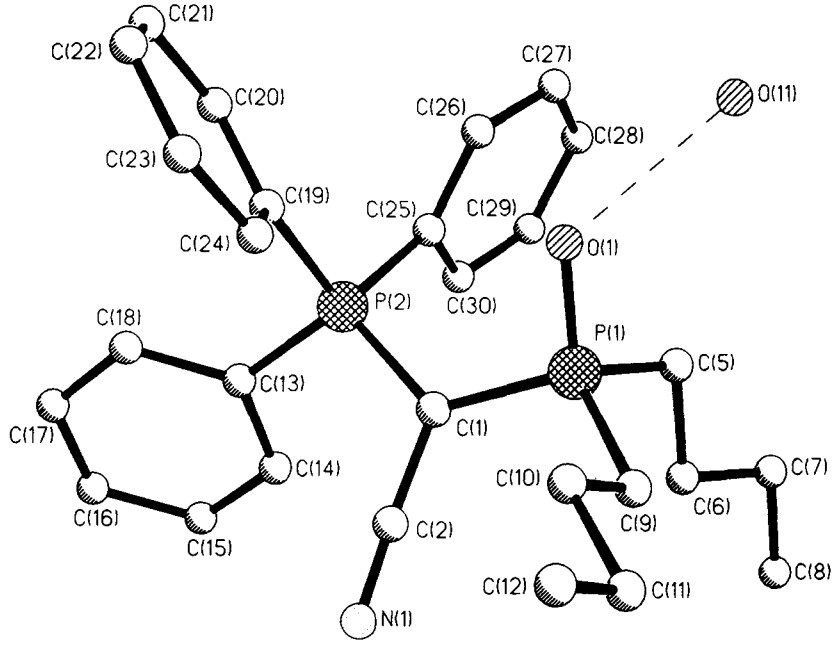


FIGURE 2 Structure of $[Ph_3P{=}C(CN){=}PBu_2{=}OH\cdots OH_2]^+ClO_4^-$ cation; a complex of BHB′+ type with H_2O molecule (the oxygen atom O-11).

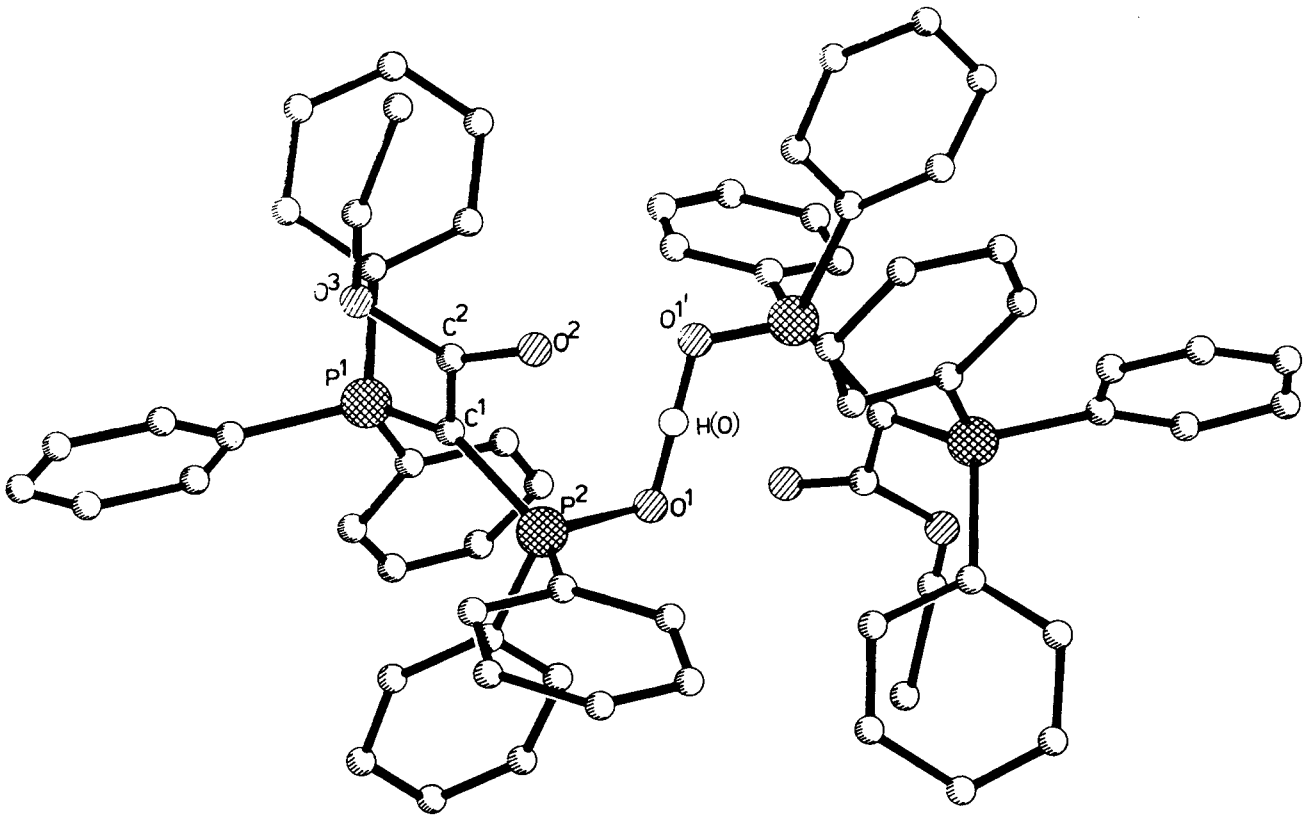


FIGURE 3 Structure of $[Ph_3P{=}C(COOEt){=}PPh_2{=}O\cdots H\cdots O{=}PPh_2{=}C(COOEt){=}PPh_3]^+$ BF_4^- cation; a complex of BHB^+ type.

spectra. The protons of $COOC_2H_5$ or $SO_2C_6H_4CH_3$ are observed as separate signals of both tautomeric forms and can be used to determine the tautomeric equilibrium constants. Nevertheless, they are best observed at low temperatures.

Tautomeric equilibria are rapidly reached and then do not change with time. The results of studies of tautomeric equilibria obtained by different methods coincide fairly well. In Tables 6 and 7 $^{31}P\{^1H\}$ NMR data in CH_2Cl_2 are given for all studied substances as the most demonstrative ones.

Bis-triphenylphosphonium salt **7**, Y = $\overset{+}{P}Ph_3$, R,R′ = Ph, Table 6, was found to exist in solutions as form (B). The same is also true for the bromide and perchlorate; moreover, in trifluoroacetic acid, where in all other cases merely (A) forms are observed, in the case of the bisphosphonium salt only the (B) form is noted. Apparently, due to a strong acidifying ability of triphenylphosphonium groups (σ_{CH}^- = 1.08), CH acidity of the bisphosphonium salt is so great that the CH-form (A) production is impossible, even in CF_3COOH.

CN-substituted compounds, **7**, Y = CN bromides with R,R′ = Ph or Bu are phosphaenols (B), whereas those with R and R′ = EtO or PhO (chlorides) at low temperatures are (A) forms. As to perchlorates, with R,R′ = Bu, both forms are observed in solutions. For R,R′ = Ph a complex of the BHB'^+ type, i.e., virtually form (B), is formed. Unlike the bisphosphonium salt, only one form (A) is observed in CF_3COOH.

In solutions of the bromide and perchlorate tosyl derivatives **7**, Y = Ts, Table 7, with R,R′ = Ph, only the (B) form is present; for perchlorate with R = Ph and R′ = Et, a tautomeric equilibrium is observed. The signals of the (A) form are doubled due to the diastereomeric anisochronism. There is also a tautomeric equilibrium for compounds with R and R′ = Bu (for bromide and perchlorate) and with R = Bu and R′ = EtO (for X = Br, ClO_4) and with R and R′ = AlkO (for bromides). In perchlorate solutions, with alkoxy and phenoxy groups at the phosphorus atom, only forms (A) are present.

Carbethoxyl derivatives, **7**, Y = COOEt, Table 6, show the tautomeric equlibrium only for R,R′ = Ph, or Bu if X = Cl. Otherwise, only the (A) forms are available. Eventually, if Y is the $CONEt_2$ group, possessing the smallest acidifying ability (σ_{CH}^- = 0.42), only the (A) forms are present (Table 6). Thus, a decrease in the electron acceptor ability of the Y groups favors predominance of the (A) forms, and vice versa.

TABLE 6 NMR ^{31}P-{^{1}H} Data for Phosphorylphosphonium Salts **7**, CH_2Cl_2[a]

$$R_2P(O)CH(Y)—\overset{+}{P}Ph_3X^- \rightleftharpoons R_2P(OH)=C(Y)—\overset{+}{P}Ph_3X^-$$

Form (A) Form (B)

Y	*R*	*X*	*Temp. (°C)*	*Form*	δ_{PO} (*d*)	δ_{PPh_3} (*d*)	J_{PP}, *Hz*	*Notes*
$Ph_3\overset{+}{P}X^-$	Ph	Br	30	B	40.9 (triplet)	23.5	20	
$Ph_3\overset{+}{P}X^-$	Ph	ClO_4	20	B	38.3 (triplet)	24.8	21	In $MeNO_2$
$Ph_3\overset{+}{P}X^-$	Ph	CF_3COO	30	B	49.2 (triplet)	22.7	20	In CF_3COOH
CN	Ph	Br	30	B	51.5 (broad s.)	22.7	27	
CN	Ph	CF_3COO	−20	A	33.4 (broad s.)	24.3	—	In CF_3COOH
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 (broad s.)	26.0	—	
CN	PhO	Cl	−80	A	6.9 (broad s.)	26.7 (broad s.)	—	
CN	EtO	Cl	−80	A	0.1 (broad s.)	24.6 (broad s.)	—	
COOEt	Bu	Cl	−70	B	79.2; 78.0	19.2; 20.3	24	Two conformers
				A	48.8	23.1	7	
COOEt	Ph	Cl	−80	B	43.8; 40.6	19.0; 20.0	40; 42	Two conformers
				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	In $CHCl_3$
$CONEt_2$	Ph	Cl	30	A	29.4	27.0	10	

[a] Refs. [31, 32].

TABLE 7 NMR ^{31}P-{^{1}H} Data for Phosphorylphosphonium Salts **7** at Y = Ts, CH_2Cl_2

$$\underset{\text{Form (A)}}{RR'P(O)—CH(Ts)—\overset{+}{P}Ph_3X^-} \rightleftharpoons \underset{\text{Form (B)}}{RR'P(OH)=C(Ts)—\overset{+}{P}Ph_3X^-}$$

R	*R'*	*X*	*Temp. (°C)*	*Form*	δ_{PO} *ppm (d)*	δ_{PPh_3} *(d)*	J_{PP}, *Hz*	*Notes*
1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*
Ph	Ph	Br	30	B	46.4	18.2	29.0	B 98%
Ph	Ph	ClO_4	30	B	45.9	17.5	26.0	B 98%
Ph	Et	Br	30	B	58.1	18.2	24.0	
Ph	Ph	ClO_4	30	B	60.7	18.3	26.0	
				A	44.4 (s.), 43.0 (s.)	20.1 (s.), 21.0 (s.)	—	Two diastereomers
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 (s)	18.2	—	
Bu	EtO	ClO_4	30	B	70.2	17.5	27.0	In $CHCl_3$
				A	45.9; 43.6 (s.)	19.5 (s.)	6.0	Two diastereomers
						19.7 (s.)	—	
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	A	−0.9 (s.)	22.0 (s.)	—	

TABLE 8 Effect of R and R′ on Tautomeric Equilibrium (A ⇄ B) of Phosphonium Salts **7** for Y = Ts, CH_2Cl_2

$$RR'P(O)CH(Ts)—\overset{+}{P}Ph_3X^- \rightleftarrows RR'P(OH)=C(Ts)—\overset{+}{P}Ph_3X^-$$

Form (A) Form (B)

			X = Br^-, t = −80°C		X = ClO_4, t = 30°C	
R	*R′*	$\Sigma\sigma^{\varphi}$	% (*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 might be expected, groups R and R′ at phosphorus strongly affect the tautomeric equilibrium position. Data on the effect of these groups are given in Table 8. The data are compared with σ^{φ} constants characterizing the effect of substituents at phosphorus on the acidity of phosphorus acids [41]. As seen, the content of (B) forms increases with a decrease in electronegativity of R and R′. It is the natural expectation since electronegative groups R and R′ increase the strength of P–OH acids, which favors the proton transfer to the carbon atom.

A special place is occupied, however, by aromatic derivatives. A phenyl group at phosphorus markedly favors phosphaenolization. The origin of this phenomenon had been repeatedly discussed for other kinds of the "phenyl anomaly." Several assumptions have been made [30, 42].

The anion character, in accordance with the anion ability to form an H-bond stabilizing phosphaenol, strongly affects the tautomeric equilibrium (A ⇄ B):

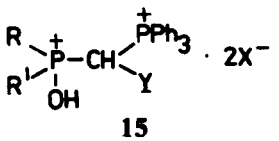
$$Cl^- > Br^- > BF_4^- \geq ClO_4^-$$

The effect of the solvent nature is also of importance. In aprotic media, the percentage of (B) form decreases with an increase in the solvent dielectric constants ϵ. As an example, we present the effect of solvents on the percentage of (B) forms for $Ph_2P(O)CH(PPh_3Cl)COOEt$ at −60°C.

	CH_2Cl_2	CH_2Cl_2 + MeCN (4:1)	$MeNO_2$
ϵ	9.14	14.8	38.57
% (B)	77.0	16.0	<45

The proton donor, chloroform, easily solvates P=O groups and, accordingly, shifts the equilibrium to the (A) form. In alcohols, where OH forms are easily solvated, the equilibrium is shifted to the (B) forms.

The effect of medium acidity on the equilibrium position (A ⇄ B) is of interest. An increase in the acidity shifts the equilibrium to (A) forms. The acid protons apparently compete with the P–OH phosphaenol protons for the H-bonds with anions, resulting in the decreasing stability of phosphaenols. A strong increase in the acid concentration leads to double protonated products **15** [43]:



15

Enthiolization of the thiophosphoryl group appreciably differs from enolization of its oxygen prototype [35]. Phosphonium salts **14** are less stable in the solid state. They all have the CH structure. The salt with two phosphonium groups, **14**, Y = $\overset{+}{P}Ph_3X^-$ cannot be obtained in the pure state because of a very low basicity of the corresponding phosphorane **13**. In CH_2Cl_2 or FSO_3H solutions, it has the mercaptoylid structure **5**, which unambiguously follows from its $^{31}P\text{-}\{^1H\}$ NMR spectrum. All other salts, **14**, regardless of the nature of Y, R,R′ and X, have the thiophosphoryl structure and are not tautomeric.

Thus, enthiolization of the thiophosphoryl group is observed only with Y = $\overset{+}{P}Ph_3$; all derivatives with CN and other groups with smaller $\Sigma\sigma_{CH}^-$ values have the thiophosphoryl structure **14** and are not tautomeric. It is possible that the area of the thiophosphoryl–mercaptoylid tautomerism should have $\Sigma\sigma_{CH}^-$ values in the range of 2.5–2.7. Unfortunately, this area still remains inaccessible.

ENOLIZATION OF THE PHOSPHORYL GROUP AND ACIDITY

It has been known for some time that the acidic properties of prototropic tautomeric substances are

TABLE 9 Acid Dissociation Constants of Thiophosphorylphosphonium Salts **14** in $MeNO_2$ and EtOH at 25°C, $R_2P(S)CH(Y)—\overset{+}{P}Ph_3X^-$

				pK_{ef}	
No.	*R*	*Y*	$\Sigma\sigma_{CH}^-$	$MeNO_2$	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

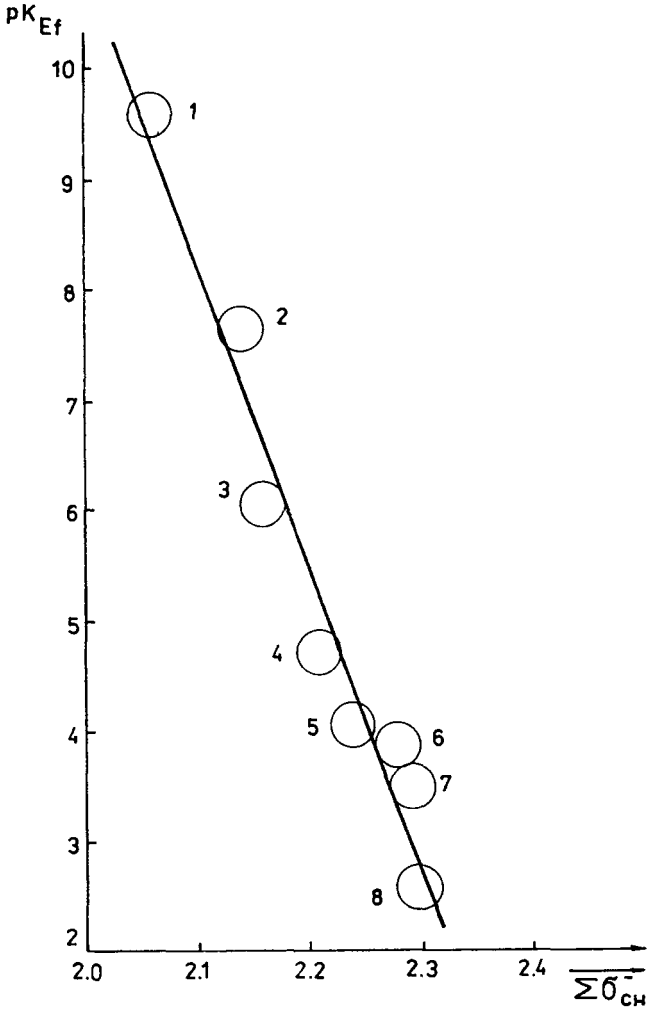


FIGURE 4 Plot of pK_{ef} vs. $\Sigma\sigma_{CH}^-$ for $RR'P(S)CH(Y)\overset{+}{P}Ph_3ClO_4^-$ in nitromethane (for number of points see Table 9).

related to the tautomeric equilibrium position in a complicated way. This position, as seen from Equation (1), is not determined by the acidity level. The experimentally determined effective dissociation constant of the equilibrium mixture, K_{ef}, is related to dissociation constants of individual forms by Equation (2) [22].

$$K_{ef} = \frac{K_1 K_2}{K_1 + K_2} \tag{2}$$

where K_1 and K_2 are dissociation constants of individual forms. The dissociation constants of individual forms can be calculated from the measured effective dissociation constants K_{ef} and tautomeric equilibrium constants K_T

$$pK_1 = pK_{ef} - \log (K_T + 1) \tag{3}$$

$$pK_2 = pK_1 + \log K_T \tag{4}$$

It is of interest to elucidate the acidic properties of CH–phosphoryl acids ((A) forms) and phosphaenols ((B) forms) and their dependence on the structures. To this end it was also reasonable to use the $\sigma\rho$-correlation analysis. However, its applicability to a quantitative description of the acidity of compounds with structures that have been investigated had to be tested on nontautomeric substances of the same type. As such, thiophosphoryl phosphonium salts **14** were used. Dissociation constants of these compounds in nitromethane and absolute ethanol were measured by the potentiometric method with a glass electrode [44]. The results of these measurements are listed in Table 9.

As apparent, these acids are fairly strong. For instance, in $MeNO_2$, the pK is 7.05 for CF_3COOH, 11.62 for $ClCH_2COOH$, and 14.41 for CH_3COOH. They are well- (in absolute ethanol even excellently) correlated with σ_{CH}^- constants (Figures 4 and 5):

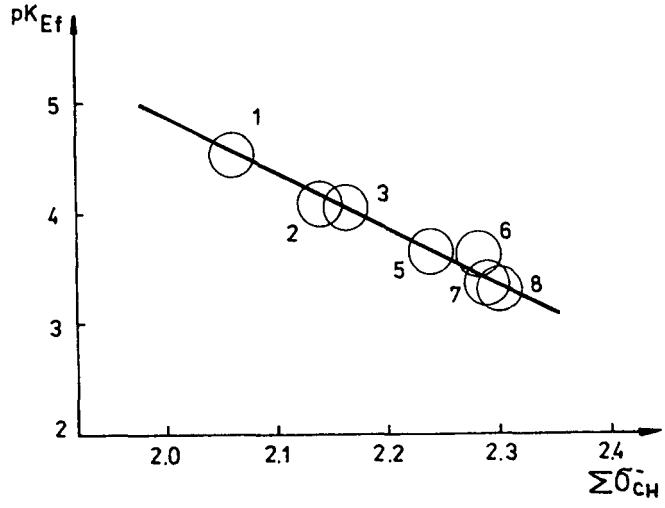


FIGURE 5 Plot of pK_{ef} vs. $\Sigma\sigma_{CH}^-$ for $RR'P(S)CH(Y)\overset{+}{P}Ph_3Cl^-$ in ethanol (for number of points see Table 9).

TABLE 10 Acid Dissociation Constants of Tautomeric Phosphoryl–Phosphonium Salts in $MeNO_2$ and EtOH at 25°C

$$RR'P(O)CH(Y)—\overset{+}{P}Ph_3X^- \rightleftharpoons RR'P(OH)=C(Y)—\overset{+}{P}Ph_3X^-$$

Form (A) Form (B)

				$MeNO_2$				*EtOH*			
No.	*RR'*	*Y*	$\Sigma\sigma_{CH}^{-}$	pK_{ef}	% (*B*)	pK_{CH}	pK_{OH}	pK_{ef}	% (*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

In $MeNO_2$:

$$pK_{ef} = 65.82 - 27.410\ \Sigma\sigma_{CH}^{-} \quad (r = 0.980)$$

In EtOH:

$$pK_{ef} = 14.94 - 5.052\ \Sigma\sigma_{CH}^{-} \quad (r = 0.998)$$

As seen, the strong differentiating effect of nitromethane is observed. Naturally there is a linear Brönsted dependence between pK in both solvents.

$$pK_{MeNO_2} = -15.72 + 5.535\ pK_{EtOH} \quad (r = 0.978)$$

The high value of the slope, markedly differing from unity, is evidence of great differences in the differentiating effect of nitromethane and ethanol.

Analogously, the acidic dissociation constants of tautomeric phosphorylphosphonium salts **7** were measured [28]. The results obtained are listed in Table 10 and compared with the equilibrium content of phosphaenol forms (B) found by ^{31}P NMR spectroscopy. It is apparent that all these substances are comparatively strong acids. Their strength in nitromethane is less than that of the thiophosphoryl acids **14** mentioned previously, by approximately 0.7 pK units on the average. In ethanol, their strengths are almost equal. The strong differentiating effect of nitromethane is also observed. With fixed substituents at phosphorus, the acid strengths decrease on going from Y = CN to compounds with Y = Ts, then to carbethoxy and further to carbamoyl derivatives. These data correspond to the changes in σ_{CH}^{-} constants of the Y groups.

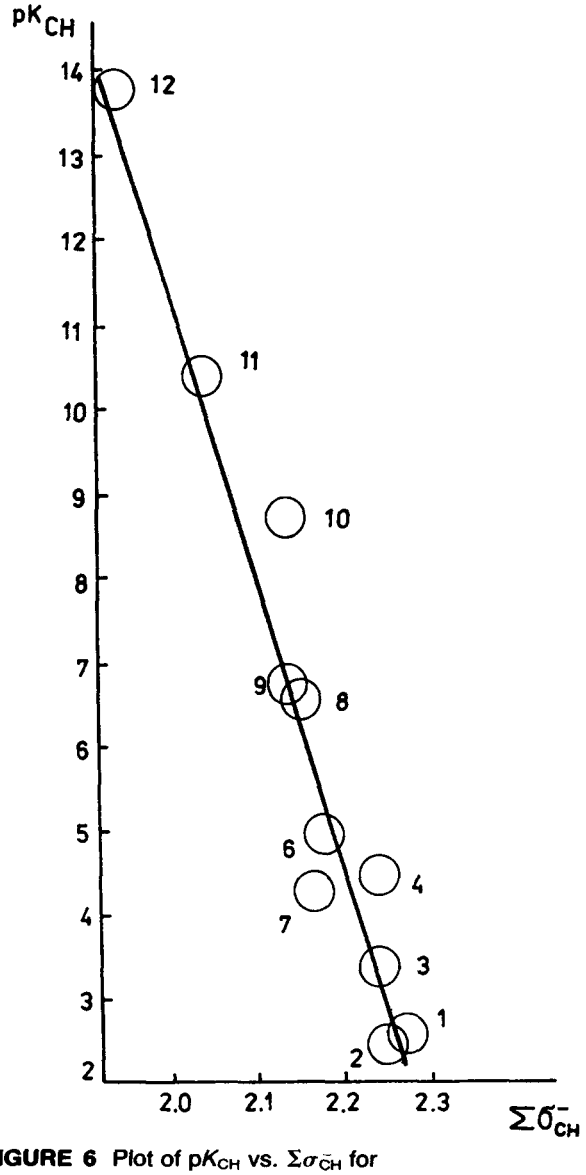


FIGURE 6 Plot of pK_{CH} vs. $\Sigma\sigma_{CH}^{-}$ for $RR'P(O)CH(Y)\overset{+}{P}Ph_3ClO_4^{-}$ in nitromethane (for number of points see Table 10).

By means of Equations (2)–(4) the dissociation constants of form (A) (pK_{CH}) and form (B) (pK_{OH}) were calculated. The results obtained are included in Table 10. It is apparent that pK_{CH} increases with decreasing $\Sigma\sigma_{CH}^{-}$, a satisfactory Hammett correlation in nitromethane and a good one in ethanol being observed (Figure 6).

In $MeNO_2$:

$$pK_{CH} = 81.99 - 35.246\ \Sigma\sigma_{CH}^{-} \quad (r = 0.977)$$

As to the pK_{CH} values in ethanol, only the last four digits in Table 10 are reliable. They give a good correlation with $\Sigma\sigma_{CH}^{-}$ in EtOH:

$$pK_{CH} = 39.61 - 17.268\ \Sigma\sigma_{CH}^{-} \quad (r = 0.996)$$

In these correlations an extraordinarily high pK° value is also observed, especially in nitromethane. The pK_{OH} dependence on the structure appears to be fairly complicated. With fixed Y values, e.g., Y = Ts, pK_{OH} satisfy the Hammett correlation with σ^{φ} constants [41] (Figure 7).

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

Thus, the acidity measurements pK_{ef} and calculations of pK_{CH} and pK_{OH} elucidate the relations between the P=O group enolization and the acidity of phosphoryl compounds.

CONCLUSION

The main conclusion from the various experiments is that the phosphoryl group *can be enolized.* The needed condition is a high acidity of the CH–phosphoryl form. Naturally, this is a necessary but not a sufficient condition. It is necessary that the acidities of the corresponding enol (B) and phosphoryl (A) forms be close, which is easily attained with sufficiently acidic CH forms. The enolization conditions of the thiophosphoryl group are stricter, which is explained by a higher acidity of mercaptoacids of phosphorus compared with those of oxygen.

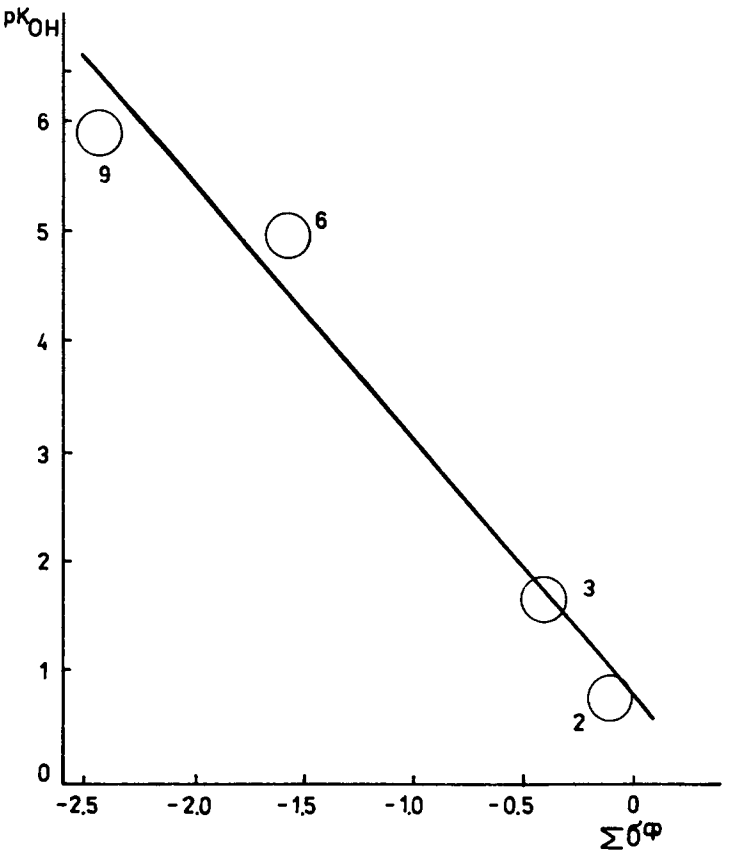


FIGURE 7 Plot of pK_{OH} vs. $\Sigma\sigma^*$ for $RR'P(OH)=C(Ts)\overset{+}{P}Ph_3ClO_4^-$ in nitromethane (for number of points see Table 10).

It can easily be shown that no one has succeeded in observing the P=O group enolization until recently, because the $\Sigma\sigma_{CH}^-$ values of the groups bonded to the central atom did not exceed 2. The latter was due to an inadequate acidifying effect of the linked groups. Thus, for instance, for "phosphonacetic ester," studied by A. E. Arbuzov and A. I. Razumov, the σ-$(EtO)_2P(O)—CH_2COOEt$ $\Sigma\sigma_{CH_2}^-$ value is 1.28, which is quite inadequate for phosphaenolization. The substances studied by O. I. Kolodyazhnyi, $Ph_2P(O)CH(SO_2C_6H_5)_2$ [13, 14], have $\Sigma\sigma_{CH}^-$ = 1.97, which is on the verge of enolizability. The introduction of electronegative substituents into the benzene ring augments the $\Sigma\sigma_{CH}^-$ value, and enolization becomes pronounced.

In summation, enolization of the phosphoryl group is entirely subject to regularities of the prototropic tautomeric acid-base equilibrium to which, naturally, enolization of the carbonyl group is also subject.

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