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The Phosphorus-Carbon Prototropic Tautomerism

T.A.Mastryukova and M.I.Kabachnik

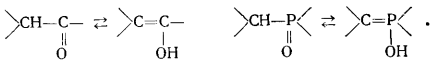
New types of prototropic tautomerism in which the proton migrates between a carbon atom and a phosphorus-containing functional group are examined. It is shown that in all cases the position of the tautomeric equilibrium is determined by the relative acidities of the different forms: the CH acidity of the forms in which the proton is located at a carbon atom and the PH or PXH acidity (X = O, S, etc.) of the tautomers with the proton in the phosphorus-containing group. The method for the estimation of the relative acidities of different forms with the aid of the σ^{ph} constants of the substituents at the phosphorus atom and the σ_C^- constants of the substituents at the central carbon atom, characterising the acidifying influence of these substituents, has attracted attention in this connection.
It has been shown that in all cases the equilibrium position is determined by the general characteristics of the protolytic acid - base tautomeric equilibrium.
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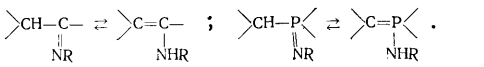
I. INTRODUCTION

By phosphorus-carbon prototropic tautomerism, we understand the type of tautomerism in which the proton migrates between a carbon atom and a phosphorus-containing functional group. In principle, phosphorus-carbon tautomeric systems can be derived from their purely organic prototypes by replacing the group accepting a proton from the carbon atom by a phosphorus-containing group. Thus, the phosphoryl-hydroxy-ylide system can be derived from the keto-enol system:



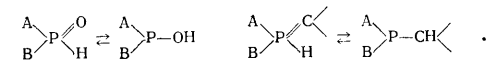
keto - enol phosphoryl - hydroxy-ylide

The phosphorimide-animoylide tautomerism can be derived similarly from the ketimine-enamine tautomerism:



Ketimine - enamine phosphorimide - aminoylide

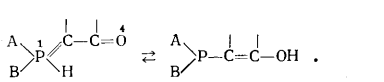
Furthermore, by virtue of the ease with which phosphorus changes its covalence from 3 to 4, diad-tautomeric systems of the type of dialkyl phosphites and their numerous analogues are widely known in the chemistry of organophosphorus compounds. By means of the reverse analogy, involving the replacement of the heteroatom linked to phosphorus by a carbon atom, it is possible to derive the diad phosphorus–carbon tautomerism:



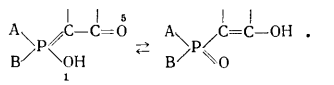
dialkyl phosphite tautomerism diad phosphorus - carbon tautomerism

It can be shown that all types of the phosphorus-carbon tautomerism constitute a single group of equilibria, a common feature of which is the transfer of a proton from the α-carbon atom to a phosphorus-containing functional group (Table 1).

Apart from the phosphorus-carbon diad and triad tautomeric systems, there is also a possibility of their vinylogue systems. Here, one can include, for example the tetrad system in which there is a proton 1,4-migration and not a 1,2-migration (diad migration):



Mention can also be made of a pentad system in which the proton is transferred from the 1-position to the 5-position:



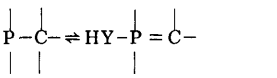
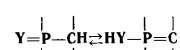
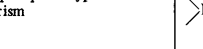
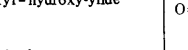
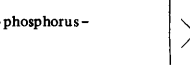
Although formally these systems do not fit the definition quoted above (in the last system, for example, the proton is transferred from the oxygen atom of the phosphorus-containing functional group to the oxygen atom of the carbonyl group, the keto-form is in this instance simultaneously an ylide form and the type of transition  is retained for the phosphorus atom, which makes it possible to classify these complex systems conventionally as of the phosphorus–carbon type. Furthermore, as will be shown below, there is always a typical phosphorus-carbon 1,2- or 1,3-transition in such systems together with the pentad or tetrad transitions from an oxygen or phosphorus atom to an oxygen atom and conversely.

Table 1. A schematic arrangement of the phosphorus–carbon prototropic systems.

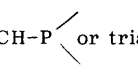
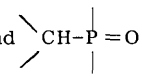
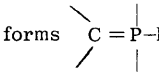
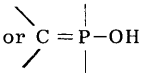


Y	Type of tautomerism	General formula
Electron pair	diad, dialkyl phosphite type of tautomerism	
O	triad, phosphoryl - hydroxy-ylide	
S	triad, thiophosphorly-mercaptoylide	
RN	triad, phosphorimide-aminoylide	
C	triad, carbon - phosphorus - carbon	

The position of any prototropic tautomeric equilibrium is known to be determined by the relative acidities of the different forms under the given experimental conditions, i.e.

$$K = c_1/c_2 = K_2/K_1 ,$$

where c_1 and c_2 are the concentrations of forms 1 and 2 and K_1 and K_2 are their dissociation constants. In practice, a tautomeric equilibrium is observed in those cases where the dissociation constants of the forms differ by not more than 1–3 orders of magnitude (naturally this limit depends on the sensitivity of the method of analysis or calculation adopted for the tautomeric system). On the other hand, if the difference between the dissociation constants is large, the equilibrium is displaced almost completely towards the form whose dissociation constant is smaller.

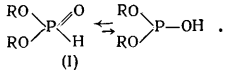
If this criterion is applied to typical phosphorus-carbon systems, namely the diad  or triad  systems it is clear that conversion into the ylide forms  or  will occur only if the acidity of the CH forms becomes comparable to or greater than the acidity of the PH or OH forms. At the same time it is known that the PH acidity and especially the OH acidity is usually higher than the CH acidity. For the CH acidity to become equal to or greater than the acidity of the XH forms, a sufficiently powerful acidifying influence of groups attached to the carbon atom is necessary. Ylide forms can therefore be observed in those cases where strongly electronegative groups such as COR, SO_2R, CN, etc. are attached to the α-carbon atom. Naturally, the ratio of the acid properties of the forms depends on many intermolecular and external factors. However, to a first approximation it may be sufficient to estimate the acidifying influences of the substituents attached to the carbon and phosphorus atoms. Such an approximate approach has helped to discover certain new types of tautomerism to which this review is devoted.

II. THE DIAD PHOSPHORUS-CARBON TAUTOMERISM

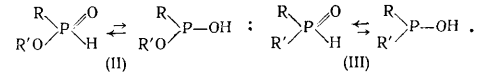
As already mentioned, the diad phosphorus-carbon system is structurally related to other diads: phosphorus-oxygen, phosphorus-sulphur, and phosphorus-nitrogen. Some important information about these systems is therefore initially presented below.

1. The Phosphorus-Oxygen, Phosphorus-Sulphur, and Phosphorus-Nitrogen Diads

Among all the types of diad tautomeric systems known in organic chemistry, the organophosphorus diads have been investigated to the greatest extent. They include in the first place dialkyl phosphites (I), the study of the tautomerism of which was initiated by A.E.Arbuzov[1] more than 75 years ago:


(I)

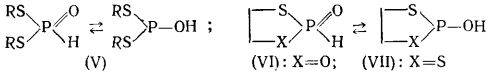
Although the conclusion that such tautomerism occurs had been reached a long time ago[2], proof of the existence of the hydroxy-form was obtained much later in kinetic isotope investigations[3,4]. Naturally, alkyl alkylphosphonites (II) and dialkylphosphonites (III) are included here also:


(II) (III)

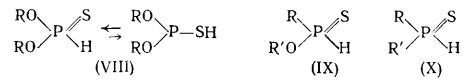
In all the compounds of this type the tautomeric equilibrium is displaced towards the form with tetracoordinate phosphorus. Only in the case of bis(trifluoromethyl)phosphinite (IV) is the form with a tervalent phosphorus atom the only one present[5]:

(IV)

It was later stated in the literature that the *S,S*-dialkyl phosphorodithioites (V) as well as the cyclic phosphorothiolites (VI) and (VII) are tautomeric mixtures of two forms[6–8]:


(V) (VI): X=O; (VII): X=S

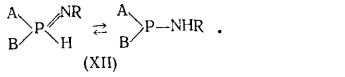
O,O-Dialkyl phosphoromonothioites (VIII), the sulphur analogues of phosphites, were first investigated by the authors of this review at the beginning of the 1950's.[9] Here too the tautomeric equilibrium is displaced towards the thione forms under the usual conditions; the *O*-alkyl phosphonothioites (IX) and dialkylphosphinothioites (X) behave similarly:


(VIII) (IX) (X)

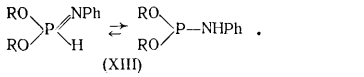
According to an estimate, this equilibrium is displaced to an even greater extent than in dialkyl phosphites and only bis-(trifluoromethyl)phosphinothioite (XI) exists solely in the thiol form[10]:

(XI)

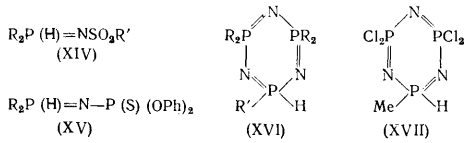
The proportions of the different forms of phosphoramidites and their analogues (XII) are different:


(XII)

Under the usual conditions, where A, B, and R are alkyl, aryl, or alkoxy-groups, the tautomeric equilibrium is displaced towards the amine form with a tervalent phosphorus atom[11]. This was first demonstrated by Kabachnik and Gilyarov[12] in relation to dialkyl N-phenylphosphoramidites (XIII).


(XIII)

In contrast to the oxygen and sulphur diads, in the case of phosphoramidites the second, i.e. the PH form could be detected for a much larger number of examples—for compounds (XIV),[13] (XV),[13] (XVI),[14] and (XVII):[15]


(XIV) (XV) (XVI) (XVII)

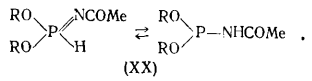
Instances of the tautomeric equilibria involving both forms have also been found[16,17]:

$$(RO)_2P(H)=N-SiMe_3 \rightleftarrows (RO)_2P-NH-SiMe_3 ;$$
(XVIII)

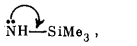
$$[Me_2N]_2P(H)=N-COMe \rightleftarrows [Me_2N]_2P-NH-COMe .$$
(XIX)

The PH forms of dialkyl phosphites (I) and their sulphur analogues (VIII) have much weaker acid properties than the OH and particularly the SH forms. The equilibrium is therefore as a rule displaced towards the PH forms. Only the introduction of two trifluoromethyl or cyclic ethylenedithiol groups at the phosphorus atom can increase the acidity of the PH form so much that it exceeds that of the OH or the SH forms, in the direction of which the equilibrium is in fact displaced[18].

The acidity of the NH forms of phosphoramidites and their analogues (XII) is lower than that of the PH forms; accordingly, the NH forms predominate in the equilibria. However, the difference between the acidities of the forms is not so great in this instance; when suitable substituents at the nitrogen and phosphorus atoms are used, it is easy to alter the relative acidities of the forms and thus influence the equilibrium position. For example, it is known that the equilibrium (XX) is displaced towards the amino-form[19]:


(XX)

However, if the strongly electron-accepting alkoxy-groups at the phosphorus atom are replaced by the more electron-donating dialkylamino-groups [see (XIX)], then the acid properties of the P–H bonds are diminished and the PH and NH forms can be detected in the tautomeric equilibrium[17]. On the other hand, if the trimethylsilyl group [see (XVIII)] is introduced at the nitrogen atom of the system (XX), then, as a result of the effect of the p–d conjugation



the nitrogen atom acquires a partial positive charge, the acidity of the N–H bond increases, and both forms again appear in the tautomeric equilibrium, which has been observed experimentally[16].

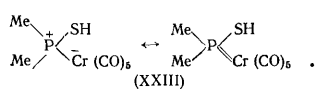
There are indications in the literature that the OH form of a dialkyl phosphite can be stabilised by incorporating it in a complex with a transition metal ion. For example, the complex (XXI), discovered in 1944 by Grinberg and Troitskaya[20,21]:

$$Pt\{P(OEt)_2OH\}_2 \cdot \{P(OEt)_2O\}_2 .$$
(XXI)

One can also refer to the complex $Mo(CO)_5[Ph_2POH]$ [22] and a number of others[23]. Dialkyl phosphorothioites form similar complexes in the SH form, for example, compound (XXII):[24,25]

$$Cr(CO)_5[Me_2PSH] .$$
(XXII)

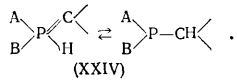
However, in discussing these and analogous complexes one must not forget that, instead of the free (solvated by solvent molecules) tautomeric forms with a tervalent phosphorus atom, one is dealing with compounds of another type [compounds (XXIII)], containing a tetracoordinate phosphorus atom:


(XXIII)

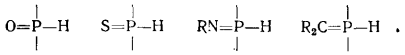
It is therefore illegitimate to consider examples such as those of "stabilisation" of phosphites with tervalent phosphorus.

2. Phosphorus–Carbon Diad Systems

As mentioned above, the phosphorus-carbon diad system (XXIV) is the carbon analogue of the dialkyl phosphite diad:

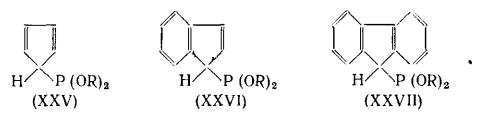

(XXIV)

This is the last of the four possible phosphorus diads:



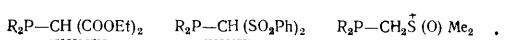
(a) The phosphorus–carbon diads existing in the CH form. Dialkyl phosphonites $(RO)_2P-CHR'_2$, alkyl phosphinites $(RO)R'P-CHR''_2$, and tertiary phosphines $R_2P-CHR'_2$ containing an α-hydrogen atom belong in the first place to phosphorus–carbon diad systems. However, they had not been considered previously from the standpoint of the possibility of the the diad phosphorus-carbon tautomerism. Indeed, these substances are always represented in the CH forms with a tervalent phosphorus atom since the acid properties of the C–H bond are still less marked than those of the N–H bond, the shift of the equilibrium towards the CH forms is even greater in this instance. Very powerful influences on the C–H and P–H bonds are necessary for the appearance of the experimentally detectable phosphinomethylene PH form.

Attempts to achieve such an influence on the CH acidity of phosphonites and tertiary phosphines have been made. Thus one of the authors of the present review and Tsvetkov[26] investigated for this purpose cyclopentadienylphosphonites (XXV), indenylphosphonites (XXVI), and fluorenylphosphonites (XXVII).


(XXV) (XXVI) (XXVII)

However, these substances proved to be pure CH forms.

Kolodyazhnyi, Gololobov, and co-workers introduced at the α-carbon atom of the R_2PCH group two alkoxycarbonyl groups [compound (XXVIII)],[27,28] two sulphonyl groups [compound (XXIX)],[29] the protonated dimethyl sulphoxylide group [compound (XXX)],[30] and certain others:


(XXVIII) (XXIX) (XXX)

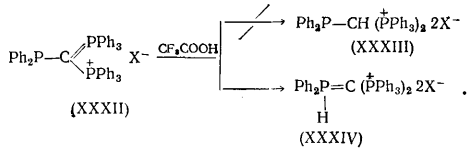
In all cases the groups R consisted of the simplest (unbranched) alkyl, phenyl, or alkoxy-groups. Only the CH forms of all these compounds could be detected in solutions by infrared spectroscopy, ^1H NMR, and NMR.[28] It has been stated[31] that the PH form of the phosphorylated acetaldehyde (XXXI) can exist in equilibrium with the CH and enol forms:

$$Ph_2P-CH_2-C(H)O \rightleftarrows Ph_2P-CH=CH-OH \rightleftarrows Ph_2P(H)=CH-C(H)O .$$
(XXXI)

However, the aldo-enol equilibrium has been demonstrated experimentally in this instance but the existence of a PH ylide form has been merely postulated.

(b) The phosphorus–carbon diad existing in the PH form. The first compound with the PH ylide structure was described in 1966 by Birum and Matthews[32]. When the phosphorany idene phosphonium salt (XXXII) was treated with trifluoro-

acetic acid, the formation of the ylide (XXXIV) with a P–H bond was observed:



(XXXII) (XXXIV)

Two triphenylphosphonium groups attached to the central carbon atom proved to have such a powerful acidifying effect on the C–H bond in compound (XXXIII) that the proton added to the phosphorus atom with formation of the PH ylide (XXXIV) and not to the carbon atom.

Indeed, the triphenylphosphonium group belongs to the class of the most highly acidifying groups. In the study of the influence of this group on the tautomeric keto-enol equilibrium, we found[33] that its effect is significantly greater than that of, for example, the ethoxycarbonyl group, as can be seen from the following data: $MeCOCH_2COOEt$ (7% of enol); $MeCOCH(COOEt)_2$ (69% of enol);[34] $MeCOCH(COOEt)\overset{+}{P}Ph_3X^-$ (100% of enol). In the latter case, total enolisation is observed not only in solutions but also in the crystalline state[33,35].

According to Issleib and Lindner[36], the triphenylphosphonium group is at the head of the series of substituents Y arranged in order of their decreasing acidifying influence on the CH acidity of the phosphonium salts $Ph_3\overset{+}{P}CH_2YX^-$:

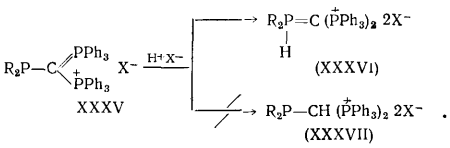
$$Ph_3P^+ > PhCO > MeCO > CN > COOR > P(S)R_2 \approx P(O)R_2 > PPh_2 > Ph > H > Me\ .$$

In terms of the Hammett constants, the phosphonium groups are also among those with the most pronounced electron-accepting properties ($\sigma > 0.9$).

The authors of this review have made a detailed study of the protonation of substances of the type of compound (XXXII). The substituents at the tervalent phosphorus atom were varied in such a way that their σ^{ph} constants, characterising the acidifying effect of the groups at the phosphorus atom, gradually diminished[37]:

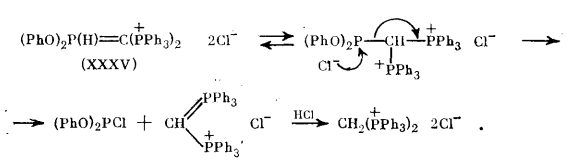
R	PhO	EtO	Ph	Me	Et	Bu
σ^{ph}	−0.06	−0.21	−0.59	−0.96	−1.10	−1.22

Phosphino-substituted phosphoranylidenephosphonium salts (XXXV) were protonated in various solvents by different acids (in an atmosphere of dry argon). According to $^{31}P\{^1H\}$ NMR data, only protonated PH forms (XXXVI) are formed in all cases[38]:



XXXV (XXXVI) (XXXVII)

These forms are characterised by a high constant J_{PH} = 450–700 Hz and other features (Table 2). All attempts to detect the CH form (XXXVII) in solution were unsuccessful. However, evidence has been adduced in support of the decomposition of compound (XXXV) with R = PhO under the influence of acids via the CH form[39]:



X-Ray diffraction analysis of compound (XXXVI, R = Bu, X = Br)[40] confirmed its structure (Fig. 1). The central carbon atom C(1) in this compound is markedly sp^2-hybridised (the sum of the angles between the bonds involving the carbon atom and the three phosphorus atoms is 359 °C), while the P(3) phosphorus atom is sp^3-hybridised, which undoubtedly indicates a PH structure.

Table 2. Parameters of the ^{31}P NMR spectra of the products (XXXVI) obtained by the protonation of the salts $R_2P^{\alpha}C[=P^{\beta}Ph_3]P^+Ph_3X^-$ (XXXV) by trifluoroacetic acid or hydrogen chloride in $CHCl_3$ or CH_2Cl_2.[38]

R	Solvent, reagent	δP^{α} (t), p.p.m.	δP^{β}(d), p.p.m.	J_{PP}, Hz	J_{PH}, Hz
Ph	CF_3COOH	8.6	25.3	22	500
Me	CF_3COOH	−1.1	25.8	19	525
Me	CH_2Cl_2, HCl	−2.1	24.5	21	525
Et	$CHCl_3$, HCl	22.5	24.7	21	460
Bu	CF_3COOH	17.2	25.4	17	450
Bu	$CHCl_3$, HCl	14.6	23.0	19	460
PhO	CH_2Cl_2, HCl *	51.5	21.5	29	698

* At −70 °C.

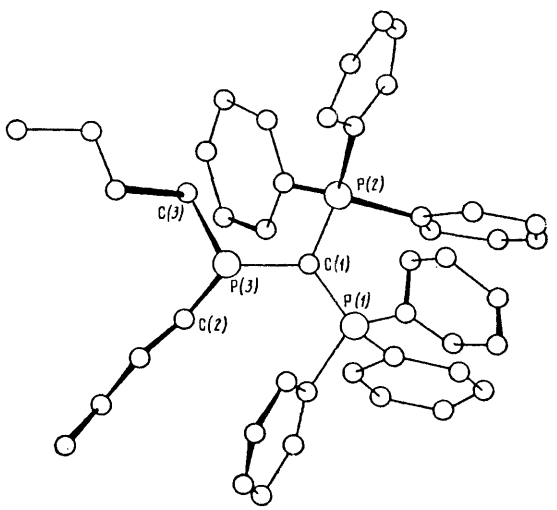


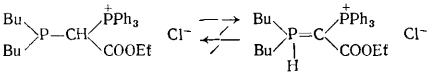
Figure 1. The structure of the $Bu_2P(H)=C(\overset{+}{P}Ph_3)_2$ cation. Angles: P(1)C(1)P(2) = 118°; P(2)C(1)P(3) = 117°; P(1)C(1)P(3) = 124°; C(1)P(3)C(2) = 115°; C(1)P(3)C(3) = 114°; C(2)P(3)C(3) = 109°; distances: C(1)P(1) = 1.69 Å; C(1)P(2) = 1.88 Å; C(1)P(3) = 1.72 Å.[40]

Certain PH ylides have been recently obtained by Kolodyazhnyi[41]. These are derivatives of phosphino-substituted malonic ester $RR'P(H)=C(COOMe)_2$, in which R = t-butyl and R′ are branched alkyl groups (for further details, see below).

(c) The phosphorus–carbon tautomeric diads. The starting point in the search for tautomeric phosphorus–carbon diad systems consisted of a comparison of the results of the

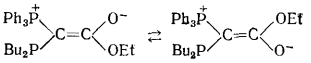
protonation of phosphino-substituted phosphoranylidenephosphonium salts (XXXV) and phosphino-substituted malonic esters (XXVIII). In the former case only the PH ylide (XXXVI) was found while in the latter only the CH acid (XXVIII) was discovered. In the former systems the CH acidity [of the (XXXVII) form] proved to be too high and the equilibrium was fully displaced towards the PH form (XXXVI). On the other hand, in systems of the second type the acidity of the CH form proved to be too small and the position of the phosphorus–carbon equilibrium was fully displaced towards this form. It was naturally postulated that, when one phosphonium and one ethoxycarbonyl group are introduced at the central carbon atom instead of two phosphonium groups [as in compound (XXXVII)] or two ethoxycarbonyl groups [as in compound (XXVIII)], one would expect the acidities of the two forms to be similar and that a true tautomeric equilibrium would result[42,43]. Naturally the equilibrium position should depend on the character of the substituents at the phosphorus atom because they also influence the relative acidities of the two forms.

The dibutylphosphinoethoxycarbonylmethylphosphonium salt (XXXVIII)



(XXXVIIIa) (XXXVIIIb)

proved to be a pure PH acid (XXXVIIIb). This ylide exists as a mixture of two conformers of the PH form, as shown by the doubling of the number of signals in the $^{31}P\{^1H\}$ NMR spectrum at a low temperature (Table 3). This kind of conformational isomerism of cisoid and transoid forms is already well known for unsubstituted alkoxycarbonylphosphinomethylenes[44,45]. It is also characteristic of the initial dibutylphosphinoethoxycarbonylmethylenephosphorane (XXXIX):



(XXXIX)

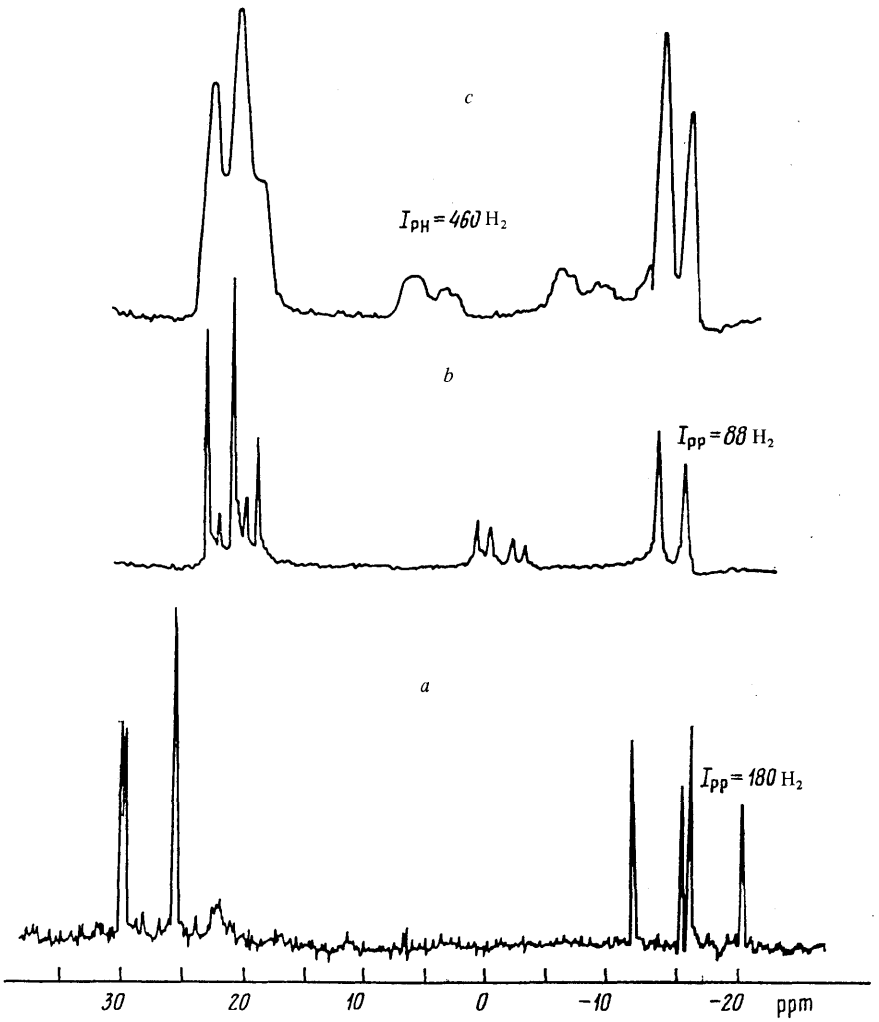
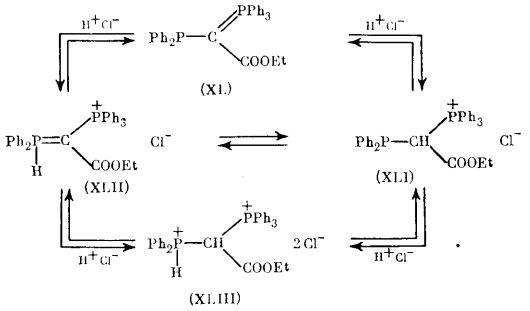


Figure 2. ^{31}P NMR spectrum of a solution of the $Ph_2PCH(\overset{+}{P}Ph_3)COOEt\ Cl^- \rightleftharpoons Ph_2P(H)=C(\overset{+}{P}Ph_3)COOEt\ Cl^-$ tautomeric mixture in CH_2Cl_2 at −80 °C: *a*) $^{31}P\{^1H\}$ NMR spectrum of the initial ylide; *b*) $^{31}P\{^1H\}$ NMR spectrum of the tautomeric mixture; *c*) ^{31}P NMR spectrum of the tautomeric mixture[42].

Consequently the acidity of the CH form again exceeded that of the PH form. However, the replacement of the two butyl groups at the tervalent phosphorus atom by two phenyl groups greatly increased the PH acidity and the protonated diphenylphosphinoethoxycarbonylmethylenetriphenylphosphorane proved to be a tautomeric substance. Its solution contains both the CH form (XLI) and the corresponding PH form (XLII). Overall, the acid-base and tautomeric transitions in this instance can be represented by the following scheme[40,42,43]:



The $^{31}P\{^1H\}$ NMR spectrum of the tautomeric mixture at −90 °C with the ratio ylide (XL) : HCl = 1 : 2 is fairly complex (see Table 3). It contains the signals of two conformers of the PH form (XLII) (four doublets at 21.4, 23.7, 0.5, and −2.4 p.p.m) and two doublet signals of the CH form (XLI) at −15.6 and 25.1 p.p.m. with J_{PP} = 88 Hz (Fig. 2).

Table 3. Parameters of the ^{31}P NMR spectra of the phosphinoylides $R_2P^{\alpha}C[=P^{\beta}Ph_3]COOEt$ and the products of their protonation with HCl.[40,42,43]

R	Compound	Solvent, reagent	t, °C	$\delta P\alpha$ (d) p.p.m.	$\delta P\beta$ (d), p.p.m.	J_{PP}, Hz	J_{PH}, Hz
Bu	(XXXIX), ylide	CH_2Cl_2	20	−33.1	27.3	156	—
Bu	(XXXIX), ylide	CH_2Cl_2	−80	−31.5	27.3	154	—
				−38.3	27.3	161	—
Bu	(XXXVIIIb), PH form	CH_2Cl_2, HCl	−80	5.7	19.4	32	460
				2.4	21.8	32	480
Ph	(XL), ylide	$CHCl_3$	20	−14.9	28.1	180	—
Ph	(XL), ylide	CH_2Cl_2	−70	−13.5	28.0	178	—
				−19.2	28.1	183	—
Ph	(XLII), PH form	CH_2Cl_2, HCl	−90	0.5	21.4	41.5	460
				−2.4	23.7	39.8	460
Ph	(XLI), CH form	CH_2Cl_2, HCl	−90	−15.6	25.1	88	—

The validity of the assignment of the signals with δ = 0.5 and −2.4 p.p.m. to the conformers of the PH form is indicated by the high splitting constant J_{PH} = 460 Hz observed when the suppression is removed. On the other hand, the assignment of signals with the splitting constant J_{PP} = 88 Hz to the CH form was confirmed by the study of the ^{13}C NMR spectrum of a solution of the pure CH form in a 10 : 1 CH_2Cl_2–CH_3CN mixture at −80 °C (see below). Under these conditions, the signal of the α-carbon atom with the chemical shift δ = 38.1 p.p.m. has a triple doublet splitting. The doublet splitting with J_{CH} = 139.7 Hz is due to the interaction with the added proton (CH group), the second doublet splitting with J_{CP} = 57.0 Hz is caused by the interaction with the phosphonium atom, and the third doublet splitting with the constant J_{CP} = 48.0 Hz is associated with the spin-spin coupling with the tervalent phosphorus atom. Only in the case of the CH form is it possible to observe such triple doublet splitting of the signal in the ^{13}C NMR spectrum.

With increase in the HCl concentration, there is initially a change in the relative signal intensities, indicating an increase of the concentration of the CH form (XLI), after which (in the presence of a large excess of HCl) the spectrum becomes greatly simplified and is converted into the spectrum of the doubly protonated form (XLIII) with a sharply reduced J_{PP} (to 7.3 Hz).

The position of the tautomeric equilibrium (XLII) ⇌ (XLI) depends on many factors. An increase of temperature favours the CH form (XLI). It has been found from the dependence of $\lg K_T$ on $1/T$ (Fig. 3) that the PH form is slightly more stable (by 0.65 kcal mol^{-1}) under these conditions than the CH form (Table 4); apparently an increase of the HCl concentration also acts like the increase of the polarity of the medium. It is of interest to note that only the CH form is present in the 10 : 1 CH_2Cl_2–CH_3CN mixture in the presence of two moles of HCl at −80 °C (see above).

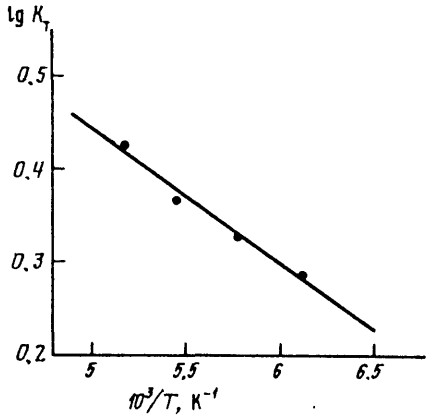


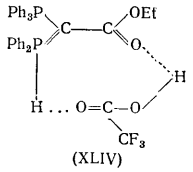
Figure 3. Temperature variation of the $Ph_2PCH(\overset{+}{P}Ph_3)_3COOEt\ Cl^- \rightleftharpoons Ph_2P(H)=C(\overset{+}{P}Ph_3)COOEt\ Cl^-$ tautomeric equilibrium constants.

Table 4. Dependence of the position of the tautomeric equilibrium between the PH and CH forms [(XLII) ⇌ (XLI)] on the solvent composition [−80 °C, (XL) : HCl = 1 : 2].[40]

Content of CH_3CN in CH_2Cl_2, %	Content of PH form, %	Equilibrium constant K_T = [PH]/[CH]
0	30	0.43
3.20	14	0.16
6.25	5	0.05
9.10	0	0

One PH form is observed in trifluoroacetic acid or in CH_2Cl_2 with an excess of CF_3COOH. It may be that trifluoroacetic acid stabilises the PH form, forming long hydrogen

bonds with the latter [see formula (XLIV)]:



(XLIV)

The next example of the phosphorus-carbon diad tautomerism was discovered somewhat later by Kolodyazhnyi[41]. It was noted above that the diphenylphosphino-derivatives of malonic ester (XXVIII) consist of 100% CH forms[27,28]. This applies also to the previously investigated derivatives of tervalent phosphorus (XXVIII) containing lower unbranched alkyl groups, the phenyl group, or an alkoxy-group at the phosphorus atom.

Continuing his persistent search for PH ylides, Kolodyazhnyi[41] investigated the analogous derivatives (XLV) and (XLVI) containing branched alkyl groups at the phosphorus atom, namely the t-butyl, s-butyl, isobutyl, and isopropyl groups, i.e. those characterised by the greatest $\pm I$ effect:

$$\underset{\text{(XLV)}}{RR'P{-}CH(COOMe)_2} \rightleftarrows \underset{\text{(XLVI)}}{RR'P(H){=}C(COOMe)_2}\ .$$

The study showed that in the crystalline state these substances are PH ylides (XLVI), where R = t-Bu, R' = iso-Pr, s-Bu, or Me_3SiCH_2. Their infrared spectra show only the absorption bands of the PH ylide. On fusion or dissolution of compounds (XLVI), bands appear in their infrared spectra in the region of 1700–1800 cm^{-1}, which are characteristic of saturated carboxylic acid esters and indicate the partial conversion of compound (XLVI) into (XLV). The ^{31}P NMR spectra also indicate the simultaneous presence of the PH ylide form (doublet with the constant J_{PH} = 435–440 Hz) and the CH form (singlet, δ = 12.5–35.5 p.p.m., depending on the nature of the alkyl groups). Integration of the signals in the NMR spectra and of the infrared bands made it possible to determine the constants K_T for the tautomeric equilibrium (XLVI)⇌(XLV). It was found that they depend not only on the character of the substituting groups at the tervalent phosphorus atom but also on the temperature and the nature of the solvent. It was observed that an increase of temperature shifts the equilibrium towards the CH form and the dependence of $\lg K_T$ on $1/T$ showed that the CH form is less favoured by energy factors (approximately to the extent of 2 kcal mol^{-1}). The influence of the solvent on the position of the tautomeric equilibrium is not very clear in this instance: the following series of solvents increasing the content of the PH form has been published[41]: C_6H_{14} < THF < C_6H_6 < CH_2Cl_2 < $CHCl_3$.

As regards the influence of the substituents at the phosphorus atom (Table 5), the author[41] assumes that the bulk of the substituting group plays a decisive role. He believes that bulky groups favour the formation of the planar system $HP{-}C^{-}(COOMe)_2$, which reduces the steric hindrance in structures (XLV) as a consequence of the interaction of the COOMe groups with the bulky substituents at the tervalent phosphorus atom. However, it is difficult to agree with his explanation. If one uses the data presented in Table 5, it can be readily seen that the (XLV)⇌(XLVI) tautomeric equilibrium constants obey satisfactorily the Hammett equation when one employs the constants σ_I^{Ph} characterising the influence of the groups attached to the phosphorus atom. The following values were then obtained for a solution in $CHCl_3$†: $\lg K_T^0 = -6.55$, $\rho = -2.351$, and $r = 0.979$ for $s = 0.14$ and $s_\rho = 0.25$ (Fig.4). On the other hand, if an attempt is made to set up a correlation between $\lg K_T$ and the Taft steric constants E_S, then the points cover the entire field of the graph and no reasonable relation can be seen.

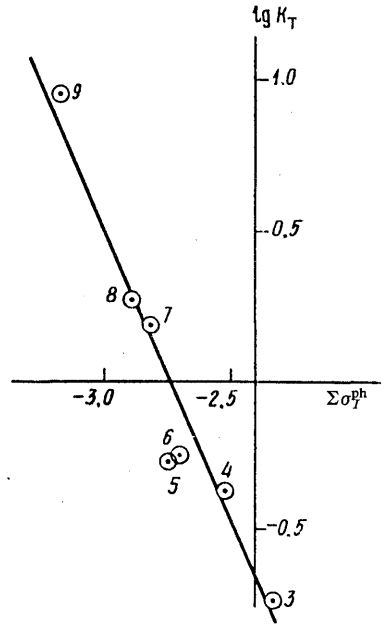


Figure 4. Dependence of the $RR'PCH(COOMe)_2 \rightleftarrows RR'P(H) = C(COOMe)_2$ tautomeric equilibrium constants on $\sum \sigma_I^{ph}$ for the groups R and R' (the numbers of the points correspond to the number of the compounds in Table 5).

Table 5. The $RR'PCH(COOMe)_2 \rightleftarrows RR'P(H) = C(COOMe)_2$ tautomeric equilibrium (20 °C, $CHCl_3$).[41]

№	R	R'	$\Sigma\sigma_I^{ph}$	Content of PH form, %	K_T
1	t-Bu	Me_2N	−1.28	0	0
2	t-Bu	Et_2N	−1.73	0	0
3	Bu	Bu	−2.44	15	0.18
4	iso-Pr	iso-Pr	−2.60	30	0.43
5	t-Bu	iso-Bu	−2.85	33	0.49
6	t-Bu	n-Bu	−2.79	35	0.54
7	t-Bu	iso-Pr	−2.85	61	1.56
8	t-Bu	s-Bu	−2.91	65	1.86
9	t-Bu	Me_3SiCH_2	−3.15	90	9.00

The parameters of the above correlation permit also other interesting conclusions. It is possible to calculate the position of the tautomeric equilibrium in the same systems but with other substituents at the phosphorus atom for which no

† The calculation was based on six points: 3,4, 6, 7, 8, and 9 (Table 5).

tautomeric relations had been observed earlier[27]. Such a calculation shows that in $CHCl_3$ the Et_2P group ($\sum\sigma^{ph} = -2.2$) should lead to an approximately 4% content of the PH form, the Ph_2P groups should give rise to less than 10^{-4}%, and the $(EtO)_2P$ group should produce an even smaller amount. This also applies to compounds with dialkylamino-groups: the content of the PH form should be ~0.3% for R = t-Bu and R′ = Et_2N and ~0.08% for R = t-Bu and R′ = Me_2N. Naturally the PH forms were not detected in solutions of these substances.

Thus the position of the diad prototropic equilibrium between the PH and CH forms in the series of phosphino-derivatives of malonic ester as well as the other instances investigated depends on the polar influences of the substituents which determine the acid strength of the CH and PH forms and thus the position of the tautomeric equilibrium.

In order to infer reliably the influence of the substituents at the α-carbon atom and at the phosphorus atom on the position of the proton, a quantitative approach to the estimation of the acidifying effect of these substituents is necessary. As mentioned above, one can use the constants σ_I^{ph} for the substituents at the phosphorus atom. The application of the Issleib and Lindner[36] series given above to the substituents at a carbon atom makes it possible to estimate the acidifying capacity of these groups only qualitatively. The authors of this review therefore recently developed a system of σ_C^- constants whereby one can carry out a correlation analysis of the dissociation constants of CH acids with a satisfactory accuracy[46]. This correlation system is naturally based on the Hammett σ^- constants and it was found that the numerical value of the constant depends on the number of substituents at the central carbon atom of the CH acid. Since there can be one, two, or three such substituents, each substituting group was characterised by three constants: $\sigma^-_{CH_3}$ for a primary carbon atom, $\sigma^-_{CH_2}$ for a secondary carbon atom, and σ^-_{CH} for a tertiary carbon atom#. The use of these constants made it possible to obtain excellent correlations of the pK_a for CH acids using the Hammett equation§. Thus it became possible to infer the acidifying influence of substituents on the strength of CH acids from the sum of the substituent constant σ_C^-¶. Table 6 lists certain constants σ_C^- characterising the acidifying influence of the groups at the carbon atom.

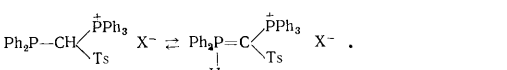
In conformity with the foregoing, for the above three types of compounds containing two identical groups at the phosphorus atom (phenyl or butyl), the sum $\sum\sigma^-_{CH}$ is 1.24 for the first type [compound (XXVIII)], 1.68 for the second type [compounds (XXXVIII) and (XLI)], and 2.16 for the third type [compound (XXXIII)]. The acidifying effect when the sum of the constants is 1.24 is insufficient for the transfer of a proton from C to P (it is insufficient for two phenyl groups at the phosphorus atom and almost insufficient for two butyl groups). The sum $\sum\sigma^-_{CH} = 1.68$ for two butyl groups gives rise to the PH structure (the CH acidity is then too great) and in the presence of two phenyl groups the CH⇌PH tautomeric system is produced. Finally, for the sum $\sum\sigma^-_{CH} = 2.16$, the proton is firmly held at the phosphorus atom (the CH acidity is too great).

Table 6. The $\sigma^-_{CH_2}$ and σ^-_{CH} constants characterising the acidifying influence of the groups on the CH acidity[46].

Group	$\sigma^-_{CH_2}$	σ^-_{CH}	Group	$\sigma^-_{CH_2}$	σ^-_{CH}
Me	0.12	0.13	COMe	0.88	0.66
Ph	0.365	0.26	COPh	0.98	0.78
p-$NO_2C_6H_4$	0.74	0.52	$PhSO_2$	0.77	0.71
COOMe	0.72	0.62	p-$MeC_6H_4SO_2$	—	0.70
COOEt	0.725	0.60	NO_2	1.26	1.12
CN	0.80	0.75	$Ph_3\overset{+}{P}$	1.22	1.08

One must bear in mind that the constants ρ of the correlation between the CH acidity and σ_C^- are fairly large (usually 10–25), which means that small changes in $\sum\sigma_C^-$ can give rise to large changes in the CH acidity.

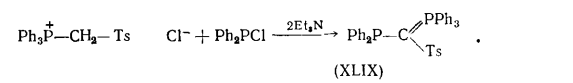
Next, studies were made on the (XLVII)⇌(XLVIII) systems with tosyl groups[47]:



(XLVII) (XLVIII)

It was assumed that investigation would reveal either a tautomeric or an ylide system (XLVIII), since the sum of the constants $\sum\sigma^-_{CH} = 1.78$ is characterisitc of the form (XLVII), exceeding the corresponding sum (1.68) for the (XLI) ⇌ (XLII) tautomeric system (investigated previously) with an ethoxycarbonyl group at the α-carbon atom; however, it is significantly smaller than $\sum\sigma^-_{CH} = 2.16$ for the PH ylide diphosphonium structure (XXXVI).

The necessary compounds were synthesised in accordance with the scheme[47]



(XLIX)

Next, the ylide (XLIX) was protonated:



On treatment with trifluoroacetic acid or HCl in a slight excess, only the PH form (XLVIII) is observed. The $^{31}P\{^1H\}$ NMR spectrum (in a 3:1 $CHCl_3$–CH_2Cl_2 mixture) shows a typical AB quartet with $\delta_1 = -2.1$ p.p.m. and $\delta_2 = 19.8$ p.p.m. (with the constant $J_{PP} = 37$ Hz). When the suppression of the spin-spin coupling between the phosphorus and the protons is removed, the signal with $\delta = -2.1$ p.p.m. is converted into a characteristic doublet with $J_{PH} = 490$ Hz, which undoubtedly indicates the presence of the PH bond. Only the PH form

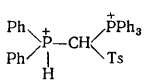
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A single reaction series can include terms with $\sigma^-_{CH_3}$, $\sigma^-_{CH_2}$, and σ^-_{CH}.

§ For the limitations of this correlation system, see Kabachnik and Mastryukova[45].

¶ Naturally, in estimating the CH acidity from the influence of the acidifying group, account must be taken also of the influence of the phosphorus-containing group. However, for many of these the values of σ_C^- are unknown and only comparisons for constant substituents at the phosphorus atom are therefore strictly legitimate.

(XLVIII) was observed also under other protonation conditions. Treatment with a large excess of HCl at −95 °C leads to the doubly protonated dication (L):

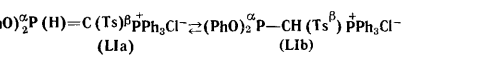


(L)

The positions of the signals in the ^{31}P NMR spectrum then change only slightly, but there is a sharp decrease of the spin-spin coupling constant: $J_{PP} = 6$ Hz (compared with 37 Hz for the monoprotonated compound). The dication is stable only at a low temperature and, on heating, the NMR spectrum of the dication is converted into that of the monocation (XLVIII).

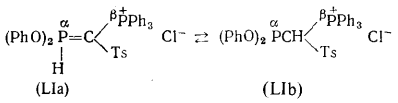
Thus the CH acidity induced by the presence of the triphenylphosphonium and tosyl groups proved to be too high and the proton migrated to the diphenylphosphino-group. However, when the phenyl groups at the tervalent phosphorus atom were replaced by phenoxy-groups, whose acidifying effect is incomparably greater ($\sigma_I^{ph} = +0.27$ for Ph and +2.83 for PhO), the PH acidity increased and an experimentally observable equilibrium between the two forms of (LI) again appeared (Table 7).

Table 7. ^{31}P NMR spectroscopic data (−80 °C, CH_2Cl_2) for the tautomeric system.



(LIa) (LIb)

Substance	$\delta_{P\alpha}$ (d), p.p.m.	$\delta_{P\beta}$ (d), p.p.m.	J_{PP}, Hz	J_{PH}, Hz
Initial ylide	173.2	16.4	14.6	—
PH form (LIa)	49.1	16.8	29.3	697
CH form (LIb)	149.5	20.0	7.4	—

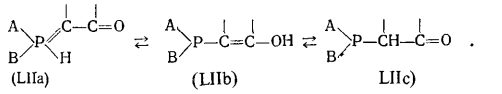


(LIa) (LIb)

The results obtained in the study of the diad phosphorus–carbon tautomerism can be summarised as follows. Table 8 lists the substituents X and Y at the carbon atom in order of decreasing acidifying capacity expressed by the sum of the constants σ_{CH}^-. The substituents at the phosphorus atom (on the left) are arranged from above downwards in order of increasing sum of the constants σ_I^{ph}, i.e. of increasing acidifying influence. Thus Table 8 lists on the left hand side the strongest CH acids and at the bottom the strongest PH acids. The upper left-hand corner represents the region of PH forms; here the carbon atom readily gives up a proton and the phosphorus atom readily accepts it. The lower right-hand corner represents the region of the CH form (the phosphorus atom readily gives up a proton and the carbon atom readily accepts it). The region of compounds with a distinct tautomeric equilibrium lies along the diagonal of Table 8. In this region the strengths of the CH and PH acids are similar and both forms are observed in the equilibrium.

3. The Tetrad Phosphorus–Carbon Tautomerism (A Vinylogue of the Diad Tautomerism)

As mentioned above, tetrad systems can be derived as vinylogues of the diad systems. The simplest examples of such tetrad tautomerism of compounds (LII) can be represented as a combination of the phosphorus-carbon diad and keto-enol tautomerisms:



(LIIa) (LIIb) LIIc)

The two tautomeric forms produced when the proton is fixed at the phosphorus atom [structure (LIIa)] and oxygen atom [structure (LIIb)] must be supplemented by the third form (LIIc), which can be produced when the proton is fixed at the α-carbon atom (as in diad tautomerism).

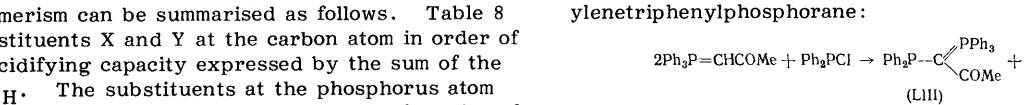
Table 8. The influence of substituents on the position of the tautomeric equilibrium*.

A, B	$\Sigma\sigma_I^{ph}$	X, Y; $\Sigma\sigma_{CH}^-$				
		$^+PPh_3$, $^+PPh_3$; 2,16	$^+PPh_3$, Ts; 1,78	$^+PPh_3$, COOEt; 1,68	COOMe, COOMe; 1,24	$^+PPh_3$, H; 1,22
t-Bu, s-Bu	−2.91	(PH)	(PH)	(PH)	CH⇄PH	(CH⇄PH)
Bu, Bu	−2.44	PH	PH	PH	CH⇄PH CH	(CH)
Ph, Ph	+0.54	PH	PH	CH⇄PH	CH	CH
PhO, PhO	+5.66	PH	CH⇄PH	(CH)	CH	CH

* Data expected on theoretical grounds are enclosed in brackets.

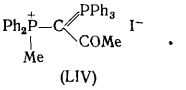
Diphenylphosphinoacetaldehyde (XXXI) (see above) could be regarded as a tautomeric substance of this kind if the existence of the PH ylide form could be demonstrated.

The products of the protonation of the diphenylphosphino-derivative of acetylmethylenetriphenylphosphorane (LIII) were investigated as the first tetrad system[48]. The phosphorane was obtained by the reaction of Ph_2PCl with acetylmethylenetriphenylphosphorane:



(LIII)

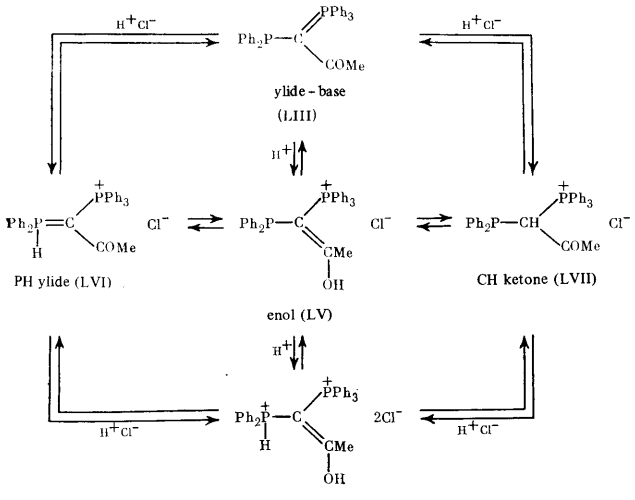
We may note that the spin-spin coupling constant in the $^{31}P\{^1H\}$ NMR spectrum of the ylide (LIII) is $J_{PP} = 184$ Hz (in CH_2Cl_2 at 20 °C). When the ylide (LIII) is methylated at the tervalent phosphorus atom, the product is the ylide (LIV) whose spectrum shows an AB quartet at 16.9 p.p.m. and 18 p.p.m. with $J_{PP} = 46$ Hz:



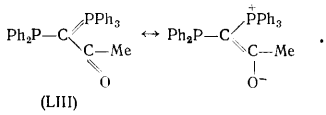
(LIV)

After extensive cooling, the multiplicity of the spectrum was found to be doubled owing to conformational isomerism.

The study of the prototropic transformations on protonation of the ylide (LIII) led to the following pattern of the acid–base and tautomeric transitions[48]:



The addition of a solution of HCl in CH_2Cl_2 to compound (LIII) at −80 °C in an argon atmosphere leads initially (in the presence of a small amount of the acid and immediately after its addition) to the enol form (LV). Its $^{31}P\{^1H\}$ NMR spectrum ($\delta_1 = -20.4$ p.p.m., $\delta_2 = 24.6$ p.p.m., and $J_{PP} = 144$ Hz) differs little from the spectrum of the ylide-base (LIII) ($\delta_1 = -18.8$ p.p.m., $\delta_2 = 25.2$ p.p.m., $J_{PP} = 184$ Hz). This is quite natural, because the electronic structure of the molecule of the initial ylide-base (LIII) differs little from that of the *O*-protonated form (LV):


(LIII)

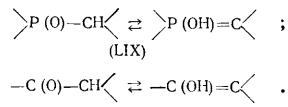
With increase of the HCl content in the reaction mixture (to 2 and 3 moles of HCl), six doublet signals with three splitting constants, equal in pairs, appear immediately. Two doublet signals are identical with those in the spectrum of the enol (LV) and therefore indicate its presence in the mixture; the other two doublets ($\delta = 2.6$ and 18.5 p.p.m., $J_{PP} = 51$ Hz) correspond to the PH form, since, after the removal of suppression the doublet at −2.6 p.p.m. splits into further two doublets with the constant $J_{PH} = 500$ Hz; furthermore, the splitting constant J_{PP} is in this case close to the constant found for the methylated derivative (LIV); the remaining two doublets refer to the CH form, which has been confirmed by repeated cross comparisons.

On further increase of the HCl concentration, the spectrum simplifies both as regards the positions of the signals (four doublets) and the character of J_{PP} and J_{PH}—it can be easily assigned to the dication (LVIII).

III. THE TRIAD PHOSPHORUS–CARBON TAUTOMERISM

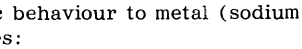
1. The Phosphoryl–Hydroxy-ylide Tautomerism

The possibility of the phosphoryl–hydroxy-ylide tautomerism (LIX), which is analogous to the keto–enol tautomerism (LX), was first suggested by Arbuzov and Razumov in 1929 in connection with the discussion of the alkylation reactions of diethoxyphosphorylacetic acid ester[49]:


(LIX)

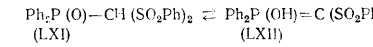
(LX)

In conformity with the views adopted at the time, they attributed a tautomeric behaviour to metal (sodium) derivatives of these substances:



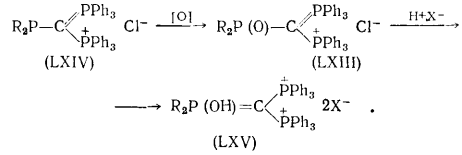
Arbuzov returned to this question in 1934 [50] and in 1947 [51], but naturally no evidence, apart from the dual reactivity of the alkali metal derivatives, was available at the time for the phosphoryl-hydroxy-ylide tautomerism.

A letter to the Editors by Kolodyazhnyi was published in 1976 [52] in which the tautomerism of phosphorylated di(benzenesulphonyl)methane (LXI)⇌(LXII) was reported:


(LXI) (LXII)

On acidification with hydrochloric acid, the sodium salt of compound (LXII) is converted into the free acid in the hydroxy-ylide form (LXII), whose structure was clearly confirmed by infrared spectroscopy. The acid crystallises from solution in benzene as the phosphoryl CH form (LXI) with an altered infrared spectrum. When the CH form is dissolved in $CHCl_3$, both forms are produced and their ratio varies with increase of temperature in favour of the phosphoryl CH form.

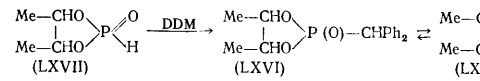
The authors of the present review and their co-workers[39] investigated simultaneously the protonation of phosphoryl-substituted phosphoranylidenephosphonium salts (LXIII) obtained by oxidising the corresponding phosphino-substituted salts (LXIV) with potassium permanganate; the formation of the hydroxy-ylide forms (LXV) was then observed:


(LXIV) (LXIII)

(LXV)

When fluorosulphonic acid is protonated, the signals in the $^{31}P\{^1H\}$ NMR spectrum referring to the triphenylphosphonium phosphorus atoms do not undergo any significant changes, while the signals due to the phosphorus in the phosphoryl group undergo a downfield shift of 12.3 p.p.m. The protonation of phosphoryl groups is known to be accompanied as a rule by a similar change in the position of their NMR signal[53, 54].

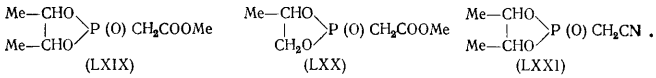
The next communication about the phosphoryl–hydroxy-ylide transitions was by Kazan chemists[55]. The authors reported that the cyclic diphenylmethylphosphonate (LXVI), obtained from the corresponding cyclic phosphite (LXVII) by reaction with diphenyldiazomethane (DDM) and subsequent oxidation, consists of the (LXVI)⇌(LXVIII) tautomeric mixture:


(LXVII) (LXVI) (LXVIII)

Unfortunately the authors did not present experimental data justifying this interesting and unexpected conclusion.

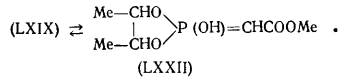
The phosphoryl–hydroxy-ylide tautomerism naturally obeys the same general laws which govern prototropic tautomerism in general. The conversion of a phosphoryl compound with an α-CH group into a hydroxy-ylide requires a powerful acidifying influence by the substituents at the central carbon atom which would equalise the strength of the CH acid with that of the P–OH acid, which is the hydroxy-ylide form. Here one must naturally take into account the influence of all the substituents—both at the carbon atom and at the phosphorus atom. From this standpoint, the butylenedioxyphosphinyl group in the CH acid (LXVI) should exert a powerful acidifying influence, while the influence of the phenyl group is moderately strong or even weak. The hydroxy-ylide form (LXVIII) contains at the phosphorus atom the butylenedioxy-group, which is a powerful electron acceptor. This form should be a fairly strong acid. Thus it would seem that one should expect the dominant form to be the phosphoryl CH form (LXVI), which is a weaker acid. On the other hand, if proton transfer nevertheless takes place despite the above reasoning, then one must accept that the influence of the butylenedioxy-group affects the CH acidity (LXVI) form to a much greater extent (increasing it sharply) than the OH acidity of the (LXVIII) form, which is enhanced to a lesser extent (a hypothesis which is in general unlikely). Further studies confirming the presence of the ylide form (LXVIII) are evidently necessary.

Other relations may be expected (and such are observed in reality) for the cyclic ethoxycarbonylmethylphosphonates (LXIX) and (LXX) or the corresponding nitriles (LXXI):



(LXIX) (LXX) (LXXI)

Here the methylene group has an environment analogous to that in the malonic ester and the manifestation of an appreciable CH acidity may be expected even in the absence of the dioxaphospholan ring; if the CH acidity becomes equal to or even approaches the OH acidity of the hydroxy-ylide form (LXXII) under the influence of the butylenedioxyphosphoryl group, then one can postulate the occurrence of the phosphoryl-hydroxy-ylide tautomerism (LXIX)⇌(LXXII), which is apparently actually observed[56]:

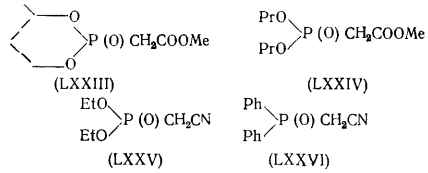


(LXXII)

Indeed the ^{1}H NMR spectrum of compound (LXIX) in CCl_4 contains the doublet signal of the P–CH_2 protons at 3.2 p.p.m. with the splitting constant $J = 21$ Hz, the doublet signal of the proton in the P=CH group at 2.9 p.p.m. with the same splitting constant, and the broad signal of the OH proton at 6.8 p.p.m.†

The ^{31}P NMR spectra also show the signals of the phosphoryl and hydroxy-ylide forms. In aqueous alcohol the equilibrium is fully displaced towards the ylide. The infrared spectrum confirms the ^{1}H NMR data. Analogous behaviour has been observed also for compounds (LXX) and (LXXI).

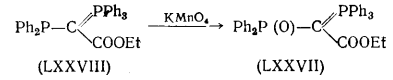
Five-membered cyclic methoxycarbonylmethylphosphonates proved to be strong acids ($pK_a = 2.71$–2.79 in 50% alcohol). The derivative of the six-membered dioxaphosphorinane (LXXIII), which has an analogous structure, is a weaker acid ($pK_a = 9.64$ and 11.05 for the two geometrical isomers), while the corresponding acyclic derivative (LXXIV) is weaker still ($pK_a = 12.10$). These substances are not tautomeric. The cyanides (LXXV) and (LXXVI) are likewise not tautomeric and their acid strengths are low ($pK_a = 11.58$ and 11.09 respectively):



(LXXIII) (LXXIV) (LXXV) (LXXVI)

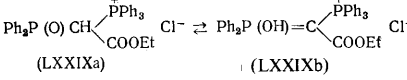
Thus in the presence of the usual acyclic substituents at the phosphoryl group, the acidifying effect of the methoxycarbonyl group COOMe ($\sigma^-_{CH} = 0.72$) and the cyano-group ($\sigma^-_{CH_2} = 0.80$) is insufficient to impart to the phosphoryl CH form an acid strength comparable to that of the hydroxy-ylide OH form, which is necessary for tautomeric behaviour. Only in the presence of an adjoining dioxaphospholan ring, as in compounds (LXIX)–(LXXI), is this condition fulfilled and prototropic transitions are observed. Incidentally, the nature of the influence of the dioxaphospholan ring is not clear (see above).

Tautomeric behaviour is to be expected when groups which cause a greater increase in the CH acidity are introduced at the α-carbon atom. This was achieved in a study by one of the present authors and his co-workers[57] after the simultaneous introduction of the triphenylphosphonium ($\sigma^-_{CH} - 1.08$) and ethoxycarbonyl ($\sigma^-_{CH} = 0.60$) groups at the α-carbon atom[57]. The synthesis of ethoxycarbonyldiphenylphosphinylmethylenetriphenylphosphorane (LXXVII) was achieved by oxidising the corresponding ethoxycarbonyldiphenylphosphinophosphorane (LXXVIII):



(LXXVIII) (LXXVII)

The phosphorane (LXXVII) is protonated by HCl with formation in solution of α-phosphorylated phosphonium salts having the CH structre (LXXIXa) and the OH structure (LXXIXb):[57]



(LXXIXa) (LXXIXb)

The salt forms crystals melting at 123–125 °C and containing the pure hydroxy-ylide form (LXXIXb) according to infrared spectroscopic data. The infrared spectrum showed a band at 1660 cm^{-1} due to the conjugated ethoxycarbonyl group (i.e. COOEt at a carbanionic centre) and a broad diffuse band due to the OH group (at 1500–2200 cm^{-1}). On dissolution in chloroform, an additional band appears in the infrared spectrum at 1730 cm^{-1} (non-conjugated ethoxycarbonyl group), which indicates the tautomeric equilibrium (LXXIXa)⇌(LXXIXb).

The ^{1}H NMR spectrum in CH_2Cl_2 contains the signals of both the CH form (LXXIXa) (a triplet at 1.12 p.p.m. and a quartet at 3.55 p.p.m. due to the protons of the exthoxy-group) and the signals of the OH form (LXXIXb) (a triplet at 0.49 p.p.m. and a quartet at 3.49 p.p.m due to the protons of the ethoxy-group; in both cases the spin-spin coupling constant $J_{HH} = 7$ Hz; in addition a broad singlet signal due to the proton of the OH group with $\delta = 10.7$ p.p.m. is observed. Evidently the signal of the CH proton is masked

† New data concerning the acid properties of compounds (LXIX) and (LXXIII) in ethanol have been published recently (O.Larsen and G.Aksnes, Phosphorus and Sulphur, 1983, 15, 219, 229). In contrast to the data quoted by Ovchinnikov et al.[56], compounds (LXIX) and (LXXIII) proved to be weak CH acids with virtually identical strengths (pK_a = 19.90 and 19.95).

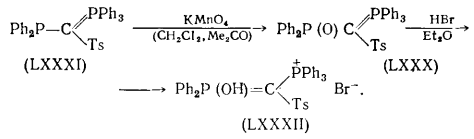
in the case of the CH form by the signals of the aromatic protons). The ratio of the tautomeric forms (LXXIXa) : (LXXIXb) = 1 : 1.8 follows unambiguously from the ratio of the signal intensities[57].

The ^{31}P NMR spectra also confirm the above conclusion. They contain the signals of the two conformers of the OH form and the signals of the CH form:

	δ_1, p.p.m.	δ_2, p.p.m.	J_{PP}, Hz
OH form, conformer 1:	44.5 p.p.m.	19.1	41
OH form, conformer 2:	41.0	20.0	44
CH form	28.1	23.9	7

We may note that the low value of J_{PP} is characteristic of the structures of the type of (LXXIXa). The position of the tautomeric equilibrium in the system investigated depends on the nature of the solvent and the temperature[57].

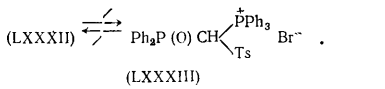
An analogous study has been carried out for compounds similar to those described previously but with the replacement of the ethoxycarbonyl group by the tosyl group[58]. The phosphorane (LXXX) with the tosyl group has been synthesised by oxidising the phosphinophosphorane (LXXXI). Next, the entirely stable hydroxy-ylide (LXXXII) with m.p. 193 to 195 °C was obtained in 92% yield by treatment with HBr in ether:



(LXXXI) (LXXX) (LXXXII)

The structure of the bromide salt of the hydroxy-ylide was investigated by X-ray diffraction (Fig. 5). The central carbon atom C(1) has in this case a planar trigonal structure (its displacement from the plane towards the bromide anion is 0.118 Å) and the (C(1)–P(1) and C(1)–P(2) bonds are shortened (1.751 and 1.764 Å), compared with the single C–P bonds, which shows that they have a bond order of 1.5. The C–SO_2 bond is also somewhat shortened (1.728 Å compared with 1.772 Å for C_{ar}–S), which shows that the sulphur atom adjoins the anionic centre. Finally, there is the O...H...Br hydrogen bond with a length of 3.078 Å. The infrared spectrum of the crystalline ylide confirms its structure.

The situation does not change when the hydroxy-ylide (LXXXII) is dissolved in deuterochloroform. The ^1H NMR spectrum of the solution shows a singlet signal due to the CH_3 proton at 2.27 p.p.m. and a broad singlet signal of the OH proton at 11.2 p.p.m., the ratio of the integral intensities is 3 : 1, which indicates the absence of the CH form of compound (LXXXIII):



(LXXXII) (LXXXIII)

The ^{31}P NMR spectrum shows only two doublet signals at 18.2 p.p.m. and 46.4 p.p.m. with the splitting constant J_{PP} = 29 Hz. Tautomerism of the type (LXXXII) ⇌ (LXXXIII) is not observed[58].

Thus the combination of the triphenylphosphonium and ethoxycarbonyl groups leads to the phosphoryl–hydroxy-ylide tautomerism and the replacement of the ethoxycarbonyl group by the tosyl group shifts the tautomeric equilibrium completely towards the hydroxy-ylide form in both the crystalline state and in solutions. An explanation of this phenomenon should be sought in the stronger acidifying influence of the tosyl group ($\sigma^-_{CH} = 0.70$) compared with the ethoxycarbonyl group ($\sigma^-_{CH} = 0.60$) on the CH acidity. The difference of 0.10 of a unit between the values of $\sum\sigma^-_{CH}$ combined with the steep slope of the relation between the CH acidity and $\sum\sigma^-_{CH}$ naturally increase sharply the CH acidity of the (LXXXIII) form and thus fully displace the equilibrium in the direction of the (LXXXII) form.

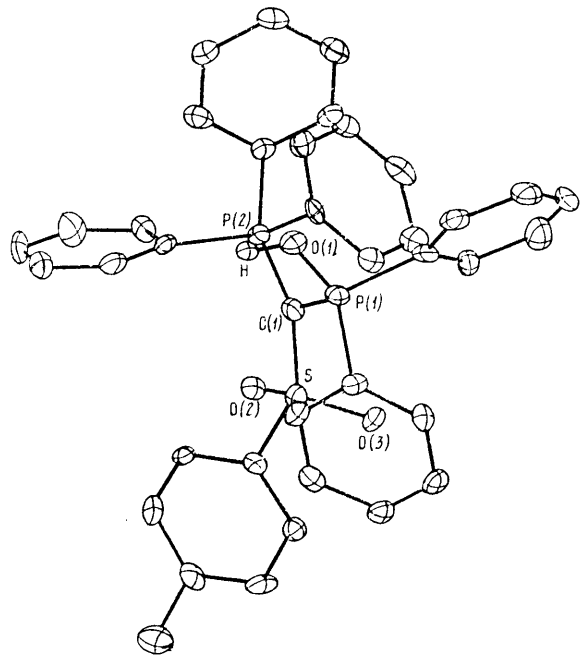


Figure 5. The structure of the cation of the bromide salt $Ph_2P(OH)=C(\overset{+}{P}Ph_3)Ts\ Br^-$; angles: P(1)C(1)P(2) = 122°; P(1)C(1)S = 121°; P(2)C(1)S = 115°.[58]

As shown above, a single alkoxycarbonyl group ($\sigma^-_{CH_2} = 0.72$) at the central carbon atom is insufficient for the tautomeric transfer of a proton to the oxygen atom of the phosphoryl group; the combination of the alkoxycarbonyl group with the triphenylphosphonium group ($\sum\sigma^-_{CH} = 1.68$) proved to be entirely sufficient for the manifestation of the tautomeric transition; on the other hand, the combination of the triphenylphosphonium group with the tosyl group ($\sum\sigma^-_{CH} = 1.78$) and also the combination of two triphenylphosphonium groups ($\sum\sigma^-_{CH} = 2.16$) lead to a "redistribution" of the CH acidity: the tautomeric equilibrium proved to be displaced in the direction of the hydroxy-ylide form.

It was therefore of interest to investigate the influence of two tosyl groups ($\sum\sigma^-_{CH} = 1.40$) at the central carbon atom in the structures (LIX) considered. Two tosyl groups should lead either to the CH form or to tautomerism between the CH and OH forms. This question has been recently elucidated by Kolodyazhnyi[60], who investigated the influence of the substituents X on the position of the tautomeric equilibrium in the

(LXXXIV)⇌(LXXXV) system:

$$\underset{\text{(LXXXIV)}}{Ph_2P(O)-CH(SO_2C_6H_4X)_2} \rightleftarrows \underset{\text{(LXXXV)}}{Ph_2P(OH)=C(SO_2C_6H_4X)_2} .$$

In a pure state these substances consist of colourless crystals, which are very stable in air. They have the structure of the CH forms (LXXXIV), as can be seen from their infrared spectra, which contain bands at 1200–1210 cm^{-1} (P=O), 1160 to 1170 cm^{-1} (sym.SO_2), 1340–1350 cm^{-1} (asym.SO_2), and 2820 to 2840 cm^{-1} (CH). They are all strong acids (Table 9). However, in solution both forms, (LXXXIV) and (LXXXV), are present, differing in the chemical shifts in their ^{31}P NMR spectra (these are 21–24 p.p.m. and 47–49.5 p.p.m. respectively). The protons of the CH and OH groups are not manifested in the ^1H NMR spectra at the usual temperature but they can be detected on cooling—the signals of the OH protons are at 10–11 p.p.m. and those of the CH protons at 6–7 p.p.m. These are doublet signals (J_{PH} = 13 Hz); at −7.5 °C they lose the doublet structure and at +30 °C they disappear.

Table 9. The influence of substituents X on acidity and the tautomeric equilibrium[60].

$Ph_2P(O)-CH(SO_2C_6H_4X)_2 \rightleftarrows Ph_2P(OH)=C(SO_2C_6H_4X)_2$ [60]
(LXXXIV) (LXXXV)

X	σ_n	K_T (THF, 25 °C)	pK_a, (50% CH_3OH)
p-Cl*	+0.227	1.20	3.55
H	0	0.25	3.60
p-Me	−0.17	0.11	3.62
p-MeO	−0.268	0.04	3.68

* K_T = 1.32 at 20 °C and 1.98 at 30 °C.

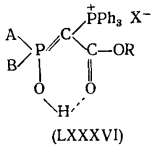
The infrared spectra of the solutions are also different for the CH and OH forms. The spectrum of the CH form (LXXXIV) shows bands at 1200 cm^{-1} (P=O), 1170 cm^{-1}, and 1350 cm^{-1} (SO_2 attached to an sp^3-hybridised carbon atom); the spectrum of the OH form (LXXXV) shows bands at 1300 cm^{-1} and 1290 cm^{-1} (SO_2 attached to an sp^2-hybridised carbon atom). Table 9 lists the (LXXXIV)⇌(LXXXV) equilibrium constants as a function of the substituent X. Using the data in Table 9, it can be shown that the tautomeric equilibrium constants obey satisfactorily the Hammett equation when the usual constants σ_p are used:

$$\lg K_T = -0.51 + 2.867\,\sigma_p \quad (r = 0.994;\ s = 0.08;\ s_p = 0.21).$$

An increase of temperature increases the relative content of the (LXXXIV) form, which indicates a greater stability of the hydroxy-ylide form (LXXXV). The equilibrium position depends on the nature of the solvent, the content of the (LXXXV) form increasing in the sequence

$$CH_2Cl_2 < CHCl_3 < CCl_4 < THF .$$

In conclusion of this section, mention must be made of the striking stability of the hydroxy-ylide forms. They are apparently stabilised by hydrogen bonds, which can be both intramolecular, as in structure (LXXXVI), and intermolecular:



(LXXXVI)

Apart from the oxygen atoms of the COOR or SO_2Ar substituents, halide ions can also function as proton acceptors in the hydrogen bonds. This problem has so far been little investigated, but the existence of the hydrogen bonds has been demonstrated. They reduce the acidity of the OH forms and hence displace the equilibrium in their direction.

2. The Thiophosphoryl–Mercaptoylide Tautomerism

This type of triad phosphorus–carbon tautomerism (LXXXVII)⇌(LXXXVIII) is the phosphorus analogue of the thioketo-enethiol tautomerism (LXXXIX)⇌(XC):

$$\underset{\text{(LXXXVII)}}{>P(S)-CH<} \rightleftarrows \underset{\text{(LXXXVIII)}}{>P(SH)=C<} \qquad \underset{\text{(LXXXIX)}}{-C(S)-CH<} \rightleftarrows \underset{\text{(XC)}}{-C(SH)=C<} .$$

All the thiophosphoryl-compounds known previously, namely tertiary phosphine sulphides $R_2P(S)-CHR'R''$, phosphinothionates $(RO)R'P(S)CHR''R'''$, and phosphonothionates $(RO)_2P(S)CHR'R''$, are thione derivatives, i.e. correspond to structure (LXXXVII). Owing to the low basicity of the thiophosphoryl group (this is equivalent to a high acidity of its protonated form), a rarer appearance of the mercaptoylide form (LXXXVIII) than of the corresponding hydroxy-ylide form was to be expected for the thiophosphoryl-mercaptoylide system (LXXXVII)⇌(LXXXVIII). In other words, the transfer of a proton from the (LXXXVII) forms to the (LXVIII) forms requires a greater CH acidity of the (LXXXVII) forms than was the case for the phosphoryl-hydroxy-ylide transitions (see the previous section).

The first representative of a thiophosphoryl compound with the (LXXXVIII) structure was obtained[61] by the authors of this review and their co-workers. When the thiophosphorylated phosphoranylidenephosphonium salt (XCI) was protonated by fluorosulphonic acid, the mercaptoylide form (XCII) was obtained:

$$\underset{\text{(XCI)}}{Me_2P(S)-C(PPh_3)(\overset{+}{P}Ph_3)}\ X^- \xrightarrow{FSO_2OH} \underset{\text{(XCII)}}{Me_2P(SH)=C(\overset{+}{P}Ph_3)(\overset{+}{P}Ph_3)}\ 2X^- .$$

S-Protonation was detected from the characteristic downfield shift of the signal in the $^{31}P\{^1H\}$ NMR spectrum by 7.2 p.p.m. (cf. Skvortsov et al.[54]).

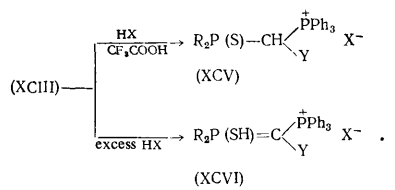
Later the same workers investigated the thiophosphoryl-mercaptoylide tautomerism in greater detail[62] and obtained unexpected results. Various thiophosphoryl-substituted phosphinomethylenes (XCIII) have been synthesised by adding sulphur to the corresponding phosphino-derivatives (XCIV):

$$\underset{\text{(XCIV)}}{R_2P-C(PPh_3)Y} \xrightarrow{S} \underset{\text{(XCIII)}}{R_2P(S)-C(PPh_3)Y} ;$$

	(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)	(i)
R	Ph	Bu	EtO	PhO	Ph	Bu	Ph	Bu	Bu
Y	Ts	Ts	Ts	Ts	COOEt	COOEt	$\overset{+}{P}Ph_3Cl^-$	$\overset{+}{P}Ph_3Cl^-$	$\overset{+}{P}Ph_3Br^-$

These compounds were protonated by various acids under different conditions. Of the two types of protonation—at the sulphur atoms, as in structure (XCVI), and at the carbon

atom, as in structure (XCV)—only one type has been invariably observed as a function of the initial compound, the protonating agent, and the reaction conditions:



(XCV)

(XCVI)

Thus the protonation of compounds (XCIII, a–f) by hydrogen halides in equimolar proportions or in the presence of an excess of the latter leads only to the CH forms (XCV, a–f). The signal of the triphenylphosphonium phosphorus in the $^{31}P\{^1H\}$ NMR spectrum then undergoes a downfield shift by 1.5–7 p.p.m. and the constant J_{PP} diminishes significantly, amounting to 32–42 Hz before protonation and to 1–2 (at most 6) Hz after protonation, which is extremely characteristic of CH protonation. Frequencies corresponding to the SO_2 and COOEt groups attached to an sp^3-hybridised carbon atom are observed in the infrared spectrum. Apart from the signals due to the protons of the butyl, phenyl, and tosyl group, the ^1H NMR spectrum of the salt (XCVb) contains doublets with $\delta = 8.8$ p.p.m. and $J_{PCH} = 12.1$ and 13.6 Hz, which indicates unambiguously the CH structure (XCV). The ratio of the integral intensities of the signals of the CH proton and the CH_3 protons of the tosyl group is then 1 : 3. Protonation of the thiophosphorylylides (XCIII, e and f) by trifluoroacetic acid is also directed solely to the central carbon atom. The hydrochlorides (XCV, a–c), formed on protonation by HCl, are crystalline substances; they are all very strong acids which readily lose HCl on storage in air, the chlorides being less stable than the bromides.

Thus in this group of compounds the strength of the SH acids exceeds significantly that of the CH acids, although the latter are fairly strong.

A different behaviour is observed on protonation of compounds (XCIII, g–i), since this should entail the protonation of extremely strong acids. Indeed, on treatment of the thiophosphoryl ylides (XCIII, g–i) with HCl in CH_2Cl_2 (even with a large excess of HCl) or on treatment with an excess of trifluoroacetic acid, the addition of a proton is not always observed at the usual temperature. Only at temperatures between −70° and −85 °C in CH_2Cl_2 on treatment with an excess of hydrogen halide or on dissolution in fluorosulphonic acid is protonation observed, but in these instances only at the suphur atom.

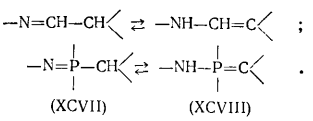
Thus, when compounds (XCIII, g and h) are treated with HSO_3F, doublet signals with the chemical shifts $\delta = 3.67$ p.p.m. for compound (XCVIg) and 3.05 p.p.m. for compound (XCVIh) and the splitting constants $J_{PSH} = 10$ and 8 Hz respectively appear in the ^1H NMR spectra. Spectra of this kind are very characteristic of thiophosphoryl compounds protonated by fluorosulphonic acid[63].

In the ^{31}P NMR spectra the signal of the thiophosphoryl phosphorus atom shifts downfield by 1–5 p.p.m. compared with the non-protonated compounds. The spin–spin coupling constant J_{PP} not only does not diminish under these conditions, as in the previous instance of C protonation, but actually increases somewhat.

Thus a system in which the (LXXXVII) and (LXXXVIII) forms are in an experimentally observed tautomeric equilibrium has been found for thiophosphoryl compounds of type (LXXXVII). If the acidity of the CH form is insufficient [the sum of the constants of the substituents at the central carbon atom $\sum\sigma^-_{CH} = 1.78$ for compounds (XCV, a–d) and, especially, 1.68 for compounds (XCV, e and f)], then only the CH form is produced. If the acidity of the CH form is high [$\sum\sigma^-_{CH} = 2.16$ for compound (XCVI, g–i)], then the proton is transferred to the sulphur atom and we detect exclusively the SH form. Apparently the region of the thiophosphoryl-mercaptoylide tautomerism involving thiophosphoryl compounds should occur for values of the sum of the constants $\sum\sigma^-_{CH}$ of the substituents at the central carbon atom between 1.78 and 2.16. The synthesis of thiophosphoryl compounds with such substituents at the α-carbon atom and the study of their thiophosphoryl-mercaptoylide tautomerism are matters for the future.

3. The Phosphorimide–Aminoylide Tautomerism

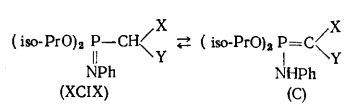
The phosphorimide–aminoylide tautomerism is the phosphorus analogue of the well known azomethine tautomerism:



(XCVII) (XCVIII)

Compared with previous cases—the phoshoryl-hydroxyylide tautomerism (LIX) and the thiophosphoryl–mercaptoylide tautomerism (LXXXVII) and (LXXXVIII)—there is not in this instance such a sharp difference between the polarities of the ends of the N = P = C triad; the relative acidities of the CH and NH forms can therefore change significantly under the influence of substituents at the nitrogen and carbon atoms. This type of tautomerism has been investigated by the Kiev chemical school[64–67]. Referring to it, in conformity with the nomenclature of the phosphorus-nitrogen compounds adopted in Kiev, as the phosphazo-ylide tautomerism, Kolodyazhnyi, Kukhar', Gololobov, and others investigated thoroughly both the methods of analysis of the tautomeric mixtures and the factors influencing the position of the phosphorimide-aminoylide equilibrium. It was established that the imide (XCVII) and iminoylide (XCVIII) forms can be clearly distinguished by means of infrared spectra and also ^1H and ^{31}P NMR. Thus, when there are two COOR groups at the carbon atom of the (XCVIII) form, the ^{31}P NMR spectrum shows a signal in the vicinity of 50 p.p.m., while for the corresponding (XCVII) form the signal is at 0 p.p.m. The ^1H NMR spectra of the (XCVII) forms contain a doublet due to the CH group in the range 3.5–4 p.p.m., while the spectra of the (XCVIII) forms contain the doublet of the NH group at 7–13 p.p.m. In the infrared spectra the vibration frequency of the COOR group at the α-carbon atom depends on the state of hybridisation of the latter and amounts to 1700–1760 cm^{-1} for the sp^3 hybridisation and to 1600–1700 cm^{-1} for the sp^2 hybridisation.

Thus the presence or absence of the tautomeric equilibrium has been established and in many instances its constants have been determined. The sharp influence of substituents at the nitrogen and carbon atoms on the equilibrium is noteworthy. Thus, in the presence of two isopropoxy-groups at the phosphorus atom, i.e. in the (XCIX)⇌(C) system



(XCIX) (C)

the equilibrium position (in CCl_4 at 28 °C) changes as follows:

X, Y	$\Sigma\sigma_C^-$	Content of NH form, %
$(COOMe)_2$	1.24	100
COOMe, Ph	0.88	0
COOMe, H	0.72	0

If the NH acidity is reduced by replacing the phenyl group at the nitrogen atom by the methyl group, then 100% of the NH form will be present not only in the first case for $\sum\sigma_C^- = 1.24$ but also for $\sum\sigma_C^- = 0.88$; even for $\sum\sigma_C^- = 0.72$, its content will still be 90%. On the other hand, if the NH acidity is increased by introducing the 2,4-dinitrophenyl group at the nitrogen atom instead of the phenyl group, then in the first case ($\sum\sigma_C^- = 1.24$) only 30% of the NH and not 100% is observed and, finally, the greatest increase of the NH acidity, resulting from the introduction of the tosyl group at the nitrogen atom, leads to the complete disappearance of the NH form in all the three instances considered. Thus the results obtained by the Kiev chemists[64-67] can be readily interpreted from the standpoint developed in the present review.

The nature of the solvent has an appreciable influence on the phosphorimide–aminoylide equilibrium. The content of the aminoylide form increases in the following series of solvents from left to right:

$$CCl_2{=}CCl_2 < CCl_4 < CH_3OH < CH_3CN < CHCl_3 \quad .$$

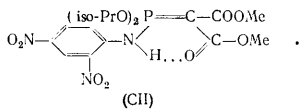
This series is apparently determined by the simultaneous operation of several factors.

An increase of temperature favours the imide form (XCVII). Thus the study of the temperature variation of the equilibrium in the (CI)⇌(CII) system

$$\underset{\underset{NC_6H_3(NO_2)_2}{\|}}{(\text{iso-PrO})_2P{-}CH(COOMe)_2} \rightleftarrows \underset{\underset{NHC_6H_3(NO_2)_2}{|}}{(\text{iso-PrO})_2P{=}C(COOMe)_2}$$

(CI) (CII)

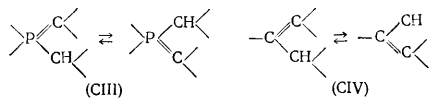
showed that $\Delta H = -5.9 \pm 0.5$ kcal mol^{-1} and $\Delta S = -21$ e.u. for a 0.2 M solution in CCl_4. The aminoylide form (CII) is energetically more favourable and more stable than the imide form (CI). The high entropy of the conversion of the ylide into the imide is noteworthy; this enabled the author of the study quoted above to postulate that the ylide form has a more rigid structure as a consequence of an intramolecular hydrogen bond:



(CII)

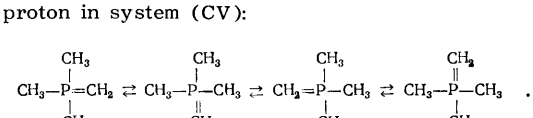
4. The Carbon–Phosphorus–Carbon Tautomerism

Here we are dealing with the phosphorus analogue (CIII) of the three-carbon tautomerism (CIV):



(CIII) (CIV)

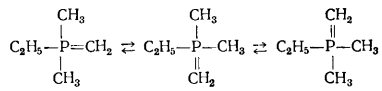
The first data on the degenerate tautomerism of this kind were published by Schmidbaur and Tronich[68], who found that the ^{1}H NMR spectra of solutions of trimethylmethylenephosphorane (carefully freed from impurities) depend on temperature and that at 100 °C the signals of the methyl and methylene protons merge owing to the degenerate tautomeric migrations of the proton in system (CV):



(CV)

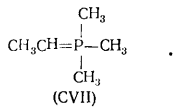
The activation energy for such transformations was estimated as 20 kcal mol^{-1}. The transformation is catalysed by added methanol, water, silanol, and in general proton donors. When traces of CH_3OH are introduced, a singlet signal is observed in the ^{1}H NMR spectrum already at −30 °C.

Tautomeric transitions (also degenerate) analogous to those of methylenetrimethylphosphorane have been observed for ethyldimethylmethylenephosphorane (CVI)[68]:



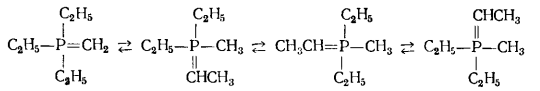
(CVI)

In the absence of catalysis by methanol, the ethyl group is not involved in the tautomerism, while the presence of methanol, the methylene protons of the ethyl group are involved in the merging of the signals, which indicates the appearance of the fourth tautomeric form (CVII), which is in equilibrium with the three previous forms:



(CVII)

The ^{1}H NMR spectrum of the compound $(C_2H_5)_3P{=}CH_2$ undergoes no temperature-induced changes below 100 °C, but, after the addition of methanol, the equilibrium of the four forms in system (CVIII) is immediately established[68]:



(CVIII)

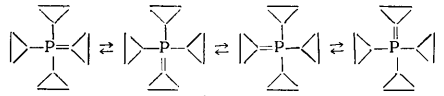
Strictly speaking the conversion of the first form specified into any one of the other three constitutes a non-degenerate tautomeric transition. However, the differences between the energy relations of the forms are in this instance very small and the system approaches a degenerate state. An analogous situation (with complete degeneracy) has been observed for triethylethylidenephosphorane $(C_2H_5)_3P{=}CHCH_3$, whose ^{1}H NMR spectrum is independent of temperature. The addition of only traces of methanol induces a rapid proton migration. As regards the mechanism of the catalytic action of methanol, it has been suggested that methanol reacts with the ylide to form phosphonium methoxide (CIX) by the reversible reaction[68]

$$Me_3P{=}CH_2 + MeOH \rightleftarrows \underset{(CIX)}{Me_4\overset{+}{P}\,\overset{-}{O}Me} \quad .$$

Next, the familiar transylidation process takes place.

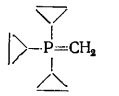
The application of ^{1}H NMR spectroscopic methods made it possible to discover many analogous instances of the degenerate tautomerism of ylides. Thus one may quote as an

example tricyclopropylcyclopropylidenephosphorane (CX) [69]:



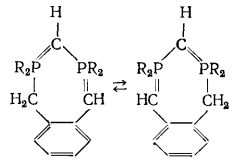
(CX)

It is of interest that the replacement of one cyclopropyl substituent by the methyl group immediately fixes the structure (CXI), as the more favourable, and proton migration ceases:



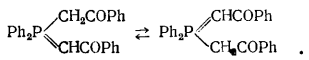
(CXI)

We may mention also the pentad system of type (CXII) [70]:



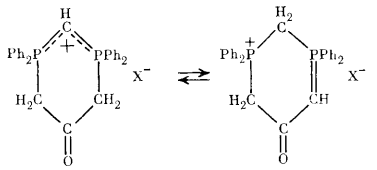
(CXII)

The introduction of strongly electron-accepting substituents into the methylene and methyl groups of trimethylmethylenephosphorane significantly reduces the barrier to tautomerisation. Thus the merging of the signals of the methylidyne and methylene groups in system (CXIII) takes place in $CDCl_3$ at −40°– −50 °C, while for a solution in SO_2 the merging takes place at −20 °C [71]:



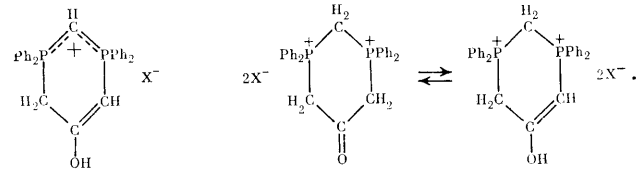
(CXIII)

The number of known cases of non-degenerate tautomerism in the triad $CH-\overset{|}{P}=C$ is much smaller. The first example of this kind was the tautomerism of 3,3,5,5-tetraphenyl-3,5-diphosphacyclohexenone, (CXIV) ⇌ (CXV), investigated by the authors of this review and their co-workers[72,73]:



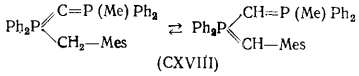
(CXIV) (CXV)

According to infrared spectroscopic data, the substance in the crystalline state has the structure (CXV): the infrared spectrum of a mull in hexachlorobutadiene shows bands at 1540–1550, 1345, and 880 cm^{-1} associated with the ν_1, ν_2, and ν_3 vibrations of the acylphosphinomethylene system, while OH bands are absent; according to NMR and infrared spectra, a solution in $CHCl_3$ contains simultaneously also the (CXIV) form (again at a low relative concentration). It is of interest that the enol form (CXVI) is not detected in the equilibrium mixture at all, while in the saturated system (CXVII) there is a distinct keto-enol equilibrium according to ^1H NMR and infrared spectroscopic data[74]:



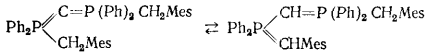
(CXVI) (CXVII)

Interesting examples of the non-degenerate tautomerism (CXVIII), (CXIX), and (CXX) in the $C=\overset{|}{P}-CH$ triad have been described recently[75]:



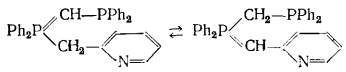
(CXVIII)

(3 : 1 ratio of different forms);



(CXIX)

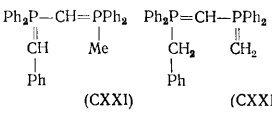
(3 : 2 ratio of different forms);



(CXX)

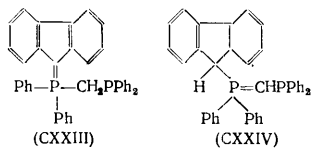
(3 : 1) ratio of different forms).

In the degenerate carbon–phosphorus–carbon tautomerism the forms involved are identical, their acidities are equal, and their contents in the equilibrium mixture are the same. For certain small differences between the structures of the forms, which are reflected in their relative CH acidities, a non-degenerate tautomerism is observed where the less acid form naturally predominates in the equilibrium mixture. On the other hand, if the structural differences become more significant, then the difference between the CH acidities increases and the equilibrium is almost completely displaced to one side. Thus the derivative (CXXI) is not tautomeric; it has the structure (CXXI) and not (CXXII):



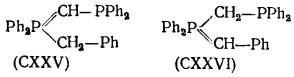
(CXXI) (CXXII)

The fluorenylidene derivative is also non-tautomeric, having the structure (CXXIII) and not (CXXIV):



(CXXIII) (CXXIV)

If the α-pyridyl substituent in system (CXX) is replaced by the phenyl substituent, which has a lower acidifying capacity, then the equilibrium is fully displaced towards the (CXXV) form and tautomerism with the (CXXVI) form is not manifested:



(CXXV) (CXXVI)

Such a sharp response of the position of the carbon–phosphorus–carbon tautomeric equilibrium to seemingly small changes in the character of the substituents at the CH groups can be explained by the very high slopes of the linear

correlations between the pK_a for the different forms and $\sum\sigma_{CH}^-$. Indeed the values of ρ in the expressions for the pK_a for non-tautomeric CH acids ($pK_a = pK_a^0 - \rho\sum\sigma_C^-$) vary from 10 to 25 as a function of the solvent, the counterion, etc.[46]

Small changes in $\sum\sigma_C^-$ induce large changes in the pK_a for the different forms. The difference between them ($\Delta pK_a = pK_1 - pK_2$) can then increase markedly, whereupon the position of the tautomeric equilibrium ($pK_T = \Delta pK_a$) is sharply altered.

IV. CONCLUSION

Not so long ago there was no information about the existence of PH ylides, P(OH) ylides, P(SH) ylides, etc. Studies in the 1970's led to the discovery of this new extensive field of organophosphorus chemistry. In this review we were concerned only with problems of the tautomerism of such ylides with the corresponding derivatives of tervalent phosphorus or phosphoryl, thiophosphoryl, etc. compounds. The prototropic migrations could be reliably treated in this instance from the standpoint of the theory of the tautomeric acid–base protolytic equilibrium. This is naturally extremely important. At the same time, it is essential to note that the proton transitions constitute only a part of the extensive chemistry of the new systems. There exists yet another very interesting field of dual reactivity of the corresponding ambident species, which can be negatively charged like the usual anions, but the corresponding neutral species are also possible if the initial protonated forms carry a positive charge. We were naturally unable to deal with this extremely interesting field of the chemical properties of new phosphorus ylides. There is a possibility also of other interesting and important reactions, for example, rearrangements, decomposition reactions, etc. Their elucidation has not so far proceeded very far, although interesting results have already been obtained. However, this is a subject for another article.

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