DYADIC PHOSPHORUS-CARBON TAUTOMERISM

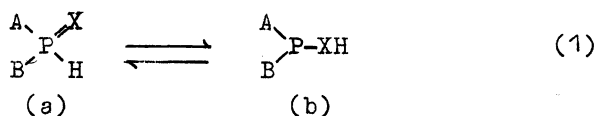T.A.Mastryukova, I.M.Aladzheva, I.V.Leont'eva, P.V.Petrovski,
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Abstract – It has been shown by means of ^{1}H, ^{13}C and ^{31}P NMR
techniques and IR-spectroscopy that in the dyadic organo-
phosphorus tautomeric systems: (a) ABP/H/=CRR' $\rightleftharpoons$ ABP-CHRR',
(b) the equilibrium position which is solvent- and tempera-
ture-dependent also strongly depends upon the substituents
on the carbon and phosphorus atoms, namely on their effect
on the relative P-H and C-H acidities. When R and R' are
electronegative groups, such as COOEt, SO$_2$Ph, etc., the
equilibrium is shifted towards form (b) (owing to the low
acidity of the CH group). If R=R'=Ph$_3$P$^+$ and A=B=Alk, Ph,
AlkO and PhO, the compounds exist only in form (a). The PH
ylide (A=B=Bu) has been isolated in the crystalline state
and its structure determined by X-ray analysis. If R=Ph$_3$P$^+$,
R'=COOEt and A=B=Bu exists the form (a), as a sole one.
When A=B=Ph the acidity of both forms is commensurated and
structures (a) and (b) exist simultaneously.

Thus, to the well known three principal types of phosphorus
dyadic tautomeric systems, represented mainly by the dialkyl
phosphites, thiophosphites and anilidophosphites, with the
equilibrium in the first two mostly shifted to the phospho-
nate (PH) form, and in the third to the NH form, there has
been added the phosphorus-carbon tautomeric system which had
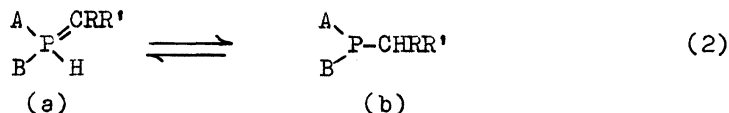previously been known only in form (b).

INTRODUCTION

Of the dyadic tautomeric compounds, the organophosphorus dyads (1)

$$\begin{array}{c} A \\ B \end{array} P \begin{array}{c} X \\ H \end{array} \quad \rightleftharpoons \quad \begin{array}{c} A \\ B \end{array} P-XH \qquad (1)$$

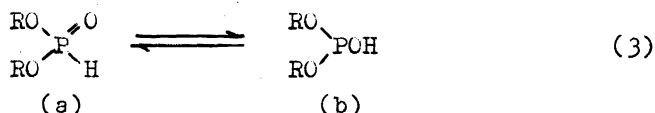$$\qquad (a) \qquad\qquad\qquad (b)$$

(X=O, S, Se and NR; A and B = various substituents) seem to have attracted
the greatest attention. Of these the principal representatives are the
dialkylphosphites that have been investigated in detail.

To this type of tautomerism should be also referred the dyadic phosphorus-
carbon system (X=CRR') with the following corresponding tautomeric equilib-
rium:

$$\begin{array}{c} A \\ B \end{array} P \begin{array}{c} CRR' \\ H \end{array} \quad \rightleftharpoons \quad \begin{array}{c} A \\ B \end{array} P-CHRR' \qquad (2)$$

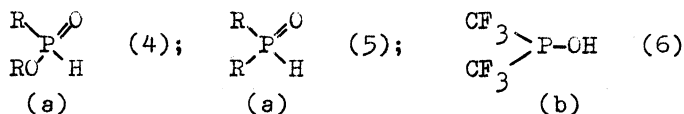$$\quad (a) \qquad\qquad\qquad (b)$$

This kind of equilibrium which has previously not been observed will serve
the subject matter of the present report.

A few words about the known organophosphorus dyads and their tautomeric
properties. Over 70 years ago A.E.Arbuzov [1] had found that all dialkyl-
phosphites are in fact phosphonates, the tautomeric equilibrium (3) being
wholly displaced towards form (a):

$$\begin{array}{ccc}
\underset{RO}{\overset{RO}{\diagdown}}P\underset{H}{\overset{O}{\diagup}} & \rightleftharpoons & \underset{RO}{\overset{RO}{\diagdown}}POH \\
(a) & & (b)
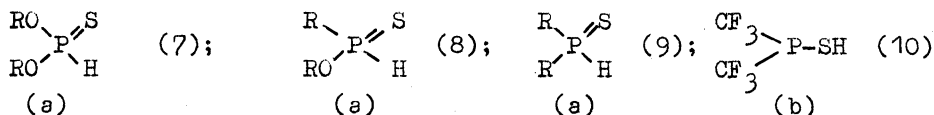\end{array} \qquad (3)$$

Although equilibrium between forms (a) and (b) was proposed long ago [2], the existence of form (b) was actually demonstrated by kinetic studies of isotope exchange [3] only much later.
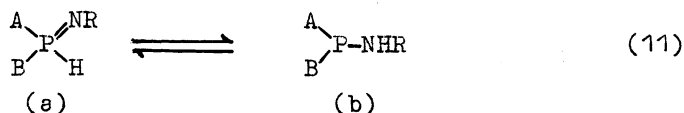
The same tautomeric equilibrium occurs among the O-alkyl-alkylphosphonites (4) and the dialkylphosphinites (5) with the exception of bis-trifluoromethylphosphinite (6), which exists only in form (b) [4].
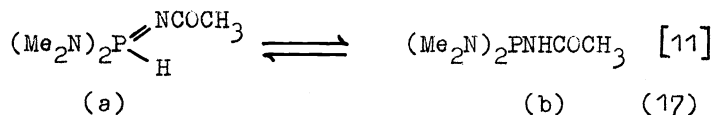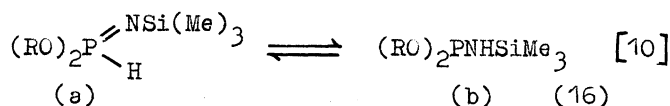
$$\underset{RO}{\overset{R}{\diagdown}}P\underset{H}{\overset{O}{\diagup}} \quad (4); \qquad \underset{R}{\overset{R}{\diagdown}}P\underset{H}{\overset{O}{\diagup}} \quad (5); \qquad \underset{CF_3}{\overset{CF_3}{\diagdown}}P-OH \quad (6)$$
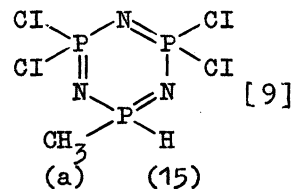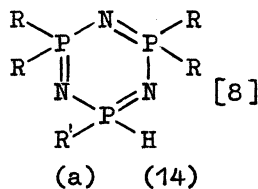$$\qquad (a) \qquad\qquad\qquad (a) \qquad\qquad\qquad\qquad (b)$$

Similar relationships hold for the sulfur-containing analogs (7-10) [5].

$$\underset{RO}{\overset{RO}{\diagdown}}P\underset{H}{\overset{S}{\diagup}} \quad (7); \qquad \underset{RO}{\overset{R}{\diagdown}}P\underset{H}{\overset{S}{\diagup}} \quad (8); \qquad \underset{R}{\overset{R}{\diagdown}}P\underset{H}{\overset{S}{\diagup}} \quad (9); \qquad \underset{CF_3}{\overset{CF_3}{\diagdown}}P-SH \quad (10)$$
$$\qquad (a) \qquad\qquad\qquad (a) \qquad\qquad\qquad (a) \qquad\qquad\qquad (b)$$
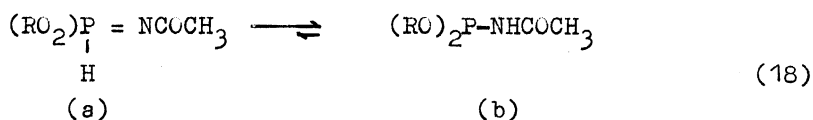
Amidophosphites, however, behave differently in the tautomeric equilibrium (11):

$$\underset{B}{\overset{A}{\diagdown}}P\underset{H}{\overset{NR}{\diagup}} \quad \rightleftharpoons \quad \underset{B}{\overset{A}{\diagdown}}P-NHR \qquad (11)$$
$$\qquad (a) \qquad\qquad\qquad\qquad (b)$$

As a rule form (b) prevails [6] and only in a few cases were both forms (or even preferentially form (a)) revealed. The following examples serve as illustration:

$$\underset{H}{\overset{R_2P}{|}} = NSO_2R' \quad [7] \qquad\qquad (a) \quad (12)$$

$$\underset{H}{\overset{R_2P}{|}} = N-P(S)(OPh)_2 \quad [7] \qquad (a) \quad (13)$$

(14) (a) ring structure with R, R', N, P [8]

(15) (a) ring structure with Cl, N, P, CH$_3$ [9]

$$(RO)_2P\underset{H}{\overset{NSi(Me)_3}{\diagup}} \quad \rightleftharpoons \quad (RO)_2PNHSiMe_3 \quad [10]$$
$$\qquad (a) \qquad\qquad\qquad\qquad (b) \quad (16)$$

$$(Me_2N)_2P\underset{H}{\overset{NCOCH_3}{\diagup}} \quad \rightleftharpoons \quad (Me_2N)_2PNHCOCH_3 \quad [11]$$
$$\qquad (a) \qquad\qquad\qquad\qquad\qquad (b) \quad (17)$$
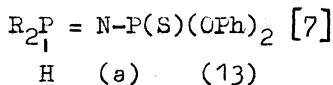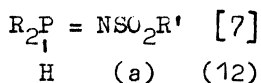
The equilibrium position of the dyadic tautomers depends upon the variegated factors controlling the acidic properties of the individual forms [12]. The acidity of the dialkylphosphite PH-forms and of their sulfur analogs is much less than that of the OH- and particularly the SH-tautomers. As a result the equilibrium is always shifted here to the former. On the other hand, the very weak dissociation tendency of the NH-bond of amidophosphites favors the form with this bond over the PH-form in the equilibrium mixture. However, form (a) will immediately appear if the relative acidities of the NH- and PH-forms will be changed in one way or another in favor of the former. Thus, while the tautomeric equilibrium of O,O-dialkyl-N-acetamido-phosphites (18)

$$(RO_2)\underset{\underset{\text{(a)}}{|}}{\overset{}{P}} = NCOCH_3 \ \underset{}{\overset{}{\rightleftharpoons}} \ \ \underset{\text{(b)}}{(RO)_2P-NHCOCH_3} \qquad\qquad (18)$$
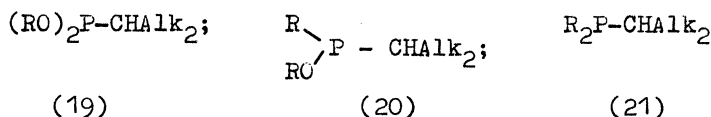
is shifted to form (b) [13], replacement of the two alkoxy-groups by two dialkylamido groups that low dissociation of the PH-bond leads to the appearence of both forms [11] (see equilibrium (17)).

A similar effect could be caused by augmenting the NH acidity, substituting a trimethylsilyl group on the nitrogen (16) [10].

1. PHOSPHORUS-CARBON DYADS EXISTING IN THE CH-FORM

If one regards the phosphorus-carbon dyad systems (2) from the above point of view, the conclusion must be drawn that the acidity of form (a) in the simpler compounds of this class, i.e. O,O-dialkyl alkylphosphonites (19), O-alkyldialkylphosphinites (20) and tertiary alkyl phosphines (21) is so much higher than that of form (b) (CH-acidity) that actually, as is well known, the sole form is (b).

$$(RO)_2P-CHAlk_2; \qquad \underset{RO}{\overset{R}{\diagdown}}P - CHAlk_2; \qquad R_2P-CHAlk_2$$

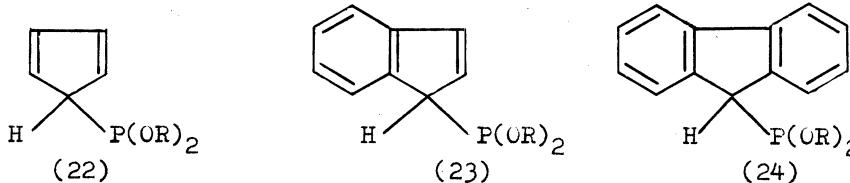$$\qquad\quad (19) \qquad\qquad\qquad (20) \qquad\qquad\qquad (21)$$

The appearance of the PH-form alongside the CH-form may be expected only when their relative acidities will be changed in favor of the CH-form. This can be achieved in two ways:

1. Augmenting the CH-acidity, for instance by inserting strong electronegative substituents on the α-carbon atom of the phosphonite (19), phosphinite (20) or the phosphine (21); (equation 2).
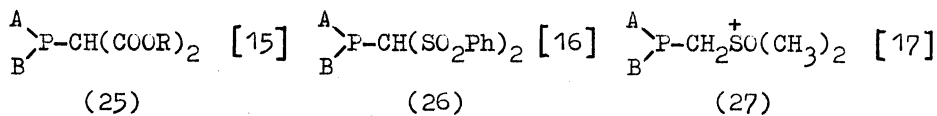
2. Decreasing the PH-acidity by means of appropriate substituents on the phosphorus or by incorporating the phosphorus atom into an appropriate ring system.

Trivalent phosphorus compounds with enhanced α-CH acidity have been described in the literature. Thus, Kabachnik and Tsvetkov [14] have studied the esters of cyclopentadienyl-(22),indenyl-(23) and fluorenyl-(24)-phosphonous acids:

$$\underset{(22)}{H\diagup\ \diagdown P(OR)_2} \qquad\qquad \underset{(23)}{H\diagup\ \diagdown P(OR)_2} \qquad\qquad \underset{(24)}{H\diagup\ \diagdown P(OR)_2}$$
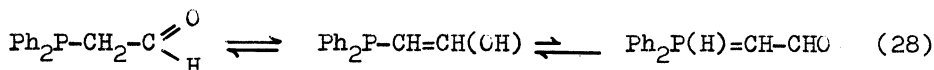
However, they turned to be of the CH-forms with no indication of the presence of an "ylidic" PH-form.

Kolodyazhnyi, Gololobov and coworkers have attached two carbalkoxy groups (25), two sulfonic groups (26), a protonated dimethylsulfoxonium group (27) and some others to the α-carbon atom of the trivalent phosphorus compounds:

$$\underset{B}{\overset{A}{\diagdown}}P-CH(COOR)_2 \ [15] \qquad \underset{B}{\overset{A}{\diagdown}}P-CH(SO_2Ph)_2 \ [16] \qquad \underset{B}{\overset{A}{\diagdown}}P-CH_2\overset{+}{S}O(CH_3)_2 \ [17]$$

$$\qquad (25) \qquad\qquad\qquad (26) \qquad\qquad\qquad (27)$$

But here again the IR, ^1H and ^{31}P-NMR spectra showed the presence of only the CH-form.

Issleib and Sokolov [18] supposed that the PH-form exists in equilibrium with the CH- and enol forms in the system (28):

$$Ph_2P-CH_2-C\diagup\overset{O}{\underset{H}{\diagdown}} \ \rightleftharpoons \ Ph_2P-CH=CH(OH) \ \rightleftharpoons \ Ph_2P(H)=CH-CHO \quad (28)$$
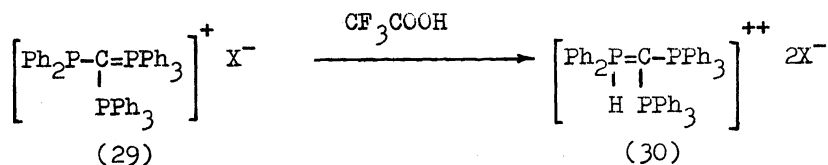
However, whereas formation of the aldo- and enol forms have been vigorously proved, this cannot be said of the PH-form, the formation of which is still in doubt.

2. PHOSPHORUS-CARBON DYADS EXISTING IN THE PH-FORM

For a number of years we have systematically studied the effect of the triphenylphosphonium group on the position of the keto-enol equilibrium of β-dicarbonyl compounds. These studies have revealed its strong enolizing effect, greatly surpassing that of many conventional electronegative "enolizing" groups. Thus, whereas acetoacetic ester is enolized to the extent of 7% and the incorporation of a carbethoxy-group at the α-position augments the enolization to 70% [19] , a triphenylphosphonium group in the α-position leads to 100% enolization in both the crystalline state and in solution [20-22]. The strong enolizing effect of triphenylphosphonium is undoubtedly due to its ability to sharply increase the CH-acidity of the keto-form while only weakly affecting the enol form. It was thus only natural to expect that if in a phosphonite or phosphine one or two triphenylphosphonium groups are attached to the CH-group the resultant enhancement of its acidity should cause the appearance of the PH-form.
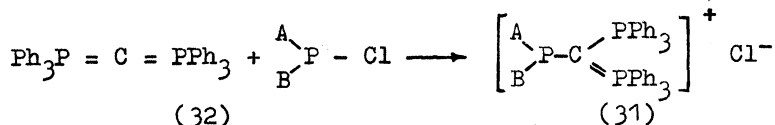
An indication of this kind is to be found in the literature. Namely, Birum and Matthews [23] observed the formation of phosphino-methylene (30) with PH-bond when they dissolved a phosphorane-phosphonium salt (29) in trifluoroacetic acid.

$$\left[\begin{array}{c} Ph_2P-C=PPh_3 \\ | \\ PPh_3 \end{array} \right]^+ X^- \xrightarrow{\ CF_3COOH\ } \left[\begin{array}{c} Ph_2P=C-PPh_3 \\ |\ \ | \\ H\ PPh_3 \end{array} \right]^{++} 2X^-$$

$$(29) \hspace{4cm} (30)$$

However, they did not consider the possibility of a dyadic phosphorus-carbon tautomerism.

In our study we deemed it necessary to first repeat the synthesis of Birum and Matthews, making a detailed investigation of the protonation of salt (29) and of salts with other substituents on the trivalent phosphorus atom [24-26].

The phosphorane-phosphonium salts of type (31) were synthesized by reacting carbodiphosphorane (32) with chlorophosphines or dialkylchlorophosphites.

$$Ph_3P = C = PPh_3 + \begin{array}{c} A \\ B \end{array}\!\!\diagdown P - Cl \longrightarrow \left[\begin{array}{c} A \\ B \end{array}\!\!\diagdown P-C \diagup^{\textstyle PPh_3}_{\textstyle PPh_3} \right]^+ Cl^-$$
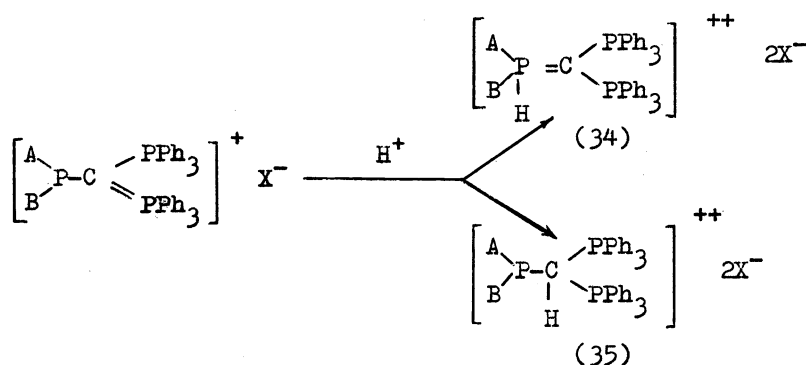
$$(32) \hspace{5cm} (31)$$

where A and B = Me, Et, Bu, Ph, EtO, PhO.

These are readily oxidizable substances that are decomposed by the moisture of the air to the phosphorane-phosphonium salt $[Ph_3P^+ -CH = PPh_3]$ Cl^- (33) and derivatives of trivalent phosphorus, the phosphonites being less stable than the phosphines. Some of their properties are listed in Table 1.

It can be seen that there are only two signals in a 2:1 ratio, showing that two phosphorus atoms of the phosphorane-phosphonium group are magnetically equivalent and the charge on the phosphorus is delocalized.

The phosphine phosphorus signal by intensity 1 is in the form of a triplet (coupling with the two equivalent phosphorus nuclei), whereas the phosphorus signal of intensity 2 is in the form of a doublet, the spin coupling constant J_{P-P} being of the order of 50-70 Hz. The phosphine phosphorus signal is in a higher field than that of the phosphonite.

The results are in good agreement with reported data [23].

In general, these salts may be protonated on either the trivalent phosphorus (34) or on the carbon (35) atoms:

$$\left[\begin{array}{c} A \\ B \end{array}\!\!P\text{-}C \!\!\begin{array}{c} \nearrow PPh_3 \\ \searrow PPh_3 \end{array}\right]^{+} X^{-} \xrightarrow{\ H^{+}\ } \begin{array}{c} \left[\begin{array}{c} A \\ B \end{array}\!\!\underset{\underset{H}{|}}{P}=C\!\!\begin{array}{c}\nearrow PPh_3 \\ \searrow PPh_3\end{array}\right]^{++} 2X^{-} \quad (34) \\[2em] \left[\begin{array}{c} A \\ B \end{array}\!\!P\text{-}\underset{\underset{H}{|}}{C}\!\!\begin{array}{c}\nearrow PPh_3 \\ \searrow PPh_3\end{array}\right]^{++} 2X^{-} \quad (35) \end{array}$$

or simultaneously on both.

TABLE 1. Properties of the phosphino-substituted phosphorane-
phosphonium salts $[ABPC(PPh_3)_2]^+Cl^-$ (31)

A = B	Yield, %	M.p. °C (dec.)	NMR ^{31}P–$\{^1H\}$			
			Solvent	δ_{P^+} ppm (d)	δ_{PIII} ppm (t)	J_{PP} Hz
Ph	73	254–7	$CHCl_3$	26.3	−1.2	74
Me	82	240–4	CH_2Cl_2	25.2	−34.8	64
Et	98	239–42	MeOH	24.0	−7.8	63
Bu	74	249–55	CH_3CN	24.2	−17.4	64
PhO	80	230–7	CH_3CN	21.3	175.7	68
EtO	–	–	$CHCl_3$	21.4	65.7	53

We investigated the protonation of the phosphorane–phosphonium salts (31)
by a variety acids in a number of absolute solvents under dry argon. Accord-
ing to the ^{31}P–$\{^1H\}$ NMR data in all cases only the PH–form (34) with the
characteristic J_{PH} constant of 450–700 Hz and a reduced J_{PP} (17–29 Hz), re-
lative to that of (31), is formed.

TABLE 2. ^{31}P–$\{^1H\}$ NMR parameters of salts (31) protonated by
trifluoracetic acid or hydrogen chloride in $CHCl_3$
or CH_2Cl_2 $[ABP(H)C(PPh_3)_2]^{++}2X^-$ (34)

A = B	Solvent	δ_{P^+} ppm (d.)	$\delta_{P(H)}$ ppm (t.)	J_{PP} Hz	J_{PH} Hz
Ph	CF_3COOH	25.3	8.6	22	500
Me	CF_3COOH	25.8	−1.1	19	525
	CH_2Cl_2	24.5	−2.1	21	525
Et	$CHCl_3$	24.7	22.5	21	460
Bu	CF_3COOH	25.4	17.2	17	450
	$CHCl_3$	23.0	14.6	19	460
PhO	CH_2Cl_2 (−70°C)	21.5	51.5	29	698

In the PMR spectrum of the protonated salt (34, A and B = CH_3) one can clearly observe the splitting of the methyl proton signal by the P-H proton; (in CF_3COOH: doublet of doublets, δ = 1,38 ppm, J_{PCH} 12 Hz and J_{HPCH} 6 Hz). Numerous attempts have been made to observe the CH-form (35) alongside the PH-form (34) by varying the substituents on the P^{III} phosphorus atom, the solvent, etc. However, no signals were observed either in the ^{31}P-NMR spectra or in the PMR spectra that could be assigned to the CH-form, despite the use of a CAT procedure.

As already noted, the phosphonite derivatives (34) are of low stability [26]. Thus, compound (34) (A=B=PhO, X=Cl) decomposes already at 0°C with rupture of the P-C bond to form the easily identified diphenylchlorophosphite (36) and the bisphosphonium salt $(Ph_3P^+)_2CH_22X^-$ (37). Quite similarly, the phosphorane-phosphonium salt (31, A=B=PhO) immediately forms the bisphosphonium salt (37) and the diphenylphosphite (38) when dissolved in CF_3COOH. The diphenylphosphite is formed from the diphenylchlorophosphite in trifluoracetic acid medium, as was shown in a special experiment. The protonated salt with the two phenyl groups (34, A=B=Ph) is, however, relatively stable at room temperature, beginning to form diphenylchlorophosphine, the phosphorane-phosphonium salt (33) or the bisphosphonium salt (37) only after standing for 24 hrs.

It is difficult to conceive of the formation of a diphenylchlorophosphite or diphenylchlorophosphine and phosphorane-phosphonium salt (33) from the phosphorus protonated PH form (34), whereas, on the contrary, it is very easy to conceive of its proceeding from the carbon-protonated CH-form (35):
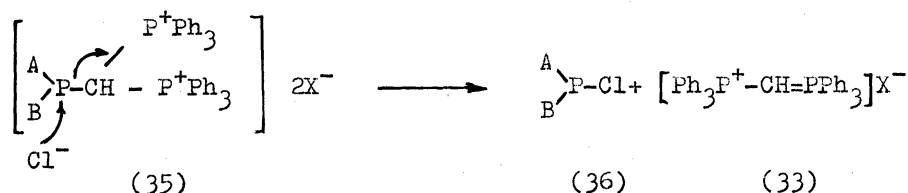
One can assume that the above-noted protonation of the phosphorus of (34) occurs at low temperatures, and that on raising the temperature the CH-form (35) is also partially formed, but that it is immediately subjected to anion attack and decomposed, as shown above. Naturally, this displaces the protonation equilibrium untill complete decomposition takes place. But this is more of a conjecture than it is actually proved.

We thus see, that the two triphenylphosphonium groups in the dyadic system (2) increase the acidity of the CH-form (b) to such an extent that the equilibrium is displaced completely on the side of the PH-form (a).

The PH-structure formed on protonation has been confirmed by X-ray analysis of the crystalline acidic hydrogen bromide salt of the dibutylphosphine substituted phosphorane-phosphonium (39).

$$\left[\begin{matrix} Bu_2P = C(P^+Ph_3)_2 \\ | \\ H \end{matrix} \right] 2Br^- \ldots HBr \cdot CH_2Cl_2$$
$$(39)$$
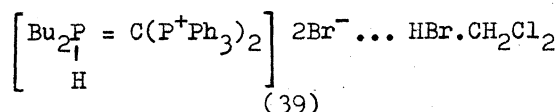
The salt forms on treating the corresponding phosphorane-phosphonium salt (31, A=B=Bu, X=Br) with dry hydrogen bromide in methylene chloride. The structure of the salt is represented in Fig. 1.

As one can see from the figure, the central carbon atom is of a planar trigonal configuration, characteristic of sp^2 hybridization. The sum of the PCP angles is 359°, the mean for each angle being $119(7)^{\circ}$ and the phosphorus atoms are out of the molecular plane by not more than $0.14(3)Å$. The phosphorus atom to which are attached the butyl groups has a slightly distorted tetrahedral configuration. Although the position of the hydrogen atom was not directly identified, the data bear strong evidence of the PH-structure, for in the case of CH-protonation the central carbon atom would have been tetrahedral (sp^3) and would not have been in the plane of the three phosphorus atoms.

Interestingly, the bromine ions in the crystalline form an almost equilateral triangle with the sides approximately $5Å$, the distance from the Bu_2P phosphorus to one of these atoms corresponding to a P-H...Br hydrogen bond.
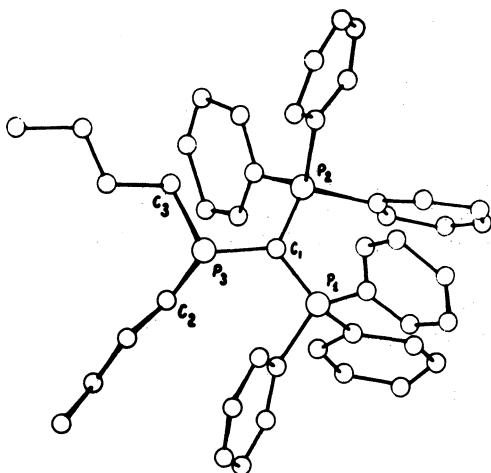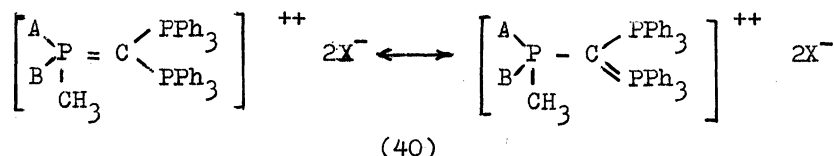
Fig. 1. The structure of cation of the crystalline salt
$[Bu_2P(H)C(PPh_3)_2]^{++}$ $2Br^-.HBr.CH_2Cl_2$

$P_1C_1P_2$	118.2°	$C_1P_3C_2$	115.3°	C_1P_1	1.69 Å
$P_2C_1P_3$	117.2°	$C_1P_3C_3$	114.2°	C_1P_2	1.88 Å
$P_1C_1P_3$	124.2°	$C_2P_3C_3$	109.2°	C_1P_3	1.72 Å

The IR-spectrum of the crystalline salt also confirms the existence of the P-H...Br hydrogen bond. The spectrum contains a broad band at 2300 cm^{-1} (also present [27] in the spectrum of $Et_3P^+H...Br^-$, 2320 cm^{-1}) and also deformation bands at 930 and 975 cm^{-1}.

As well as adding a proton, the salts (31) readily react with numerous electrophilic reagents. Methylation with methyl iodide yields the triphosphonium methanes (40), in which the onium charge is delocalized among the three phosphorus atoms, similar to the protonated PH salt (34).

$$\left[\begin{array}{c} A \\ B \end{array}\!\!>\!\!\begin{array}{c} \\ P = C \\ | \\ CH_3 \end{array}\!\!<\!\!\begin{array}{c} PPh_3 \\ \\ PPh_3 \end{array}\right]^{++} 2X^- \longleftrightarrow \left[\begin{array}{c} A \\ B \end{array}\!\!>\!\!\begin{array}{c} \\ P - C \\ | \\ CH_3 \end{array}\!\!<\!\!\begin{array}{c} PPh_3 \\ \\ PPh_3 \end{array}\right]^{++} 2X^-$$
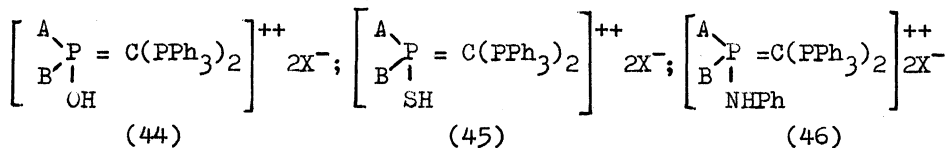
(40)

Oxidation by oxygen, addition of sulfur or reaction with phenylazide gives the corresponding phosphinoxides (41), sulfides (42) or imides (43).

$$\left[\begin{array}{c} A \\ B \end{array}\!\!>\!\!\begin{array}{c} \\ P - C \\ \| \\ O \end{array}\!\!<\!\!\begin{array}{c} PPh_3 \\ \\ PPh_3 \end{array}\right]^{+} X^-; \quad \left[\begin{array}{c} A \\ B \end{array}\!\!>\!\!\begin{array}{c} \\ P - C \\ \| \\ S \end{array}\!\!<\!\!\begin{array}{c} PPh_3 \\ \\ PPh_3 \end{array}\right]^{+} X^-; \quad \left[\begin{array}{c} A \\ B \end{array}\!\!>\!\!\begin{array}{c} \\ P - C \\ \| \\ NPh \end{array}\!\!<\!\!\begin{array}{c} PPh_3 \\ \\ PPh_3 \end{array}\right]^{+} X^-$$

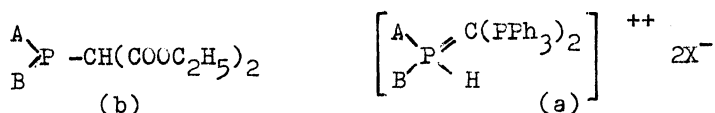(41)   (42)   (43)
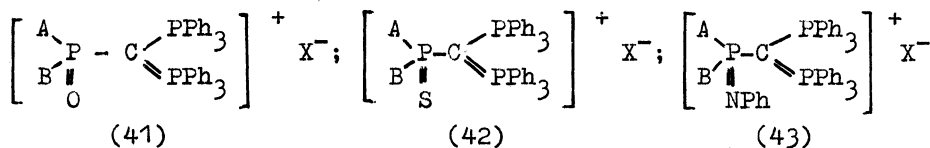
These, now triad systems, can be protonated on the oxygen, sulfur or nitrogen atoms to form mesomeric hydroxy (44), mercapto (45) or aminophosphonium ylides (46).

$$\left[\begin{array}{c} A \\ B \end{array}\!\!>\!\!\begin{array}{c} \\ P = C(PPh_3)_2 \\ | \\ OH \end{array}\right]^{++} 2X^-; \quad \left[\begin{array}{c} A \\ B \end{array}\!\!>\!\!\begin{array}{c} \\ P = C(PPh_3)_2 \\ | \\ SH \end{array}\right]^{++} 2X^-; \quad \left[\begin{array}{c} A \\ B \end{array}\!\!>\!\!\begin{array}{c} \\ P = C(PPh_3)_2 \\ | \\ NHPh \end{array}\right]^{++} 2X^-$$

(44)   (45)   (46)
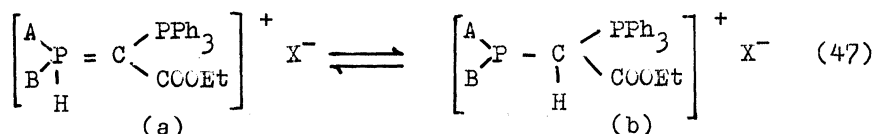
The structures of all these compounds have been vigorously established. Although beyond the scope of the present report it is nevertheless of interest that introduction of two phosphonium groups into the tertiaty methylphosphonium oxide leads to the rarely encountered "enolization" of the P=O group [28].

3. PHOSPHORUS–CARBON DYADS EXISTING AS AN EQUILIBRIUM MIXTURE OF THE PH– AND CH–FORMS
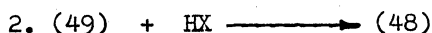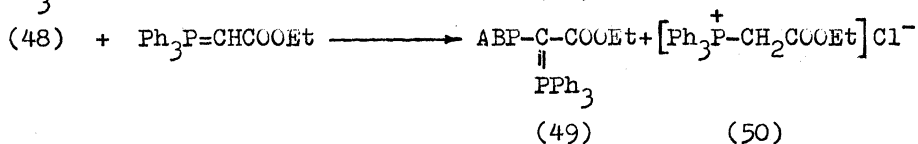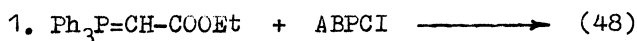
We have seen that in the potentially tautomeric system (2) only form (b) exists when R and R' are carbethoxy groups, because acidity of the CH group is then insufficient for a proton shift to the phosphorus atom. If, however, R and R' are both triphenylphosphonium groups, the CH-acidity increases so that the proton migrates to the phosphorus atom to give form (a).
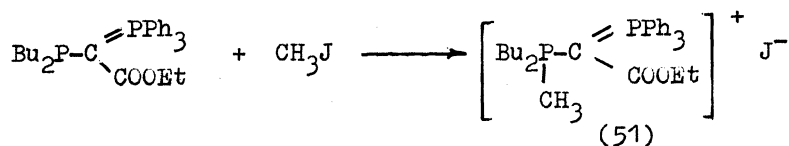
$$\underset{B}{\overset{A}{>}}P-CH(COOC_2H_5)_2 \qquad \left[\underset{B}{\overset{A}{>}}P\underset{H}{\overset{C(PPh_3)_2}{<}}\right]^{++} 2X^-$$

$$\text{(b)} \qquad\qquad\qquad \text{(a)}$$

One might, therefore, have expected that if the central carbon atom carried one carbethoxy- and one triphenylphosphonium group the CH and PH acidities should become commensurated and both forms (a) and (b) should exist in a solution. This, indeed, has been confirmed experimentally.

$$\left[\underset{\underset{H}{|}}{\overset{A}{>}}\overset{A}{\underset{B}{>}}P=C\overset{PPh_3}{\underset{COOEt}{<}}\right]^+ X^- \rightleftharpoons \left[\underset{\underset{H}{|}}{\overset{A}{\underset{B}{>}}}P-C\overset{PPh_3}{\underset{COOEt}{<}}\right]^+ X^- \quad (47)$$

$$\text{(a)} \qquad\qquad\qquad\qquad \text{(b)}$$

A study was made of the tertiary (triphenylphosphonium carbethoxymethyl)-phosphine salts (48, A=B=Bu or Ph), prepared according to the method of Issleib and Lindner [29]:

1. $Ph_3P=CH-COOEt$ + ABPCI $\longrightarrow$ (48)

   (48) + $Ph_3P=CHCOOEt$ $\longrightarrow$ $ABP-\underset{\underset{PPh_3}{||}}{C}-COOEt + \left[Ph_3\overset{+}{P}-CH_2COOEt\right]Cl^-$

   $\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ (49) $\qquad\qquad$ (50)

2. (49) + HX $\longrightarrow$ (48)

The reaction of triphenylphosphino-carbethoxymethylenephosphorane with di-butyl- or diphenylchlorphosphine yields the phosphine-substituted ylide (49), since the initially formed phosphonium salt (48) is immediately trans-ylidated by a second triphenylphosphino-carbethoxymethylenephosphorane mole-cule. Compound (49) with two phenyl groups on the phosphorus atom (49, A=B=Ph) is a crystalline substance that readily oxidizes in solutions. The dibutyl derivative (49, A=B=Bu) is an unstable viscous oil that can be kept only at low temperatures in an atmosphere of argon. It was therefore charac-terized by converting it with methyl iodide into the stable, easily crystal-lizable phosphorane-phosphonium salt (51) (m.p. 148–150°C).

$$Bu_2P-C\overset{PPh_3}{\underset{COOEt}{<}} + CH_3J \longrightarrow \left[Bu_2P-\underset{\underset{CH_3}{|}}{C}\overset{PPh_3}{\underset{COOEt}{<}}\right]^+ J^-$$

$$\text{(51)}$$

The $^{31}P-\{^1H\}$ spectrum of this salt displays two phosphonium phosphorus signals (δ_1=19.5 and δ_2=27.5 ppm) as doublets with a low coupling constant J_{PP}=31 Hz. Table 3 lists the NMR parameters of the initial phosphinomethy-lenes (49).

It can be seen from the table that at room temperature ^{31}P signals of the ylides are in the form of separate doublets, the high field signal belonging to the trivalent phosphorus and the low field signal – to the ylide phos-phorus. At low temperatures each doublet is split into two, as the result of hindered rotation about the partial C–C double bond to yield cisoid and transoid conformers.
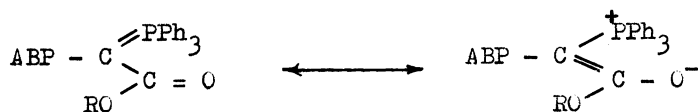
Similar conformational isomerism was observed by Bestmann and coworkers [30] and Grey [31]. We have found low temperature conformational isomerism also in the case of the P-protonated forms.

TABLE 3. $^{31}P-\{^{1}H\}$ NMR parameters of phosphino-substituted ylides $\text{ABPC(PPh}_3\text{)COOEt}$ (49).

A = B	Solvent	t°C	$\delta_{P^{III}}$ ppm (d)	δ_{P^+} ppm (d)	J_{PP} Hz
Bu	CH_2Cl_2	20	-33.1	27.3	156
	CH_2Cl_2	-80	-31.5	27.3	154
			-38.3	27.3	161
Ph	$CHCl_3$	20	-14.9	28.1	180
	CH_2Cl_2	-70	-13.5	28.0	178
			-19.2	28.1	183

Issleib and Lindner [29] have investigated the action of HCl at room temperature on the ylide (49), but have isolated only degradation products.

$$\text{Ph}_2\text{P-C(=PPh}_3\text{)COOEt} + HCl \longrightarrow \text{Ph}_2\text{PCl} + (50)$$
$$(49)$$
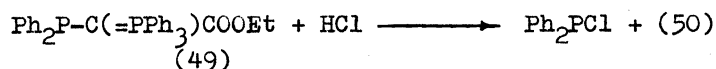
The degradation is similar to that described above for the diphenoxy- or diphenyl-(ditriphenylphosphoniomethyl)-phosphine salts. However, we found that if the hydrogen chloride or trifluoroacetic acid treatment is carried out at low temperatures in CH_2Cl_2 solution under argon or if it is carried out under other such mild conditions, instead of decomposition the ylides yield the corresponding protonated forms (47).

The action of acids on the ylides (49) depends on A and B substituents on the trivalent phosphorus. For example, treatment of the dibutyl derivative with HCl or HBr at -80°C in CH_2Cl_2 or with CF_3COOH at room temperature gives only P-protonation as can be seen from the ^{31}P-NMR spectral data. The low temperature spectrum reveals the formation of two conformers, cisoid and transoid (Table 4).

TABLE 4. $^{31}P -\{^{1}H\}$ NMR parameters of the HCl protonated ylides (49) in CH_2Cl_2 at -80°C.

A = B	Form	$\delta_{P/H/}$ ppm (d)	δ_{P^+} ppm (d)	J_{PP} Hz	J_{PH} Hz
Bu	(a)	5.7	20.2	34	460
		2.4	21.8	31	480
Ph	(a)	1.1	21.5	41.5	460
		-2.2	23.9	44.0	460
	(b)	-14.1 (P^{III})	25.1	90	-

In the proton undecoupled ^{31}P-NMR spectrum one observes a doublet for the protonated phosphorus with a coupling constant J_{PH} 460 Hz. This constant in

addition to the small J_{PP} (34 Hz) constant provides unambigious proof of the existence of a PH-bond, i.e. of structure (47a).

A different picture is given by the diphenyl derivative (49, A=B=Ph), whose spectra, obtained in CH_2Cl_2 solution in the presence of 1.5 mol HCl at -80° show besides the signals corresponding to the cisoid- and transoid-conformers of the PH-form (Table 4) also signals (see last line in Table 4) with chemical shifts differing only slightly from those of the initial ylide (49, A=B=Ph, Table 3), but with much smaller P-P coupling constants $J_{PP}=90$ Hz. We ascribe this group of signals to the CH-form (b) since it is known from the literature [32, 33], that conversion of phosphine-substituted ylides into the corresponding phosphonium salts (52) leads to similar changes in $\delta_{P^{III}}$ and J_{PP}.

$$\text{>}P = C - P\text{<} \quad \longrightarrow \quad \left[\text{>}P - CH - P\text{<}\right]^+ X^- \qquad (52)$$
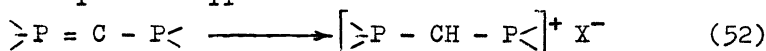
This conclusion is confirmed by ^{13}C-NMR spectral data obtained under conditions when only the CH-form is present (see below). It can be seen that the ^{13}C signal of the central carbon atom ($\delta = 38.1$ ppm) is split into 3 doublets, a doublet due to CH coupling (J_{CH} 139.7 Hz) each line of which is split into a doublet of doublets with constants $J_{CP^+} = 57$ Hz and $J_{CP(H)}=48$ Hz (the phosphorus atoms are non-equivalent). Such triple doublet couplings of the central carbon atom could only occur when it is in the CH form.

Thus, in CH_2Cl_2 at -80°C the hydrogen chloride salt (A=B=Ph) exists in both the CH- and PH-forms (47, a,b). Further study has shown that both forms are in mobile tautomeric equilibrium. This can be seen from the dependence of the relative percentage of the forms in solution upon the temperature, as determined from the integral intensities of the signals (Table 5).

TABLE 5. Temperature dependence of the tautomeric equilibrium of the CH and PH forms (47, A=B=Ph) in CH_2Cl_2 in the presence of a 2-fold of HCl.

$t^\circ C$	Content, %	
	CH – Form	PH – Form
-80	73	27
-90	70	30
-100	68	32
-110	66	34

A rise in temperature from -110° to -80° favors the CH-form; but further increase causes decomposition of this form. Signal broadening occurs with the rise in temperature, indicating the occurence of exchange processes; the signals of the PH-form undergo broadening more rapidly, than those of the CH form, perhaps because of increasing rate of conformational interconversions.

The relative percentage of the tautomeric forms depends also on the acidity of the medium. It can be seen from the data in Table 6 that the content of the CH-form increases with increase in acidity. At constant acidity the percentage of this form increases also with increase in polarity of the medium. This is illustrated in Table 7 with a mixture of CH_2Cl_2 and acetonitrile.

With a 10:1 CH_2Cl_2:CH_3CN content at -80° in the presence of 2 M HCl only the CH-form is present. However, when the temperature is raised to -30° and in the presence of a large excess of CF_3COOH only the PH form is present.

In a large excess of HCl but not of trifluoroacetic acid at -90° both forms are transformed to the dication (53).
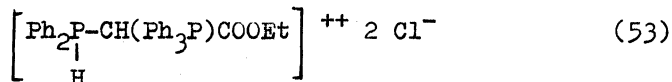
$$\left[\begin{matrix} Ph_2P-CH(Ph_3P)COOEt \\ | \\ H \end{matrix} \right]^{++} \; 2 \; Cl^- \qquad (53)$$

TABLE 6. Dependence of the equilibrium position of the CH
and PH forms of (47, A=B=Ph) on the ylide (49):
HCl ratio (CH_2Cl_2; $-80°C$).

Ratio	Content, %	
ylide (49):HCl	CH-Form	PH-Form
1 : 0	0	0
1 : 1.5	33	67
1 : 2	70	30
1 : 3	85	15
1 : 8	95	5

TABLE 7. Dependence of the equilibrium position of the CH
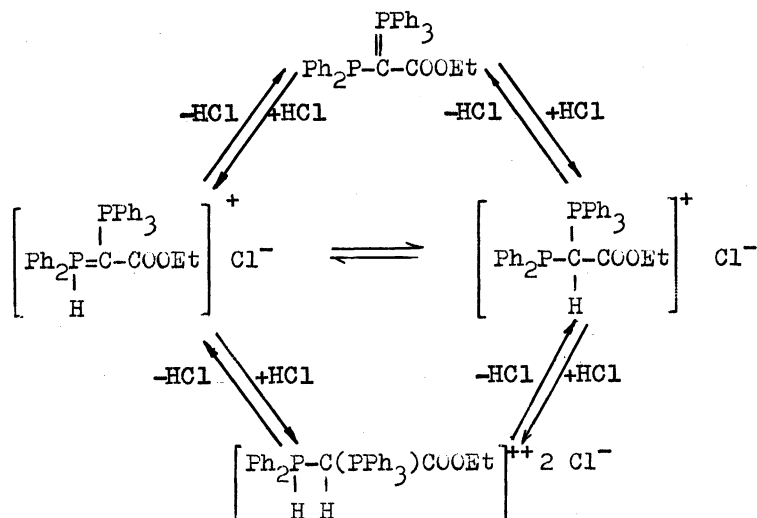and PH forms (A=B=Ph) on the solvent composition
(49):HCl ratio 1:2; $-80°C$

Concentration of CH_3CN in CH_2Cl_2, %	Content, %	
	CH-Form	PH-Form
0	70	30
3.20	86	14
6.25	95	5
9.10	100	0

The NMR ^{31}P-{^1H}-spectrum of the dication in the 10:1 CH_2Cl_2:CH_3CN solvent
shows two phosphonium signals at $\delta = 5$ and 23 ppm ($J_{PP}=7.3$ Hz). In the
proton undecoupled spectrum the first signal becomes a doublet with
$J_{PH}=520$ Hz, evidence of PH protonation. It should also be mentioned that
the ^{31}P-NMR spectrum of the dication (53) is close to that of the bisphos-
phonium salt (54), represented in [32].

$$\left[\begin{array}{c} Ph_2P-CH_2-PPh_2 \\ CH_3 \quad\quad H \end{array} \right]^{++} \quad 2\ CF_3COO^- \quad\quad\quad (54)$$
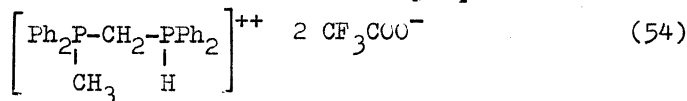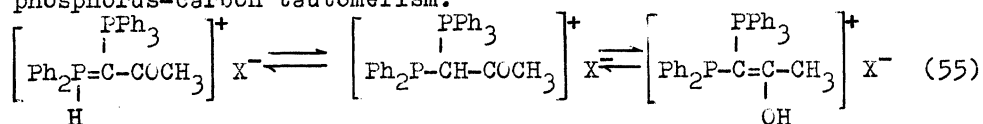
Dication (53) is stable only at low temperatures. With rise in temperature
the signal first broadens and then splits into two separate groups corres-
ponding to the CH and PH forms. These temperature-induced changes are
completely reversible.

The prototropic equilibrium can thus in summary be represented by the fol-
lowing scheme:

$$
\text{Ph}_2\text{P}-\overset{\overset{\displaystyle \text{PPh}_3}{\|}}{\text{C}}-\text{COOEt}
$$

$$-HCl \Big/ +HCl \qquad\qquad -HCl \Big\backslash\ +HCl$$

$$
\left[\begin{array}{c}\overset{\displaystyle \text{PPh}_3}{\underset{\displaystyle}{|}} \\ \text{Ph}_2\overset{}{\underset{|}{P}}=\text{C}-\text{COOEt} \\ \text{H}\end{array}\right]^{+} \text{Cl}^{-}
\qquad \rightleftharpoons \qquad
\left[\begin{array}{c}\overset{\displaystyle \text{PPh}_3}{|} \\ \text{Ph}_2\text{P}-\text{C}-\text{COOEt} \\ \overset{|}{\text{H}}\end{array}\right]^{+} \text{Cl}^{-}
$$

$$-HCl \Big\backslash\ +HCl \qquad\qquad -HCl \Big/ +HCl$$

$$
\left[\text{Ph}_2\overset{|}{\underset{\text{H}}{P}}-\overset{|}{\underset{\text{H}}{C}}(\text{PPh}_3)\text{COOEt}\right]^{++} 2\,\text{Cl}^{-}
$$

We carried out a similar study of the corresponding acetyl derivatives
(55). In this case the usual keto-enol tautomerism occurs as well as the
dyadic phosphorus-carbon tautomerism:

$$
\left[\begin{array}{c}\overset{\displaystyle \text{PPh}_3}{|} \\ \text{Ph}_2\overset{}{\underset{|}{P}}=\text{C}-\text{COCH}_3 \\ \text{H}\end{array}\right]^{+}\!\!\! \text{X}^{-}
\rightleftharpoons
\left[\begin{array}{c}\overset{\displaystyle \text{PPh}_3}{|} \\ \text{Ph}_2\text{P}-\text{CH}-\text{COCH}_3\end{array}\right]^{+}\!\!\! \text{X}^{-}
\rightleftharpoons
\left[\begin{array}{c}\overset{\displaystyle \text{PPh}_3}{|} \\ \text{Ph}_2\text{P}-\text{C}=\text{C}-\text{CH}_3 \\ \text{OH}\end{array}\right]^{+}\!\!\! \text{X}^{-} \quad (55)
$$

Here, too, the equilibrium interconversion of all three forms have been
unequivocally demonstrated.

We thus see that the known examples of dyadic tautomerism of oxygen, sulfur
and nitrogen organophosphorus systems can now be supplemented by phospho-
rus-carbon dyadic tautomerism.

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