THE STRUCTURE AND REACTIVITY OF ORGANO-PHOSPHORUS COMPOUNDS

R. F. Hudson

Cyanamid European Research Institute, Cologny, Geneva, Switzerland

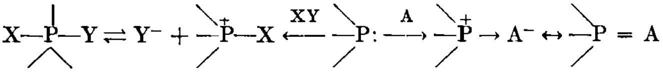
I. Introduction

Structural and mechanistic investigations of organo-phosphorus compounds have received considerable stimulus in recent years because of the importance of nucleic acids, coenzymes, and allylic pyrophosphates in living systems (*170*). Thus an organic phosphorus chemistry analogous to organic carbon chemistry has rapidly developed. The reactions of such compounds are usually classified under organic chemistry since the same experimental techniques are used, and some of the reactions are common to both elements. From an electronic point of view however, reactions at a phosphorus atom should undoubtedly be classified as inorganic, and the relationship between the structure and reactivity of organophosphorus compounds is therefore of interest in theoretical and mechanistic studies of inorganic chemistry.

In the present review we shall be concerned primarily with the structural description of 4- and 5-coordinated compounds in an attempt to provide a general basis for the interpretation of their reactivity. Before doing so the general basis of phosphorus chemistry will be discussed briefly.

The electronic structure of elementary phosphorus, $1s^2\ 2s^2,\ 2p^6\ 3s^2\ 3p^3$ shows that three $3p$ orbitals are available for σ-bonding, thus giving rise to the trivalent compounds PX_3. The valency angles* in phosphine (93°) show less sp^3 hybridization than in ammonia (106–107°), but the bond angles in the halides PX_3 (100–102°) are close to those in NF_3 (102.5°), which are probably determined by nonbonded repulsions.

The reactivity of such compounds, and most of phosphorus chemistry are determined by the behavior of the 3*s* electrons, and the main reactions may be represented briefly as follows,



Tervalent phosphorus compounds are very reactive, passing readily into the sp^3 hybridized state by protonation, alkylation, the addition to Lewis acids (*18*, *174*) and by complexing with transition metal ions (*27*). Many of these reactions have been reviewed recently, and the participation of ultimate *d*-orbitals in complex formation has been discussed (*2*).

Further the trivalent phosphorus atom is highly electrophilic, and in this way resembles bivalent sulfur. Thus displacement reactions with nucleophilic reagents proceed rapidly, e.g.,

$$R_2PCl + R_2PH \rightarrow R_2P - PR_2 + HCl.$$
$$R_2PCl + R'_2NH \rightarrow R_2PNR'_2 + HCl.$$
$$R_2PCl + ROH \rightarrow R_2POR' + HCl.$$

Trans-esterification (*91*, *92*) of trialkyl phosphites is a rapid process, but it is not known whether the reaction proceeds via a quasi-phosphonium derivative,

$$(R'O)_3P + ROH \rightleftarrows (R'O)_3\overset{+}{P}H + RO^- \rightarrow RO(R'O)_2P + R'OH$$

although in acid solution this intermediate is rapidly de-alkylated (*67*).

$$(RO)_3P + HX \rightleftarrows (RO)_3\overset{+}{P}H + X^- \rightarrow RX + (RO)_2P(O)H \rightleftarrows (RO)_2POH.$$

Systematic investigations of nucleophilic displacement at the trivalent phosphorus atom of the kind recently made with sulfur compounds are necessary before the reactivity can be discussed further.

The substitution of alkyl groups in phosphine (*87a*) produces large increases in basicity (e.g., $PH_3 \rightarrow Me_3P$; $\Delta pK \simeq 22.5$) in contrast to the

---

* Unless stated otherwise, bond lengths and bond angles are taken from "Tables of Interatomic Distances and Configuration in Molecules and Ions," *Chem. Soc. Spec. Publ.* **11,** 1958.

small changes for amines (e.g., $NH_3 \rightarrow Me_3N$; $\Delta pK < 1$), which may be attributed to strong inductive effects, probably produced partly by hybridization changes, steric effects being relatively unimportant. (See however the nucleophilic order (*87b*) $Me_2PEt > MeEt_2P > Me_3P > Et_3P$.)

Aromatic groups reduce the basicity (*43*) but the effect is smaller than for the corresponding amines. Thus for methylamine and aniline, $\Delta pKa = 6.2$, whereas for methyl phosphine and phenyl phosphine, a value of $\Delta pKa \simeq 2$ may be estimated. This large difference may be attributed to weaker p_π-p_π bonding for the second row element on interaction of the lone pair electrons with the benzene ring, as predicted by the ultraviolet spectrum of triphenyl phosphine (*106*).

The short lived molecules P_2, PO, and PN are probably stabilized by $3p_\pi$ bonds in view of the short bond lengths and relatively high dissociation energies. These are compared with the corresponding values for the nitrogen compounds in Table I.

TABLE I

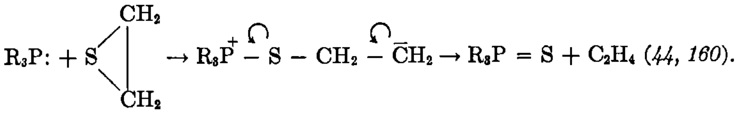
A COMPARISON OF BOND LENGTHS AND BOND ENERGIES OF DIATOMIC COMPOUNDS OF PHOSPHORUS AND NITROGEN

Bond	DAB	r_{AB}	Molecule	DAB	r_{AB}
P—P	50	2.18	P_2	116	1.894
P—N	67	1.80	PN	164	1.491
P—O	84	1.76	PO	143	1.448
P—S	55	2.14	PS	—	1.92
P—C	62	—	PC	159	1.562
N—N	12	1.40	N_2	225	1.095
N—O	48	1.36	NO	162	1.15

Apart from the existence of these unstable diatomic molecules, and the molecule HCP (*68*) there is little evidence of multiple bonding in trivalent phosphorus compounds, although several workers (*152*, *179*) have reported the dimer $(PhP)_2$. The structure of this and the alkyl analogues is in doubt as most workers believe them to be in the form of tetramers (*114*, *136*) or higher cyclic polymers, and the structure $(CF_3)_5P_5$ has been investigated by X-ray analysis (*165*). These compounds are very reactive and in contrast to the corresponding azo compounds, the P-P bond is invariably broken (*89*, *90*, *103*).

The typical reactions of phosphines acting as nucleophiles lead to either phosphonium derivatives, or by oxidation to the quinquevalent state giving phosphoryl or thiophosphoryl derivatives. Thus oxygen and sulfur are rapidly removed from many compounds in reactions which may be regarded formally as nucleophilic displacements on oxygen and sulfur, e.g.,

$$R_3P: + HOOH \rightarrow R_3\overset{+}{P}-OH + \bar{O}H \rightarrow R_3P = O + H_2O \ (93).$$

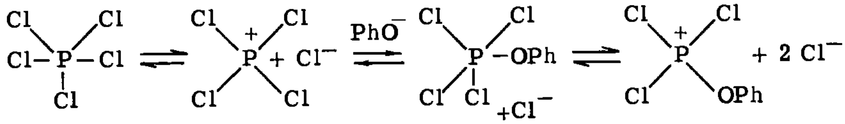


In many cases however, as for example in auto-oxidation (*22*) these are radical reactions.

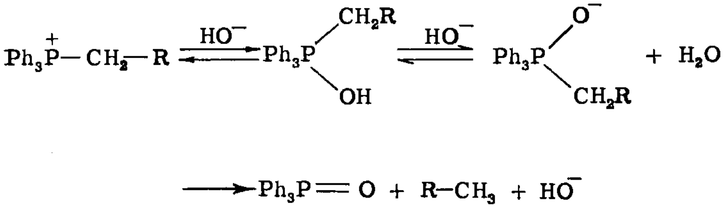
The basic structure of a phosphoryl compound is an sp^3 hybridized σ-bonded system, although the XPX angles are significantly less than 109°. This is usually attributed (*138*) to the influence of π bonding in the P=O group, although the use of $3d_\pi$ orbitals for this purpose is highly controversial (see below). The bond angle decrease may alternatively be due to nonbonded repulsions.

Owing to the highly polar P=O bond, the phosphorus atom is highly electrophilic. Displacement reactions at this center are therefore rapid, and phosphorylations, which will be discussed in more detail in a subsequent section have been widely investigated.

The bonding in phosphonium salts and pseudo-phosphonium salts is assumed to be sp^3, although the bond angles have not been measured. Electronegative atoms interact strongly at the phosphonium center to produce 5-coordinated intermediates and rapid interchange of the groups, e.g., (*154*, *155*).



The highly electrophilic nature of the phosphorus atom is shown by the displacement of carbanions by hydroxide (*63*) and alkoxide (*71*, *88*) ions, e.g.,



and by the reaction of phosphorus pentachloride with olefins (*13*) which are very weak nucleophiles.

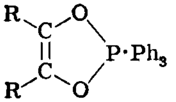
$$\overset{+}{P}Cl_4 + CH_2{=}CH_2 \rightarrow \bar{C}H_2-CH_2-\overset{+}{P}Cl_3 + Cl^- \rightarrow ClCH_2-CH_2-\overset{+}{P}Cl_3.$$

These and similar displacements involving phosphoryl and thiophosphoryl compounds may be regarded as passing through five coordinated transition states, sometimes producing stable intermediates. Before chemical reactivity is discussed in more detail therefore, the bonding and stereochemistry of these five coordinated compounds will be discussed further.

II. The Electronic Structure of PX_5

In the solid state PCl_5 and PBr_5 exist in ionic forms as $P^+Cl_4PCl_6^-$ and $P^+Br_4Br^-$ (*29*, *146*), respectively, but in the gaseous phase both adopt the trigonal bipyramidal configuration like PF_5 and PCl_3F_2.* In the case of PCl_5 (*54*, *131*, *153*) the axial and radial bonds are not equivalent (2.04 ± 0.06 and 2.19 ± 0.02), but in PF_5 they were assumed to be equivalent in the structural determination.

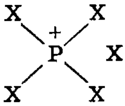
More recently, pentacovalent molecules with less electronegative ligands, e.g., Ph_5P (*185*) and



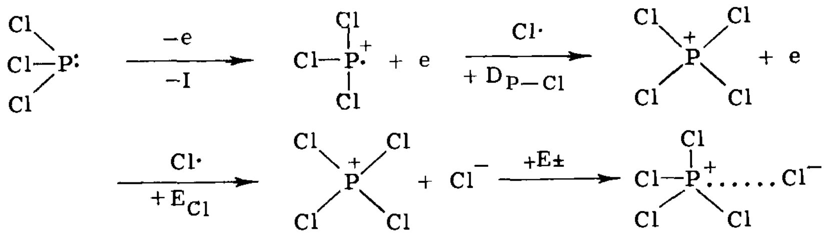
have been prepared, but the detailed structures of these are unknown.†

The 6-covalent ions, PF_6^- and PCl_6^- (only found in solid PCl_5), show octahedral symmetry (*29*) as anticipated.

In view of the high energy of 3*d* orbitals, and the influence of electronegative groups on the stability of 5-covalent molecules, Pauling (*137*) concluded that *d*-orbitals are not used and suggested resonance between the structures



That such a structure is energetically possible is readily shown by the following simple argument. Consider the sequence of processes



---

* See "Interatomic Distance," *Chem. Soc. Spec. Publ.* **11**, pp. M.54 and M.55, 1958.

† Note added in proof. Wheatley (*182a*) has shown that Ph_5Sb, Ph_5As and Ph_5P have square-pyramidal structures.

The total bond energy is given by

$$D_{P-Cl} + E_{Cl} + E \pm - I.$$

This gives a value of 47 kcal/mole ($I_{PCl_3} = 12.3$ ev) and 87 kcal/mole if allowance is made for the initial P-Cl partial ionic character in PCl_3, compared with the experimental value of 78 kcal/mole (*169*).

According to Pauling the 5 atoms are held by the 3*s* and 3*p* orbitals, together with electrostatic attraction with the unit negative charge distributed over the 5 chlorine atoms. Although this explanation is energetically reasonable, the stereochemistry is not predicted, although the five "4/5 electron pair" bonds will take up a position of minimum electronic repulsion.

For this reason the use of *d* orbitals is usually invoked in spite of the high promotion energy. This is not known accurately, but an approximate value has been estimated (*69*) from the following excitation energies.

(1) $3s^2 3p^3 \rightarrow 3s 3p^4 \sim 8$ ev

(2) $3s^2 3p^3 \rightarrow 3s^2 3p^2 3d \sim 9$ ev

The combined value of 17 ev is overestimated by several electron volts by the repulsion of two *p* electrons in the same orbital in transition (1), but the actual valency state will be 2–3 ev higher than the lowest energy state given by (1) + (2). Thus the approximate value, 17 ev may be compared with the corresponding value 23 ev for nitrogen. Since the transition (1) gives the difference in energy of an electron in the 3*p* and 3*s* levels, the sum of this energy and the ionization potential of phosphorus (which refers to a 3*p* electron) gives an approximate value of 19 ev for the ionization potential of an *s* electron in the free atom.

The ionization potential (~10 ev for PH_3) and consequently the energy of the 3*d* level are reduced considerably by molecule formation, due to the presence of the additional electrons in the 3*p* orbitals, but the 3*d* promotional energy remains considerably greater than the energy of bond formation in PCl_5 (~3 ev). This is the main objection to the use of 3*d* orbitals in second row elements.

In an orbital description of the 5-coordinated system, the angular functions are such that hybridization of the *s*, and *p* orbitals with a *d* orbital leads to a bipyramidal arrangement (*111*). For effective hybridization the exponents characterizing the radial functions must be of similar size. Detailed calculations of Slater radial functions for ultimate 3*d* orbitals have been used to calculate the overlap integrals between the *s*, *p*, and *d* orbitals of the same atom and between these orbitals and a p_σ orbital of a chlorine atom (*34*, *104*). Maximum overlap and hence maximum binding energy is given by a small contribution from the *d*-orbital, hence the bonding is determined mainly by the sp^3 orbitals. Moreover the axial and radial bonds give maximum overlap for slightly different lengths, the former being slightly the longer.

Calculations of the ($3d_\sigma - 3p_\sigma$) overlap integrals for the P-Cl bond show that the *d*-orbitals are too diffuse for effective bonding when the nuclear charges Z calculated by Slater rules, are equal. The overlap integral is very sensitive to the effective charges on the atoms (see Fig. 1), and becomes comparable to the corresponding values for *s* and *p* orbitals when*

$$\frac{\alpha_P - \alpha_{Cl}}{\alpha_P + \alpha_{Cl}} \sim 0.2$$

This and similar calculations (*35*) have led to the idea that *d*-orbitals are contracted by perturbation by the ligands. It has been suggested that the electrons in the 3*d*-orbital of the phosphorus atom are partially ionized and located on the chlorine atoms (*34*). This creates a positive charge on the phosphorus atom, which by causing preferential contraction of the more polarizable *d*-orbitals makes these compatible with the 3*p*-orbitals. In valency bond terms the resulting structure could be regarded as a resonance hybrid of the ionic ($PX_4^+X^-$) and covalent, PX_5, forms.

In a modified treatment, Craig and Magnusson (*35*) have shown that orbital contraction may be produced by the electrostatic field of the ligands, each regarded as a point charge Z_s, without ionization of the electron from the 3*d* orbital, due to the high polarity of the sp^3d hybridized bonds.

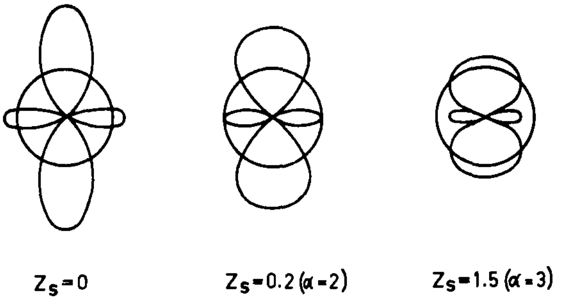


Fig. 1. The contraction of a d_{z^2} orbital in the presence of perturbing ligands (*35*) with effective charges Z_s.

However, the increase in the central charge caused by the perturbing ligands *increases* the 3*d* promotional energy considerably, as an inner orbital is stabilized relative to a projecting orbital. For example, the energy of an electron in a 3*d*-orbital is increased by 8 ev by 6 unit charges at a distance

---

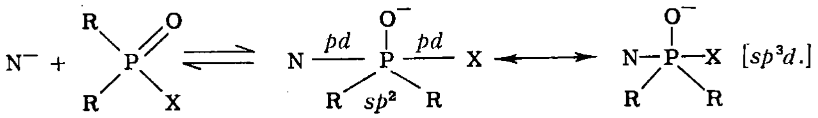
* $\alpha = Z/n$, where n is the effective principal quantum number.

of 4 a.u. assuming a spherical field, although this value is somewhat less for an octahedral field.

It follows therefore that the increase in the promotional energy is greater than the gain in energy by *d*-orbital hybridization and the importance of d_σ-orbitals in phosphorus chemistry is probably very small.

III. Configuration of the Transition State

Although the contribution of d_σ-orbitals to the ground states of 5-coordinated phosphorus compounds may be small, the importance will increase in excited states and *pd* hybridization may well stabilize the transition state of a displacement at 4 coordinated phosphorus. According to Gillespie (*69*) three of the 4 original sp^3 bonds rehybridize to give sp^2 bonds leaving a more diffuse *p*-orbital which hybridizes with the $d_z{}^2$-orbital to give *pd* hybrids (I). These bonds will be relatively polar, and the structure is very similar to an S_N2 transition state, viz.,

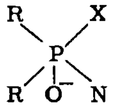


(I) (II)

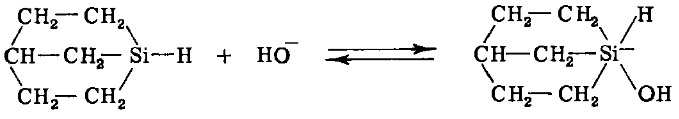
This description of the transition state is supported by the absence of O^{18} exchange of the phosphoryl oxygen atom in the hydrolysis of chlorides (*53*) fluorides (*84*) and esters (*80*), suggesting that the two P-O bonds of a possible intermediate diol are not equivalent, as would be the case in (II).

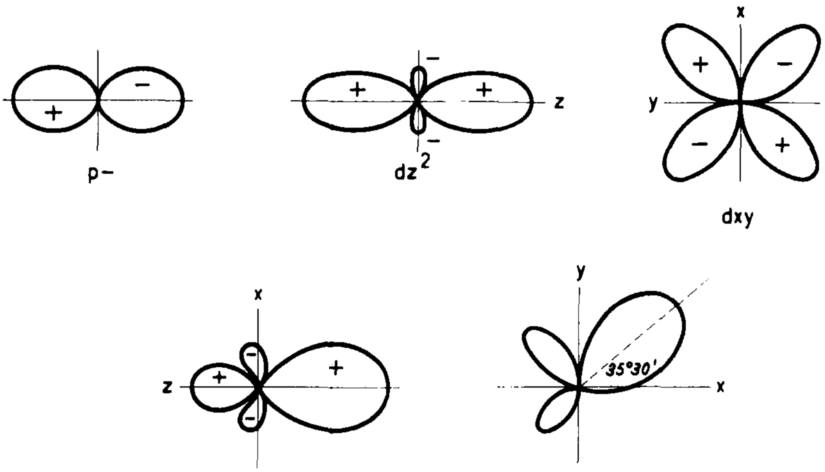
Alternative forms of hybridization are possible, and Gillespie (*69*) has shown that an sp^3-orbital may hybridize with a suitably orientated *d*-orbital (d_{xy}) to give two equal *spd* bonds, mutually inclined at 71°.

In this structure, (III), 3 bonds remain in the sp^3 hybridized state. Although there is so far no evidence for this structure in phosphorus reactions, the high reactivity of the bridgehead silicon compounds (*164*) may be due to this transition state.



(III)





p-   dz²   dxy

pd-hybrid   spd – hybrid

FIG. 2. *pd* and *spd* hybrid orbitals (*69*).

Evidence on the nature of the transition state for phosphorus may be obtained from optical activity studies, since structure (I) would lead to inversion, structure (II) to inversion and retention, and structure (III) to retention of configuration, and considerable advances in this direction have been made in the past 2–3 years.

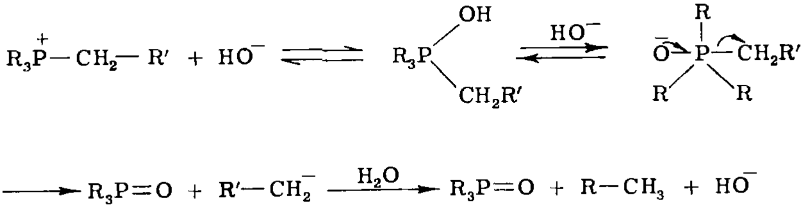
IV. Reactions of Phosphonium Compounds

Differences in the reactions of quaternary phosphonium and ammonium salts also suggest that *d*-orbitals may be used in the former cases. Thus although halide ions and other reagents which are highly reactive towards the saturated carbon atom give de-alkylation (*62*), viz.,

$$R_4\overset{+}{N}—CH_2R' \xrightarrow{Y^-} R_3N + R'CH_2Y$$

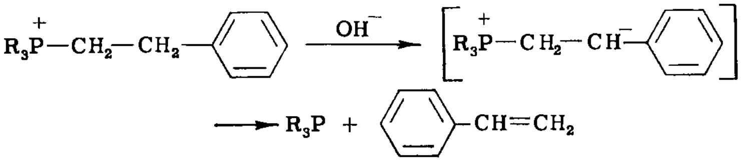
$$R_3\overset{+}{P}—CH_2R' \xrightarrow{Y^-} R_3P + R'CH_2Y$$

hydroxide (*88*) and alkoxide (*71*) ions, which produce β-elimination with quaternary ammonium compounds (*102*), give the corresponding paraffins with phosphonium salts. Kinetic studies (*189*) have shown these reactions to be second order with respect to base, suggesting the following mechanism,



Recent work with optically active phosphonium salts has shown that this reaction is stereospecific (*116*) giving the phosphinoxide which was originally characterized by Meisenheimer (*125*, *126*). This reaction probably involves inversion of configuration in view of the comparison with the Wittig reaction given below.*

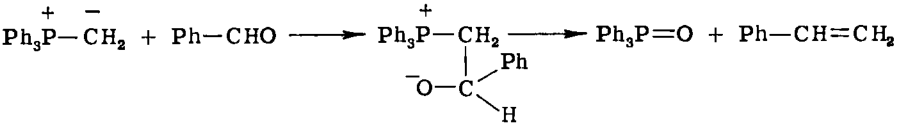
In view of the strongly electrophilic nature of the phosphorus atom, β-elimination from phosphonium compounds is only observed (*63*) when the incipient carbanion is stabilized by conjugation, e.g.,



Alternatively strong bases can remove an α-proton (*166*, *184*) to give the phosphomethylene (or ylid), the stability of which is usually attributed to $d_\pi - p_\pi$ bonding (see p. 362)

$$R_3\overset{+}{P}-CH_2R + Ph-Li \rightarrow R_3P{=}CH_2R + C_6H_6.$$

Phosphine methylenes are very reactive towards electrophilic reagents in particular towards the carbonyl group (*186*) giving the celebrated Wittig reaction (*158*). The intermediate has been isolated in the reaction of benzaldehyde (*186*) so the reaction presumably occurs by way of a four-membered ring with entering and leaving groups on the same side of the phosphorus atom.

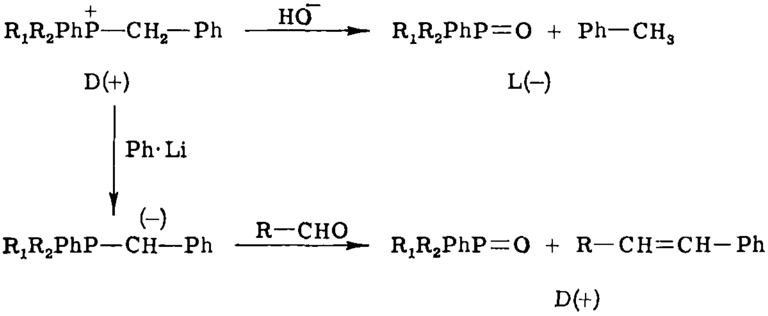


$$Ph_3\overset{+}{P}-\overset{-}{C}H_2 + Ph-CHO \longrightarrow Ph_3\overset{+}{P}-CH_2-\overset{-}{O}-C(Ph)(H) \longrightarrow Ph_3P{=}O + Ph-CH{=}CH_2$$

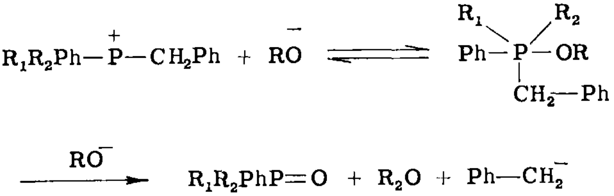
By carrying out this reaction with the optically active methyl ethyl phenyl benzyl phosphonium salt an optically pure phosphinoxide was obtained with opposite rotation to that obtained by the displacement reaction with hydroxide ions. By assuming that, of these two processes, the Wittig reaction is the more likely to proceed with retention of configuration, it follows that the displacement proceeds with complete inversion (*15*)

---

* The work of Horner *et al.* (*93a*) supports this view.

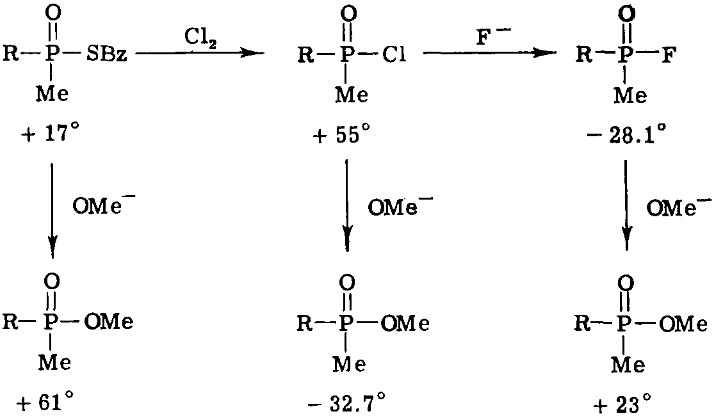


It is significant that in the corresponding displacement by alkoxide ions, the phosphinoxide is racemic (*135*), thus indicating that a 5-coordinated intermediate is formed, the decomposition of which is slow compared with the reversion to the original ions, viz.,



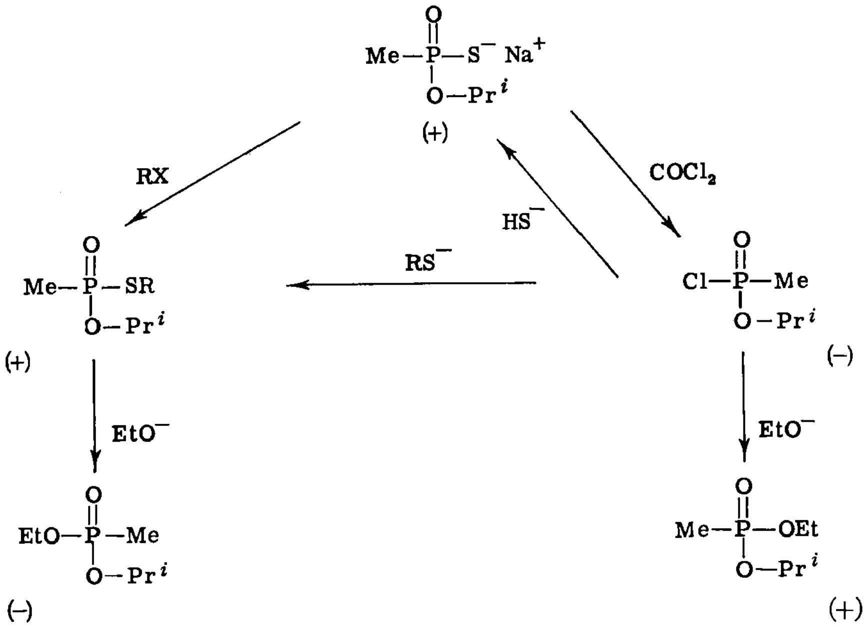
V. Stereochemical Change on Phosphorylation

Optical activity studies of phosphorylation are particularly difficult owing to the frequently rapid racemization (probably due to traces of anions present) of the compounds. Several workers have carried out cycles which show that inversion of configuration occurs predominantly in some reactions. Thus Green and Hudson (*74*) have carried out the following series of reactions.



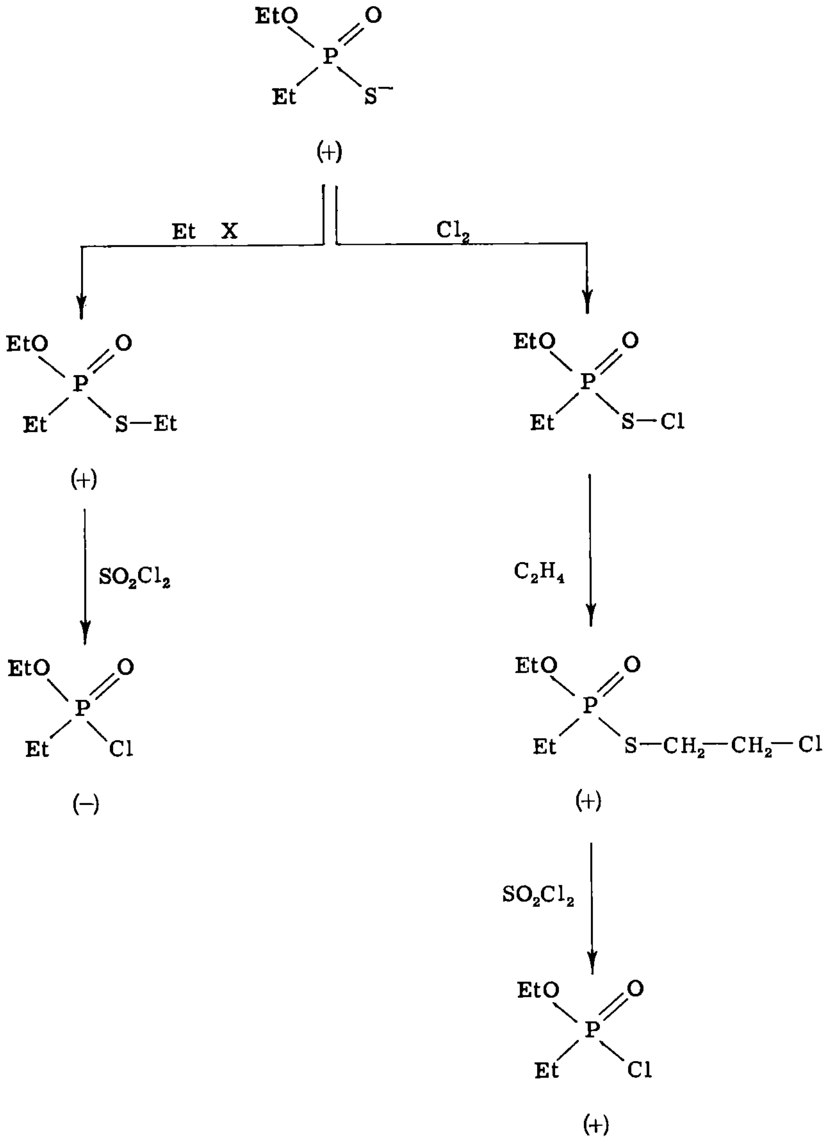
In these experiments the products were not isolated, as the reactions were known to proceed to completion, and distillation reduces the activities considerably. All activity measurements were made in benzene solution. Traces of fluoride ions were shown to racemize the phosphinic fluoride very rapidly.

A similar scheme has been established by Aaron and co-workers (*1*), who based the investigations on the chloridate as follows.

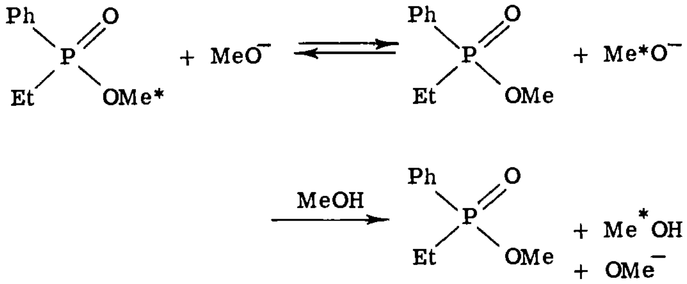


The chloridates were found to racemize very rapidly owing to traces of chloride ions or hydrochloric acid, and consequently products of low optical purity were obtained in these displacements and in the similar reactions carried out by Michalski and Ratajczak (*127*).

By assuming that the two displacements involving ethoxide ions involve similar stereochemical changes, Aaron *et al.* (*1*) concluded that the compounds $Pr^iO(RS)P(O)Me$ and $Pr^iO(Me)POCl$ of different sign have different configurations. However this assumption must be applied with caution in view of the various observations with silicon compounds (*163*) that products of different sign are obtained by making relatively small changes in the reaction conditions. Moreover Michalski and Ratajczak obtained the same chloridate with different rotations, by chlorination of two different thiolates with the same sign of rotation,



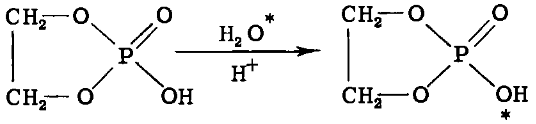
Very recently, the displacement of the methoxide group of methyl ethylphenylphosphinate by methoxide ions has been shown to be completely stereospecific proceeding with inversion of configuration (*75*). Thus the rate of racemization of the ester was found to be exactly twice the rate of displacement of the methoxide group labelled with C^{14},



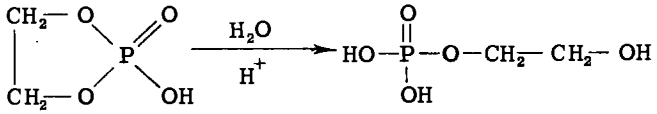
It appears therefore that, as in the case of silicon (*163*) inversion is the preferred configurational change in homogeneous solution.

By considering the reactions of strained cyclic esters (*115*), Haake and Westheimer (*80*) have shown recently that both O^{18} exchange (a) and hydrolysis (b) of ethylene hydrogen phosphate, proceed at similar rates in acid solution.

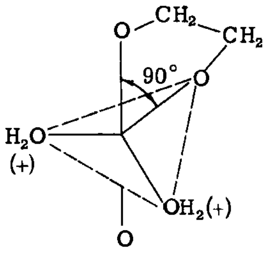
(a)



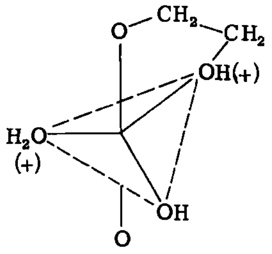
(b)



Since the rate of hydrolysis is about 10^7 times greater than the corresponding rate for diethyl phosphate, due to the release from steric strain on formation of the transition state (*181*), the O-P-O angle in the ring is considered to be the same in the transition states of (a) and (b). After considering various possibilities, transition states with O-P-O angles of 90° were considered to be the most likely, corresponding to a trigonal bipyramid or a square pyramid. In view of the less favorable electronic distribution in the latter case (*111*) these observations suggest that the transition state adopts the *sp³d* hybridized form as follows:

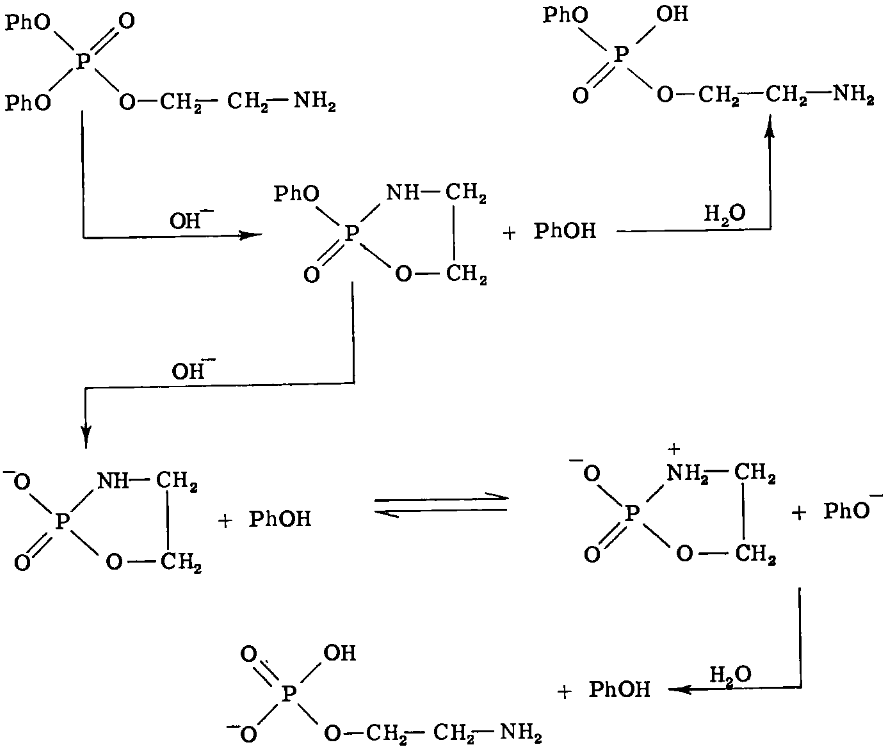


and

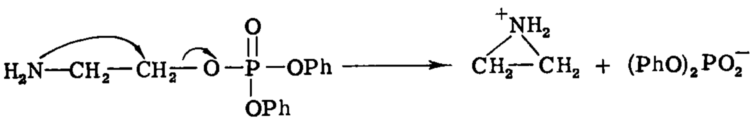


This configuration requires the *sp*^{3}*d* bonds in the basal plane to be weaker than the axial bonds, leading to inversion of configuration. This is an interesting suggestion, which requires further investigation with suitable conformations at the phosphorus atom.

The comparable rates of (a) and (b) suggest that displacement of the noncyclic group attached to a phosphorus atom which is also part of a 5-membered ring is extremely rapid. This may explain the rapid alkaline hydrolysis of 2-aminoethyl diphenyl phosphate with the liberation of two moles of phenol (*55*) since the monophenyl 2-aminoethyl ester is unreactive in alkaline solution, according to the scheme.



In dilute alkaline media, the reaction proceeds by the usual ionization reaction giving ethylene imine and its cyclic dimer (*20*)



$$H_2N{-}CH_2{-}CH_2{-}O{-}P(=O)(OPh){-}OPh \longrightarrow CH_2{-}CH_2(^+NH_2) + (PhO)_2PO_2^-$$

Although studies of the configurational changes accompanying displacement are in a very early stage, the following tentative conclusions may be drawn:

(a) Displacements usually proceed through an S_N2 bimolecular transition state with the *pd* bonds weaker than the radial sp^2 bonds.

(b) In view of possible sp^3d and *spd* hydridization however, reaction may proceed by retention of configuration in suitable cases with velocities comparable to those observed in the more usual mechanism.

VI. The Symmetry of d_π–p_π Bonds

In carbon chemistry, changes in π-bonding affect the reactivity to such an extent that in many reactions conjugation changes outweigh σ-bond effects. It is very important therefore to ascertain whether conjugation is possible in phosphorus compounds.

Considering initially an isolated P=O double bond, π-bonding can be formed as follows (*34*).

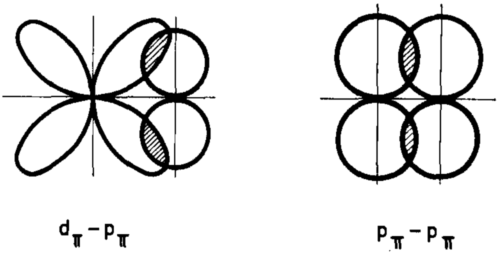


FIG. 3. A comparison of p_π—p_π and d_π—p_π overlap.

As with σ-bonds, *d*-orbitals are found to be too diffuse (if $Z_a = 0$) for significant overlap, but the overlap integral increases with positive charge on the phosphorus atom, thus conferring conditional stability to the *d*-orbitals (*34*), (Fig. 4). This is quite different from p_π-p_π overlap which is maximum when the two p_π-exponents are equal. Here overlap occurs in the region between the nuclei giving strong bonding, whereas d_π-p_π overlap occurs in the region of the oxygen atom, so that a d_π-p_π bond is necessarily polar. The bond is therefore weaker than a corresponding p_π-p_π bond, since overlap occurs in a region away from the phosphorus nucleus (*34*).

The symmetry and overlap will be affected considerably by the nature of the groups σ-bonded to the phosphorus atom. Thus the overlap will be most efficient if the O-P bond lies not only in the common nodal plane of the two orbitals but also in the plane defined by the vectors of maximum density of the *d*-orbitals. This situation is found in the C_{3v} symmetry of the system POX_3, which could give two strong π-bonds between the phosphorus and oxygen atoms, using the d_{xz} and d_{yz} orbitals.

The orbitals in the *xy*-plane can overlap with the p_π-orbitals of the three X groups to give symmetrical overlap with the degenerate d_{xy} and $d_{x^2-y^2}$ orbitals (Fig. 5). The overlap is less than in the case of the P=O bond, since the p_π-orbitals lie out of the *xy* plane. The X groups can therefore conjugate weakly between themselves but not with the P=O group, thus giving a type of conjugation also possible for other symmetries, which is not found in p_π-p_π conjugation.

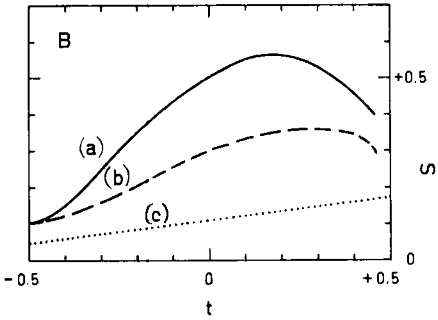


FIG. 4. Overlap integrals (*34*) for $3p_\pi$—$3d_\pi$ as functions of t (= $(\alpha_A + \alpha_B)/(\alpha_A + \alpha_B)$) with several values of p(= $\frac{1}{2}(\alpha_A + \alpha_B)r$) where $\alpha_A = Z_A/n_A$ (Z_A is the effective atomic number of A and n_A the effective principal quantum number of atom A) and r is the internuclear distance in Bohr units.

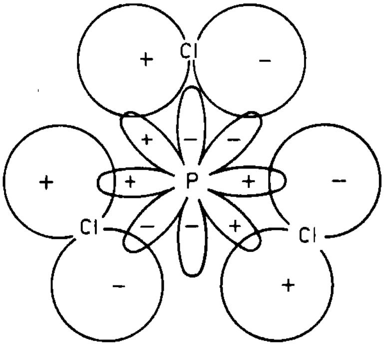


FIG. 5. Overlap (d_π—p_π) of the X_3 group of POX_3 (C_{3v}) (*123*).

If it is assumed that the P=O triple bond is considerably stronger than the π bonds formed by the other groups (*123*), this orientation provides a convenient basis for discussing d_π conjugation in the completely unsymmetrical case ABCP=O. In discussing the effect of substituents (the p_π exponents of which are usually less than those of the O atom) on the reactivity of phosphorylating agents (Section X), this symmetry will be used.

When strongly conjugating groups are present however, (in particular in the case of oxyanions) other symmetries have to be considered (*105*), the most important of which, PO_4^{3-} and $R_2PO_2^-$, will be described briefly below.

In the absence of electrostatic fields, the five 3*d*-orbitals are degenerate. However the electron pairs of σ-bonds and the lone pair electrons of the ligands split the energy levels in a way which has been discussed in great detail in the case of penultimate *d*-orbitals (*78*). Since ultimate *d*-orbitals are not screened so well from the ligands, a similar splitting must occur here.

Tetrahedral symmetry (T_d) is such that the coordinates x, y, and z bisect the edges of the tetrahedron. Figure 2 shows that the d_{xy}-, d_{xz}-, and d_{yz}-orbitals have considerable amplitudes along the valency bonds, whereas the d_{z^2} and $d_{x^2-y^2}$ tend to avoid them. Thus the orbitals are split into two groups, a doubly degenerate group of lower energy ($d\nu$) and a triply degenerate group of higher energy ($d\epsilon$).

Reference to Fig. 6 shows that the $d\nu$-orbitals have the correct symmetry to form π-bonds with p_π-electrons of the four groups to give two systems of molecular π-orbitals (*40*, *188*). The overlap integral for this symmetry is given in Table II.

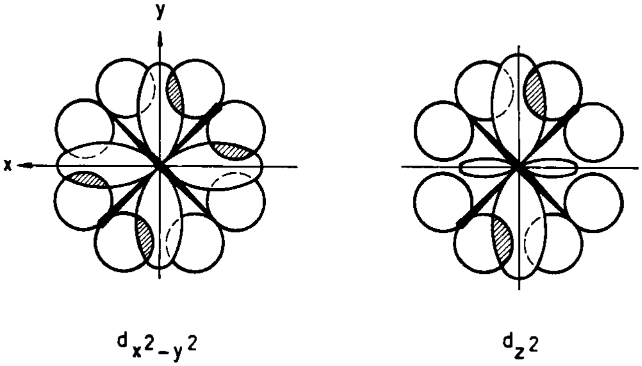


FIG. 6. Overlap (d_π—p_π) for the PX_4 system (Td).

In the more general case, the following factors have to be considered (*105*): (a) maximum d_π-p_π overlap for the C_{3v} system is not in general observed for other 4-coordinated systems; (b) the orientation depends on the number and nature of the σ-bonded groups, e.g., the magnitude of the p_π-exponents.

In view of the strongly polar character of the $\overset{+}{P} \rightarrow \overset{-}{O}$ bond this will tend to take up the position of maximum d_π-p_π-bonding (*123*). An increase in the p_π-exponents of the groups A, B, and C will result in a decrease in $P = O$ π-bond energy (see Table VI).

In view of this competition for the d_π-orbitals and the relatively strong

$P = O$ π-bonds, other groups may use alternative *d*-orbitals in spite of the increased ligand field energy. Such π-bonding, which would not affect the $P = O$ bond except through polarity changes, is sometimes referred to as back coordination.

Of particular interest is the R_2XO_2 system (where X = S or P) of symmetry C_{2v} for which the appropriate MO's have been considered in detail by Moffitt (*129*).

Here the formation of two molecular orbitals may be represented as follows (Fig. 7).

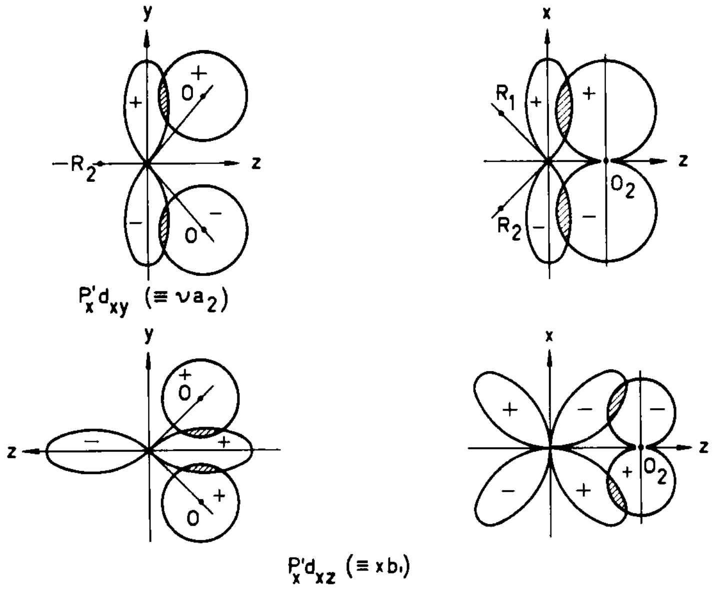
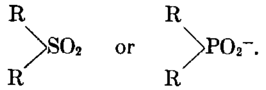


FIG. 7. Orbital overlap for the C_{2v} system showing (*112*) the formation of two different kinds of molecular orbitals (νa_2 and xb_1) for the groups



R_2SO_2 or $R_2PO_2^-$.

These orbitals can conjugate in two essentially different ways (*112*): (a) by using the νa_2-orbital, strong conjugation is possible with p_π-orbitals on the groups R, to give a molecular orbital, the plane of which is rotated through 90° on passing through the phosphorus atom; this is equivalent to the conjugation described for the T_d system (Fig. 6); (b) this is a donor type of orbital which cannot conjugate with the xb_1 molecular orbital of the XO_2 group, as shown in Fig. 8.

This kind of conjugation like that described for the POX_3 system should not therefore affect the properties of the P═O group.

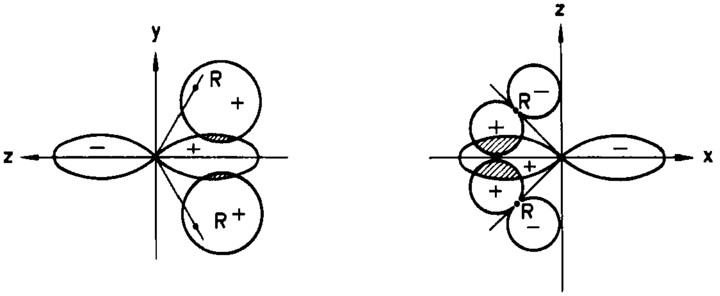


Fig. 8. Conjugation of the groups R in R_2SO_2 and $R_2PO_2^-$ with the xb_1 orbital (112).

Jaffé (*105*) has pointed out that the *p*-orbital of the oxygen atoms in the *xy*-plane can conjugate strongly to give an orbital (wa_1) of the kind given in Fig. 9. This allows no conjugation with the R_2 groups, and hence is an alternative strong bonding orbital for the SO_2 or PO_2^- group.

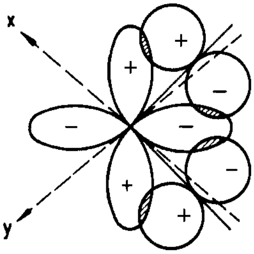


Fig. 9. An alternative strong bonding molecular orbital (wa_2) for the XO_2 system, incapable of conjugating with the R groups (*105*).

The relative group overlap integrals of the orbitals considered are given in Table II in terms of the overlap integral *S*, for an isolated P═O bond.

The symmetry group C_{2v} also characterizes the stereochemistry of the very interesting phosphonitrilic compounds (*134*). Since p_π-orbitals of nitrogen are strongly conjugating, phosphorus and nitrogen should form relatively strong π-bonds. In these compounds, owing to the cyclic system, the p_π-orbital of the nitrogen atom can be orientated in one direction only (Fig. 10). Here the d_{yz}-orbital interacts with the p_z-orbital of the nitrogen atom to give p_π-p_π type of symmetry.

Owing to field splitting, this orbital is probably of higher energy than the d_{xz}-orbital which has symmetry of the kind shown in Fig. 11.

Construction of the appropriate molecular orbitals (*33*) leads to a doubly degenerate set of d_π-p_π orbitals, the special feature of which is that they do

TABLE II

OVERLAP INTEGRALS FOR VARIOUS CONFIGURATIONS IN TERMS OF THE VALUE FOR THE ISOLATED P=O BOND

Compound	Configuration	Orbitals	Overlap integral
MA_2R_2	Tetrahedral C_{2v}	xb_1	$(2/3)^{\frac{1}{2}}S$
		νa_2	$(4/3)^{\frac{1}{2}}S$
		wa_1	$4/3S$
	Square C_{2v}		$2^{\frac{1}{2}}S$
MA_4	Tetrahedral, Td		$2(2/3)^{\frac{1}{2}}S$
	E, or T_2		
	Square D_{4h} or octahedral Oh		$2S$

not conform to the Huckel 8-n rule. On the contrary, conjugation in the tetramer (Fig. 11b) is greater than in the trimer (Fig. 11a) as indicated by the symmetry considerations represented in a simple way in Fig. 11.

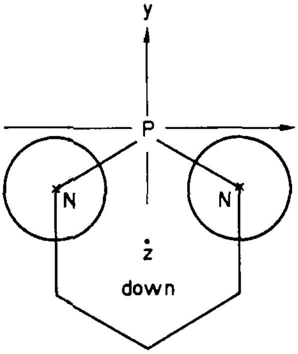
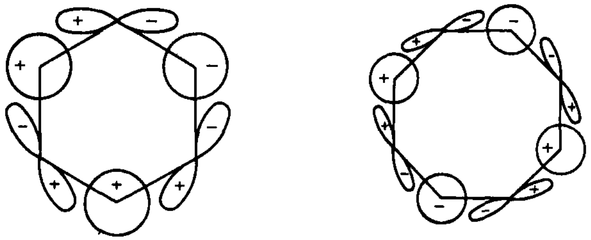


FIG. 10. Orientation of the nitrogen p_π-orbitals in the phosphonitrilic chloride system, (C_{2v}) *(47)*.

Experimental data does not support a conventional aromatic structure for these compounds, e.g., the uv spectra is quite different from that of benzene and the broad maximum at 200 mμ is independent of the number of atoms in the ring *(161)*. The chlorides are not particularly inert, being readily replaced by nucleophilic reagents, e.g., fluoride ions, alkoxide ions and amines *(134)*.

For these reasons an alternative structural interpretation has been proposed *(47)*, involving hybridization of the d_{xz} and d_{xy} orbitals to give two degenerate orbitals with the plane lying close to the P-N bonds (Fig. 12). In this structure the N-P-N bonds may conjugate whereas the P-N-P



(a) (b)

FIG. 11. Representation of conjugation in the phosphonitrilic trimer and tetramer.

bonds may not, giving rise to separate units similar to the allylic system. This interpretation retains the idea of π-bonding, and explains the equivalence of the P-N bonds, but predicts a nonaromatic structure. Further experimental evidence is required before the aromatic nature of these compounds can be ascertained.

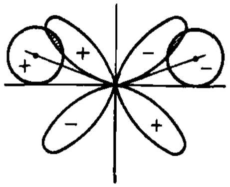


FIG. 12. Alternative conjugation of the "allylic" type in the phosphonitrilic chloride system (*47*).

VII. Experimental Evidence for d_π–p_π Bonding

A. Bond Lengths and Bond Energies

Although the orientation is highly favorable, the importance of d_π-p_π-bonding using ultimate d-orbitals is still a subject of controversy in view of the large difference in the energies of $3p$ and $3d$ levels.* Thus by constructing nonlocalized molecular orbitals for structures of T_d symmetry (Fig. 6), Wolfsberg and Helmholtz (*188*) have calculated the energies of excitation from the ground state non-bonding p_π-orbital (t_1) to the lowest excited state, that is an antibonding $3d_\pi$-$3p_\pi$ hybrid ($3t_2$). The high energies for the perchlorate ion corresponding to absorption in the far ultraviolet suggests that the d-orbital exponent is too small for effective hybridization.

---

* See "Atomic Energy Levels." National Bureau of Standards Circular No. 467, Vol. I, p. 163, 1949.

Similarly PO_4^{3-} and SO_4^{2-} ions do not absorb* below 7–8 ev (*21*) suggesting that in these cases also the energies of the *d*-orbitals are too high for significant mixing with the corresponding *s*- and *p*-orbitals.

Conjugation in these systems must therefore be regarded as very weak compared with p_π-p_π-bonding involving first row elements.

With the advent of the Lewis theory the P=O bond was assumed to be a coordinate bond (*120*), but the bond shortening of the oxy ions of phosphorus and sulfur was subsequently explained (*140*) in terms of d_π-p_π bonding. The correlation between bond order and bond lengths has recently been discussed in detail by Cruickshank (*40*). Assuming that each of the two equivalent d_π-p_π-orbitals (Fig. 6) is capable of π-bonding to four oxygen atoms, each P-O bond has a bond order of 0.5, in valence-bond terminology. For other structures the bond order is given by the number of π electrons available, e.g. for $ROPO_3^{2-}$, the RO-P π-bond order is 0.25, the P-O bond order is 0.583. In this way a linear relation between bond order and bond length is obtained (Fig. 13).

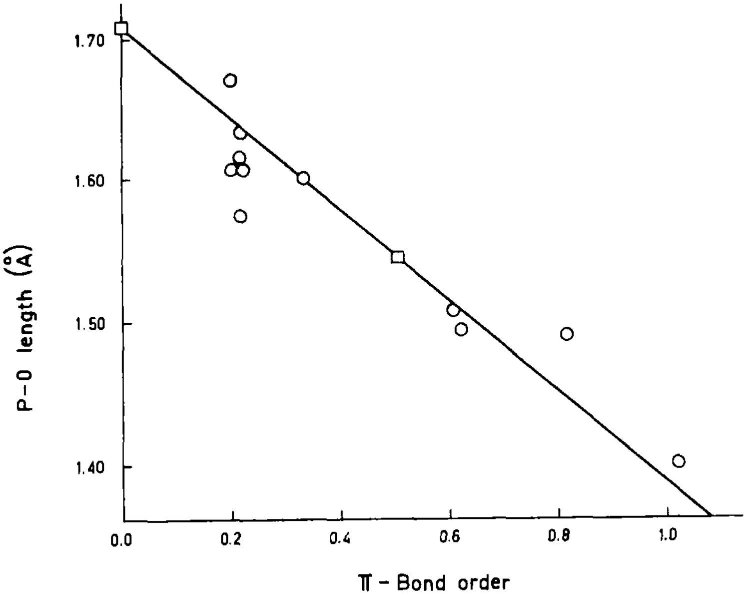


FIG. 13. The relationship between π-bond order and bond length for phosphoric acid derivatives (*40*).

---

* The author wishes to acknowledge interesting discussions on this subject with Dr. Chr. Klixbüll Jørgensen of the Cyanamid European Research Institute, Geneva.

The significance of the bond shortenings has also been discussed by Phillips *et al.* (*142*), who drew attention to the high bond energies (Table III).

TABLE III
P=O DISSOCIATION ENERGIES

$D_{P=O}$ (kcal/mole)	Basis of determination	Reference
115	ΔH_f of P_4O_6 and P_4O_{10}	(*113*)
127.5	ΔH_f of PCl_3 and $POCl_3$	(*132*)
129.8	ΔH of oxidation of PF_3	(*56*)
121.8	ΔH_f of PCl_3 and $POCl_3$	(*26*)
119.3	ΔH_f of PBr_3 and $POBr_3$	(*26*)
131.0	ΔH of oxidation of $EtPCl_2$	(*133*)
134.1	ΔH of oxidation of $(Pr^iO)_3P$	(*133*)
138.3 ± 4	ΔH of oxidation of Pr_3^nP	(*28*)
~137	ΔH of oxidation of Bu_3^nP	(*28*)

The values are seen to vary considerably with the other groups attached to the phosphorus atom. By assuming the minimum value of 115.3 kcal for the P=O bond energy (*113*), Neale and Williams (*133*) obtained values for the energies of several single bonds including values of about 95 kcal/mole for the P-OP bond and about 104 kcal/mole for the P-OH bond. These values are compared with the values for trivalent phosphorus compounds in Table IV.

TABLE IV
SINGLE BOND ENERGIES FOR THE POX_3 AND PX_3 SYSTEMS (*133*)

Bond	D_{-P-X} in POX_3	D_{PX} in PX_3
P—Cl	80	78
P—Br	65	63
P—OH	104	84
P—F	120	117
P—OP	96	~80(?)
P—H	78	77

With the exception of the values for the P-O bonds, the agreement between the two series is surprisingly close in view of the hybridization differences. Smaller values would be obtained for the tetrahedral σ-bonds if higher values were taken for the P=O energy.

Although the estimated P=O bond energies (Table III) are significantly greater than the P—O bond energies, and approach the value for PO (Table I), no allowance has been made for changes in hybridization and *for increased ionic attraction of the four* bonds. Thus the P-Cl bonds in PCl_4 are stronger than the bonds in PCl_3 (which is taken as the reference in thermochemical work) as shown by the shorter bond lengths (Table V).

TABLE V
Bond Lengths in Phosphorus Halides

Bond	PX_3	$\overset{+}{PX_4}$	PX_5	PX_6^-
P—Cl	2.04	1.98	2.04[a] 2.19[a]	2.07
P—Br	2.23	2.13	—	—
P—F	1.535	—	1.54	
	(1.52)[b]	—	(1.57)[b]	1.73

[a] Axial and radial bonds.
[b] Alternative values.

This may be attributed alternatively to π-bonding involving the chlorine atoms (see Table VI). By using a relationship between bond length, modified for polarity differences, and π-bond character, proposed by Pauling (*139*), Van Wazer (*175*) has estimated the degree of π-bonding per atom (Table VI) for the phosphoryl halides. It is seen that the π-bond order of P=O decreases in the order Br > Cl > F, i.e., the order of increasing competition for the available *d*-orbitals (p. 364). No simple relation is found however between π-bonding of the halogen atoms, i.e., *F* = Br > Cl, and their electronic structure.

TABLE VI
π-Bond Character in Phosphorus Oxyhalides (*175*)

Molecule	POF_3	$POCl_3$	$POBr_3$
π-bonds/σ-bond[a]	0.4	1.0	1.1
in P—O bond[b]	0.3	0.9	1.0
π-bonds/σ-bond[a]	0.3	0.0	0.3
in P—X bond[b]	0.2	0.1	—
π-bonds in molecule[a]	1.3	1.0	2.0
π-bonds in molecule[b]	0.9	1.2	1.9

[a] Based on σ-bond distance calculated according to Schomaker and Stevenson (*159*).
[b] Based on σ-bond distance calculated according to Huggins (*101*).

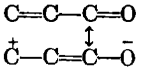
By comparison with amine oxides and boron-ether adducts, in which cases coordinate bonds are formed, Phillips *et al.* (*142*) estimated that the P → O coordinate bond has an energy of 40–70 kcal/mole compared with the values of 115–150 actually observed (Table III). Moreover the bond moment of the phosphorus oxygen bond in $(CH_3)_3P{=}O$ leads to an estimate of ca 47% partial ionic character (27% in the sulfide) compared to 70% for $(CH_3)_3NO$ (*121*). Since nitrogen is more electronegative than phosphorus, the partial ionic character of P → O should be greater than that of N → O if both were coordinate.

This comparison of bonds formed with second row and first row elements has been criticized by Wells (*180*) who also pointed out that a comparison of the lengths of P-OP and P=O bonds is not valid owing to the different coordination numbers of oxygen. The decrease in polarity of the coordinate bond in $Me_3N \rightarrow O$ compared with the estimated value for $\overset{+}{N} \rightarrow \overset{-}{O}$ must be due to polarization. In view of the greater polarizability of the phosphorus atom, the bond shortenings may well be electrostatic in origin as suggested by Pitzer (*144*).

He also pointed out that the inner shell repulsions are quite different for first and second row elements. Thus for N_2 the valency shell repulsion is important in determining the internuclear distance, whereas for P_2 repulsion between an inner shell of one atom and a valency shell of the other is more important. In a combination of oxygen and phosphorus therefore the equilibrium distance will be shorter than given by the Schomacher-Stevenson rule (*159*).

B. SPECTRA

In organic compounds, the strongest evidence for conjugation comes from spectra. Thus in an isolated C=O bond, the uv-absorption can be represented satisfactorily as an $n \rightarrow \pi$ transition, and conjugation, in the classical sense, e.g., in



$$\begin{array}{c} C{=}C{-}C{=}O \\ \updownarrow \\ \overset{+}{C}{-}C{=}C{-}\overset{-}{O} \end{array}$$

leads to optical exaltation, and a decrease in the carbonyl stretching frequency.

The spectroscopic behavior of the corresponding phosphorus compounds in general is quite different. The infrared (*9*, *10*) and Raman spectra (*3*) of a large number of phosphorus compounds have been examined, and the P=O vibration frequency shown to increase regularly with the electronegativity of the substituent (Fig. 14) (*9*). This generalization together with the regular decreases in the frequency increments with successive substitution is characteristic of an inductive effect.

Hydrogen bonding of the phosphoryl oxygen atom (*3*, *4*), which is known to be nucleophilic (*76*), suggests that the P=O bond is conjugated. Since in d_π-p_π-bonding, the overlap is a sensitive function of the charge on the phosphorus atom, and most conjugating groups are electronegative, conjugative electronic release to the P=O group would be difficult to detect.

Some evidence for conjugation is given by the phosphoroamidates. In some cases, R_2N groups give two bands for the P=O group, one of greater and one of lower frequency (*11*) than the alkyl compound. Thus Me_2NPOCl_2 and $Me_2N(EtO)POCl$ show bands at 9.94 and 10.11, and 13.70 and 14.20, respectively. A single band is observed if the Me_2N group is replaced by an NH_2 group. The two bands might be due to rotational isomers, the higher frequency being produced by induction, the lower by conjugation promoted by steric control.

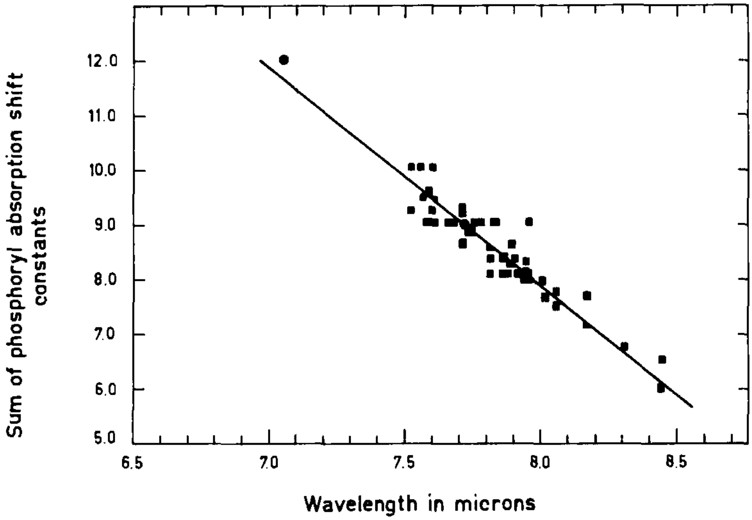


FIG. 14. The relationship between the wavelength of the P=O stretching mode and shift constants related to the electronegativities of the substituents (*9*).

The ultraviolet spectra of a number of aryl phosphonic and diaryl phosphinic acids have been studied (*8*, *64*, *106*, *107*, *145*), and in no case is a large change in the benzene spectrum observed, and in particular the fine structure remains unaltered. The intensity is however increased by a factor of 1.5–5.0, and a bathochromic shift of about 10 mμ is observed (*106*). These small changes could be explained by weak conjugation between the benzene ring and the phosphorus atom. If this is so, substitution of a stronger conjugating group should lead to an exalted spectrum (*162*), and recently the spectra of tri α pyrrole phosphinoxide and the corresponding methiodide have been found (*77*) to be similar to the spectra of the corresponding ketones with similar extinction coefficients (~10^4). The wavelength shift is however appreciably less than for the carbonyl derivatives, indicating weaker π-bonding.

The NMR spectra of phosphorus compounds, compiled by van Wazer

(*176*) also suggest different bonding for P^{III} and P^{IV} compounds. Thus trivalent phosphorus compounds show large changes in nuclear shielding, and large chemical shifts (~500 ppm), being attributed to changes in hybridization as shown by changes in bond angles. For 4-coordinated compounds the shifts are very small (50–100 ppm) probably due to the variation in the distribution of π bonds between the four groups. Electron shielding of the central nucleus by substituting atoms at the phosphoryl, or thiophosphoryl, group increases in the following order.

$$\mathrm{Se} < \mathrm{S} < \mathrm{C}_{\mathrm{aliphatic}} < \mathrm{C}_{\mathrm{aromatic}} \simeq \mathrm{P} < \mathrm{N} \simeq \mathrm{Cl} < \mathrm{H} < \mathrm{O} < \mathrm{F}$$

i.e., with the exception of H and P the order of electronegativity. This is opposite to the predictions of a simple polar theory, since the more electronegative elements are the most shielding. These results are rationalized if the second substituent withdraws electrons from a previously formed π bond of the P═O or P═S linkage in agreement with the bond length deduction (Table VI).

Finally, recent quadruple Cl^{35} coupling spectra measurements (*123*) are also in agreement with weak d_π-p_π-bonding, and the shifts in the coupling frequencies for the phosphonyl compounds (*123*) although smaller, are related fairly closely to the corresponding values for carbonyl compounds. Thus, as discussed above, the strong P═O bond and weaker conjugating groups X of the C_{3v} system probably use different $3d_\pi$-orbitals, and consequently π-bonding of the groups X in general affects the P═O stretching frequency, νP═O, by the inductive effect only.

Thus a plot of the N.Q.R. coupling frequency against $\nu_{P=O}$, gives two approximately parallel lines, one for conjugating and the other for nonconjugating substituents.

C. Acid-Dissociation Constants

The transmission of electrical effects across a phosphorus atom as influenced by π-bonding, should also be reflected in acid dissociation constants. Thus Jaffé *et al.* (*108*) have shown that *p*-substituted benzene phosphonic acids (*8*) obey the Hammett relation.

TABLE VII

Values of the Reaction Constants of the Hammett Equation for the Dissociation of Acids and the Refractivity of the Corresponding Central Ion (*108*)

	ρ	Ion	Ion refractivity
$ArCO_2H$	1.00	C^{4+}	88
$ArAsO_3H_2$	0.95	As^{3+}	76
$ArPO_3H_2$	0.76	P^{3+}	67

The reaction constants ρ for phosphonic, arsonic, and benzoic acids are similar, and vary with the ionic refractivity of the central atom (Table VII).

This correlation suggests that the differences in ρ are determined by the transfer of electronic effects from the substituent to the OH group. Pressman and Brown (*147*) have however argued against the influence of a charged central arsenic atom in the dissociation of the arsonic acids.

D. CHEMICAL EVIDENCE FOR $3d_\pi$ BONDING

The stability of phosphinemethylenes relative to the corresponding nitrogen derivatives (*186*) is normally attributed to p_π-d_π bonding as mentioned in a previous section.

The reactivity of the α-proton in several cations has been investigated quantitatively by Doering and Hoffmann (*49*) who showed that tetramethyl phosphonium and trimethyl sulfonium ions undergo base catalyzed deuterium exchange much more rapidly than the tetramethyl ammonium ion (Table VIII). The orders P > As > Sb and S > Se > Te suggest that the rate is not determined simply by electronegativity differences and that the high reactivities of the P^+ and S^+ ions are due to conjugation, viz.,

TABLE VIII
RATE OF DEUTERATION OF TETRAMETHYL CATIONS OF NITROGEN, PHOSPHORUS, ARSENIC, AND ANTIMONY AND OF THE TRIMETHYL CATIONS OF SULFUR, SELENIUM AND TELLURIUM (*49*)

Ion (central atom)	N^+	P^+	As^+	Sb^+	S^+	Se^+	Te^+
Exchange rate, log k	−9.75	−3.37	−4.61	−5.62	−2.44	−4.09	−4.63

$$\mathrm{Me_3\overset{+}{P}{—}CH_3 \xrightarrow{HO^-} \underset{+\ H_2O}{\phi_3P{=}CH_2} \xrightarrow{D_2O} \phi_3\overset{+}{P}{—}CH_2D + DO^-}$$

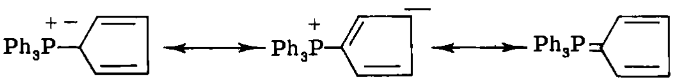
Phosphine methylenes can be formed more readily than originally anticipated, e.g., by the weakly basic phenoxide ion as in the following case (*187*)

$$\mathrm{(PhO)_3\overset{+}{P}{—}CH_3 + PhO^- \rightleftharpoons (PhO)_3{—}P{=}CH_2 + PhOH}$$

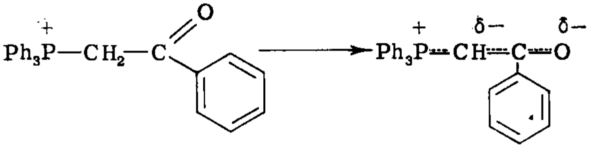
and by the formation of an allenic di-methylene (*149*)

$$\mathrm{Ph_3P{=}C{=}CPPh_3}$$

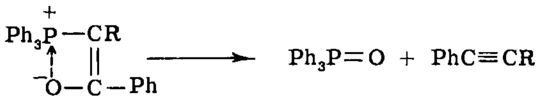
Phosphinemethylenes stabilized by conjugation may be readily prepared in the free state.* Thus the 9-fluorenyl trimethyl phosphonium ion, but not the corresponding ammonium ion gives an isolable fluorenylidide (*143*). Similarly a stable phosphonium cyclopentadienylide has been isolated and the structure investigated by Ramirez (*151*). The u-v spectrum indicates strong conjugation with the ring, and the dipole moment corresponds to approximately equal contributions from the covalent and ionic forms.



The structure is also stabilized by α-carbonyl groups as in the phosphobétaines (*150*), the carbonyl frequency in which is low owing to the following conjugation



On prolonged heating, these reagents undergo an internal Wittig reaction (*173*), viz.,

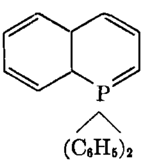


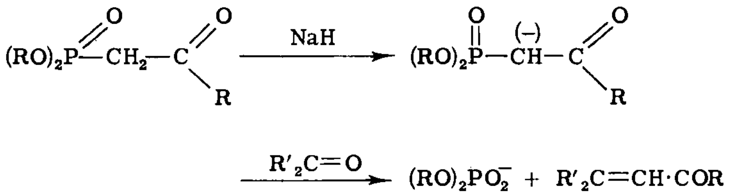
The strong conjugation in these betaines also explains the rapid racemization of optically active ethyl α-trimethyl phosphonium propionate under conditions where the corresponding ammonium salt is unaffected (*14*).

Similar reagents have been prepared from phosphate esters containing conjugating groups in the α-position (*177*), which undergo the following reaction.

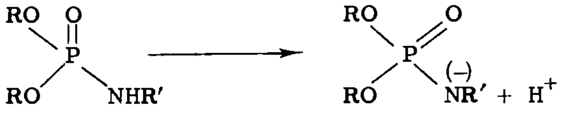
---

* Märkl (*123a*) has recently reported the preparation of

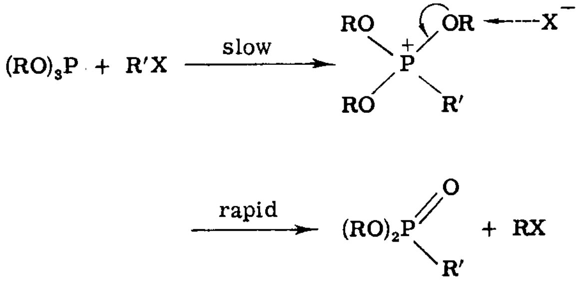




Similarly active reagents may be made from the phosphoramidates (*178*),



The main driving force in the Wittig type of rearrangement is the strong P=O bond formed, which is indicative of double bond formation. This affinity is characteristic of many reactions of phosphorus compounds, e.g., in the Arbusov rearrangement (*5*)

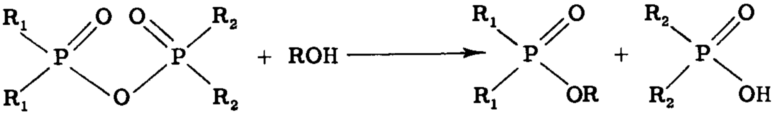


The intermediate has been isolated recently in the form of the borofluoride and perchlorate salts (*48*).

VIII. Phosphorylation

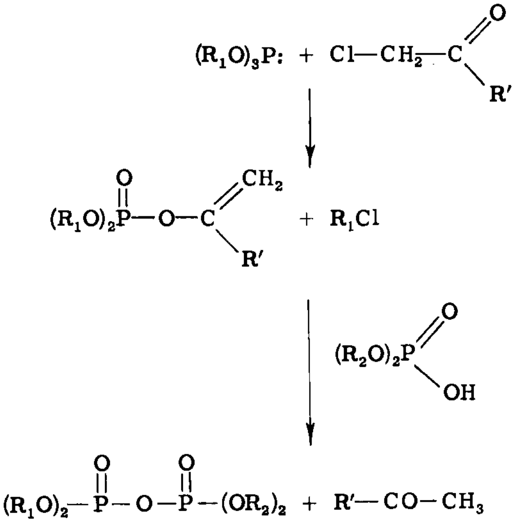
Quantitative investigations of the reactivity of phosphorus compounds have been limited to phosphorylation and related reactions at the phosphoryl group (*51*, *70*, *86*, *97*, *118*). Such studies which have been made only recently, have been stimulated by the great increase in preparative organo-phosphorus chemistry within recent years, and by the biological importance of phosphorylation.

From a mechanistic point of view, phosphorylation reactions may be subdivided in the following way: (a) nucleophilic displacement of an acidic group by a nucleophilic reagent, as for example in classical phosphorylation reactions of the following type, which are analogous to acylation.



These may be regarded as simple bimolecular displacements, the lability of the groups increasing with their acidity in the case of unsymmetrical pyrophosphates (*171*); (b) the conversion of a nonphosphorylating agent into a phosphorylating agent, followed by reaction of an acid (in the Brønsted sense), e.g.,

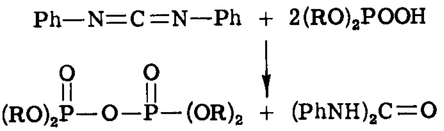
1.



(36,141)

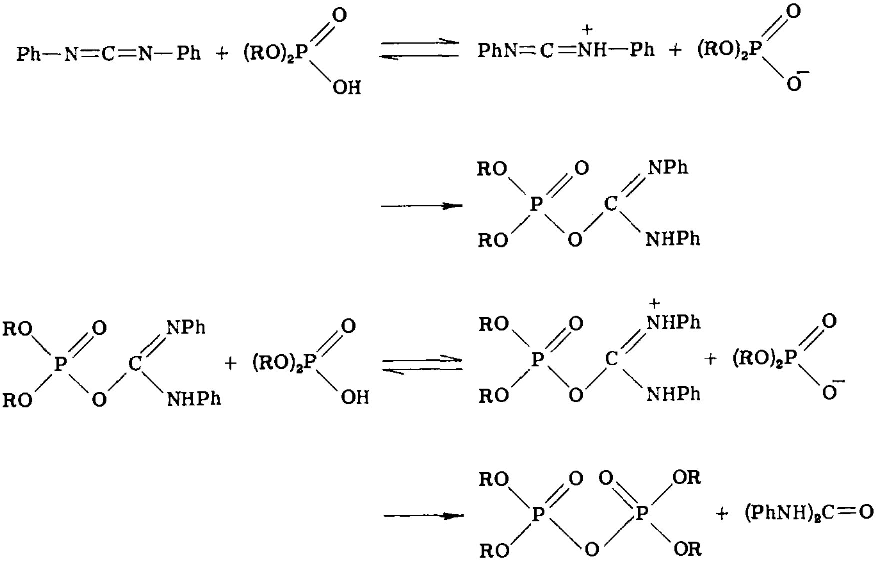
and

2.

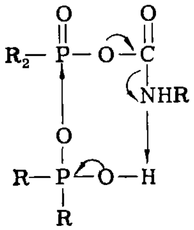


$$\mathrm{Ph{-}N{=}C{=}N{-}Ph} + 2(\mathrm{RO})_2\mathrm{POOH} \longrightarrow (\mathrm{RO})_2\overset{\overset{\mathrm{O}}{\|}}{\mathrm{P}}-\mathrm{O}-\overset{\overset{\mathrm{O}}{\|}}{\mathrm{P}}-(\mathrm{OR})_2 + (\mathrm{PhNH})_2\mathrm{C{=}O}$$

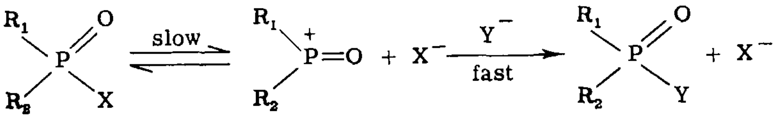
Since the first use of carbodimides (*110*), other similar reagents, e.g., isocyanates (*38*, *122*) and trichloro acetonitrile (*37*) have been used. These reactions may be regarded as proceeding through the protonated form, followed by a nucleophilic displacement of the kind given in (a), e.g.,



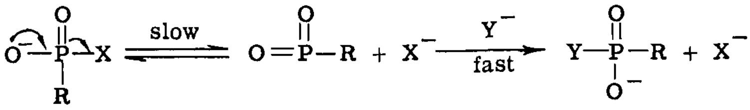
The phosphorylation stage essentially involves the attack of an anion on the phosphorus atom containing a positively charged leaving group, although this process may involve a cyclic transition state in some cases, e.g.,



(c) the possibility of pre-ionization (*83*), as in the formation of carbonium and acylium ions, followed by rapid phosphorylation,



or alternatively the unimolecular release of a group from a phosphorus anion, e.g.,



From a theoretical point of view these reactions can be classified into two groups (a) bimolecular displacement on the phosphorus atom and (b) unimolecular ionization followed by rapid phosphorylation. The influence of the nucleophilic reagent, the reaction conditions and the structure of the phosphorus compound will be reviewed in the following sections.

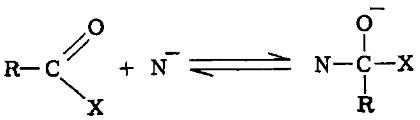
IX. The Influence of the Nucleophile on Phosphorylation

The similarity between phosphoryl and carbonyl compounds is further shown by the relative reactivity of various nucleophiles (*94*). It is well known (*167*) that highly polarizable ions and molecules, e.g., Br^-, I^-, CNS^-, $S_2O_3^{=}$, and $(NH_2)C{=}S$ are particularly reactive towards the saturated carbon atom. The reactivity tends to follow the oxidation reduction potential (*57*), suggesting that the variations in the energy required to remove an electron from the nucleophile are more important (because of the influence of electronic repulsion) than the corresponding bond energy changes,

$$(N^-)_{aq} \longrightarrow \tfrac{1}{2}N_2 + e + aq \qquad \Delta F = \mathscr{F}E_r$$

The rate is therefore controlled mainly by the apparent electron affinity (which includes solvation energy), E_A.

On the other hand, reactivity towards a more electrophilic (positively charged) center is more sensitive to bond energy changes (*58*). Thus the transition state structure for acylation may be close to that of the addition intermediate (*12*),



$$\Delta E = E_A - D_{C-N} + \text{const}$$

Since changes in the bond energy D_{C-N} are usually greater than the changes in E_A, the nucleophilic reactivity tends to follow the bond forming energy, and hence the pKa of the conjugate acid of the nucleophile (*58*).

Nucleophilic reactivity may therefore be represented in general by an equation of the kind

$$\log (k/k_0) = \alpha pKa + \beta E_r$$

first proposed by Edwards (*57*), where the relative magnitude of α and β gives a measure of the influence of bonding in the transition state.

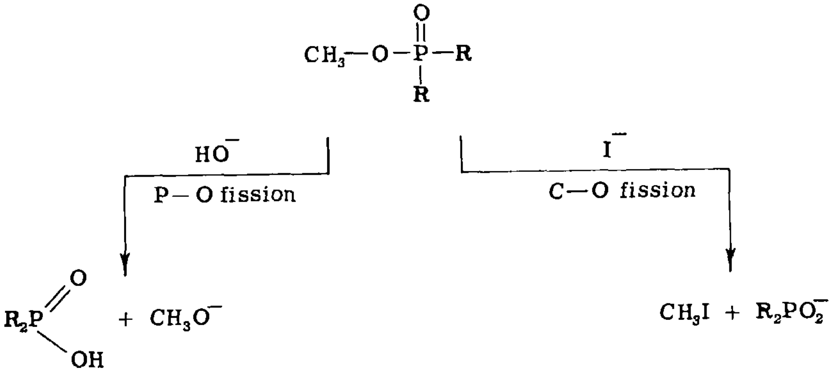
It follows therefore that strongly basic ions are readily acylated whereas the more polarizable ions, e.g., I^-, RS^-, are less reactive.

A similar reactivity order has been observed for phosphorochloridates (*50*), viz.,

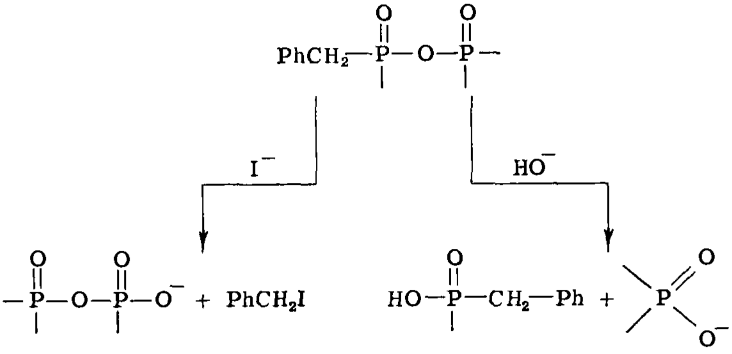
$$F^- > HO^- > PhO^- > EtOH > PhS^-, CH_3CO_2^-$$

and recent data by Miller (*128*) have shown that the reactivities of oxyanions (RO^-) and the corresponding sulphur anions (RS^-) follow the corresponding *pKa*'s closely. The high reactivity of the fluoride ion does not follow the Edwards equation, but is probably due to the high P-F bond energy (cf. the high Si-F bond energy).

The completely different nucleophilic order towards the saturated carbon atom and the phosphoryl phosphorus atom has been used to predict the position of bond fission in the hydrolysis of esters of quinquevalent phosphorus (*85*).



and is the basis of anionic de-benzylation of pyrophosphates introduced by Clark and Todd (*32*),

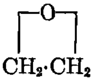


The nucleophilic order towards the phosphoryl group thus suggests (*58*, *94*) that the bond forming energy is high in the transition state, which probably resembles the addition intermediate (see p. 354).

The degree of bond formation in the transition state is also indicated by the coefficient α of the Brønsted equation (*99*), $\log k = \alpha pKa +$ constant, which relates reactivity and acid dissociation constant for a series of similar nucleophiles.

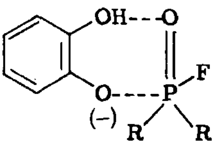
TABLE IX

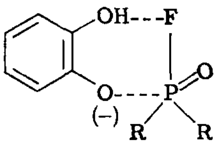
A COMPARISON OF THE BRØNSTED COEFFICIENT α FOR REACTIONS OF NUCLEOPHILES WITH ALKYLATING, ACYLATING, AND PHOSPHORYLATING AGENTS (*99*)

Compound	Nucleophiles	α	Reference
$MeOSO_3^-$	$R·C_6H_4O^-$	0.16	[a]
$Cl·CH_2·COO^-$	$R·COO^-$	0.20	[b]
$Br·(CH_2)_3·OH$	$R·C_6H_4O^-$	0.22	[c]
 $CH_2·CH_2$	$R·C_6H_4O^-$	0.32	[d]
$EtO·COCl$	$R·C_6H_4O^-$	0.78	[c]
p-$NO_2·C_6H_4·O·COCH_3$	$R·C_6H_4O^-$; $R·C_5H_4N$	0.80	[e]
$(CH_3CO)_2·O$	$R·C_5H_4N$	0.92	[f]
$Et_2N(OEt)P(O)CN$	R_2CNO^-	0.50	[g]
$(EtO)_2P(O)OP(O)(OEt)_2$	R_2CNO^-	0.70	[g]
$Pr^iO·(Me)·POF$	$R·CONHO^-$	0.82	[g]
$Pr^iO·(Me)·POF$	$R·C_6H_3(OH)O^-$	0.90	[h]

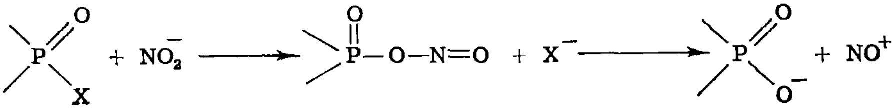
[a] Green and Kenyon, *J. Chem. Soc.* p. 1595 (1950).
[b] Smith, *J. Chem. Soc.* p. 521 (1943).
[c] Hudson and Loveday, *J. Chem. Soc.* p. 1068 (1962).
[d] Goldsworthy, *J. Chem. Soc.* p. 1254 (1926).
[e] Bruce and Lapinski, *J. Am. Chem. Soc.* **80**, 2265 (1958).
[f] Gold and Jefferson, *J. Chem. Soc.* p. 1409 (1953).
[g] Green, Saville, Sainsbury, and Stansfield, *J. Chem. Soc.* p. 1583 (1958).
[h] Epstein *et al.*, *J. Am. Chem. Soc.* **78,** 341 (1956).

The value of α is observed to increase with the electronegativity of the substituents (*72*) which produce a decrease in the electron density at the reaction center, thus increasing the charge transfer and bond forming energy in the transition state. The value of α is further increased when the charge transfer is assisted by hydrogen bonding as in the reaction with substituted catechols (*60*).

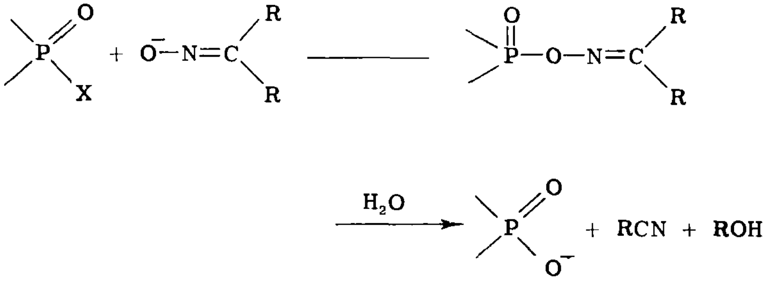




Basic oxyanions, e.g., oxime anions (*73*, *81*), ClO^- (*59*), HO_2^- (*124*) are considerably more reactive towards both phosphoryl and carbonyl centers (Table X), than predicted from the reactivity of the hydroxide ion and the Brønsted relation. The nitrite ion, which is also very reactive gives rise to an incipient nitroso cation (*119*) as shown by the formation of a dye with phenylene diamine (*130*).



and oxime anions give similar rearrangements and fragmentation (*73*)



Various interpretations have been advanced for the high reactivities of these anions, including bifunctional catalysis (*59*), the influence of the electron pair on the atom adjacent to the oxygen atom (*58*), and the influence of solvation and conjugation (*94*), but a completely satisfactory explanation is still lacking. It should be noted that the high reactivity is quite general and is therefore characteristic of the anion and not of the nature of the bonding (e.g., the use of *d*-orbitals) at the electrophilic center.

TABLE X

The Reactivity of Nucleophiles Towards Isopropyl Methylphosphonofluoridate (B) and Tetraethyl Pyrophosphate (A) (*72*)

Nucleophile	$k_{(A)}$	$k_{(B)}$	*pKa*	k_A/k_B
H_2O	0.0017	0.0001	0	17
NH_2OH	26	2.6	6	10
ClO^-	267	600	7.4	0.45
$Ac_2C{:}NO^-$	35	73	7.4	0.48
$AcCH{:}NO^-$	59	240	8.3	0.24
$BzCO_3NHO^-$	160	1020	8.8	0.16
$AcCMe{:}NO^-$	16	380	9.3	0.043
HO_2^-	2180	94,000	11.8	0.023
HO^-	21	2000	14	0.011

From the above discussion it may be inferred that bond formation is advanced in the transition state (*94*), and hence the reactivity is probably increased by electron withdrawal from the phosphorus atom. This influence is considered further in the following discussion of the effect of structural changes on the reactivity of the phosphorus compound.

X. Substituent Effects in Bimolecular Phosphorylation*

Since most phosphorylations are bimolecular reactions, the rates are affected by steric and electronic factors. Owing to the greater coordination number of phosphorus, steric hindrance is more important than in acylation, and this must be carefully considered before an electronic interpretation of a change in reactivity is assumed. Most of the published reactivity data is unfortunately difficult to analyze for this reason.

The importance of steric hindrance was shown (*52*) by the reactivity order, primary > secondary > tertiary in the reactions of amines with di-isopropyl phosphorochloridate. The rate differences are somewhat less when isopropyl methyl-phosphonochloridate is used (*109*). Similarly the rate of reaction of the latter with alcohols is decreased by substitution of alkyl groups in the alcohol, although the activation energy decreases owing to the increased basicity (*98*).

The substitution of alkyl groups in the groups R_1 and R_2 of derivatives of phosphonic acids decreases the reactivity, as shown for example by the data of Table XI for the alkaline hydrolysis of phosphonates (*96*). Similar observations have been made for the chloridates (*97*), fluoridates (*86*), anhydrides (*172*), and *p*-nitrophenyl esters (*70, 118*).

TABLE XI
THE ALKALINE HYDROLYSIS OF DIALKYL METHYLPHOSPHONATES $(R'O)_2P(R)O$ (*96*)

R′(R=Me)	Me	Et	Pr^i	neo-Pentyl
Relative rate	600	40	1	0.33
E* (kcal/mole)	13.5	14.0	14.9	13.6
10^{-4} PZ	1900	360	27	1.5

R(R′=Pr^β)	Me	Et	Pr^n	Bu^n	Bu^t
Relative rate	1	0.16	0.062	0.039	0.002
E* (kcal/mole)	14.9	16.2	15.9	16.2	—
10^{-5} PZ	2.7	2.8	0.75	0.69	—

As in the case of reactions at a saturated carbon atom (*61*), steric and

---

* In view of the excellent summary given by Heath (*86*), individual papers containing rate data prior to 1956 are not normally cited, particularly as few attempts have been made to differentiate between steric and electronic influences.

inductive effects cannot be separated. However di-neopentyl methyl phosphonate is considerably less reactive than the diethyl ester (*98*), although the activation energies are the same (Table XI). Both reactions involve displacement at the phosphorus atom, and the large difference in the PZ factors is attributed to the steric influence of the bulky neopentyl groups. Similarly diethyl t-butylphosphonate (*96*) is considerably less reactive than the corresponding methylphosphonate, and triphenylmethyl phosphonyl chloride ($Ph_3C{\cdot}POCl_2$) is reported to be unreactive towards water (*6*).

The very low reactivity of $(Me_3N)_3P{=}O$ towards alkali (*86*) is almost certainly mainly steric in origin (cf. the relatively low reactivity of Pr_3^iSiCl), although this has been attributed to conjugation (*86*), and the low reactivity of derivatives of tetra-alkyl phosphoroamidic acids (*42*, *86*) may be explained similarly (see below). Considerable care must therefore be exercised in discussing the reactivity of phosphorus compounds in electronic terms.

A. Electronic Effects

In view of the large steric effects which may be exerted, our attention will be limited to rate increases which are observed in spite of steric hindrance increases, and to comparisons where the steric effects are approximately constant (homomorphs).

Following the usual practice in organic chemistry, the effect of changes in σ-bond and π-bond energies will be discussed separately.

There is at present little data on the influence of the inductive effect on σ bonds. In general phenyl groups and halogen atoms in either groups R_1 or R_2 increase the rate of solvolysis and alkaline hydrolysis as shown by the data in Tables XII, XIII and XIV.

TABLE XII

The Inductive Effect Produced by Substitution in the OR Group of Derivatives of Phosphoric and Phosphonic Acids

Compound	k[d]	E (kcal/mole)	Compound	k[d]
$(C_2H_5O)_2POCl$[a]	11	13.4	$EtO(Me)POCl$[b]	181
$(PhCH_2O)_2POCl$[a]	8.5	14.6	$PhO(Me)POCl$[b]	87.6
$(PhO)_2POCl$[a]	5.1	11.9	$EtO(Me)POF$[c]	60.7
			$Br(CH_2)_2O(Me)POF$[c]	162

[a] Reaction in ethanol at 40° (*51*).
[b] Reaction in 5% aqueous acetone at 0° (*117*).
[c] Alkaline hydrolysis (*66*).
[d] Relative values.

Although these effects are small, it is seen that electron attracting substituents usually increase the reactivity particularly in alkaline hydrolysis.

TABLE XIII

THE RATE OF ALKALINE HYDROLYSIS (25°, pH 8.3) OF O-ETHYL O-*p* NITROPHENYL ALKYLPHOSPHONATES—$EtO(R)P(O)O{\cdot}C_6H_4{\cdot}NO_2$ (*66*)

R	10^4k, min^{-1}	*R*	10^4k, min^{-1}
$CH_3{\cdot}CH_2{\cdot}CH_2$	4.17	$Ph{\cdot}CH_2$	7.05
$Cl{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2$	7.5	Ph	26.4

This is to be expected in view of the increased electrostatic interaction between a negative ion and the electrophilic center. In solvolysis the bond forming and bond breaking energies are similar and hence the rate differences are small. This is shown clearly by the data (*130*) in Table XIV.

TABLE XIV

THE INFLUENCE OF α-CHLORINE ATOMS IN THE METHYL GROUP OF PHOSPHONOCHLORIDATES AND PHOSPHONATES ON THEIR REACTIVITY (*130*)

	Me	Et	$Cl{\cdot}CH_2$
Solvolysis of $EtO(R)POCl$ *in* 5° *aqueous acetone at* 0°			
10^3k min^{-1} (0°)	87.6	29.7	107 (1.3°)
E_A kcal/mole	8.5	8.9	10.9
$\log_{10}$ PZ	4.0	3.9	5.9
Alkaline hydrolysis of $RP(O)(OEt)_2$			
k_2 l mole^{-1} hr^{-1} (60°)	9.36	4.41	111
E_A, kcal/mole	14.0	14.2	12.0
$\log_{10}$ PZ	6.5	6.3	6.8

The rate increases are considerably less than observed with the corresponding carbonyl compounds [e.g., the relative rate of alcoholysis of $Cl{\cdot}CH_2{\cdot}COCl$ and CH_3COCl (*17*) is about 20], which may be attributed to the weaker bonding in the 5 coordinated transition state (see p. 354).

B. CONJUGATING GROUPS

When the atom of group R attached to the phosphorus atom contains lone pair (p_π) electrons, the rate may be also modified by d_π-p_π conjugation which may stabilize the ground state as described on p. 362. Substitution of a chlorine atom usually increases the reactivity by a small factor (2–3) as shown by the following comparisons (*130*) $(EtO)POCl_2$ and $EtO(Me)$-$POCl$; $MePOCl_2$ and $POCl_3$, suggesting that the inductive effect is slightly more important than conjugation.

Replacement of an alkyl group by an alkoxy group (*51*, *70*, *86*, *97*, *118*)

TABLE XV
THE EFFECT OF ALKOXY AND ALKYLAMINO GROUPS ON THE REACTIVITY OF SOME PHOSPHONYL COMPOUNDS

Reference	Compound	Conditions	Temperature	k
(97)	Et_2POCl	95% acetone—5% water (v/v)	0	1.500×10^{-3} sec^{-1}
(97)	MeOP·EtOCl	95% acetone—5% water		98×10^{-3} sec^{-1}
(97)	$(MeO)_2POCl$	95% acetone—5% water		1.75×10^{-3} sec^{-1}
(72)	Et_2POF	OH^- in water	25	50.000 l. mole^{-1} hr^{-1}
(72)	EtOPEtF	OH^- in water	25	1.200/mole^{-1} hr^{-1}
(72)	$(EtO)_2POF$	OH^- in water	25	110 mole^{-1} hr^{-1}
(70)	$EtO{\cdot}P{\cdot}Pr^n(O)O{\cdot}C_6H_4{\cdot}NO_2$-p	OH^- in water	37.5	4.17×10^{-4} min^{-1a}
(70)	$(EtO)_2P(O){\cdot}OC_6H_4$-$NO_2$-p	OH^- in water	37.5	6.14×10^{-4} min^{-1a}
(85)	$Et_2P{\cdot}(O){\cdot}OMe$	OH^- in water	80	5.9^b
(85)	$(MeO)_2P{\cdot}(Et){\cdot}O$	OH^- in water	80	4.2^b
(85)	$(MeO)_3PO$	OH^- in water	80	1.0^b
(86)	$(Pr^iO)_2POF$	water	25	1.2×10^{-4} sec^{-1}
(86)	$(Pr^iNH)_2POF$	water	25	2.3×10^{-6} sec^{-1}

[a] Pseudounimolecular constants.

[b] Relative reactivity per OMe group.

however invariably decreases the rate (Table XV) which has been attributed to π-bonding in the ground state (*51*, *86*, *97*).

These rate decreases may alternatively be attributed (*97*) to increased σ-bond energies, (as shown by the increased infrared frequencies (*9*) if d_π-p_π bonding is discounted. This explanation is however unlikely for the following reasons (*97*): (a) electron-withdrawing groups usually increase the reactivity; (b) alkyl amino-groups decrease the reactivity further (Table XV), which is the reverse of the inductive effect predicted by the electronegativities. The reduced reactivity produced by an amino group (*42*, *86*) is explained by increased π-bonding with the phosphorus atom. This effect, if indeed present, is considerably less than for the corresponding carbon compounds as shown by comparing the values given in Table XV with the value of ca 10^4 for the relative reactivity of a chloroformate and acid chloride (*97*).

Moreover phenyl groups which produce large rate decreases in carbonyl compounds owing to the conjugation $\mathrm{Ph}\overset{\curvearrowright}{—}\mathrm{C}\overset{\curvearrowright}{=}\mathrm{O}$, increase the rate of solvolysis of phosphorochloridates (*51*, *98*) and the rate of alkaline hydrolysis of the corresponding phosphonates (*96*).

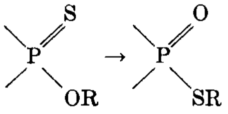
Although few rate studies have been made with derivatives of thioic acids, the effect of an RS group is considerably less than that of the corresponding alkoxy group (*86*).

In general therefore, the following rate order is observed (in particular for solvolysis)

$$\mathrm{Cl} > \mathrm{Ph} > \mathrm{R} > \mathrm{RS} > \mathrm{RO} > \mathrm{RNH}$$

which is the order of increasing p_π-p_π conjugation in organic compounds. Since this gives a measure of the exponent of the p_π electrons of the group, d_π-p_π bonding should increase in the same order (although this may be modified to some extent by conditional stability). This rate order and the magnitude of the effects observed support the contention of weak d_π-p_π bonding in phosphoryl compounds and cannot be explained on inductive effects alone.

The substitution of sulfur for oxygen in the phosphoryl group (*86*) reduces the solvolysis rate of phosphorochloridates and phosphonochloridates by about 10^2 ($\Delta E \sim 2.5$ kcal/mole), and similar rate reductions are found in the hydrolysis of aromatic esters (*86*). Since the π-bond energy for the P═S group is probably less than for the P═O group, as indicated by the thiono-thiolo rearrangement (*65*)



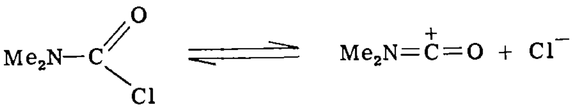
thionates would be more reactive than the oxygen analogs if conjugation were dominant. The rate factor suggests that electrostatic factors are more important in this case. It should be noted that thiocarbonyl compounds are less reactive than the corresponding carbonyl derivatives (*16*) indicating that even here π-bond energy changes are less significant than the polarity and solvation energy changes.

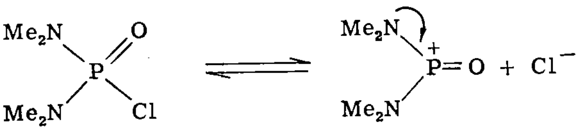
XI. Ionization Reactions

The reactivity data discussed in the previous section can be interpreted satisfactorily on the hypothesis that d_π-p_π conjugation in the ground state, which is weak compared with p_π-p_π bonding, opposes the (electron withdrawing) inductive effect which normally increases the reactivity. If this interpretation is correct, it should be possible for reactions to proceed through ionization intermediates to give ions of the kind postulated in the $POCl_3$ solvo system (*79*)

$$2POCl_3 \rightleftharpoons POCl_2^+ + POCl_4^-$$

when the π-bonding energy is greater than the P-X bond energy.* A mechanism of this kind has been suggested for the solvolysis of phosphoroamidic chlorides (*83*), to account for the lack of reaction with hydroxide ions, and the rate sequence. $(R_2N)_2POCl > R_2N(OEt)POCl$, since carbamyl chlorides are known to react by an ionization mechanism (*82*)





It is known that hydroxide ions increase the rate of hydrolysis of the corresponding fluorides (*86*) and anhydrides (*86*), although the rate increases are relatively small.

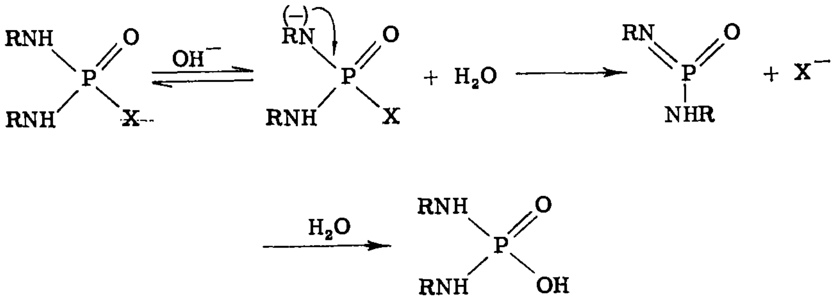
Further kinetic investigations (*41*, *157*) have suggested that the hydrolyses of tetra-alkyl phosphoroamidic chlorides are bimolecular, although bond breaking is more important in the transition state than in other cases considered (*41*). In particular nitrite (*41*) and azide (*157*) ions increase the rate of reaction, in the latter case giving stable azides (*157*).

The corresponding derivatives of primary amines are very sensitive to

---

* These ions would be stabilized by p_π—p_π bonding, probably involving $(pd)_\pi$ hybrids.

alkali (Table XVI), and Westheimer (*182*) suggested a mechanism involving preliminary ionization of the α-proton:



$X = Cl, F, (RNH)_2PO_2$

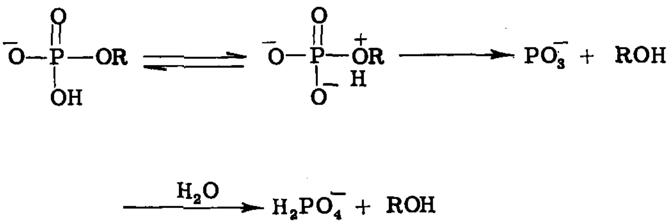
Support for this suggestion was provided by the observation that 2:6 lutidine increases the rate of solvolysis of phosphoroamidic chlorides but has no effect on the homomorphic phosphorochloridates (*41*).

TABLE XVI

ALKALINE HYDROLYSIS OF PHOSPHORODIAMIDIC FLUORIDES RR′POF AT 25° (*86*)

R	R′	$k(OH^-)$ min^{-1}	E (kcal/mole)
$\mathrm{Pr^iNH}$	$\mathrm{Pr^iNH}$	48.9	11.2
MeNH	$\mathrm{Me_2N}$	17.6	11.2
EtNH	$\mathrm{Me_2N}$	12.3	11.4
$\mathrm{Bu^nNH}$	$\mathrm{Me_2N}$	11.1	11.4
$\mathrm{Pr^iNH}$	$\mathrm{Me_2N}$	8.43	11.9
$\mathrm{Me_2N}$	$\mathrm{Me_2N}$	4.7×10^{-3}	16.6
$\mathrm{Et_2N}$	$\mathrm{Me_2N}$	2.88×10^{-4}	16.6
$\mathrm{Et_2N}$	$\mathrm{Et_2N}$	2.5×10^{-5}	17.1

Similar mechanisms have been postulated for other reactions involving phosphoryl compounds in the ionized form. Thus the very high reactivity of mono-alkyl phosphates (*7*, *45*) in the pH range where the mono-ionized form is present in maximum concentration (Fig. 15), has been interpreted by the following mechanism (*23*), or a modification thereof (*24*).



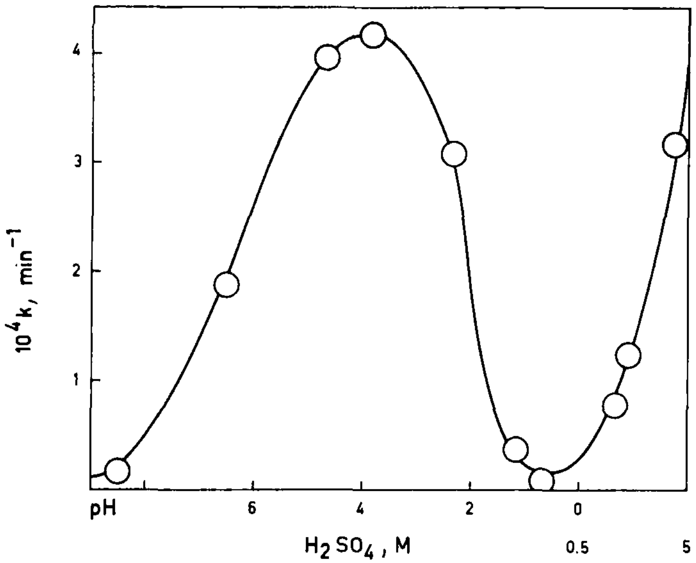
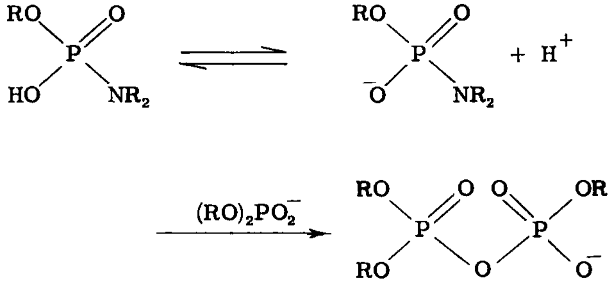


FIG. 15. The change in the rate of hydrolysis of 1-methoxy propyl 2-phosphate with pH of the solution (*24*).

By comparison, dialkyl phosphates are very inert, suggesting that this mechanism requires conjugation of two P-O groups. Similarly the corresponding amidates probably react by the bimolecular mechanism as in the pyrophosphate synthesis (*25*, *30*).



Recent investigations of the mechanism of hydrolysis of phosphoryl chloride (*100*) have shown that the first rapid stage, giving dichlorophosphoric acid, is followed by a slow reaction involving the dichlorophosphate anion which gives two equivalents of chloride ion simultaneously in acid and in alkaline solution.

Since amines strongly catalyse the second stage, this reaction probably proceeds by a bimolecular displacement involving a water molecule. The

$$POCl_3 + H_2O \xrightarrow{k_1} 2H^+ + Cl^- + Cl_2PO_2^- \cdot$$

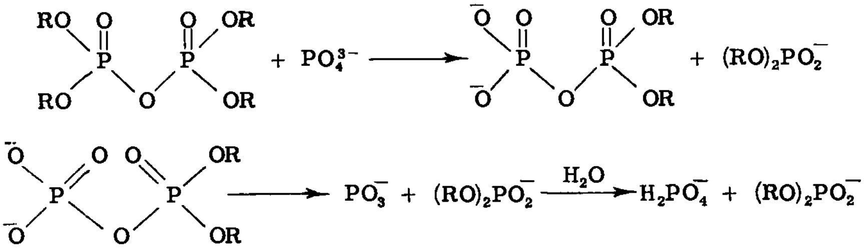
$$Cl_2PO_2^- + H_2O \xrightarrow{k_2} H^+ + Cl^- + ClPO_3H^-$$

$$ClPO_3H^- \rightleftharpoons H^+ + ClPO_3^{2-} \xrightarrow{k_3} PO_3^- + Cl^- \xrightarrow{H_2O} H_2PO_4^- + Cl^-$$

where $k_1 \gg k_2 \ll k_3$

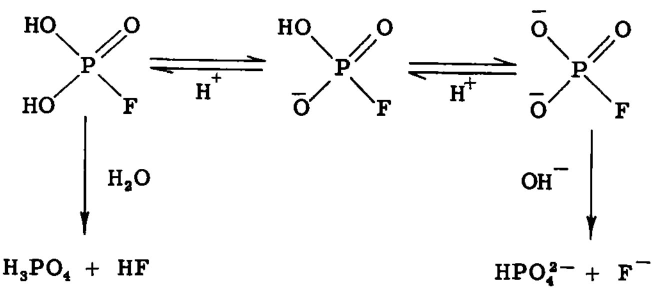
rate order $k_3 \gg k_2$ suggests that the third stage proceeds by the unimolecular mechanism, as shown in the above scheme.

This rate sequence is also observed with the corresponding pyro-esters. Thus the catalysis of the hydrolysis of tetra-alkyl pyrophosphates by phosphate ions has been explained by the following mechanism (*19*, *156*),



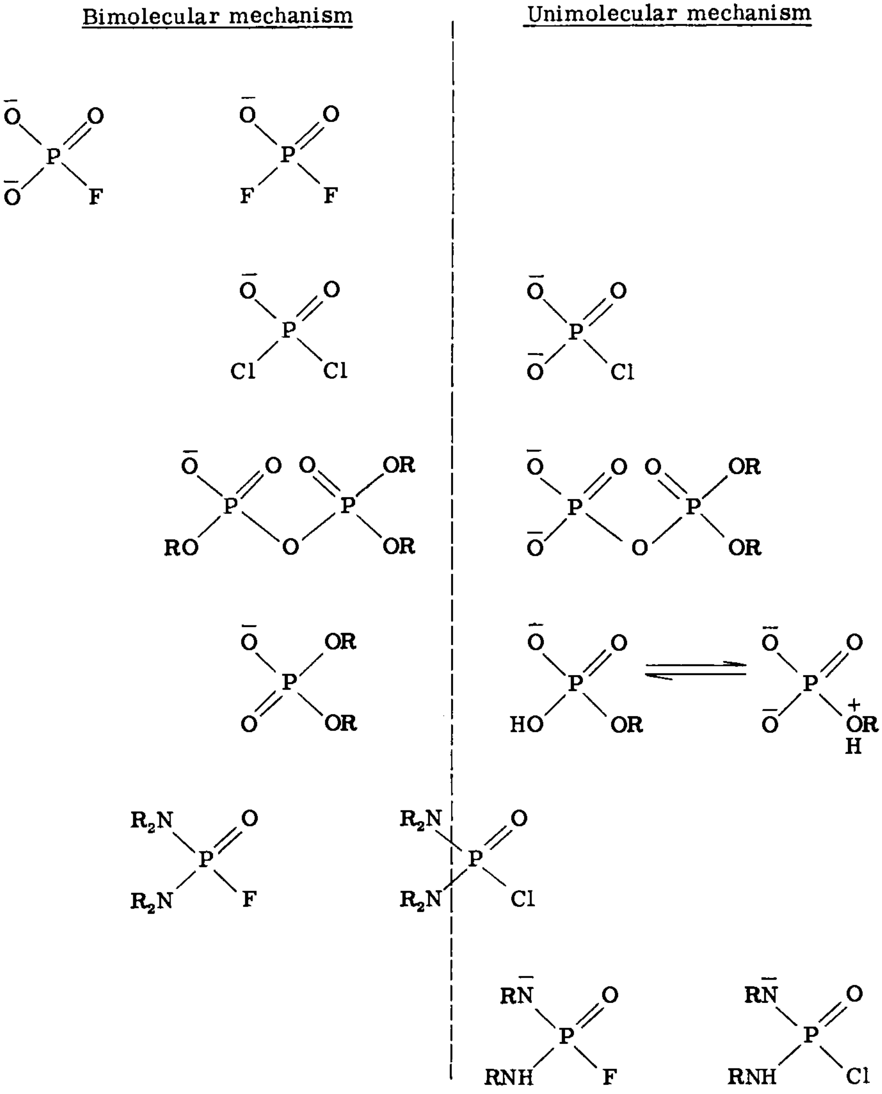
The corresponding triesters are relatively stable, and can be readily isolated (*39*).

The rate order $k_3 \gg k_2$ is the inverse of that expected for bimolecular reactions as shown by the reactions of the corresponding fluorides (*46*). The hydrolysis of mono-fluorophosphoric acid is catalyzed by alkali and acid (*46*) according to the scheme.

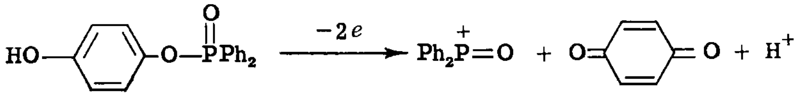


The unimolecular mechanism also explains the rapid rate of decomposition of β-chloroethylphosphonic acid in dilute alkaline solution (*168*) formed by the action of the olefin on phosphorus pentachloride (p. 350).

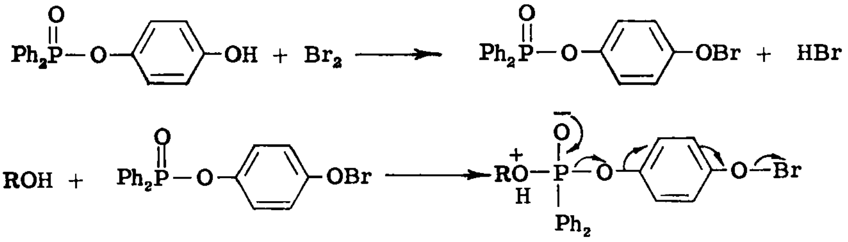
The rate data discussed in this section defines fairly clearly the conditions leading to an ionization mechanism, in terms of conjugation energy in the intermediate, and the P-X bond energy. These conclusions can be summarized diagrammatically in the following way (*95*),



The concept of an intermediate phosphoryl ion as a strong phosphorylating agent, has led to the discovery of oxidative phosphorylation (*31*, *183*), which may be represented in a general form as follows,



Although the mechanism of this interesting reaction has not been established, it probably proceeds by bimolecular phosphorylation involving a reactive intermediate. When halogens are used as the oxidizing agent, a scheme of the following kind can be proposed,



References

1. Aaron, H. S., Uyeda, R. T., Frack, H. F., and Miller, J. I., *J. Am. Chem. Soc.* **84,** 617 (1962).
2. Ahrland, S., Chatt, J., and Davies, N. R. *Quart. Revs.* (*London*) **12,** 265 (1958).
3. Aksnes, G., *Acta Chem. Scand.* **14,** 1475 (1960).
4. Aksnes, G., and Gramstad, T., *Acta Chem. Scand.* **14,** 1485 (1960).
5. Arbusov, A. E., *J. Russ. Phys.-Chem. Soc.* **38,** 1906 (1906).
6. Arbusov, A. E., and Arbusov, B., *J. Russ. Phys.-Chem. Soc.* **61,** 217 (1929).
7. Bailly, M. C., *Bull. soc. chim. France* **9,** 340, 405 (1942).
8. Banks, C. V., and Davis, R. J., *Anal. Chim. Acta.* **12,** 418 (1955).
9. Bell, J. V., Heisler, J., Tannenbaum, H., and Goldenson, J., *J. Am. Chem. Soc.* **76,** 5185 (1954).
10. Bellamy, L. J., "Infra-Red Spectra of Complex Molecules," p. 311. Wiley, New York, 1954.
11. Bellamy, L. J., and Beecher, L., *J. Chem. Soc.* p. 1701 (1952).
12. Bender, M. L., *Chem. Revs.* **60,** 53 (1960).
13. Bergmann, E., and Bondi, A., *Ber.* **63,** 1158 (1930); **64,** 1455 (1931); **66,** 278, 286 (1933).
14. Biilmann, E., and Jensen, K. A., *Bull. soc. chim. France* [5] **3,** 2306 (1936).
15. Bladé-Font, A., VanderWerf, C. A., and McEwen, W. E., *J. Am. Chem. Soc.* **82,** 2396 (1960).
16. Böhme, H., *Ber.* **74,** 248 (1941).
17. Branch, G. E. K., and Nixon, A. C., *J. Am. Chem. Soc.* **58,** 2499 (1936).
18. Brown, H. C., *J. Chem. Soc.* p. 1248 (1956).
19. Brown, D. M., and Hamer, N. K., *J. Chem. Soc.* p. 1155 (1960).
20. Brown, D. M., and Osborne, G. O., *J. Chem. Soc.* p. 2590 (1957).

21. Buck, R. P., Singhadeja, S., and Rogers, L. B., *Anal. Chem.* **26,** 1240 (1954).
22. Buckler, S. A., *J. Am. Chem. Soc.* **84,** 3093 (1962).
23. Bunton, C. A., Llewellyn, D. R., Oldham, K. G., and Vernon, C. A., *J. Chem. Soc.* p. 3574 (1958).
24. Butcher, W. W., and Westheimer, F. H., *J. Am. Chem. Soc.* **77,** 2420 (1955).
25. Chambers, R. W., and Khorana, H. G., *Chem. & Ind.* (*London*) p. 1022 (1956).
26. Charnley, T., and Skinner, H. A., *J. Chem. Soc.* p. 450 (1953).
27. Chatt, J., and Williams, A. A., *J. Chem. Soc.* p. 3061 (1951).
28. Chernick, C. L., and Skinner, H. A., *J. Chem. Soc.* p. 1401 (1956).
29. Clark, D., Powell, H. M., and Wells, A. F., *J. Chem. Soc.* p. 642 (1942).
30. Clark, V. M., Kirby, G. W., and Todd, A. R., *J. Chem. Soc.* p. 1497 (1957).
31. Clark, V. M., Kirby, G. W., and Todd, A. R., *Nature* **181,** 1650 (1958).
32. Clark, V. M., and Todd, A. R., *J. Chem. Soc.* p. 2030 (1950).
33. Craig, D. P., *J. Chem. Soc.* p. 997 (1959).
34. Craig, D. P., Macoll, A., Nyholm, R. S., Orgel, L. E., and Sutton, L. E., *J. Chem. Soc.* p. 332 (1954).
35. Craig, D. P., and Magnusson, E. A., *J. Chem. Soc.* p. 4895 (1956).
36. Cramer, F., *Angew. Chem.* **72,** 239 (1960).
37. Cramer, F., Pawelzik, K., and Baldauf, H. J., *Ber.* **91,** 1049 (1958).
38. Cramer, F., and Winter, M., *Ber.* **92,** 2761 (1959).
39. Cramer, F., and Wittmann, R., *Ber.* **94,** 322 (1961).
40. Cruickshank, D. W. J., *J. Chem. Soc.* p. 5486 (1961).
41. Crunden, E. W., and Hudson, R. F., *Chem. & Ind.* (*London*) p. 748 (1959).
42. Crunden, E. W., and Hudson, R. F., *J. Chem. Soc.* p. 3591 (1962).
43. Davies, W. C., and Addis, H. W., *J. Chem. Soc.* p. 1622 (1937).
44. Davis, R. E., *J. Org. Chem.* **23,** 1767 (1958).
45. Desjobert, A., *Bull. soc. chim. France* **14,** 809 (1947).
46. Devonshire, L. V., Ph.D. Thesis, University of Oklahoma, 1954. Quoted by Van Wazer, J. R., "Phosphorus and Its Compounds," p. 817. Wiley (Interscience), New York, 1958.
47. Dewar, M. J. S., Lucken, E. A. C., and Whitehead, M. A., *J. Chem. Soc.* p. 2423 (1960).
48. Dimroth, K., and Nürrenbach, A., *Angew. Chem.* **70,** 27 (1958).
49. Doering, W. von E., and Hoffmann, A. K., *J. Am. Chem. Soc.* **77,** 521 (1955).
50. Dostrovsky, I., and Halmann, M., *J. Chem. Soc.* p. 508 (1953).
51. Dostrovsky, I., and Halmann, M., *J. Chem. Soc.* p. 502 (1953).
52. Dostrovsky, I., and Halmann, M., *J. Chem. Soc.* p. 512 (1953).
53. Dostrovsky, I., and Halmann, M., *J. Chem. Soc.* p. 1004 (1956).
54. Downs, J., and Johnson, R. E., *J. Chem. Phys.* **22,** 143 (1954).
55. Durant, G. J., Turnbull, J. H., and Wilson, W., *Chem. & Ind.* (*London*) p. 157 (1958).
56. Ebel, F., and Bretscher, E., *Helv. Chim. Acta* **12,** 450 (1929).
57. Edwards, J. O., *J. Am. Chem. Soc.* **76,** 1540 (1954).
58. Edwards, J. O., and Pearson, R. G., *J. Am. Chem. Soc.* **84,** 16 (1962).
59. Epstein, J., Bauer, V. E., Saxe, M., and Demek, M. M., *J. Am. Chem. Soc.* **78,** 4068 (1956).
60. Epstein, J., Rosenblatt, D. H., and Demek, M. M., *J. Am. Chem. Soc.* **78,** 341 (1956).
61. Evans, A. G., Evans, M. G., and Polanyi, M., *J. Chem. Soc.* p. 558 (1947).
62. Fenton, G. F., Hey, L., and Ingold, C. K., *J. Chem. Soc.* p. 989 (1933).

63. Fenton, G. F., and Ingold, C. K., *J. Chem. Soc.* p. 2342 (1929).
64. Freedman, L. D., and Doak, G. O., *J. Am. Chem. Soc.* **77,** 6221 (1955).
65. Fukuto, T. R., and Metcalf, R. L., *J. Am. Chem. Soc.* **76,** 5103 (1954).
66. Fukuto, T. R., and Metcalf, R. L., *J. Am. Chem. Soc.* **81,** 372 (1959).
67. Gerrard, W., and Whitbread, E. G. G., *J. Chem. Soc.* p. 914 (1952).
68. Gier, T. E., *J. Am. Chem. Soc.* **83,** 1769 (1961).
69. Gillespie, R. J., *J. Chem. Soc.* p. 1002 (1952).
70. Ginjar, L., Ph.D. Thesis, Leiden, Netherlands, 1960.
71. Grayson, M., and Keough, P. T., *J. Am. Chem. Soc.* **82,** 3919 (1960).
72. Green, A. L., Sainsbury, G. L., Saville, B., and Stansfield, M., *J. Chem. Soc.* p. 1583 (1958).
73. Green, A. L., and Saville, B., *J. Chem. Soc.* p. 3887 (1956).
74. Green, M., and Hudson, R. F., *Proc. Chem. Soc.* p. 227 (1959).
75. Green, M., and Hudson, R. F., *Proc. Chem. Soc.* p. 307 (1962).
76. Green, M., and Hudson, R. F., *Proc. Chem. Soc.* p. 217 (1962).
77. Griffin, C. E., and Polsky, R. A., *J. Org. Chem.* **26,** 4772 (1961).
78. Griffith, J. S., and Orgel, L. E., *Quart. Revs. (London)* **11,** 381 (1957).
79. Gutmann, V., *Monatsh. Chem.* **83,** 164 (1952).
80. Haake, P. C., and Westheimer, F. H., *J. Am. Chem. Soc.* **83,** 1102 (1961).
81. Hackley, B. E., Plapinger, R., Stolberg, M., and Wagner-Jauregg, T., *J. Am. Chem. Soc.* **77,** 3651 (1955).
82. Hall, H. K., *J. Am. Chem. Soc.* **77,** 5993 (1955).
83. Hall, H. K., *J. Org. Chem.* **21,** 248 (1956).
84. Halmann, M., *J. Chem. Soc.* p. 305 (1959).
85. Harper, D. C., and Hudson, R. F., *J. Chem. Soc.* p. 1356 (1958).
86. Heath, D. F., *J. Chem. Soc.* p. 3796 (1956).
87a. Henderson, W. A., and Streuli, C. A., *J. Am. Chem. Soc.* **82,** 5791 (1960).
87b. Henderson, W. A., and Buckler, S. A., *ibid.* p. 5794.
88. Hey, L., and Ingold, C. K., *J. Chem. Soc.* p. 531 (1933).
89. Hoffmann, H., and Grünewald, R., *Ber.* **94,** 186 (1961).
90. Hoffmann, H., Grünewald, R., and Horner, L., *Ber.* **93,** 861 (1960).
91. Hoffmann, F. W., Ess, R. J., and Usinger, R. P., *J. Am. Chem. Soc.* **78,** 5817 (1956).
92. Hoffmann, F. W., Roth, R. G., and Simmons, T. C., *J. Am. Chem. Soc.* **80,** 5937 (1958).
93. Horner, L., and Jurgeleit, P. W., *Ann. Chem. Liebigs* **591,** 138 (1955).
93a. Horner, L., Winkler, H., Rapp, A., Mentrup, A., Hoffmann, H., and Beck, P., *Tetrahedron Letters* No. 5, 161 (1961).
94. Hudson, R. F., *Chimia (Switz.)* **16,** 173 (1962).
95. Hudson, R. F., *Ann. Chim. (Rome)* **53,** 47 (1963).
96. Hudson, R. F., and Keay, L., *J. Chem. Soc.* p. 2463 (1956).
97. Hudson, R. F., and Keay, L., *J. Chem. Soc.* p. 1859 (1960).
98. Hudson, R. F., and Keay, L., *J. Chem. Soc.* p. 1865 (1960).
99. Hudson, R. F., and Loveday, G. W., *J. Chem. Soc.* p. 1068 (1962).
100. Hudson, R. F., and Moss, G. E., *J. Chem. Soc.* p. 3599 (1962).
101. Huggins, M. L., *J. Am. Chem. Soc.* **75,** 4123, 4126 (1953).
102. Ingold, C. K., and Vass, C. N., *J. Chem. Soc.* p. 3125 (1928).
103. Issleib, K., and Seidel, W., *Ber.* **92,** 2681 (1959).
104. Jaffé, H. H., *J. Chem. Phys.* **21,** 258 (1953).
105. Jaffé, H. H., *J. Phys. Chem.* **58,** 185 (1954).
106. Jaffé, H. H., and Freedman, L. D., *J. Am.Chem. Soc.* **74,** 1069 (1952).

107. Jaffé, H. H., and Freedman, L. D., *J. Am. Chem. Soc.* **74,** 2930 (1952).
108. Jaffé, H. H., Freedman, L. D., and Doak, G. O., *J. Am. Chem. Soc.* **75,** 2209 (1953).
109. Keay, L., *J. Org. Chem.* **28,** 329 (1963).
110. Khorana, H. G., and Todd, A. R., *J. Chem. Soc.* p. 2257 (1953).
111. Kimball, G. E., *J. Chem. Phys.* **8,** 188 (1940).
112. Koch, H. P., and Moffitt, W. E., *Trans. Faraday Soc.* **47,** 7 (1951).
113. Koerner, W. E., and Daniels, F., *J. Chem. Phys.* **20,** 113 (1952).
114. Kuchen, W., and Buchwald, H., *Ber.* **91,** 2296 (1958).
115. Kumamoto, J., Cox, J. R., and Westheimer, F. H., *J. Am. Chem. Soc.* **78,** 4858 (1956).
116. Kumli, K. F., McEwen, W. E., and VanderWerf, C. A., *J. Am. Chem. Soc.* **81,** 3805 (1959).
117. Larsson, L., *Acta Chem. Scand.* **11,** 1131 (1957).
118. Larsson, L., *Svensk Kem. Tidskr.* **70,** 10 (1958).
119. Lees, E. B., and Saville, B., *J. Chem. Soc.* p. 2262 (1958).
120. Lewis, G. N., *J. Am. Chem. Soc.* **38,** 762 (1916).
121. Linton, E. P., *J. Am. Chem. Soc.* **62,** 1945 (1940).
122. Lipmann, F., Spector, L., and Jones, M. E., *J. Am. Chem. Soc.* **77,** 819 (1955).
123. Lucken, E. A. C., and Whitehead, M. A., *J. Chem. Soc.* p. 2459 (1961).
123a. Märkl, G., *Angew. Chem.* **75,** 168 (1963).
124. Marsh, D. J., and Neale, E., *Chem. & Ind.* (*London*) p. 494 (1956).
125. Meisenheimer, J., Casper, J., Höring, M., Lauter, W., Lichtenstadt, L., and Samuel, W., *Ann. Chem. Liebigs* **449,** 213 (1926).
126. Meisenheimer, J., and Lichtenstadt, L., *Ber.* **44,** 356 (1911).
127. Michalski, J., and Ratajczak, R., *Chem. & Ind.* (*London*) p. 1241 (1960).
128. Miller, B., *J. Am. Chem. Soc.* **84,** 403 (1962).
129. Moffitt, W. E., *Proc. Roy. Soc.* **A200,** 409 (1950).
130. Moss, G. E., Ph.D. Thesis, University of London, 1961.
131. Moureu, H., Magat, M., and Wetroff, G., *Compt. rend. acad. sci.* **205,** 276 (1937).
132. Neale, E., and Williams, L. T. D., *J. Chem. Soc.* p. 2156 (1954).
133. Neale, E., and Williams, L. T. D., *J. Chem. Soc.* p. 2485 (1955).
134. Paddock, N. L., and Searle, H. T., *Advances in Inorg. Chem. Radiochem.* **1,** 347 (1959).
135. Parisek, C. B., McEwen, W. E., and VanderWerf, C. A., *J. Am. Chem. Soc.* **82,** 5504 (1960).
136. Pass, F., and Schindlbauer, H., *Monatsh. Chem.* **90,** 149 (1959).
137. Pauling, L., "Nature of the Chemical Bond," p. 232. Cornell Univ. Press, Ithaca, New York, 1940.
138. Pauling, L., "Nature of the Chemical Bond," p. 84. Cornell Univ. Press, Ithaca, New York, 1940.
139. Pauling, L., *J. Phys. Chem.* **56,** 361 (1952).
140. Pauling, L., and Brockway, L. O., *J. Am. Chem. Soc.* **59,** 13 (1937).
141. Perkow, W., Ullerich, K., and Meyer, F., *Naturwissenschaften* **39,** 353 (1952).
142. Phillips, G. M., Hunter, J. S., and Sutton, L. E., *J. Chem. Soc.* p. 146 (1945).
143. Pinck, L. A., and Hilbert, G. E., *J. Am. Chem. Soc.* **69,** 723 (1947).
144. Pitzer, K. S., *J. Am. Chem. Soc.* **70,** 2140 (1948).
145. Polestack, W. J., and Zimmerman, H. K., *J. Phys. Chem.* **60,** 787 (1956).
146. Powell, H. M., and Clark, D., *Nature* **145,** 971 (1940).
147. Pressman, D., and Brown, D. H., *J. Am. Chem. Soc.* **65,** 540 (1943).
148. Ramirez, F., Mitra, R. B., and Desai, N. B., *J. Am. Chem. Soc.* **82,** 2652 (1960).

149. Ramirez, F., Desai, N. B., Hansen, B., and McKelvie, N., *J. Am. Chem. Soc.* **83,** 3539 (1961).
150. Ramirez, F., and Dershowitz, S., *J. Org. Chem.* **22,** 41 (1957).
151. Ramirez, F., and Levy, S., *J. Am. Chem. Soc.* **79,** 67 (1957).
152. Reesor, J. W. B., and Wright, G. F., *J. Org. Chem.* **22,** 385 (1957).
153. Rouault, M., *Compt. rend. acad. sci.* **207,** 620 (1938); *Ann. Phys.* **14,** 78 (1940).
154. Rydon, H. N., *Chem. Soc. (London) Spec. Publ.* **No. 8,** 61 (1957).
155. Rydon, H. N., and Tonge, B. L., *J. Chem. Soc.* p. 3043 (1956).
156. Samuel, D., and Silver, B., *J. Chem. Soc.* p. 4321 (1961).
157. Samuel, D., and Westheimer, F. H., *Chem. & Ind. (London)* p. 51 (1959).
158. Schöllkopf, U., *Angew. Chem.* **71,** 260 (1959).
159. Schomaker, V., and Stevenson, D. P., *J. Am. Chem. Soc.* **63,** 37 (1941).
160. Schuetz, R. D., and Jacobs, R. L., *J. Org. Chem.* **23,** 1799 (1958).
161. Shaw, R. A., *Chem. & Ind. (London)* p. 54 (1959).
162. Sklar, A. L., *Revs. Modern Phys.* **14,** 232 (1942).
163. Sommer, L. H., *Angew. Chem.* **74,** 176 (1962).
164. Sommer, L. H., and Bennett, O. F., *J. Am. Chem. Soc.* **81,** 251 (1959).
165. Spencer, C. J., and Lipscomb, W. N., *Acta Cryst.* **14,** 250 (1961).
166. Staudinger, H., and Braunholtz, W., *Helv. Chim. Acta* **4,** 897 (1921).
167. Swain, C. G., and Scott, C. B., *J. Am. Chem. Soc.* **75,** 141 (1953).
168. Swan, J., and Maynard, J. A., *Proc. Chem. Soc.* p. 61 (1963).
169. Syrkin, Y. K., and Dyatkina, M. E., "The Structure of Molecules," p. 261. Butterworths, London, 1950.
170. Todd, A. R., *Proc. Natl. Acad. Sci. U. S.* **45,** 1389 (1959).
171. Todd, A. R., *Chem. Soc. (London) Spec. Publ.* **No. 8,** 91 (1957).
172. Toy, A. D. F., *J. Am. Chem. Soc.* **70,** 3882 (1948); **72,** 2065 (1950).
173. Trippett, S., and Gough, S. T. D., *Proc. Chem. Soc.* p. 302 (1961).
174. Van Wazer, J. R., "Phosphorus and Its Compounds," p. 197. Wiley (Interscience), New York, 1958.
175. Van Wazer, J. R., *J. Am. Chem. Soc.* **78,** 5709 (1956).
176. Van Wazer, J. R., Callis, C. F., Shoolery, J. N., and Jones, R. C., *J. Am. Chem. Soc.* **78,** 5715 (1956).
177. Wadsworth, W. S., and Emmons, W. D., *J. Am. Chem. Soc.* **83,** 1733 (1961).
178. Wadsworth, W. S., and Emmons, W. D., *J. Am. Chem. Soc.* **84,** 1316 (1962).
179. Weil, T., Prijs, B., and Erlenmeyer, H., *Helv. Chim. Acta* **35,** 616 (1952).
180. Wells, A. F., *J. Chem. Soc.* p. 55 (1949).
181. Westheimer, F. H., *Chem. Soc. (London) Spec. Publ.* **No. 8,** 12 (1957).
182. Westheimer, F. H., *Chem. Soc. (London) Spec. Publ.* **No. 8,** 181 (1957).
182a. Wheatley, P. J., *Proc. Chem. Soc.* p. 251 (1962).
183. Wieland, T., and Pattermann, F., *Angew. Chem.* **70,** 313 (1958).
184. Wittig, G., and Geissler, G., *Ann. Chem. Liebigs* **580,** 44 (1953).
185. Wittig, G., and Rieber, M., *Ann. Chem. Liebigs* **562,** 187 (1949).
186. Wittig, G., and Schöllkopf, U., *Ber.* **87,** 1318 (1954).
187. Wittig, G., Weigmann, H. D., and Schlosser, M., *Ber.* **94,** 676 (1961).
188. Wolfsberg, M., and Helmholz, L., *J. Chem. Phys.* **20,** 837 (1952).
189. Zanger, M., VanderWerf, C. A., and McEwen, W. E., *J. Am. Chem. Soc.* **81** 3806 (1959).