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Chemistry of Phosphinylidene Compounds—Advances and Prospects of Development

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Research in this field is surveyed, and features of individual classes of compounds having this functional group in common are compared. An attempt is made to outline possible developments in certain promising scientific directions. Attention is paid mainly to investigations made during recent years. A list of 506 references is included.

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I. INTRODUCTION

The evolution of the chemistry of organophosphorus compounds has created a large region uniting many classes of compounds having a phosphinylidene functional group OPH< in common. It comprises acids of tervalent phosphorus, their partial esters, thiolic esters, amides, certain anhydrides, etc., which can all be regarded as phosphinylidene derivatives. Their preparation, structure, reactions, and practical applications have now been widely investigated. Individual aspects of the results have been discussed in monographs and reviews. Thus Tsvetkov and Kabachnik published a comprehensive work[1] on the preparation and analysis of such derivatives. Other articles[2,3] were devoted to problems of alkylation. Individual classes of compounds—dialkyl phosphites[4,5], phosphonous acids and their derivatives[6], phosphinous acids[7]—have been subjects of compilations. The above reviews were written during the early and middle 1960s, and cover information that has become almost classical. Investigations made during recent years, which have been pursued especially vigorously, have not yet been summarised or examined from general points of view. The resulting need to fill the gap is intensified by certain circumstances, of which special note should be made.

1. The number of known classes and types of phosphinylidene derivatives has increased appreciably, which has permitted both comparison of the properties of a wide range of compounds having the same functional group and the first conclusions on the influence of structure of their reactivity. Moreover, it has become possible to pass from a qualitative to a quantitative treatment of the results.

2. A stereochemical principle has appeared. The first individual geometrical and optical isomers of partial phosphites, phosphonites, and phosphinous acids have been obtained. Research has begun on dynamic stereochemistry, in particular on the conformational dependence of the reactivity of phosphites.

3. Abundant preparative information has accumulated, and fundamentally new reactions of phosphinylidene compounds have been suggested. The widespread uses of several transformations discovered during the 1940–1950s has made it necessary to honour the debt to their authors and introduce the appropriate names into chemical vocabulary.

4. Physicochemical laboratories have been attracted to the study of phosphinylidene compounds. It is significant that not only structural and kinetic but also preparative problems have been solved in them, revealing unexpected possibilities for organophosphorus synthesis.

5. Methods used in the chemistry of phosphinylidene compounds have been applied to naturally occurring compounds and polymers. Original results have been obtained, indicating a promising future for these lines of investigation.

6. Work on the technology of dialkyl phosphites and related derivatives has ended in industrial realisation. Data have been obtained on the use of phosphinylidene derivatives to solve many practical problems.

The present Review has been prepared in the light of the above circumstances. It reflects (but does not always fully cite) the advances of the past decade. The Reviewer has seen his task in not only systematising and analysing published information but also assessing tendencies and the prospects for development of the most interesting lines of research. Judgments on such problems are, of course, controversial in character.

II. SYNTHESIS

Published information usually covers the preparation of phosphorous diesters, multisubstituted phosphonous esters, and oxides of secondary phosphines. During recent years, however, other related types of compounds have become accessible, including relatively unstable derivatives; in several cases stereoisomeric forms have been isolated and studied.

In the present Section information on the formation of phosphinylidene compounds is presented in a sequence based on chemical structure—(1) organic derivatives of phosphorous acid, (2) phosphonous acids and their derivatives, (3) phosphinous acid, (4) derivatives of hypophosphorous acid, and (5) oxides of primary phosphines and other compounds—where preparations of each class or type of compounds are separated into two groups: the first group comprises reactions in which the initial substances already contain a phosphinylidene function, and the second those in which it is formed. Where possible, data on the structure of stereoisomers are included.

1. Organic Derivatives of Phosphorous Acid

(*a*) Diesters

Dialkyl (diaryl) phosphites. The most thoroughly studied and important type of phosphinylidene derivatives comprises dialkyl and diaryl phosphites. They are widely used as intermediates in the production of pesticides [8] and complexing agents [9,10], as stabilisers for polymers [11,12], additives to oils [13,14], components of flame-proofing compositions [15], etc.

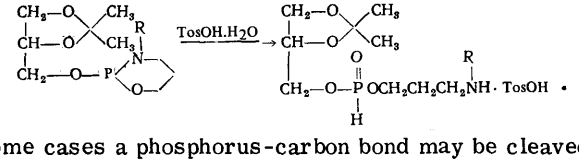
To prepare many dialkyl (diaryl) phosphites it is advisable to phosphinylate alcohols (phenols) with simple derivatives. This includes transesterification, whose advantages include high yields and mild conditions due to the absence of aggressive by-products, as well as simplicity of control. Transesterification has been used to prepare various symmetrical and unsymmetrical phosphites [16-18], phosphinylated terpenes [14], and polyfunctional systems, mainly hydroxylated phosphorous esters formed from simple dialkyl phosphites and glycols [19-21]

$$(RO)_2P(O)H + HOR'OH \begin{cases} \xrightarrow{1:1} ROP(O)-O-R'OH \\ \xrightarrow{1:2} HOR'OP(O)-OR'OH \end{cases}$$

The products are phosphites of a new type, of interest for macromolecular chemistry. Their preparation by other routes is complicated or altogether impossible. However, transesterification has its limitations. Thus negative results have been obtained in the phosphinylation of 2-trichloromethylpropan-2-ol with simple dialkyl phosphites [22]. Because of such difficulties attention has been attracted to the alcoholysis of amides [23-25] and thiolic esters [26] of phosphorous acid, as well as the corresponding mixed anhydrides [27], which are milder reagents.

It has been proposed to obtain dialkyl phosphites of diverse structure by esterifying phosphorous acid [28,29], which is of industrial interest [30]. Similarly, monoalkyl phosphites can also be esterified [31,32]; those of more complicated structure, e.g. nucleoside phosphites, are esterified in the presence of condensing agents [33]. Phosphorous acid and monoalkyl phosphites can be alkylated to dialkyl phosphites by means of diazo-compounds [34,35], orthoesters [36], oxiran [37], and alkyl halides [38].

A large group of reactions yielding dialkyl or diaryl phosphites is based on the use of three-coordinated phosphorous derivatives. An important approach is hydrolysis of $(RO)_2PX$ systems, where X = Cl, [22,39] OAlk†, [40-42] or NH_2. [43-45] The hydrolysis of complex phosphoramidites requires meticulous selection of conditions; thus treatment of the cyclic 2,3-isopropylideneglycerol phosphoramidite with water gives a mixture of products, but with the hydrate of toluene-*p*-sulphonic acid the required compound is formed in almost quantitative yield [44]:



In some cases a phosphorus-carbon bond may be cleaved. An example is the hydrolysis of completely esterified carborane-phosphonites [46]:

$$RCB_{10}H_{10}CP(OC_2H_5)_2 + H_2O \rightarrow (C_2H_5O)_2P(O)H + RCB_{10}H_{10}CH .$$

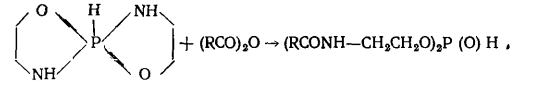
†A reaction mechanism differing from the traditional mechanism is discussed in Ref. 42.

The preparation of acid phosphites by decomposing the neutral esters is especially valuable. Some esters, primarily those of tertiary alcohols, are degraded thermally [47]. More often, however, decomposition is effected by the use of acids—phosphorous acid [48] or dialkyl phosphorodithioates [49]—of which the latter ensure the highest rates because of the strongly nucleophilic character of the anion. An especially popular method is to dealkylate neutral phosphites with hydrogen chloride: for example [16]

$$CH_3OPCl_2 + 2C_6H_5OH \rightarrow [CH_3OP(OC_6H_5)_2 + HCl] \rightarrow (C_6H_5O)_2P(O)H + CH_3Cl .$$

A similar dealkylation completes a series of processes in the industrial production of dialkyl phosphites from phosphorus trichloride and alcohols. A continuous scheme has been suggested [50] for the process.

Much attention has been paid to the preparation of dialkyl phosphites from phosphorus sesquioxide and other anhydride systems. Direct alcoholysis of the oxide, a promising starting material for organophosphorus synthesis, leads to its complete conversion into an equimolecular mixture of mono- and di-alkyl phosphites [51]. If the reaction is conducted in boiling xylene, i.e. under conditions of azeotropic removal of water, monoalkyl phosphites are completely converted into the dialkyl esters, and a single product is formed [52]. When the technical "alcoholysate" is heated, monoalkyl phosphites disproportionate into the dialkyl esters and phosphorous acid [53]. It has been proposed to obtain dialkyl phosphites also by alcoholysis of anhydrides of alkyl dihydrogen phosphites [54,55] and by the deacylation of acyl phosphites [56,57]. An autodeacylation stage is probably involved also in passing from diaminospirophosphoran to bisacylaminoethyl phosphites [58]:



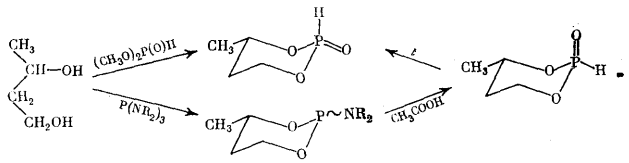
A special case of the formation of phosphorous diesters is the hydrolysis of α-oxo-phosphonates [59] and their imines [60]. It has been little studied, but is promising for the industrial production of dialkyl phosphites from white phosphorus, alcohol, and oxygen [61].

Alkylene (arylene) phosphites. Cyclic acid phosphites were first mentioned at the beginning of the century, but subsequently their study began only during recent years, when it has become possible to synthesise symmetrical and unsymmetrical 5–8-membered systems derived from glycols, dihydric phenols, and higher polyols. The most detailed investigation has been made on 1,3,2-dioxaphosphans—esters of 1,3-diols—which are of chemical and stereochemical interest, and structurally similar to certain bioregulators [62].

Simple and functionally substituted derivatives are usually obtained by transesterification [63-66]. Another popular approach involves modifying cyclic derivatives containing a three-coordinated phosphorus atom, by the hydrolysis of phosphorochloridites [67-71] and neutral mono- and bicyclo-phosphites [42,72], the acidolysis of phosphoramidites [63,64,66,73], or the aminolysis of pyrophosphites [74]. In several cases it is advisable to effect the preparations via thermally labile t-butyl intermediates [47,75,76].

Stereochemical factors must be taken into account in preparing substituted alkylene phosphites, owing to the possible formation of geometric isomers. A significant advance has been the development of directed methods for obtaining isomers. For example, 1-methyltrimethylene

phosphite is formed mainly as the *cis*-isomer when obtained by transesterification, but as the *trans*-isomer when obtained by the acidolysis of 1-methyltrimethylene phosphoramidites; the latter isomer is unstable, and changes its configuration when heated[63];

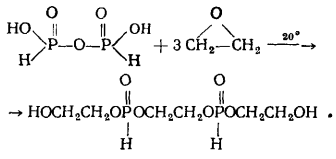


The orientation of the phosphinyl group and other structural factors in these rings have been investigated by proton nuclear magnetic resonance[63,64,66,68,69,77,78], dipole moments[63,77], infrared spectroscopy[69,79], and X-ray diffraction[80]. Moreover, several aspects of the dynamics of trimethylene phosphites—conversion of labile into stable geometric isomers[42,69,81], conformational equilibrium of symmetrical forms[79,82]—have been studied quantitatively. Geometric isomers of ethylenic phosphites do not exhibit ready interconversion[70]. Thus an appreciable difference exists between five- and six-membered cyclic phosphinylidene derivatives.

Alkylene diphosphites. These compounds, whose investigation has only just begun, have been obtained by transesterification[83]:

$$2\,(RO)_2P(O)H + HOR'OH \rightarrow RO{-}P(O)(H){-}OR'O{-}P(O)(H){-}OR\ .$$

Opportunities for their technical use have been shown[84,85]. An unusual reaction giving an important product utilises pyrophosphorous acid and oxiran[86]:



Poly(alkylene phosphites) and phosphites of polyhydroxylated polymers. It has been proposed[87-90] to obtain oligomeric and polymeric acid phosphites by the interaction of equimolecular quantities of simple dialkyl phosphites and glycols. The process develops differently according to the size of the alkylene radical: either a polyester is produced immediately or an initially formed alkylene phosphite polymerises. Unfortunately, many aspects of this promising reaction have not yet been elucidated.

A particular but important method for obtaining these polyesters is thermolysis of bis-2-chloroethyl phosphite. It is assumed that initial cyclisation to ethylene phosphite is followed by its condensation[91,92]. Polytransesterification has been extended also to triols, tetraols, and hexitols[93,94]. Several polyphosphites of hexitols have been suggested for use as additives to transformer oils[94].

Macromolecular acid phosphites of a different type are obtained by treating hydroxylated polymers with simple phosphinyl compounds. It is significant that these phosphinylating agents are more reactive than corresponding derivatives of quinquevalent phosphorus [Sic.] They have special advantages over various chlorides that are popular phosphinylating agents for lower alcohols and polyols, for their use does not liberate hydrogen chloride, which degrades or modifies many polymers. The phosphinylation of cellulose has been investigated in the greatest detail, for which purpose dialkyl phosphites[95-97], monoalkyl phosphites[96,97], and phosphorous acid[97] have been proposed. Polyphosphites, like other products of polymer-analogous reactions, are not chemically homogeneous. Amylopectin[98], lignin[99], polyallyl[100] and polyvinyl[101] alcohols, and soluble phenol–formaldehyde resins[102] undergo phosphinylation similarly to cellulose.

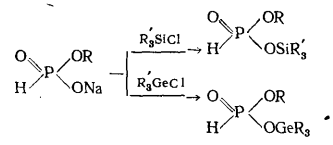
Trialkylsilyl phosphites. Silyl phosphites are definite analogues of the alkyl esters. They are usually obtained by the action of various silylating agents on phosphorous acid[103-106]:

$$(HO)_2P(O)H + 2R_3SiX \rightarrow (R_3SiO)_2P(O)H$$

$$X = Cl,\ OCCH_3,\ OSiR_3,\ NHSiR_3\ .$$

Excess of the agent is not advisable, since neutral silyl phosphites might be formed. An interesting variant of this reaction, convenient for preparative purposes, is the interaction of phosphorous acid and a trialkylsilane in the presence of colloidal nickel[107]. Disilyl phosphites can be obtained by the alcoholysis or silanolysis of trisilyl phosphites[108], and also by the oxidation of disilyl hypophosphites[109].

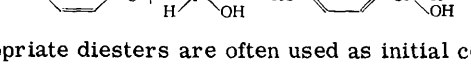
Alkyl silyl phosphites are formed by the reaction of monoalkyl phosphites with hexa-alkyldisiloxanes[110] and with trialkylchlorosilanes[105]; germanium derivatives are obtained similarly[105]:



(*b*) Monoesters

Phosphorous monoesters have been known for a long time, but their active investigation began only during recent years, probably stimulated by the discovery of interesting opportunities for their bio-organic use, as well as in solving practical problems[111]. As the first and second hydroxy-groups in phosphorous acid are esterified at different rates, a simple and convenient method has been developed for obtaining monoalkyl phosphites[28]. Phosphorous acid is poorly esterified by phenols, in contrast to alcohols[112]. The presence of a condensing agent—a carbodi-imide[113] or a sulphonyl chloride[113]—is advisable for the phosphinylation of complicated compounds (e.g. nucleosides). Phosphorous acid can be converted into monoalkyl esters by heating with alkyl halides[38] or t-butyl esters[114].

Other methods are transesterification[31,96] and the addition of hypophosphorous acid to quinones[115]:



Appropriate diesters are often used as initial compounds in obtaining monoalkyl phosphites, and are dealkylated by nucleophiles[58,116] or phosphorous acid[111].

Another approach involves the use of derivatives of three-coordinated phosphorus. Thus it has been suggested that Menshutkin acid chlorides, including nucleosides, should be hydrolysed[117-119] or treated with t-butyl alcohol[120,121]. Hydrolysis has been applied also to neutral

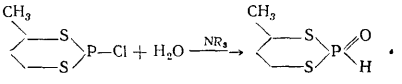
phosphites [122], phosphorodiamidites[123], and the corresponding spirophosphorans [124].

(*c*) Thiolic esters

Compounds of the type $OPH(SR)_2$ and $OPH(SR).OR$ began to be investigated only during the 1970s, when a fundamental difference from other phosphinylidene derivatives immediately became apparent. An attempt to prepare dithiolic esters by the thiolysis of tetra-alkyl phosphorodiamidites was reported; the products were neutral trithiolic esters, formed by disproportionation of the dithiolic esters [24,125]:

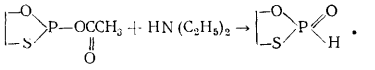
$$(R_2N)_2P(O)H + 2'RSH \rightarrow [(R'S)_2P(O)H] \rightarrow (R'S)_3P .$$

The required compounds are formed by the hydrolysis of dialkyl phosphorochloridodithiolites [26,125]. The clearest results are obtained with dithiols giving cyclic products [125]:



Cyclic chloridodithiolites are converted into phosphinylidene derivatives also by treatment with t-butyl alcohol [126]. Diethyl phosphorodithiolite is assumed to be formed in the hydrolysis of triethyl phosphorotrithiolite [127].

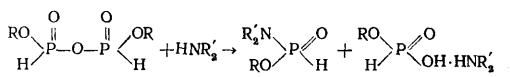
Only one phosphoromonothiolite—the ethylene ester—has been investigated. It has been prepared by hydrolysis of the corresponding chloride [128] and similar reactions, e.g. [128,129]



(*d*) Amides

Phosphinylidene compounds containing a phosphoramide bond are of very great chemical interest. Various derivatives of this class—$OPH(NR_2)_2$, $OHP(NR_2).OR'$, $OHP(NR_2).OH$—are now known. Many diamides of phosphorous acid can be obtained by transamidation [24]. However, simple derivatives are mostly prepared by hydrolysis [130] or acidolysis [130,131] of fully amidated phosphorous acid. The required compounds can be obtained from triamides and propiolactone [132], and also from silyl phosphorodiamidites and alcohols [133]. It has been suggested that cyclic amides can be obtained by hydrolysing appropriate acid chlorides [66] or by treating them with t-butyl alcohol [134]. Data have appeared on the stereochemistry of these rings [135]. Salts of phosphorodiamidous acids are formed by reducing complete amides of phosphoric acid with alkali metals [136].

Phosphoramidous esters have been obtained by transamidation of simpler compounds [23], partial alcoholysis of diamides [24], and aminolysis of anhydrides containing a phosphinylidene group [137]: for example



Another method is hydrolysis of phosphoramidochloridous [137,139] or phosphorodiamidous [23,138,139] esters, as well as alcoholysis of anhydrides of phosphoramidous acids [54].

Monoamides of phosphorous acid have been described in only one patent [140]:

$$P_4O_6 + HNR_2 \rightarrow R_2N{-}P(O)H(OH)\cdot R_2NH .$$

(*e*) Acid halides

Results on the preparation of acid halides of phosphorous acid, containing a phosphinylidene group, have not yet been analysed in reviews on the phosphorus chemistry. It has evidently been assumed that these compounds are too unstable to exist. Nevertheless, such acid halides have been obtained.

Attempts have been made to prepare phosphorodichloridous acid by the action of hydrogen chloride on diamides of phosphorous acid, but the product isolated was phosphorus trichloride. The initial substance had obviously disproportionated under the reaction conditions, like other phosphinylidene compounds containing electron-accepting groups [24]:

$$(R_2N)_2P(O)H + HCl \rightarrow [Cl_2P(O)H] \rightarrow PCl_3 .$$

Another route to an acid dichloride consists in treating phosphorus trichloride with diethyl phosphite: formation of a product was detected by n.m.r. at −40°C. [141]

A very interesting result has recently been obtained [142]:

$$ROPCl_2 + R'COOH \xrightarrow{<30^\circ} RO{-}P(O)H(Cl) + R'COCl .$$

2′,3′-Isopropylideneadenosine phosphorochloridite has been prepared by selective hydrolysis of the corresponding Menshutkin acid chloride. The product was then oxidised and hydrolysed to 2′,3′-isopropylideneadenylic acid [119].

Phosphorodifluoridous acid is obtained by redox reactions [143,144] and cleavage of its anhydrides by nucleophilic compounds [145,146]: for example

$$F_2PH + H_2O \rightarrow F_2P(O)H + H_2 ,$$

$$F_2P(O)N(CH_3)_2 + 3HI \rightarrow F_2P(O)H + (CH_3)_2\overset{\oplus}{N}H_2\overset{\ominus}{I} + I_2 .$$

The product could be distilled (b.p. 67.7°C) and its structure proved. It disproportionates on storage [145,146]. Phosphoromonofluoridous acid and its deuteriated derivatives have been obtained by treating phosphorus trichloride with aqueous hydrofluoric acid [147]. It is easily converted into stable salts. Its methyl ester has been prepared by the reaction [146]

$$F_2P(O)H + F_2POCH_3 \rightarrow PF_3 + CH_3OP(O)FH .$$

2. Phosphonous Acids and their Derivatives

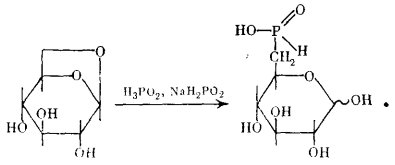
(*a*) Phosphonous acids

Phosphonous acids have been little studied as a class of compounds, but are of chemical interest and show promise for practical application. Alkylphosphonous acids are best obtained by the radical phosphinylidenation of alkenes [148-151]:

$$RCH{=}CH_2 + NaH_2PO_3 \xrightarrow[H^\oplus]{RO\cdot} RCH_2{-}CH_2{-}P(O)H(OH)$$

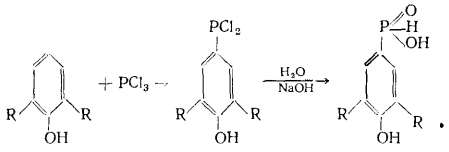
The method has been extended to several polymeric phosphonous acids [152] and also to functionally substituted

systems [153,154]. The phosphinylidenation of hetero-unsaturated compounds—Schiff bases [155,156], hydrazones [157], oximes [158], etc.—has been studied. Certain anhydroaldopyranoses (e.g. levoglucosan) on reaction with hypophosphorous acid give 6-deoxy-6-glycophosphonous acids [153]:



The process probably involves formation and rearrangement of the hypophosphite, like the reaction of polyallyl alcohol with hypophophorous acid [159].

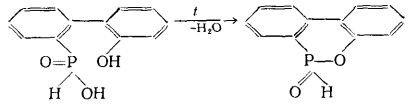
Alkyl- and aryl-phosphonous acids are often obtained by hydrolysis of their acid chlorides and other derivatives [6]. When especially pure products are required, hydrolysis must be replaced by treatment with t-butyl alcohol [160]. Acid dichlorides may yield fairly unusual acids: an example is the reaction [161]



Individual phosphonous acids are formed by the oxidation or the disproportionation of oxides of primary phosphines [162].

(*b*) Phosphonous monoesters

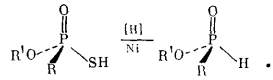
Acid phosphonites have been obtained by esterifying phosphonous acids with alcohols [28] and polyols [150,163,164]. In the latter case primary hydroxy-groups are phosphinylated preferentially. Esterification of phosphonous acids by phenols has not been reported. This reaction may well be possible under certain conditions, in view of the transformation [165-167]



For preparative purposes it is often more convenient to phosphinylate by transesterification. This process has been widely used with diols [168-170], tri- and tetra-ols, [83] carbohydrates [171], and cellulose [95].

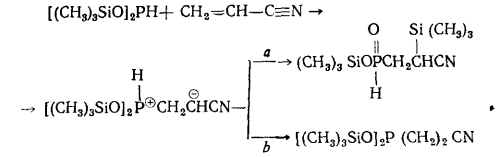
Another route starts from three-coordinated phosphorus derivatives, most frequently acid dichlorides, whose alcoholysis in the presence of amines has become widely used [172-174]. Sometimes it is convenient to treat dichlorophosphines with an equimolecular quantity of the alcohol (phenol) and t-butyl alcohol [175,176]. Acid phosphonites are formed also by the alcoholysis of phosphonous anhydrides [54,55], and the hydrolysis and acidolysis of neutral phosphonites [1] and phosphonoamidites [123,171].

In contrast to most classes of phosphinylidene compounds, acid phosphonites are often obtained from phosphorus(V) derivatives, for which purpose degradative reactions—hydrolysis of phosphonimidates [60], photochemical alcoholysis of phospholen oxides [177,178]—can be used. A very original method is the reduction of acid phosphonothioates with hydrogen over Raney nickel. This reaction can be used for the stereoselective formation of optically active compounds [179]:



Deselenation of phosphonoselenoates occurs similarly [180,181]. Optically active phosphonites can be obtained by stereospecific inclusion on cyclodextrans [182].

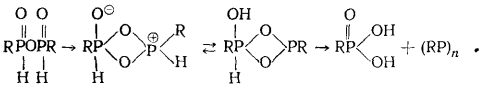
It has been proposed to obtain silicon [105,106,183], germanium [105], and antimony [184] analogues of acid phosphonites from the phosphonous acids and the corresponding heteroorganic halides. More complicated compounds of this type with additional functional groups are formed from disilyl hypophosphites and carbonyl compounds [185,186] or acrylonitrile [187]. The latter reaction apparently begins with formation of an adduct, which can then be transferred in two ways—(*a*) and (*b*):



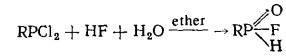
At low temperatures the rates of reactions (*a*) and (*b*) are comparable; at high temperatures $k_a > k_b$.

(*c*) Monoamides and monohalides of phosphonous acids

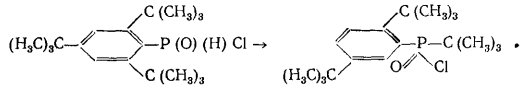
These compounds have been very little studied. The monoamides can be obtained by partial hydrolysis [171] or by acidolysis [131] of the full amides. The latter reaction is usually complicated by anhydridisation [131]; the resulting anhydride is unstable and disproportionates:



Phosphonous monofluorides have recently been obtained by a very simple process [188]:

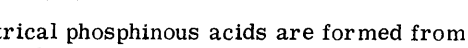


These compounds distil without decomposition. The corresponding chlorides are formed by acidolysis of alkyldichlorophosphines [189,190]. They are unstable and are readily dehydrochlorinated, which again emphasises the difference between chlorides and fluorides of phosphorus. 2,4,6-Tri-t-butylphenylphosphonochloridous acid exhibits its instability by isomerising [191]:



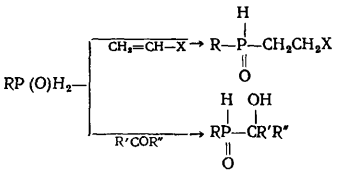
3. Phosphinous Acids

In laboratory practice it is convenient to obtain dialkyl- and diaryl-phosphinous acids from simple dialkyl phosphites and Grignard reagents [1,192,193]:



Unsymmetrical phosphinous acids are formed from acid phosphonites by an analogous scheme. A stereochemically directed preparation could be achieved by using optically active phosphonites [194].

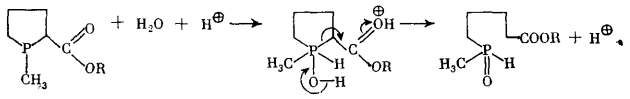
Buckler and Epstein [162] made a series of syntheses from oxides of primary phosphines together with alkenes, which might be functionally substituted, and also carbonyl compounds:



X=CN, C(O)NH$_2$.

The latter reaction has recently been extended to the preparation of phosphinous acids of the phosphan series [195].

Much research has been devoted to obtaining phosphinous acids from compounds already containing the essential molecular skeleton. Thus dimethylphosphinothious acid is hydrolysed by alkali to dimethylphosphinous acid [196]. This hydrolysis is unusual: the phosphinothioyl group in sulphides of tertiary phosphines is not converted into phosphinyl under similar conditions [196]. Thorough studies have been made of the hydrolysis of acid chlorides [60,161,197-199], anhydrides [200], esters [197,201], and amides [197] and of the thermolysis of t-butyl phosphinites [202]. The oxidation of secondary phosphines has been investigated in detail [203,204]. We can include here the acid hydrolysis of a cyclic phosphine [205]:



Other studies have been made on the preparation of phosphinous acids from phosphorus(V) derivatives. Reduction of phosphinous esters with lithium tetrahydroaluminate [194] and the desulphurisation (deselenisation) of phosphinothious (phosphinoselenous) acids with Raney nickel have been suggested; Michalski has obtained optically active products by using optically active acids [206]. Reducing processes applied to oxides of tertiary phosphines may be accompanied by rupture of a phosphorus–carbon bond [207]. α-Substituted phosphine oxides are degraded especially readily [60,208]. It is interesting that the phosphorus atom retains its configuration during their decomposition [208].

Unsymmetrical phosphinous acids have quite recently been used for fine structural investigation. Thus phenyl-s-butylphosphinous acid, which contains chiral carbon and phosphorus atoms, has been studied by n.m.r., which detected the presence of two pairs of diastereomers [209].

4. Hypophosphorous Esters and Oxides of Primary Phosphines (Phosphinyl Compounds)

Alkalyl hypophosphites were first obtained by Kabachnik et al. [210] by treating hypophosphorous acid with diazoalkanes:

$$H_2P(O)OH + RCHN_2 \rightarrow H_2P(O)OCH_2R.$$

These compounds have been obtained also by the action of hypophosphorous acids on orthocarbonyl compounds [211,212], neutral phosphites [213], and alcohols [214-216]. This last reaction was extended to diols [214,217] and hydroxylated polymers [101,218]. It has been shown recently that acid hypophosphites can be obtained by hydrolysis of the neutral compounds [219]. Hypophosphites, especially simple members of this group, are extremely labile and change when kept for a short time [210,213,219], but they can be stabilised by alcohols [214,219].

Monosilyl hypophosphites have been obtained by alcoholysis of the disilyl compounds and by silylation of ammonium hypophosphite with trialkylchlorosilanes [108]. Oxides of secondary phosphines can be obtained by oxidising primary phosphines with hydrogen peroxide, and also by the action of phosphine itself on carbonyl compounds [162]:

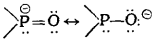
$$PH_3 + RCOR' \rightarrow [RR'C(OH)PH_2] \rightarrow RR'CHP(O)H_2.$$

III. CHEMICAL REACTIONS

The phosphinylidene group provides a clear example of a functional group having a high and diverse reactivity. These compounds have therefore become key reagents in organophosphorus synthesis and important subjects for research on theoretical aspects of reactivity. Yet the character and the scale of development of the chemistry of phosphinylidene compounds have created the problem of a rational classification of their reactions, which are numerous and of diverse kinds. Evidently this could be most usefully based on the electronic factors determining the primary reaction step. We can then distinguish the processes indicated below.

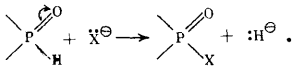
1. Acid–base equilibria and salt formation. Here we include dyadic protropy.

2. Electrophilic reactions involving an ambident anion

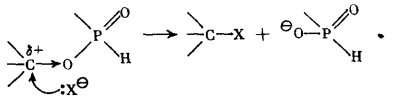


or the tautomeric form $>\ddot{P}-OH$.

3. Nucleophilic reactions occurring at the phosphorus atom bearing a partial positive charge:



Dialkyl phosphites and similar ester systems possess another centre, more open to attack by an anion:



4. Radical reactions resulting from homolysis of a phosphorus–hydrogen bond.

5. Phosphinylation, consisting in the introduction of a phosphinylidene group into the molecule of a nucleophilic compound and accompanied by loss of an anionoid group from the phosphorus. Incorporation of an amphoteric reagent at the X–P bond may be a particular case of such phosphinylation.

Unfortunately, it is not yet possible to use this scheme as a basis for the systematic arrangement of published information, since the mechanisms of many reactions have been little investigated or are altogether obscure. Furthermore, there is a large group of transformations whose initial stages are evidently related but whose subsequent stages are so different that they ultimately yield products of diverse chemical nature. Such conditions obviously justify use of a system based primarily on the mechanisms of the reactions undergone by phosphinylidene

compounds but also allowing for the structure of the reaction products and other chemical circumstances. A convenient form of such an approach will be to divide the reactions into the five groups below.

1. Acid–base interactions, including tautomerism, salt formation, and complex formation.
2. Replacement of the hydrogen atom in the phosphinylidene group by a hydrocarbon radical or group.
3. Reactions not involving the phosphinylidene functional group.
4. Reactions accompanied by a decrease in the coordination number of the phosphorus atom.
5. Other reactions of phosphinylidene compounds.

This scheme does not include many widely used reactions, consisting in the replacement of groups attached to the phosphinylidene group, e.g. alcoholysis of esters, thioesters, and amides and the action of Grignard reagents on dialkyl phosphites. We have already discussed such processes in Section II, as methods for passing from one phosphinylidene compound to another.

1. Acid–Base Interactions, Salt Formation and Complex Formation

(*a*) Phosphinylidene compounds as acids and bases

Little experimental research has been done on the acidity of phosphinylidene compounds. Grayson[192] used potentiometric titration to study several arylphosphinous acids, under conditions that were not comparable for different specimens. Hammond[220] assessed the acidity of diethyl phosphite in water from results on isotope exchange‡. Moedritzer[221] showed by n.m.r. that the acidities of dibutyl phosphite and ethanol in diglyme were closely similar. These studies made in the early 1960s did not attract attention because of the disconnected and fragmentary character of the results. Systematic investigation was probably hindered by experimental difficulties and the low acidity of the compounds.

Kabachnik et al.[222] have just made a fundamental study of the acidity of dialkyl phosphites, alkyl phosphonites, and phosphinous acids by the use of transmetallation in dimethyl sulphoxide. The dissociation constants of these derivatives increase significantly in the above sequence. This work[222] is distinguished by rigorous assessment of the experimental characteristics of the proposed method and discussion of possible errors. Another recent paper[223] has described the use of potentiometric titration with sodium propoxide in propanol to study the acidity of alkylene phosphites, and has reached conclusions on the abnormally high acidity and other unexpected chemical features. Unfortunately, the account of the actual experiment is so condensed that assessment is extremely difficult. The acidity of dimethyl phosphite in its phosphorus(III) form appears unexpectedly low[225].

An unusual approach to estimating the acidity of phosphinylidene compounds is to determine J_{P-H} in the n.m.r. spectra, which depend on the *s* character of the phosphorus orbital involved in bond formation[226–228]. The acidity of dialkyl phosphites is apparent also in their interaction with trialkyl phosphites, which has been determined thermographically[229].

‡Kinetic study of deuterium exchange has been used to compare the acidities of individual types of phosphinylidene compounds[194,198,224].

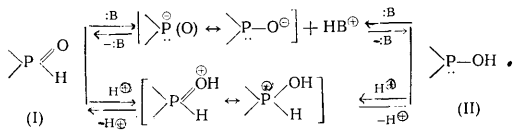
Little investigation has been made of the basicity of phosphinylidene compounds. Fluorosulphuric acid protonates dialkyl phosphites at the phosphinyl oxygen atom[230]; the process is monitored by n.m.r. Phosphinous acids are protonated considerably more readily; thus the first member of the series forms a hydrochloride stable at 50°C.[199]

Many phosphinylidene compounds form complexes with α-hydroxy-nitriles and other acidic alcohols, as is evident from the existence of azeotropes[231], and also with phenols and other compounds containing a mobile hydrogen atom[228,232–234]. The stability of the phenol complexes permits assessment of the electronic effect of substituents in the test compounds. Examination of this aspect reveals features of the various classes of phosphinylidene compounds[234]. The method enables the influence of stereochemical factors to be ascertained. Thus in six-membered cyclic phosphites the stability of complexes is determined by the orientation of the phosphoryl group. Certain judgments on the acid–base properties of dialkyl phosphites and several other phosphinylidene compounds can be based on study of the isotope effect in chemical shifts in n.m.r. spectra[40,235,236].

In connection with acid–base properties we must consider the association of phosphinylidene compounds, which depends significantly on their structure and sometimes also their stereochemistry. Dialkyl phosphites hardly associate at all[232,234]. Alkylene phosphites, in contrast, often form dimeric complexes[67,234,237,238]. It is interesting that six-membered cyclic phosphites with an equatorial phosphoryl group give more stable association complexes than do geometric isomers with an axial phosphoryl group[234]. Phosphorothiolites associate considerably more strongly than do phosphites[125].

(*b*) Tautomerism of phosphinylidene compounds

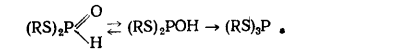
The dyadic prototropy of these derivatives, whose study constitutes one of the classic problems of organophosphorus chemistry, has been discussed in detail in several reviews and monographs[239,240]. It is catalysed by acids and bases:



(I) (II)

Dialkyl phosphites have been the most thoroughly investigated. At equilibrium they exist almost exclusively in form (I): kinetic data on deuterium exchange indicate that the concentration of form (II) reaches ~10^{-4}%. Phosphinylidene compounds containing substituents more electronegative than alkoxyl should contain more appreciable concentrations of form (II), which probably already applies to alkylene phosphites. The infrared spectrum of 1,2-dimethylethylene phosphite contains a band due to an acidic hydroxyl[72]. Potentiometric titration indicates that the series of five- and six-membered alkylene phosphites are real prototropic systems[233]. However, the preliminary character of the above studies must be borne in mind.

Cyclic ethylene phosphorothiolite has a considerable content of form (II).[128] Dialkyl phosphorodithiolites probably contain such a large quantity of form (II) that they summetrise spontaneously into phosphorotrithiolites[24,26,125]:



Bisthiocarbamoylphosphorodithiolites[241] and also phosphorodichloridous acid[24] undergo similar conversion. Phosphorodifluoridous acid is fairly stable[146]. This situation is consistent with the principles of prototropy: the aggregate electronic effect of fluorine on the polarity of the phosphorus–hydrogen bond is smaller than that of chlorine; hence the chloridous acid will have a greater content of form (II), which will undergo disproportionation.

The highest content (almost 100%) of form (II) has been found in bistrifluoromethylphosphinous acid[200]. Because of the stability of the phosphorus–carbon bond disproportionation does not take place here. Unfortunately, synthetic investigations on fluorinated phosphinous acids are very few. Penta- and tetra-fluorinated dimethylphosphinous acids, which might be supposed to contain comparable contents of forms (I) and (II), have not yet been prepared.

(*c*) Salt formation and complex formation

The tradition has become established in monographs and reviews on organophosphorus chemistry of not dealing separately with the preparation and properties of metal derivatives of phosphinylidene compounds, which are usually considered only as intermediate species in certain standard reactions. Interest in such derivatives, especially complexes of transition metals, has now increased sharply. Specific structural factors have been elucidated, and a catalytic effect has been detected[242–244].

The metal derivatives can be divided into salts and complexes, though the boundary is not always sharp. An alternative classification is based on the site—oxygen or phosphorus—at which the metal atoms are mainly localised. The latter scheme is adopted in the present Review.

Oxygen–metal derivatives. Alkali metals and their hydrides and alkoxides form with phosphinylidene compounds salts in which the phosphorus atom is usually three-coordinated[245]§. Salt formation is not accompanied by change in the configuration of the molecule[206,246,247]. Different phosphinylidene compounds react with metals at different rates: among the most reactive are dialkyl phosphites[206], while tetra-alkyldiamides of phosphorous acid are unreactive[248]. On treatment with Grignard reagents, however, the latter are smoothly converted into magnesium salts[193,248] having a phosphite type of structure.

Walther has prepared thallium(I) and thallium(III) derivatives of phosphinous acids[197,249,250]:

$$R_2P(O)H \begin{cases} \xrightarrow{C_2H_5OTl} R_2POTl \\ \xrightarrow{(CH_3)_2TlN(CH_3)_2} R_2POTl(CH_3)_2 \end{cases}.$$

Titanium(IV) derivatives of these acids have been investigated¶. They were prepared not from the phosphinylidene compounds but from their ester[251] or anhydride[252] derivatives:

$$R_2POR' + TiCl_4 \rightarrow R_2P{-}OTiCl_3 .$$

Various complexes are formed by means of the phosphoryl oxygen. Thus dialkyl phosphites give interesting adducts with boron trifluoride[253].

Various physical methods have been used in a systematic investigation[254–257] of complexes with tin halides. The tendency to complex formation is determined by the structure of the ligands:

$$(RO)_2P(O)H < (RO)(R_2N)P(O)H < (R_2N)_2P(O)H \equiv R_2P(O)H .$$

Complexes of dialkyl phosphites with uranium have also been described[258]. Their structure, like that of many others, has been proved by comparing the infrared and n.m.r. spectra of the products with the corresponding spectra of the initial compounds.

Phosphorus–metal derivatives. The *P*-mercuration of phosphinylidene compounds has been studied in detail. Biphosphinyl systems are formed by the action of mercury(II) oxide on dialkyl phosphites; if mercury halides are added to the reaction mixture, halogenomercuric derivatives separate[259,260]:

$$2(RO)_2P(O)H + HgO \rightarrow [(RO)_2P(O)]_2Hg \xrightarrow{HgX_2} 2(RO)_2P(O)HgX .$$

The structure of the products has been proved by n.m.r. and by X-ray diffraction[260,261]. Arsenation of phosphinous acids has been accomplished[249]:

$$R_2P(O)H + R'_2AsN(C_2H_5)_2 \rightarrow R_2P(O)AsR'_2 .$$

Molybdenum complexes have been obtained from the hexacarbonyl and phosphonous acids, as well as by the alkaline hydrolysis of chlorophosphine complexes of molybdenum pentacarbonyl; in these products phosphorus is attached to an acidic hydroxyl, which can be methylated with diazomethane or form salts with tertiary amines[262]:

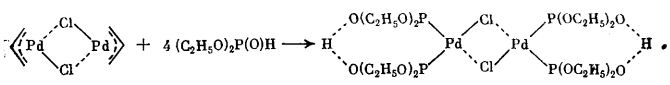
$$\left.\begin{matrix} R_2P(O)H + Mo(CO)_6 \\ R_2PCl \cdot Mo(CO)_5 \end{matrix}\right\} \rightarrow \underset{|}{\overset{OH}{R_2P}} \cdot Mo(CO)_5 \begin{cases} \rightarrow R_2P(OCH_3) \cdot Mo(CO)_5 \\ \rightarrow [R_2\overset{\oplus}{P}Mo(CO)_5]\overset{\ominus}{O}\overset{|}{N}HR'_2 \end{cases}.$$

More complicated complexes of molybdenum with residues of dialkyl phosphites have been obtained from neutral phosphites that have undergone an Arbuzov type of rearrangement:

$$[(\pi\text{-}C_5H_5)Mo(CO)_3]_2 + P(OR)_3 \rightarrow (\pi\text{-}C_5H_5)Mo(CO)_2P(OR)_3P(O)(OR)_2 .$$

Neutral phosphonites are transformed similarly[263].

In the investigation of metal derivatives there has been a tendency during recent years to pay greater attention to elements of Group VIII. Strict structural data were first obtained by workers show showed[264] that dialkyl phosphites form complexes with simple palladium salts in which a new bond has been formed between the metal and a phosphorus atom bearing a free hydroxyl. New possibilities have since been demonstrated[243,265] for this process. Thus bis-π-allylpalladium dichloride forms a complex with diethyl phosphite in which the chloride bridges have been left undisturbed†:



The product is reduced by sodium tetrahydroborate to a mononuclear complex, which catalyses the hydrogenation of acetylenes, dienes, and aromatic nitro-compounds[243].

§A recent paper suggests that the bonding of sodium may be determined by the nature of the solvent. In alcohol sodium is attached to phosphorus[209].

¶Attempts to obtain complexes from dialkyl phosphites and titanium tetrachloride led to degradative reactions[254].

†The n.m.r. spectra of this and similar compounds have been studied[266].

Analogous complexes have recently been prepared from the geometric isomers of 1-methyltrimethylene phosphite. Complex formation does not affect the configuration of the phosphorus atom. The stereoisomeric complexes differ in several properties. Reduction of the primary complexes may yield new, hydride complexes, whose catalytic activity is appreciably determined by their geometry[244]. Platinum complexes are obtained similarly to those of palladium. It has been proposed to prepare them from dialkyl or diaryl phosphites, phosphinous acids[265,267,268], or phosphonites[269].

The structure of complexes obtained from cobaltocene and dialkyl phosphites has been determined by X-ray examination[270]. On treatment with an acid a complex loses one cobalt atom, which can subsequently be replaced by another metal to give a polymetallic system[270,271]. Complexes of a different type have been prepared by reaction between dimethylglyoxime derivatives of cobalt and trimethyl phosphite; the process is accompanied by demethylation of the ester and complex formation between cobalt and phosphorus[272].

It has been proposed to apply an Arbuzov type of reaction to obtain dialkyl-phosphite[273] and phosphinous[197] complexes of dicarbonylcyclopentadienyliron from the corresponding neutral esters: for example

$$(\pi\text{-}C_5H_5)\,Fe\,(CO)_2Cl + P\,(OR)_3 \rightarrow (\pi\text{-}C_5H_5)\,Fe\,(CO)_2\,[P\,(O)\,(OR)_2] + RCl\ .$$

The ruthenium complexes have the most complicated structure, and are often formed in unusual ways. Thus reaction between dodecacarbonyltriruthenium and triaryl phosphites leads initially to partial displacement of carbon monoxide; further heating of the reaction mixture is accompanied by *o*-metallation and degradation of the phosphite ligand[274,275].

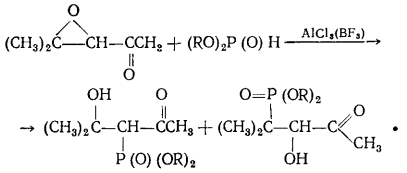
We finally note that complexes of phosphinylidene compounds are formed also by the action of diethyl phosphite on the Dewar form of tetrakistrifluoromethylthiophen, complex formation being due to isomerisation of thiophen into the usual form[276]. Complexes of dialkyl phosphites with hydrogen peroxide are also worthy of attention[277].

2. Substitution of Hydrogen Atom in Phosphinylidene Functional Group

(*a*) Electrophilic reactions

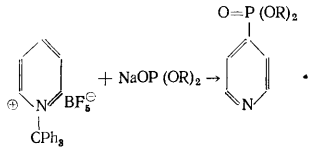
Alkylation and related processes. An important method for alkylating phosphinylidene anions is the Michaelis–Becker reaction[3]. Detailed investigation of its stereochemistry has shown that alkylation of salts of acid phosphonites[246,247] and of phosphinous acids[206] leaves the configuration at the phosphorus atom unchanged. Another group of studies of the dual reactivity of the anions has established that the direction of alkylation (at phosphorus or oxygen) may be determined by the chemical nature of the reagents[259,278] and by the solvation of the anion[279]. The influence of functional groups in the molecules on the ease of alkylation of the anions has been investigated, and in particular diaryl phosphites are found to act on α-chloro-isocyanates with remarkable ease: the reaction takes place without preliminary salt formation[280]. This has been established also for several hydroxy- and amino-benzyl systems[281–283]. Unusual conditions of alkylation apply to the use of sodium chloroacetate[284].

Special attention is merited by reactions of the Michaelis–Becker type in the presence of acid catalysts, which probably ensure regeneration of the tautomeric form of the phosphinylidene compound in which the phosphorus atom is tervalent. Moreover, these catalysts may activate also the alkylating reagents. An example is the action of dialkyl phosphites on epoxy-ketones[285]:



Study of the Michaelis–Becker reaction was initially directed mainly at the alkylating agents. In recent years investigation of the phosphorus component has developed. Thus the reaction has been extended to salts of amidic esters[286] and diamides[136,224] of phosphorous acid. Readily available magnesium salts can be used for alkylation of the latter[193], although exceptions are found[284].

The reaction has been extended to aromatic systems. In liquid ammonia, aryl iodides react with salts of dialkyl phosphites when exposed to light of wavelength 350 nm.[287] Salts of *N*-oxides of pyridine and quinoline, as well as pyridinium salts, heteroarylate anions of dialkyl phosphites[288–290], with γ-regioselectivity observed for sterically hindered systems[290]:

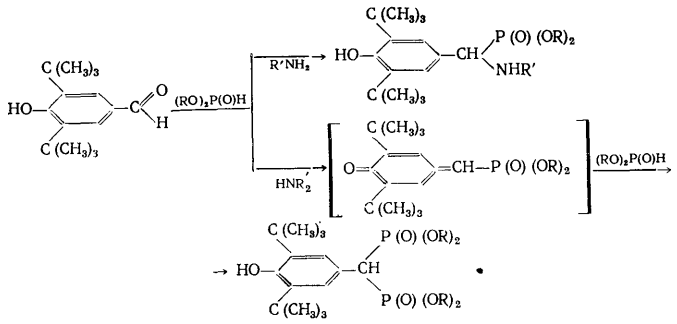


The reaction between dialkyl phosphites and diazoacetic esters in the presence of copper sulphate is chemically cognate with the Michaelis–Becker reaction[34,35]. The first stage probably involves formation of a carbene, which deprotonates the phosphite, after which the classic scheme is followed.

A large number of papers have been published on α-aminoalkylation, based on a reaction discovered in the early 1950s by Kabachnik et al.[291] and described somewhat later by Fields[292]. It consists in the simultaneous or successive action of ammonia (or a primary or secondary amine) on an oxo-compound and a phosphinylidene derivative. This synthetic method, which has come to be called the Kabachnik–Fields reaction, has found widespread and diverse use. Two trends characterise its development during recent years.

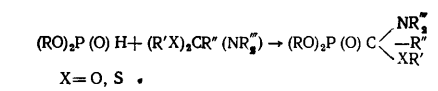
The first consists in the application of many types of phosphinylidene compounds and aminoalkylating agents. Good results are obtained by working not only with dialkyl phosphites and the other usual phosphinylidene compounds but also with dialkyl phosphites containing functional groups[19,25], with polyphosphites[97], monoalkyl phosphites[31], phosphonous acids[155], phosphinous acids[293–295], phosphorous acid[296–299], hypophosphorous acid[155,300] and its esters[216], and phosphorous amides[301]. Among aminoalkylating agents that have been used are hexamethylenetetramine[302] and other cyclic amines[303], oxazolidines[304], α-amino-peroxides[305], combinations of formaldehyde with sulphonamides[306] and of indol-3-ylacetaldehyde with amines[307], etc. The reaction has been extended to hydrazinoalkylation[157]. This method has its peculiarities: thus dialkyl phosphites react with 3,5-di-t-butyl-4-hydroxybenzaldehyde and primary amines according to

the general scheme, but differently with morpholine and piperidine. It is assumed that in this case a quinoid intermediate is formed, which adds a second phosphite molecule[281]:



The second trend is to use the Kabachnik–Fields reaction to solve practical problems. It has now been employed for the production of important complexones[9,10,296,297,308], pesticides[309,310], flameproofing agents[306], intermediates in the synthesis of heterocycles[391], etc. Furthermore, complicated lactam antibiotics have been synthesised from α-amino-phosphonates[303].

Definite interest attaches to the α-alkoxy- and α-alkylthio-aminoalkylation of phosphinylidene compounds[311,312]:



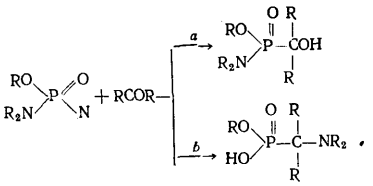
X = O, S .

The products react with dialkyl phosphites to give aminodiphosphonates. Phosphinous acids are immediately converted by bisdialkylaminoalkenes into aminodiphosphine oxides[311]. Acid phosphites and phosphonites react with orthoesters to form αα-dialkoxy-phosphonates and -phosphinates[313,314].

Addition to unsaturated polar compounds. The alkylation of phosphinylidene compounds by unsaturated polar compounds has proved synthetically very fruitful[2]. Conversions of this type are closely similar to the above and develop also by a carbonium mechanism.

Addition at the C=O bond. Phosphinylidene compounds undergo α-hydroxyalkylation on treatment with aldehydes and ketones. As a consequence of the work of Abramov (after whom the reaction is named) the method has been widely used. The main features‡ and the limits of applicability have now been determined, and the stereochemical direction of the reaction has been demonstrated[315]. The process usually occurs in the presence of bases, which convert the phosphinylidene compounds into the corresponding, highly nucleophilic anions. Kinetic study has shown a third-order reaction[316]. Recent results indicate[225] that addition of dimethyl phosphite at a carbonyl group in the presence of triethylamine occurs in the form $(CH_3O)_2.POH$, not as the anion $(CH_3O)_2PO^-$. Neutral phosphites as well as the usual bases can serve as catalysts[317]. Autocatalysis has been noted[201] in the addition of strongly basic phosphinylidene compounds, e.g. oxides of secondary phosphines. Bases are not employed with phosphonous acids[319]; acid catalysis probably occurs here, its role being to maintain the necessary concentration of the form of the phosphinylidene compound in which the phosphorus atom is tervalent. Acid catalysis operates also when neutral phosphinylidene compounds are used[320,321].

The Abramov reaction has been studied in greatest detail on dialkyl phosphites, partial phosphonites, and phosphinous acids[2]. Other classes of phosphinylidene compounds—diphosphites[84] and polyphosphites[88,97,322], phosphonous acids[189,300,319] and chlorides[189,323], phosphorous[324] and hypophosphorous[300] acids, alkyl dihydrogen phosphites[31,325], monoalkylphosphine oxides[162], monoalkyl hypophosphites[211,326,327], disilyl phosphites[328], phosphorodithiolites[125,128], and also diamides[241] and amidic esters[329,330] of phosphorous acid—have come to be used in recent years. With amides not only the classic reaction (*a*) but also the anomalous reaction (*b*) may occur[241,330]:



Route (*a*) is favoured by basic catalysts; reaction (*b*) occurs in their absence (further discussion of these reactions will be found below).

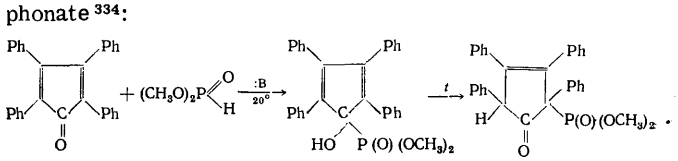
Several quantitative rules have been established for the reaction velocity: e.g. reactivity increases in the sequence

$$(RO)_2P(O)H < (RO)(R_2N)P(O)H < R_2P(O)H\ ^{331}.$$

Rates of conversion of dialkyl phosphites are hundredfold those for phosphorous acid[324].

Addition of phosphinylidene compounds to carbonyl compounds is reversible. It is often accompanied by secondary processes. α-Halogeno-carbonyl compounds with dialkyl phosphites are converted via a stage of halogenated α-hydroxy-phosphonates into enol phosphates; this reaction has been widely investigated and begun to be employed in industry[2,8§]. Rearrangement of non-halogenated hydroxy-phosphonates into phosphate systems began to be studied considerably later[2]. It is interesting that, depending on the quantity of basic catalyst present, the reaction of phosphinylidene with carbonyl compounds may or may not be accompanied by phosphonate–phosphate rearrangement[333].

Another type of rearrangement associated with the Abramov reaction is observed in the study of cyclic ketones. Thus tetraphenylcyclopentadienone and dimethyl phosphite in the presence of a tertiary amine or an alkoxide at 20°C give the hydroxycyclopentadienylphosphonate, which on further heating isomerises into a keto-phosphonate[334]:



Under these conditions diphenylphosphinous acid is converted directly into a keto-derivative[335]. Other features

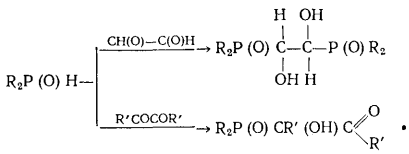
‡It must be remembered that the Abramov reaction may be accompanied by several side-processes, e.g.[318]

$$(C_6H_5)_2POLi + CH_3COCH_3 \rightarrow (C_6H_5)_2P(O)C(CH_3)_2CH_2COCH_3.$$

§Another type of reaction between dialkyl phosphites and α-halogenated carbonyl compounds is used in the preparation of αβ-epoxy-phosphonates[332].

of the reaction have been reported[336-339]. Additional complications may arise with high-temperature reactions (at 160–180°C). Thus the action of the anion of diphenylphosphinous acid on benzaldehyde and benzoylferrocene yields alkenes and their oxides[207]. Methylindanedione with dimethyl phosphite gives complicated di-indane systems[340].

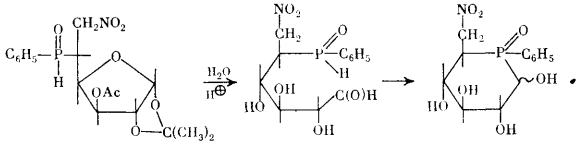
The above facts do not diminish the merits of the Abramov reaction, but merely indicate how thoroughly it has been studied. During the past decade the reaction has found widespread use in the laboratory. Thus it has been applied to diverse carbonyl compounds, which has permitted development of a broad field in the chemistry of polyfunctional organophosphorus systems. Considering first the addition of phosphinylidene to dicarbonyl compounds, we note that glyoxal readily forms 1,2-diphosphinylethylene glycols with phosphinous acids, but α-diketones react differently[199]:



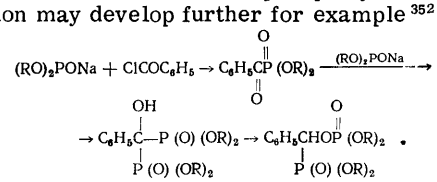
2-Methyl- and 2,2-dimethyl-indane-1,3-diones react similarly to α-diketones with dialkyl phosphites[340,341]. Several of the indane hydroxy-phosphonates obtained possess an anticonvulsant effect[341]. Pentane-2,4-dione yields 1 : 1 and 1 : 2 adducts depending on the proportions of the reactants; the latter adduct readily cyclises[342]. γ-Keto-aldehydes and γ-diketones on reaction with dialkyl phosphites and phosphinous acids give only 1,4-dihydroxytetramethylenediphosphonates (phosnin oxides).[343,344]

Reaction between dialkyl phosphites and epoxy-ketones leads to other complicated hydroxy-phosphonates[285]. Dihydroxy-phosphonates can be prepared from hydroxyketones[345]. Keto-acids and their esters have also been examined on treatment with various phosphinylidene compounds. The usual adducts are formed with temperature control[320,321], but phostones on heating[320,346]. The latter are obtained also by the action of phosphonous acids on $\alpha\beta$-unsaturated ketones[319].

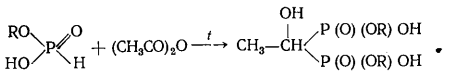
During recent years the Abramov synthesis has been used in the study of carbohydrates. The reaction is applied either to the aldo-form of a monose[347-349] or to a cyclic keto-sugar[350,351]. An interesting case is the transcyclisation of an aldo-phosphonous acid[204]:



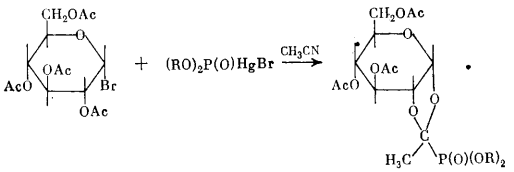
Among other types of carbonyl compounds detailed studies have been made on chlorides and anhydrides of carboxylic acids. With equimolecular proportions of the reactants and temperature control acid chlorides give α-oxo-phosphinyl derivatives on reaction with acid phosphites, phosphonites, and phosphinous acids[331,352,353]. In the presence of an excess of the phosphinylidene compound the reaction may develop further for example[352]:



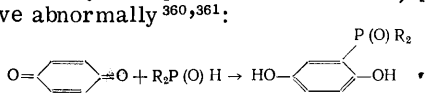
If excess of the acid chloride is used, it may acylate the initially formed oxo-phosphonate to a vinyl phosphonate[354]. Anhydrides of carboxylic acids react with oxides of secondary phosphines similarly to acid chlorides[355]. When anhydrides add to monoalkyl phosphites, the process develops differently, and the phosphonate–phosphate rearrangement does not occur[356¶]:



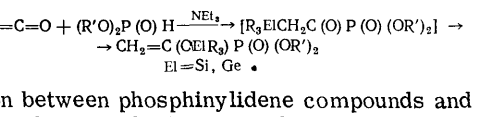
Carboxylic esters do not usually add phosphinylidene compounds and their salts. However, Paulsen has shown[259] that tetra-*O*-acetyl-α-*D*-glucopyranosyl bromide is able to react with mercurated dialkyl phosphites:



The addition of phosphinylidene compounds to quinones has been subjected to detailed discussion. When dialkyl phosphites are used, monophosphinylated quinols are formed[358,359]. The reaction may be supposed to develop according to the classic scheme and to conclude in phosphonate–phosphate rearrangement. Hypophosphorous acid adds similarly to a quinone[115]. However, phosphinous acids behave abnormally[360,361]:



Among compounds in which the carbonyl group forms part of a cumulated system keten readily reacts with dialkyl phosphites to form α-oxo-phosphonates and their enol acetates[2]. Silylated and germylated ketens react somewhat differently with dialkyl phosphites and phosphinous acids[362]:



Reaction between phosphinylidene compounds and isocyanates has been studied more widely. In the presence of basic catalysts and tin derivatives dialkyl phosphites form carbamoylphosphonates[2,90,363,364]. Monoalkyl phosphites[325], acid phosphonites[365], oxides of primary phosphines[162], and magnesium[248] and silicon[366] derivatives of phosphorodiamidous acids react similarly. In the absence of bases dialkyl phosphites[367], phosphorothiolites[128], and diamides of phosphorous acid[241,248,368] may react differently, with preservation of the tervalent phosphorus atom. Under other conditions dialkyl phosphites and isocyanates give phosphoramidines[369].

Addition at the C=N bond. Phosphinylidene compounds undergo α-aminoalkylation by the action of azomethines and similar compounds. The reaction has been introduced into synthetic practice mainly by Pudovik, author of a series of experimental papers and a comprehensive

¶The action of monoalkyl phosphites on carboxylic acid anhydrides does not always produce systems in which phosphorus–carbon bonds are preserved, as is indicated by the reaction of nucleoside phosphites[357]:

general account[2]. Investigations on the catalysis (basic and acidic) and the kinetics of the reaction have established the influence of traces of moisture on its rate and other aspects[370-372].

The addition of phosphinylidene compounds at the C=N bond has broad synthetic value. Good results are obtained not only with dialkyl phosphites, acid phosphonites, and phosphinous acid[2] but also with phosphonous acids[10], hypophosphorous acid[373], monoalkyl phosphites[325], and diamides of phosphorous acid[248,301]. Various Schiff bases have been used, including those containing functional groups[374,375], derivatives of ferrocene[376] and carbohydrates[349,377], imino-chlorides[378], acylimines[379], alkoxyimines[380], chloroacylimines[280], etc. Usually systems with additional functional groups hardly differ from simple azomethines, but in some cases complications arise. Thus salicylideneamines often give poor results on reaction with dialkyl phosphites[381], probably owing to the electronic effects of the *ortho*-hydroxyl (cf. Ref. 281).

Addition of phosphinylidene compounds to azomethines accompanied by accumulation of more than one electron-accepting group on a single carbon atom may lead to rearrangement[378,382-384]:

$$C_6H_5N{=}C\,[P(O)R_2]_2 + R_2P(O)H \rightarrow C_6H_5NHC\,[P(O)R_2]_3 \rightarrow C_6H_5N(P(O)R_2){-}CH\,[P(O)R_2]_2 .$$

A similar rearrangement takes place also with α-amino-phosphonates, if they have first been converted into sodium or potassium (but not lithium) derivatives[385].

Interesting preparations have been based on systems containing two azomethine groups—Schiff "bisbases"[156], hydrobenzamide[386], hydrazones[387], toluene-*p*-sulphonyl-hydrazones[388], and azines. In the latter case acid phosphites, phosphonites, and hypophosphites form 1:1 and 1:2 adducts[387,389,390]. Individual publications on this topic, e.g. Ref. 391, are open to objection. The observed formation of α-amino-phosphonates can be explained by the benzonitrile breakdown of hydrazones obtained in the first stage:

$$(C_2H_5O)_2P(O)CHPhNH{-}N{=}CHPh \xrightarrow{(C_2H_5O)_2PONa} \rightarrow (C_2H_5O)_2P(O)CH(NH_2)Ph + PhC{\equiv}N .$$

Addition of phosphinylidene compounds to oximes is undoubtedly of synthetic interest. There was an indication that this reaction had been accomplished, but a later paper[392] has denied such a possibility.

Among systems containing a triple bond between carbon and nitrogen atoms aryl isocyanides react with dialkyl phosphites and phosphinous acids[380]:

$$Ar\overset{\oplus}{N}{\equiv}\overset{\ominus}{C}: + >P(O)H \rightarrow >P(O)CH{=}NAr \xrightarrow{>P(O)H} [>P(O)]_2CHNHAr .$$

Nitriles add phosphonous acids in the presence of bases[393-396]: for example

$$R_2P(O)H + N{\equiv}C{-}CH_2{-}C{\equiv}N \xrightarrow{RONa} R_2P(O)\overset{NH}{\overset{\|}{C}}CH_2C{\equiv}N .$$

The second nitrile group is unaffected. Different assessments have been made of the possibility of the addition of dialkyl phosphites to nitriles, for a negative result[394] has been followed[397] by the positive result

$$R'C{\equiv}N + 2(RO)_2P(O)H \xrightarrow{HCl} R'C(NR_2)[P(O)(OR)_2]_2 .$$

An important factor influencing the course of the reaction is acid catalysis; unfortunately, acids cause several complications, which make it difficult to assess the preparative merits of the method.

Addition at the C=S bond. Addition to isothiocyanates[2,325,398] recalls the corresponding preparation with isocyanates but differs in certain respects[366]. In several cases the addition of dialkyl phosphites and phosphinous acids to isothiocyanates concludes in rearrangement[399]:

$$>P(O)H + R{-}N{=}C{=}S \rightarrow RN(H){-}C(=S){-}P< \xrightarrow[80-140^\circ]{>PONa} RN{=}CHS{-}P(=O)< .$$

Addition to carbon disulphide[400]:

$$(RO)_2P(O)H + S{=}C{=}S \xrightarrow{NaOH} (RO)_2P(O)C(S)SNa$$

has been less investigated. The resulting salts would probably be promising for the production of organo-thiophosphorus compounds, including pesticides, complexing agents, oil additives, etc.

Addition at the N=O, S=O, and N=N bonds. Compounds containing these groups have been little investigated in their reactions with phosphinylidene compounds. Trifluoronitrosomethane adds to dialkyl[401] and monoalkyl[325] phosphites. If a nitroso-compound contains an α-chlorine atom, the process is more complicated[401]:

$$R_2CN{=}O + (R'O)_2P(O)H \rightarrow \left[R_2C(OH)(Cl){-}N{-}P(O)(OR')_2\right] \rightarrow R_2C{=}N{-}O{-}P(O)(OR')_2 .$$

Addition at a S=O bond has been reported in the isolated examples of the reactions of dialkyl[402] and monoalkyl[325] phosphites with sulphur iminoxide. The action of dialkyl[403] and monoalkyl[325] phosphites on individual azo-compounds involves cleavage of the azo-bond.

In view of the tendency of modern chemical research to investigate complicated systems intermediate in nature between organic and inorganic we may suppose that comprehensive studies will be made in the near future on the addition of phosphinylidene compounds to unsaturated El=El′ bonds, e.g.

$$>Si{=}N{-}, \quad >P{=}C< .$$

Addition to the C=C bond. Addition of phosphinylidene compounds at an electrophilic C=C multiple bond is a very common synthetic process[2]. During recent years especial attention has been paid to new aspects of its use. Thus the reaction has been extended to phosphinous[199,201] and phosphonous[319] acids, four-membered cyclic partial phosphonites[404], alkyl phosphorochloridites[142] and alkylphosphonous monochlorides[190], monoalkyl phosphites[325], phosphorothiolites[26], mono- and di-amides[224,286] of phosphorous acid, alkyl hypophosphites[212], and oxides of primary phosphines[162]. Rates of reaction of individual types of phosphinylidene compounds have been compared, and aspects of catalysis considered; rules already observed for addition to other electrophilic compounds are found to apply[224,405].

The range of unsaturated compounds that add phosphinylidene compounds is extremely wide—esters of unsaturated carboxylic acids[26,319]†, unsaturated heterocycles[375], nitro-compounds[406,407], fulvenes[408], allene-phosphonates[409] and other unsaturated phosphonates[410], and also 3,5-dinitrobenzoic acid[411]. Unfortunately, nitro-aromatic compounds have been little investigated in

†The addition of dimethyl phosphite to perfluoroacrylic esters follows an unusual course[417].

this reaction, so that the wide opportunities for arylphosphonate synthesis and analysis of phosphinylidene compounds have not yet been realised.

Attention should be directed especially at unsaturated ketones and aldehydes, which, depending on the conditions and the catalysts used, can add phosphinylidene compounds not only at the ethylenic but also at the carbonyl bond [331,340,412-416]‡. It is significant that these reactions are subject to different types of control—kinetic at the carbonyl bond, but thermodynamic at the ethylenic bond[416]. The peculiarity of the addition of phosphinous acids and phosphonites having benzyl groups attached to the phosphorus atom is noteworthy [418].

Phosphinylidene compounds add to C=C–$\ddot{X}$ systems. During recent years investigations have been made on vinyl acetate [419], glycals [420], keten acetals [313], thioketen acetals and aminals [421], and amino- and alkoxy-acetylenes [422,423]. These reactions have been examined only in general outline.

Oxidation, addition of sulphur, imination, and related processes. Oxidation. Oxidation has been studied in connection with general aspects of the reactivity of phosphinylidene compounds and extension of the possibilities of organophosphorus synthesis. Many papers and patents have been published in which these compounds are intermediates in the production of acids containing quinquevalent phosphorus, including important technical products and natural compounds.

Dialkyl phosphites are oxidised to dialkyl phosphates by treatment with nitrogen dioxide [424,425]. The reaction has been extended to alkylene polyphosphites [87] and several other types of complicated derivatives. Other suggested oxidants are aqueous potassium permanganate [426] and oxygen in the presence of copper and vanadium catalysts [427]; in the latter case oxidation is complicated by dealkylation. Simple dialkyl phosphites have been oxidised with nitric oxide [428] and with 1,3-diphenyl-1,3-dithioacetone [429].

Acid phosphonites are oxidised more readily than are the corresponding phosphites, and phosphinous acids are still more easily oxidised; oxygen [201] or hydrogen peroxide [60] can be used as oxidant. It is interesting that diferrocenylphosphinous acid is comparatively inert towards oxidation [430].

A fairly detailed study has been made of the oxidation of monoalkyl phosphites. Suggested oxidants are nitrogen dioxide [31], potassium permanganate [122], and mercury(II) chloride [117]. The oxidative phosphinylation of alcohols [431] and nucleosides [117,118,432] merits especial attention. Detailed investigations have been made on the oxidation of phosphonous acids, mainly with metal salts [433,434] but also with oxides of primary phosphines [162]. The oxidation of phosphorous amides by nitrogen dioxide involves rupture of the phosphorus–nitrogen bond [368].

Besides direct oxidation, indirect methods are often used, e.g. halogenation followed by hydrolysis. Despite the advantages of oxidation, it must be emphasised that frequently the suggested methods are not general in character. It is significant also that research is actually lacking on such current trends as catalysis on complexes, photochemistry, and in particular oxidation by singlet oxygen. Thus study of the oxidation of phosphinylidene compounds retains its urgency.

‡See also the comments on quinones and cyclic ketones in the above paragraphs on the C=O system.

Addition of sulphur. Kabachnik et al. showed that dialkyl phosphites add sulphur in dioxan medium, and still more readily in the presence of tertiary amines [239]. Alkylene polythiophosphates [87] and cycloalkylene phosphorothioates have been prepared in this way [67,68]; retention of the configuration of the phosphorus atom has been established in the latter case. Dimethyl phosphite adds sulphur also on reaction with 1,3-diphenyl-1,3-dithioacetone [429]. Acid phosphonites also add sulphur in dioxan medium or in the presence of amines [172,435]. Retention of configuration by the phosphorus atom in this reaction has been demonstrated by the use of optically active phosphonites [180,436]. Phosphinous acids add sulphur with evolution of heat [201,430]. Phosphorous diamides [286] and amidic esters [437] react less vigorously with sulphur.

Phosphinylidene compounds add also selenium under conditions similar to the above [67,68].

Imination. The first results on this process were obtained by Kabachnik et al., who treated salts of dialkyl phosphites with diazomethane [239]:

$$(RO)_2PONa + CH_2N_2 \rightarrow (RO)_2\begin{matrix}ONa\\ \diagdown\\ N{-}N{=}CH_2\end{matrix} \xrightarrow{CH_3COOH} (RO)_2P(O)NH{-}N{=}CH_2 .$$

Pudovik et al. [439] have observed similar reactions between diethyl phosphite or its trialkylsilyl derivative and diazoacetic ester. The reactions of diphenyl phosphite [239] and also of trialkylsilyl derivatives of dialkyl phosphites [440] with phenyl azide can probably be included in this group. Azo-coupling occurs similarly [403,441]:

$$(RO)_2P(O)H + ArN_2^{\oplus} \rightarrow (RO)_2P(O)N{=}N{-}Ar .$$

Halogenation. Phosphorous diesters are readily converted by chlorine into phosphorochloridates. The reaction is strictly stereodirected with retention of configuration by the phosphorus atom [77,315], and has been extended to more complicated compounds, including various types of polyphosphites [85,89]. Chlorination can be effected also by sulphuryl chloride [102], chlorosuccinimide [77], and copper(II) chloride [442]. Acid phosphonites [171] and thiolic [125] and amidic [286] esters of phosphorous acid undergo similar chlorination. With monoalkyl phosphites chlorination is completed by anhydridisation; when the reaction is conducted in water, monoalkyl phosphates separate [31].

Fluorination (by means of a perchloryl fluoride) [443], bromination [33], and thiocyanation [444] of phosphinylidene compounds have been reported, but development of these processes has been slight, probably because of experimental complexity.

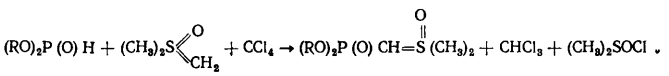
Todd–Atherton reaction. This reaction provides a very convenient and effective method for the oxidative phosphinylation of nucleophiles by the action of a phosphinylidene compound, tetrachloromethane (or similar halide), and a base [445]. The first stage can be written

$$\rangle P(O)H + CCl_4 + B \rightarrow \rangle P(O)Cl + HCCl_3 + HCl\cdot B .$$

If nothing more is added to the mixture, an acid chloride is formed [240]. This process has advantages over other methods for the preparation of phosphorus acid chlorides. If, however, a nucleophile is also added to the reaction mixture, phosphinylation takes place.

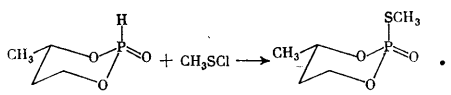
The Todd–Atherton reaction has been applied not only to simple dialkyl phosphites but also to hydroxyalkyl and other functionally substituted phosphites [19,25,45,66], diphosphites [446], polyphosphites [97,102], acid phosphonites [181,447,448], diphosphinites [170], phosphonous acids [449,450], amides of

phosphorous acid[138,139,446], monoalkyl phosphites[33], and hypophosphorous acid[450] and esters[215,217]. The popularity of the reaction is due also to the wide range of nucleophiles used—alcohols and phenols[45,451], water[450], amines, which may be functionally substituted and heterocyclic[19,138,446,452], esters of amino-acids[453], hydroxylamine[454], oximes[455], silyl vinyl ethers[456], oxiran[448], etc. An unusual and interesting process is the *C*-phosphinylation of dimethylsulphoxonium methylenylide[457]:



Zwierzak has recently begun to study the Todd–Atherton reaction in a two-phase system with quaternary ammonium salts as catalysts[458]. This variant of the reaction has great advantages for preparative purposes and shows promise for industrial application.

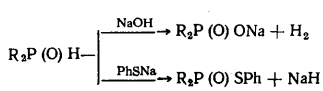
Thiolation. Phosphinylidene compounds are converted into thiolophosphoric esters by the action of organic sulphenyl chlorides, thiocyanates, and disulphides and of sulphenamides. The configuration of the phosphorus atom is preserved during thiolation: for example[459]



The reaction is of general value, and applies to acid phosphites[88,460], acid phosphonites[435], phosphinous acids[192], and monoalkyl phosphites[113]. Among the latter have been investigated nucleoside phosphites, which with diphenyl sulphide give nucleoside phosphorothiolates, of interest as reagents for producing an internucleotide bond. When disulphides are used, the composition of the reaction mixture must always be strictly controlled, the possibility of a secondary process being taken into account[461].

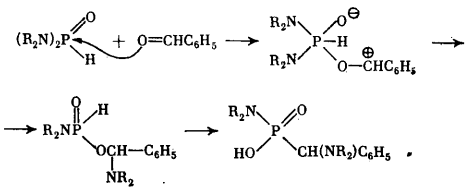
(*b*) Nucleophilic reactions

It is unlikely that a general reaction with nucleophiles will be discovered for phosphinylidene compounds. Indeed, when these compounds are esters, bifurcation occurs: both the phosphorus atom and the ester carbon atom are attacked, leading to dealkylation in the latter case. Attack on phosphorus by a nucleophile containing mobile hydrogen involves preferential displacement not of hydrogen but of an alkoxide ion: i.e. phosphinylation will occur without significant change in the nature of the phosphorus compound. When amidic or thiolic phosphinylidene compounds are used, phosphinylation of a nucleophile containing mobile hydrogen will become still more dominant. The best compounds for the investigation of nucleophilic hydrogen substitution are thus phosphinous acids[360]:

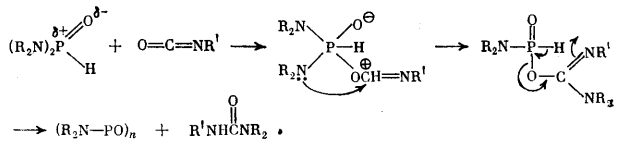


The reaction with alkali was subsequently extended to other compounds[462,463].

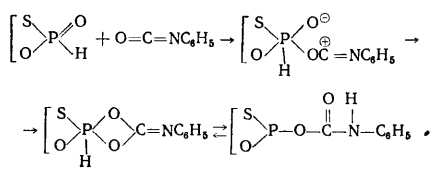
Certain complicated reactions between amides of phosphorous acid and carbonyl compounds probably begin with nucleophilic attack on the phosphorus atom: for example[241]



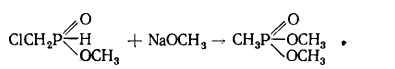
Although not all aspects of this reaction have yet been studied, an intermediate incorporation stage has already been established by nuclear magnetic resonance. The possibility of the incorporation of two molecules of the carbonyl compound has also been demonstrated[241,368]. The reaction of amides of phosphorous acid with isocyanates obviously involves a similar transformation, which has an unusual conclusion[241,248,368]:



Incorporation of carbon disulphide at a phosphorus–nitrogen bond may be supposed to develop similarly[241]. The "anomalous" action of phenyl isocyanate on ethylene phosphorothioite[128] and dimethyl phosphite[367] is more problematic, but even here the first stage probably consists in nucleophilic attack by oxygen on phosphorus:



The interaction of α-substituted phosphonous acids[464] and their partial esters[465] with nucleophiles is probably of the same type: for example



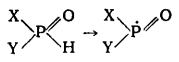
Such reactions have no general significance: chloromethylphosphonous acid reacts with ammonia to give aminomethylphosphonous acid[466].

On the whole the action of nucleophiles on phosphinylidene compounds has been little investigated. Papers have been concerned mainly with the preparative aspect, while the chemistry of the processes has been discussed seldom and usually only speculatively. Nevertheless, what has been done is very valuable, since it relieves us of a certain monotony in the development of the chemistry of phosphinylidene compounds and opens up great prospects for synthetic work.

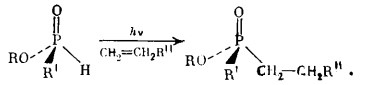
(*c*) Radical reactions

The ever increasing interest taken in radical processes in organic chemistry is evident also in the present field. The most systematic study has been made of the addition of phosphinylidene compounds to alkenes. Features and possibilities of this reaction have been surveyed in a recent monograph[467], so that here we shall consider only fundamental papers and also the most recent publications.

In the addition of phosphinylidene compounds to alkenes radicals can be generated by chemical[468,469], photochemical[470], or radiation-chemical[471-473] methods:

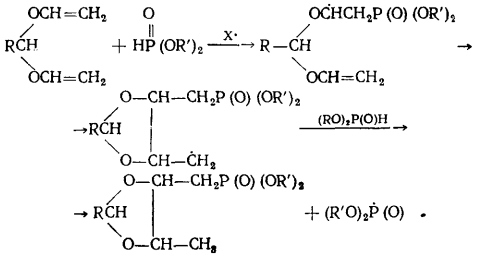


The structure of phosphoranyl radicals has been clarified in the course of a recently concluded controversy[468,469,471]. The resulting radicals are able to preserve the configuration of the initial phosphinylidene compounds, which enables optically active organophosphorus compounds to be synthesised[436]:



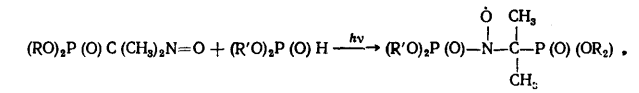
The ideas of dynamic stereochemistry have been extended to other aspects of radical addition. Thus it has been found that the conformational state of the original phosphinylidene compound governs its reactivity[468].

Synthetic investigations have been widely developed. Alkyl hypophosphites have also been brought into reaction with alkenes; under the given conditions addition occurred only once[215]. In the early work homolytic addition was applied almost exclusively to alkenes, but subsequently perfluoroalkenes[474], unsaturated heterocycles[470,475], allylic derivatives of heterochain polymers[152], etc. have been used. Diene systems exhibit noteworthy behaviour: for example[199,476]:



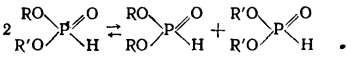
Cyclisation is akin to telomerisation[478] and the radical rearrangements observed in the addition of dialkyl phosphites to certain terpenes[477].

Under the conditions of radical reactions phosphinylidene compounds are able to phosphinylate aromatic compounds[479] and add to acetylene in the presence of transition-metal complexes as catalysts[480]. Homolytic addition is especially interesting in cases in which the heterolytic process cannot be accomplished, as in the recently discovered reactions with nitroso-compounds[481,482], nitro-compounds[483], and oximes[483]: for example



3. Reactions Not Involving the Phosphinylidene Functional Group

Phosphinylidene compounds in which the phosphorus atom is attached to electron-accepting groups are widely used in phosphinylation, e.g. in transesterification. The possibilities and peculiarities of such reactions have already been discussed in Section II. A somewhat related process is disproportionation, i.e. exchange of substituents at the central functional group. Thus unsymmetrical dialkyl phosphites give two new symmetrical esters even on storage[18], and this process may be reversed[484]:



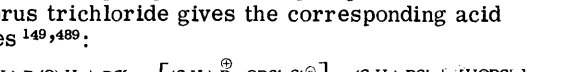
More complicated cases of disproportionation involve the cyclisation of diphosphites[83] and the oligomerisation of alkylene phosphites[71,74]. The mechanism of disproportionation has not been investigated; it is most likely catalysed by traces of alcohols or other compounds having a mobile hydrogen atom and capable of forming labile adducts with phosphinylidene compounds.

A second type of reaction is exemplified by dealkylation of the esters, which has been studied almost exclusively on dialkyl phosphites. The kinetics and the mechanism have now been studied under conditions of acid and alkaline hydrolysis[485] and treatment with metal salts[116,486]. Dealkylation of dialkyl phosphites is used in the preparation of monoalkyl phosphites (Section II), which include products of practical importance[487]. Isolated results have appeared on the dealkylation of partial phosphonites[488], which resemble dialkyl phosphites in this respect.

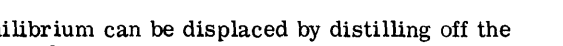
4. Reactions with Decrease in Coordination of Phosphorus

Reactions in which phosphinyl (phosphinothioyl, phosphinimidyl) groups are formed are usually preferable in the chemistry of organophosphorus compounds. Especial interest therefore attaches to the opposite reactions, which have been studied in greatest detail for phosphinylidene compounds.

Treatment of phosphonous and phosphinous acids with phosphorus trichloride gives the corresponding acid chlorides[149,489]:

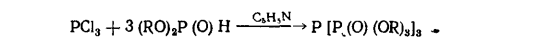


Alkylene phosphites react similarly with the trichloride[490], and also dialkyl phosphites and other phosphinylidene compounds with dialkyl phosphorochloridites[141,491,492]: for example



The equilibrium can be displaced by distilling off the volatile product.

The reactions usually begin with formation of pyrophosphites or other similar anhydride systems; the hydrogen chloride liberated then degrades the primary product in conformity with an Arbuzov reaction, forming either the initial or new products. If reaction occurs in the presence of a base, the anhydride can be isolated[141,491]. Anhydrides can be obtained also by several related methods[491,493]. It is very important that phosphinylidene compounds (or their salts) can be phosphinylated not only at oxygen but also at phosphorus[141,491§]: for example

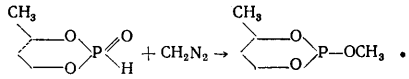


P-Phosphinylation occurs also when phosphinous acids are treated with acetic anhydride[494] or silicon tetrachloride[495]. In most cases chlorosilanes[496,497], like silylamines[133,498,499] give with phosphinylidene compounds silyl

§In some cases the direction of phosphinylation is determined by steric factors[491].

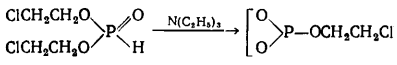
phosphites. The latter are of great interest, e.g. in the chemistry of nucleic acids [497]. Phosphonous acids react similarly with silylating reagents [106,187,500]; intramolecular silylation is possible here [187].

Reaction with aliphatic diazo-compounds was first studied on 1-methyltrimethylene phosphite treated with diazomethane and compounds containing mobile hydrogen as catalysts [446]:

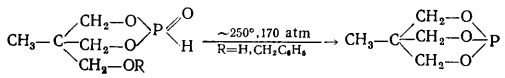


Fresh examples of this reaction have recently been given [501] with discussion of further reactions in the system comprising cyclic phosphite and diazo-compound. The reaction of 3-hydroxy-2,2-dimethylpropyl hypophosphite with diazomethane to yield the cyclic neutral 2,2-dimethyltrimethylene hypophosphite is of fundamental interest [217].

The ready intramolecular *O*-alkylation of bis-2-chloroethyl phosphite [502]



is noteworthy. The cyclisation [42,503]

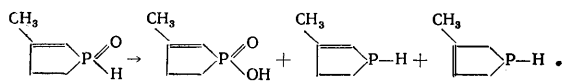


can be regarded as of the same type. One factor governing these not altogether usual transformations is evidently preferential formation of cyclic and bicyclic phosphite structures.

Several other reactions involving a decrease in the coordination number of the phosphorus atom have been considered above.

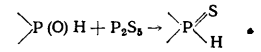
5. Other Reactions of Phosphinylidene Compounds

Investigations of the redox disproportionation of phosphinylidene compounds, begun earlier [240], have been continued during recent years. New cases of disproportionation have been found, concluding in peculiar chemical phenomena, e.g. isomerisation of one of the products [202]:

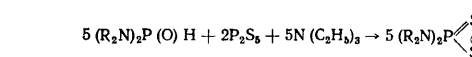


Studies have begun on the disproportionation of alkyl hypophosphites [213,327] and pyrophosphonous acids [504]. A distinguishing feature of this work is clarification of the destiny of the phosphorus intermediates; phosphenes RP have been examined in greatest detail—the rules of their oligomerisation and other transformations.

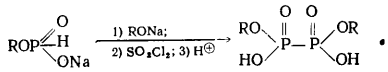
Phosphorus pentasulphide may convert phosphinylidene compounds into phosphinothioylidene derivatives:



The replacement of oxygen by sulphur involves no significant change in configuration of the phosphorus residue [179]. When amides of phosphorous acid are used, products containing two sulphur atoms are formed [505]:



An unusual reaction for phosphinylidene compounds occurs [506] when salts of monoalkyl phosphites are treated successively with an alkoxide, sulphuryl chloride, and an acid to give acid hypophosphites:



In conclusion it may be noted that the chemistry of phosphinylidene compounds, established as early as the nineteenth century, continues its successful development. One reason for such "longevity" is the appearance of fertile trends, such as steric regulation of reactions and investigation of the structure and catalytic properties of metal derivatives. At the same time the classic problems are acquiring a fresh interpretation and development by the application of modern physical methods and theoretical views. As a consequence these problems are beginning to interlock with new trends, which holds promise for further development in this field of chemistry.

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