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Phosphinates ("Hypophosphites") and Their Reactivity

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Results are given on the preparation, structure, and physicochemical properties of phosphinates, and their reactivity is discussed. A list of 234 references is included.

CONTENTS

I. Introduction 46
II. Structure, physicochemical properties, and methods of preparation 46
III. Chemical properties 49

I. INTRODUCTION

Simple compounds containing an active phosphorus–hydrogen bond can be used in general methods for preparing phosphines and phosphonic acids, phosphonous acids, and their derivatives. Various homolytic and heterolytic reactions yielding compounds containing a phosphorus–carbon bond have been applied to various phosphines, as well as phosphonic and phosphinic acids, derivatives, and analogues. However, the chemistry of phosphinates and their reactivity have hitherto been little studied, although research in this field was begun as early as the end of the nineteenth century[1] and various lines have been actively followed up to the present time. Esters[2] and organic ammonium salts[3,4] of phosphinic acid containing a four-coordinated phosphorus atom (phosphinates) are known already. A novel group of compounds having a three-coordinated phosphorus atom—full esters (dialkoxyphosphines)[5-7], diamides[8], and amidoesters[9] of phosphonous acid—have been obtained recently.

Table 1. Change in ^{31}P chemical shifts on the protonation of phosphoryl compounds[37].

Phosphoryl compound	Chemical shift, ppm	Phosphoryl compound	Chemical shift, ppm
Phosphinic acid	-24.0	Methylphosphonic acid	-15.0
Phosphonic acid	-13.6	Phosphonates and phosphonamides	-8.0--12.0
Phosphoric acid	-2.3	Trialkyl phosphates	0

However, only phosphinates have yet found extensive practical application, not only as initial reactants for the preparation of various organophosphorus compounds but also as reductants in the protective coating of metals[10-12], in analytical chemistry[13,14], in the chemical modification of antibiotics[15,16], as inhibitors of certain enzymes[17], and in other most diverse applications. Practical interest attaches also to many compounds obtainable from phosphinates: they possess biological activity[18-20], are surface-active agents, antioxidants, and flotation agents[21], find application in photography for the preparation of developers that do not darken with time[22], and enter into the composition of fluxes for low-temperature soldering[23].

The present Review discusses methods of preparation and the physicochemical and chemical properties of phosphinates. A considerable number of interesting papers of fundamental character have appeared in this field during recent years. However, among the reviews that have appeared[24-28] only three early publications—a short chapter in van Wazer's monograph[26] and Frank's[24] and Kosolapoff's[25] general surveys of the chemistry of organophosphorus compounds—devote an extremely modest space to the reactions of phosphinates. The present paper makes an attempt to fill in some measure the gap existing in the review literature on the chemistry and the reactivity of phosphinates.

II. STRUCTURE, PHYSICOCHEMICAL PROPERTIES, AND METHODS OF PREPARATION

1. Structure, Physicochemical Properties, and Method of Preparation of Phosphinic Acid and its Inorganic Salts

Phosphinic ("hypophosphorous") acid was first obtained in 1816 by Dulong[29], who identified it as containing a minimal number of oxygen atoms (two). This acid, in which phosphorus is in a lower oxidation state (+1) than in its other acids[30], corresponds to the formula H_3PO_2.

Physicochemical data indicate that the two hydrogen atoms are covalently bound to the phosphorus. Thus the phosphorus-31 nuclear magnetic resonance spectrum of aqueous phosphinic acid is a triplet having intensities 1:2:1, with a chemical shift of -13.0 ppm.[31-35]. The ^1H n.m.r. spectrum of the protons attached to phosphorus is a doublet: the chemical shift is 7.14 ppm, and the spin–spin coupling constant $J_{HP} = 566$ Hz (solution in perdeuteroacetone)[36]. Protonation of phosphinic acid is accompanied by an appreciable change in the phosphorus-31 chemical shift (Table 1).[37]

The vibrational infrared and Raman spectra of the free acid and its salts indicate four-coordinated phosphorus[38-40]. Comparison of experimental spectra with parameters of a calculated vibrational model showed that the phosphinate ion corresponds to a model with equalised phosphorus–oxygen bonds[40]. The phosphorus–hydrogen frequencies correspond to vibrations of the phosphino-group of characteristic frequency and form. Detailed study of the infrared spectra of phosphinic acid and several of its inorganic salts[41,42] also showed appreciable lowering of phosphorus–hydrogen stretching frequencies on passing from the acid to its inorganic salts (Table 2).

Results of X-ray structural investigations correlate with the spectroscopic data. The former indicate[43,44] that the $H_2PO_2^-$ ion is a tetrahedron having C_{2v} symmetry: one axis passes through a phosphorus–hydrogen bond, and another

through a phosphorus–oxygen bond. Comparison of interatomic distances and bond angles in ions of the free acid and of ammonium phosphinate shows (Table 3) that the state of the bonds with oxygen atoms remains unchanged within the limits of error in the measurements, whereas the phosphorus–hydrogen bonds, which determine the reactivity of phosphinates, are appreciably longer in the ammonium salt, with a smaller angle between the bonds. This indicates a diminution in the polarity of the phosphorus–hydrogen bond. Hence not only ammonium phosphinate but also other salts of phosphinic acid should be less reactive than the acid itself in heterolytic reactions.

Table 2. Infrared spectral data on phosphinic acid and its inorganic salts[41].

Compounds	ν_{P-H}, cm^{-1}	ν_{PO_2}, cm^{-1}	
		asym.	sym.
KH_2PO_2	2312, 2375	1230	1040
KH_2PO_2(aq)	2314, 2363	1180	1042
$Ba(H_2PO_2)_2$	2350	1170, 1147	1090, 1078
$La(H_2PO_2)_2$	2385, 2380	—	—
$Sm(H_2PO_2)_2$	2370, 2305	—	—
$Sr(H_2PO_2)_2$	—	1150	1082, 1054
NaH_2PO_2(aq)	—	1175	1045
H_3PO_2	2434, 2415, 2395	1225, 1135	1068

Table 3. Interatomic distances and bond angles in ammonium phosphinate and the free acid[43,44].

Bond	H_3PO_2	$NH_4H_2PO_2$
	interatomic distance, A	
P–O	1.505∓0.015	1.51∓0.01
P–H	1.39∓0.01	1.50∓0.01
	bond angle, °	
O–P–O	117.0	120
O–P–H	108.3	117
H–P–H	105.3	92

Considerable difficulties arise in obtaining pure phosphinic acid[45]; among numerous methods of preparation described in reviews[26–28] only a few, giving good yields of the pure acid, are of interest. Hitherto a method of practical value has involved treating white phosphorus with a boiling lime slurry[46] and other alkali[47]. Pure phosphinic acid can be obtained by oxidising phosphine in an aqueous suspension of iodine[48]: phosphine obtained from calcium phosphide and dilute hydrochloric acid is passed into the stirred suspension of iodine in a flask until the solution becomes colourless; hydrogen iodide and water are removed under reduced pressure (40 mmHg), after which pure phosphinic acid remains. The safest laboratory method for obtaining the acid involves passing an aqueous solution of an alkali-metal phosphinate through an ion-exchange resin, then concentrating the acid on a water-bath, and drying over phosphorus pentoxide in a high vacuum[49].

It was suggested[50] that chemically pure phosphinic acid could be isolated in crystalline form by continous extraction with diethyl ether. Quite recently three methods have been described for obtaining the crystalline acid from accessible inorganic salts[36]. Double decomposition between barium phosphinate and sulphuric acid followed by removal of water by low-temperature high-vacuum sublimation (lyophilic drying) gives a product which retains its physicochemical characteristics when kept in hermetically sealed vessels for a long time. However, prolonged storage of the contaminated liquid acid is not possible even when all precautionary measures are taken (cold, hermetic sealing, storage in an atmosphere of an inert gas).[51]

Decomposition of impure phosphinic acid by disproportionation can take place in the absence of air:

$$2H_3PO_2 \rightarrow H_3PO_4 + PH_3 .$$

In the presence of water hydrogen is evolved:

$$H_3PO_2 + H_2O \rightarrow H_3PO_3 + H_2\uparrow .$$

At elevated temperatures decomposition is more fundamental in character, with the formation of red or yellow phosphorus[45]. The instability of phosphinic acid in air is attributed to its strong reducing properties, which are used both in organic synthesis, e.g. for the reduction of acids[52], and in industry—to obtain chemical protective coatings (nickel and chromium plating) of better quality than electroplating[53,54].

Pure phosphinic acid comprises white crystals in the form of lobes, melting at 26.5 °C. It is a strong monobasic acid (pK 1.1).[55] Its monobasicity indicates that phosphorus has coordination number 4 in this structure. Phosphinates of alkali and alkaline-earth metals are obtained both by trivial processes (double decomposition)[45,56] and by specific methods involving change in the coordination of the phosphorus atoms[57–60].

Phosphinates are produced industrially by the action of hydroxides of alkali and alkaline-earth metals on white phosphorus: e.g.

$$8P + 3Ca(OH)_2 + 6H_2O \rightarrow 3Ca(H_2PO_2)_2 + 2PH_3$$
$$Ca(H_2PO_2)_2 + Na_2CO_3 \rightarrow 2NaH_2PO_2 + CaCO_3 .$$

Phosphinates of rare-earth metals $M_{II}(H_2PO_2)_3$ have been prepared in which M = Sc, Y, La, as well as double phosphinates $CeM'(H_2PO_2)_6$ with M' = Er, Tm, Yb, Lu.[61–65] Their physicochemical characteristics have been studied[66].

Table 4. Organic salts of phosphinic acid.

Compound	M.p., °C	Ref.
$C_6H_5\overset{+}{N}H_3\bar{O}P(O)H_2$ *	115	3
4-CH_3CONH–C_6H_4–$\overset{+}{N}H_3\bar{O}P(O)H_2$ *	178	2
C_6H_5–NH–$\overset{+}{N}H_3\bar{O}P(O)H_2$ *	—	3
$CH_3\overset{+}{N}H_3\bar{O}P(O)H_2$	—	4
$C_2H_5\overset{+}{N}H_3\bar{O}P(O)H_2$	—	4
$(CH_3)_2\overset{+}{N}H_2\bar{O}P(O)H_2$	—	4
$(C_2H_5)_3\overset{+}{N}H\bar{O}P(O)H_2$	—	68

* Dissolves readily in water.

2. Structure, Physicochemical Properties, and Methods of Preparation of Organic Derivatives of Phosphinic Acid

Organic derivatives of phosphinic acid were first obtained in 1948[3]. Very little is known about the organic salts[3,4,67,68] (Table 4), only two of which have been isolated in pure form

and characterised[3]. Dialkylmetal salts of general formula $(CH_3)_2MPH_2O_2$ (where M = Al, Ga, In) have been reported comparatively recently[69].

Many attempts to obtain phosphinic esters have proved unsuccessful[70-72]. In 1960 Kabachnik et al.[2] were the first to accomplish the direct esterification of phosphinic acid with diazoalkanes to obtain monoalkyl phosphinates (Table 5):

$$RCHN_2 + HOP(O)H_2 \rightarrow ROP(O)H_2 + N_2.$$

This reaction confirms the suggestion that the acid is monobasic. Later several alkyl phosphinates were prepared from phosphinic acid and orthocarbonyl compounds (acetals)[73]. This is less important than the previous method for preparative purposes, since it yields a difficultly separable mixture of compounds formed by interaction between the esters and carbonyl by products:

$$(RO)_2CR'R'' + HOP(O)H_2 \rightarrow ROP(O)H_2 + O{=}CR'R'' + ROH$$
$$ROP(O)H_2 + O{=}CR'R'' \rightarrow ROP(O)CR'R''$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad |\quad |$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad H\quad OH$$

Table 5. Esters of phosphinic acid*.

Compound	Yield, %	B.p., °C (mmHg)	n_D^{20}	d_4^{20}	Ref.
$CH_3OP(O)H_2$	—	25—25.5 (2.5)	1.4275	1.2177	2
$CH_3OP(O)H_2$	47	25—25.5 (2.5)	—	—	73
$C_2H_5OP(O)H_2$	—	31—32 (2)	1.4250	1.1120	2
$C_2H_5OP(O)H_2$	39	33—35 (1.3)	—	—	73
$C_2H_5OP(O)H_2$	45	30—32 (1)	1.3945	—	89
$C_3H_7OP(O)H_2$	77	90—100 (10)**	1.4222	1.0447	77
$C_3H_7OP(O)H_2$	70	29—30 (0.07)	1.4280	—	89
$C_4H_9OP(O)H_2$	82	120—125 (10)**	1.4288	1.0045	77
$C_4H_9OP(O)H_2$	84	52—60 (1.5)	—	—	78
iso-$C_4H_9OP(O)H_2$	91	110—115 (10)**	1.4275	0.9760	77
iso-$C_4H_9OP(O)H_2$	71	56—63 (3)	—	—	78
$C_5H_{11}OP(O)H_2$	92	70—80 (0.2)**	1.4332	1.0126	77
$C_6H_{13}OP(O)H_2$	85	—	1.4530	—	75
$C_6H_{13}OP(O)H_2$	83	105—110 (0.2)**	1.4355	0.9614	77
$C_7H_{15}OP(O)H_2$	93	100—110 (0.004)**	1.4390	0.9619	77
$C_8H_{17}OP(O)H_2$	85	120—130 (0.006)**	1.4430	0.9709	77
$C_9H_{19}OP(O)H_2$	89	160—165 (0.006)**	1.4460	1.9524	77
$C_{10}H_{21}OP(O)H_2$	78	130—140 (0.002)**	1.4465	—	77
$C_{12}H_{25}OP(O)H_2$	87	63—64 (m.p.)	—	—	5
$HOCH_2C(CH_3)_2CH_2OP(O)H_2$	97	—	1.4620	—	5
$H_2(O)PO(CH_2)_6OP(O)H_2$	95	—	1.4730	—	5
$CH_3CH(OH)(CH_2)_2OP(O)H_2$	98	—	1.4590	—	5
$HOCH_2CH_2OP(O)H_2$	84	—	1.4505	1.4259	77
$C_6H_5CH_2OP(O)H_2$	87	160—170 (0.05)**	1.5415	1.1496	77
$(CH_3)_3SiOP(O)H_2$	61.5	65—67 (10)	1.4219	1.0024	90
$(C_2H_5)_3SiOP(O)H_2$	56	62—64 (1)	1.4421	0.9720	90
$H_2(O)PO(CH_2)_{16}OP(O)H_2$	87	76—78 (m.p.)	—	—	75
$-CH_2-CH-O-P(O)H_2$	—	170—187 (m.p.)	—	—	75
$C_4H_9OP(S)H_2$	65	59—64 (1.5)	—	—	78
iso-$C_4H_9OP(S)H_2$	47	65—72 (2.5)	—	—	78

* Table 5 omits several phosphinic esters for which constants have not been given—6-hydroxyhexyl phosphinate[87], poly(allyl phosphinate)[87], and cellulose phosphinate[79].

** Temperature of bath.

Nifant'ev et al. proposed a simpler and more convenient method for obtaining alkyl phosphinates[74-76]:

$$HOP(O)H_2 + ROH \xrightarrow{-H_2O} ROP(O)H_2 .$$

The reaction is accomplished by azeotropic distillation of water using a Dean and Stark trap. It can be conducted either in the absence or in the presence of a catalyst such as zinc chloride, aluminium chloride, sodium acetate, etc.; excess of one of the reactants is used to accelerate the reaction. Several lower alkyl phosphinates are very unstable when purified by vacuum distillation. If the products are contaminated with the alcohol or phosphinic acid, however, they can be stored and are convenient for use. Many alkyl phosphinates have been obtained by this method[77] (Table 5); the products were freed from unchanged acid and excess of the alcohol by vacuum treatment in molecular distillation apparatus. However, after many redistillations they could not be isolated in analytically pure form.

An interesting process for obtaining phosphinic esters consists[78] in the hydrolysis of dialkoxyphosphines. Fundamentally novel alkyl phosphinates—alkyl phosphinothionates $ROPH_2S$ (Table 5)—have been obtained by essentially the same method, by oxidising dialkoxyphosphines with hydrogen sulphide:

$$(RO)_2PH \xrightarrow{+H_2S} ROP(S)H_2 .$$

Not only monohydric alcohols but also glycols react readily[5] with phosphinic acid, to form hydroxyalkyl phosphinates and alkylene bisphosphinates:

$$HOROH + HOP(O)H_2 \begin{cases} \xrightarrow{1:1} HOROP(O)H_2 \\ \xrightarrow{1:2} H_2(O)POROP(O)H_2 \end{cases} .$$

Alkylene bisphosphinates, like esters of phosphinic acid with monohydric alcohols, are unstable in pure form. In contrast, hydroxyalkyl phosphinates are stable on storage, probably as a consequence of their specific structure[5].

Phosphinic esters are formed also by the phosphorylation of certain high-molecular polyhydroxy-compounds, peptides, and monosaccharides[79-84]. The action of phosphinic acid on cellulose yields phosphinates[80] containing up to 14% of phosphorus:

$$Cell\text{-}OH + H_3PO_2 \xrightarrow{-H_2O} Cell\text{-}O\text{-}P(O)H_2 .$$

The degree of esterification of the cellulose increased steadily with rise in temperature from 80 to 120 °C. With further rise in temperature (under otherwise similar conditions), however, the phosphorus content of the reaction product diminished. This was attributed[80] to partial decomposition of phosphinic acid above 120 °C, to give phosphine, removed from the sphere of reaction[85], and phosphonic acid, which is also an esterifying reagent[86-88]:

$$3H_3PO_2 \xrightarrow{>120°} PH_3 + 2H_3PO_3 .$$

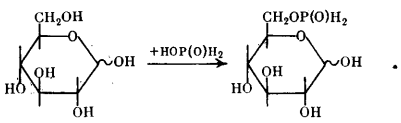
The phosphorylation of cellulose with ammonium phosphinate[79,80] showed the latter to be a more active esterifying agent than in phosphinic acid. However, the reaction products contain not only chemically bound phosphorus but also a greater or smaller quantity of nitrogen.

Research on the phosphorylation of polyols was continued with the acylation of polyvinyl alcohol by phosphinic acid[82,83]:

$$-CH_2-\underset{|}{\overset{OH}{CH}}- + H_3PO_2 \rightarrow -CH_2-\underset{|}{\overset{O-P(O)H_2}{CH}}- .$$

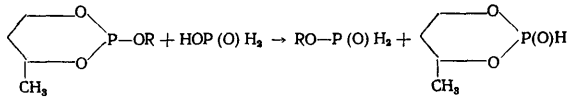
The resulting high-molecular polyphosphinate was quite stable in comparison with the unstable lower alkyl phosphinates, which break down into the initial reactants.

Study of the acylation of phosphinic acid of polyallyl alcohol and its low-molecular analogues (isobutyl alcohol and hexamethylene glycol)[84] has received a second-order reaction. Monosaccharides—glucose[76] and xylitol[81]—also react with phosphinic acid:



With xylitol the process is complicated: the formation phosphorylation products is accompanied by partial dehydration of the xylitol.

The above method of preparing phosphinic esters, though simple and convenient, is unsuitable for obtaining the simplest alkyl phosphinates. Great practical interest attaches to the dealkylation of cyclic full esters of phosphorus acid with phosphinic acid, by a modification of the Arbuzov reaction[89]:



This method gives a somewhat higher yield of ethyl phosphinate than does the process suggested by Fitch[73] (Table 5). The lower phosphinates obtained are very unstable, and can be stored only in an inert gas at temperatures below 0 °C: in air they ignite. Paper chromatography and ^{31}P n.m.r.spectra have established that the products contain the corresponding dialkyl phosphites, whose quantity increases during storage. Formation of the latter is due to disproportionation of the alkyl phosphinates, which gives also phosphine:

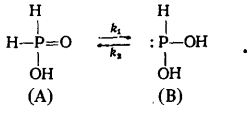
$$2RO{-}P(O)H_2 \rightarrow PH_3 + (RO)_2P(O)H_2 .$$

Organosilicon esters of phosphinic acid—trialkylsilyl phosphinates—have recently been obtained[90] by the alcoholysis of bistrialkylsilyl phosphonites:

$$(R_3SiO)_2PH + C_2H_5OH \rightarrow R_3SiOP(O)H_2 + R_3SiOC_2H_5 .$$

3. Tautomerism of Phosphinates

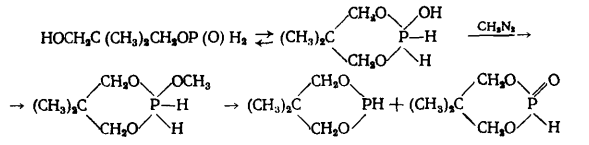
Although all the inorganic and organic phosphinates mentioned in the preceding subsections indicate that phosphinic acid is monobasic, many investigations show the occurrence of tautomerism:



Kinetic examination of the oxidation of phosphinic acid showed[91-100] that the active form is present in extraordinarily small quantities, only one-billionth (10^{-12}) part of $(HO)_2PH$ in $HOPH_2O$. As van Wazer[26] maintains, the rate-determining stage in the oxidation of phosphinic acid in acid medium by various reagents[101-105] in moderate or considerable concentrations is probably conversion of the "passive" form (A) into the "active" form (B). The rate is essentially unaffected by the nature or the concentration of the oxidant, but increases with increase in acidity. Other kinetic investigations—study of hydrogen[106,107] and oxygen[108] isotope exchange and also of the reaction mechanism[109]—confirm the tautomerism of phosphinic acid. A monograph[110] also regards the acid as tautomeric: the negative results of attempts to detect the "active" form $(HO)_2PH$ in certain spectroscopic investigations[111] are attributed to its low content in the equilibrium mixture.

The tautomerism of phosphinic acid and several other acids of phosphorus[112-114] provides an explanation of their nucleophilic reactions. The rate of conversion of "passive" into "active" form is small, so that it was difficult to count on obtaining from ordinary phosphinic acid (with the object of a final proof of tautomerism) esters of its "active" form, i.e. dialkoxyphosphines. Attempts to obtain dichlorophosphine $PHCl_2$—the initial acid chloride for the synthesis of dialkoxyphosphines—were also unsuccessful[115].

In 1969, however, appeared the first paper[5] on the preparation of a member of this class of compounds—2,2-dimethyltrimethylene phosphonite—from the phosphinic monester—3-hydroxy-2,2-dimethylpropyl phosphinate:



This was followed by the publication of several fundamental researches on this problem[6,8,9,78,116-119]. Lutsenko et al.[6] suggest obtaining dialkoxyphosphines by the reduction of dialkyl phosphorochloridites with di- and tri-alkylstannanes:

$$(RO)_2PCl + R_3SnH \rightarrow (RO)_2PH + R_3SnCl .$$

Bistrialkylsilyl phosphonites have been prepared[7,120] from ammonium phosphinate and trialkylsilylamines:

$$NH_4OP(O)H_2 + 2R_3SiNR_2 \rightarrow (R_3SiO)_2PH + NH_3 + 2HNR_2$$
$$NH_4OP(O)H_2 + (R_3Si)_2NH \rightarrow (R_3SiO)_2PH + 2NH_3 .$$

Reaction with trialkylchlorosilanes in the presence of a secondary or tertiary amine B gives the same products[121]:

$$NH_4OP(O)H_2 + 2R_3SiCl + : B \rightarrow (R_3SiO)_2PH + NH_4Cl + : B \cdot HCl .$$

The yield reaches 35–45%. High yields (80–90%) are obtained by another method[121], based on the reaction of phosphinic acid with *NN*-dialkyltrialkylsilylamines:

$$HOP(O)H_2 + 2R_3SiNR_2 \rightarrow (R_3SiO)_2PH + 2HNR_2 .$$

The formation of dialkoxyphosphines, together with the kinetic results, enables us to postulate the existence of an "active" form of phosphinic acid as the principal motive force of the nuclephilic reactions, which will be discussed in Section III.

The tautomerism of organic salts of phosphinic acid has not been studied, although its presence is suggested by studies of chemical properties.

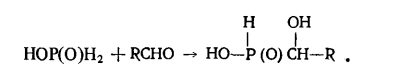
III. CHEMICAL PROPERTIES

Study of the reactivity of phosphinic acid and its inorganic salts had already begun by the end of the past century. The preparation of organic phosphinates (esters and organic salts) during recent years has given a fresh impetus to the intensive study of various reactions involving phosphinates. The present Section is devoted to a comparative analysis of the reactivity of phosphinic acid, its salts, and its esters.

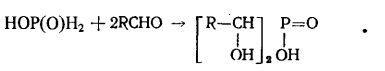
1. Reactions with Aldehydes and Ketones

Most reactions of phosphinates with aldehydes (ketones)* lead to the formation of phosphinic acids. The addition of phosphinic acid to aromatic, aliphatic, and unsaturated aldehydes (ketones) was first accomplished during 1888–1904 by Ville and by Marie[1,122,123,24-26]. Since then the reactions have aroused theoretical interest[109,124-126], and the possibility of practical utilisation of the adducts has emerged[127-131].

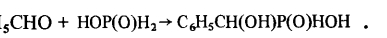
Depending on the molar proportions of phosphinic acid and aldehyde or ketone two series of derivatives may be formed[15, 124, 132–147]. Equivalent proportions give 1-hydroxyalky (or aryl) phosphinic acids:



When excess of the carbonyl compound is present, a second molecule of the latter is added:

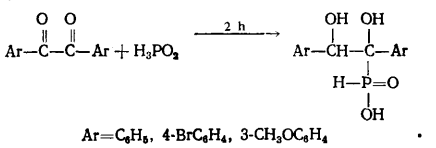


Reaction between phosphinic acid and aldehydes or ketones takes place with some difficulty, requiring heating for many hours. With benzaldehyde, for example, reaction occurs at 60–108 °C:[109]



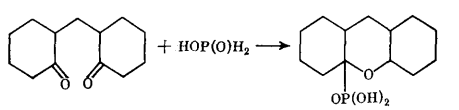
Since the equilibrium is shifted towards the initial reactants in such reactions[47], and also because of the tendency of phosphinic acid to undergo disproportionation on prolonged heating, the yields are low.

Phosphinic acid reacts considerably more rapidly with 1,2-diketones, and as a consequence the yields of condensation products—1,2-diaryl-1,2-dihydroxyethylphosphinic acids—reach 70–80%:[140]

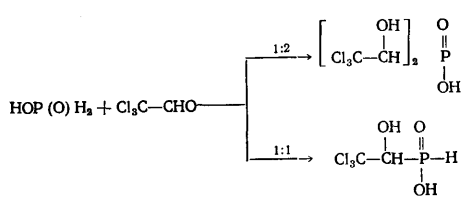


Ar=C_6H_5, 4-BrC_6H_4, 3-$CH_3OC_6H_4$

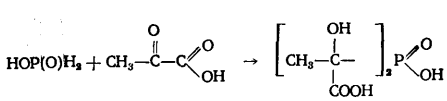
The readier addition of ketones in this case is due to the presence of two neighbouring electron-accepting (carbonyl) groups, which promote the nucleophilic addition of reactants containing phosphorus–hydrogen bonds. The action of phosphinic acid on the 1,5-diketone, methylene-2,2′-bis-cyclohexanone, is unusual[147] in that heating in acetic acid gives a 50% yield of a product regarded as a phosphonate:



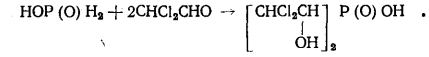
Compounds containing a polarised group react considerably more readily, i.e. at lower temperatures and with high yields. The action of anhydrous phosphinic acid on chloral in an inert solvent gives a mixture of di- and mono-substituted phosphinic acids in yields of 80% and 65% respectively[137,138]:



Pyruvic acid reacts after 2 h, to give a 46% yield of di-(1-carboxy-1-hydroxyethyl)phosphinic acid[141]:



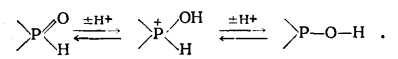
A substituted phosphinic acid is obtained also with dichloroacetaldehyde, but a period of 18 h is required and the yield is much lower (21%):[136]



Thus reaction is hindered with less strongly electrophilic reagents (dichloroacetaldehyde), in contrast to chloral: prolonged heating is necessary, and a lower yield of the desired product is obtained.

The reaction mechanism of the condensations has been studied with the action of phosphinic acid on formaldehyde and on benzaldehyde as examples[109]. These reactions are catalysed by hydrochloric acid, but their rate is independent of the hydrogen-ion concentration. They are first order with respect to the carbonyl component and to phosphinic acid in its undissociated form.

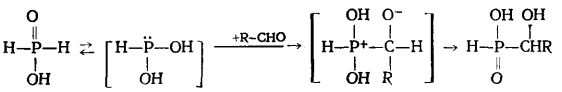
According to Kirby[110] tautomeric conversion in compounds containing a phosphinylidene group under conditions of acid catalysis corresponds to a two-stage process:



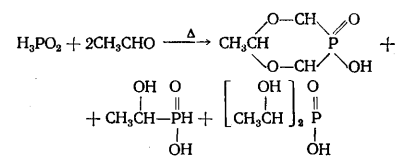
Such catalysts can apparently activate not only the phosphorus component but also the carbonyl reagent:



In view of recent studies on the mechanism of tautomeric transition of certain phosphinates into the active state with a lone pair of electrons on the phosphorus atom, and all the above considerations in relation to this problem, the addition of phosphinic acid to aldehydes can be represented by the scheme



In the cases of acetaldehyde and paraldehyde the usual adducts with phosphinic acid are accompanied by aldol condensation products, and the presence of at least two stereoisomers of the six-membered rings is postulated[125]:

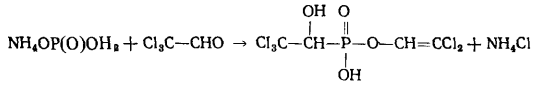


The reactivity of salts of phosphinic acid towards aldehydes has been little studied. Replacement of the acid by its potassium salt on reaction with chloral in hydrochloric acid enables the expected condensation product to be obtained[139], but the process is very slow, requiring several weeks, and gives a low yield (29%) apparently because of mutual insolubility:

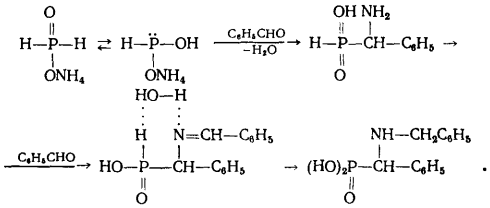
Reaction between salts of phosphinic acid and carbonyl compounds can be conducted successfully only at higher temperatures than those for the acid itself, and for a prolonged time, though in many cases the yield is high. This supports the view that the salts are more stable than phosphinic acid. Thus good yield (respectively 71% and 93%) are

obtained in the action of sodium phosphinate on 1,2,5,6-tetrahydrobenzaldehyde[135] and on paraform[148].

Unexpected results were obtained by Taube et al.[4,149], who used the little studied ammonium phosphinate as phosphorylating agent. Thus condensation of the latter with chloral gave not the expected substituted ammonium phosphinate, whatever the proportions of the reactants, but 2,2-dichlorovinyl hydrogen 2,2,2-trichloro-1-hydroxyethylphosphonate[149]:

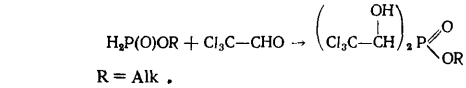


α-Benzylaminobenzylphosphonic acid was obtained by the reaction between ammonium phosphinate and benzaldehyde[4]:



The formation in the latter reaction of a phosphonic acid instead of the expected α-aminobenzylphosphinic acid is attributed to an intramolecular redox process.

The use of phosphinic esters in such reactions is of undoubted theoretical interest. It will permit comparison of the effect of replacing the acidic hydrogen by an alkyl radical: increasing the acidity of the phosphorus–hydrogen bond should favour nucleophilic addition. Indeed, the reaction of phosphinic esters with several carbonyl compounds (e.g. chloral) is exothermic and considerably more rapid than in the case of phosphinic acid[150]:



R = Alk .

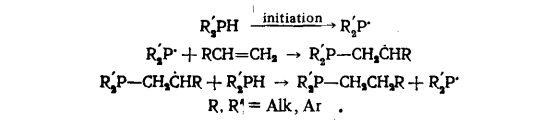
Thus the results reported in this subsection suggest the sequence of phosphinates

$$ROP(O)H_2 > HOP(O)H_2 > MOP(O)H_2,$$
R = Alk; M = Metal or NH_4

of diminishing reactivity in nucleophilic addition (to aldehydes and ketones).

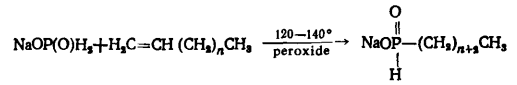
2. Reactions with Unsaturated Compounds

Free-radical addition to alkenes is a general reaction of compounds containing a phosphorus–hydrogen bond (phosphines, phosphonates, and phosphinates):

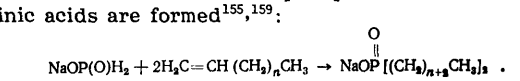


The reactions are initiated by ultraviolet irradiation or the usual sources of free radicals (organic peroxides), and take place by a radical–chain mechanism contrary to Markovnikov's rule.

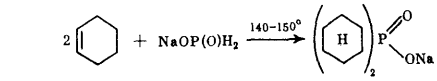
The reactions of inorganic phosphinates with unsaturated compounds usually give high yields[152–159]. For example, sodium phosphinate when heated to 120 °C with oct-1-ene in methanol in the presence of a peroxide gives a 100% yield of the salt of octylphosphonous acid[156]. Other alkylphosphonous acids have been obtained similarly from compounds having a terminal double bond:



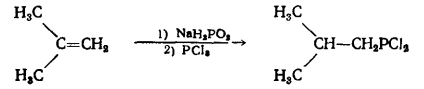
When the molar ratio of alkene to phosphinate is 2: 1, dialkylphosphinic acids are formed[155,159]:



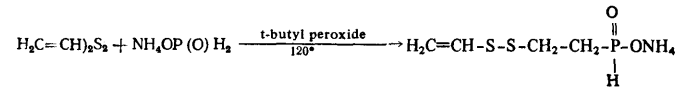
Sodium phosphinate reacts with allyl alcohol also in the presence of a peroxide[160,161]. Isolation of the reaction products presents considerable difficulties, probably owing to the occurrence of secondary processes. For the same reason individual addition products of the phosphinate to allyl cyanide and allyl acetate could not be isolated[162]. The resulting mixture was identified as the chlorides of 3-acetoxypropylphosphinic acids. The action of cyclohexene on sodium phosphinate in the presence of t-butyl peroxide gives a 77.5% yield of dicyclohexylphosphinic acid[83,163]:



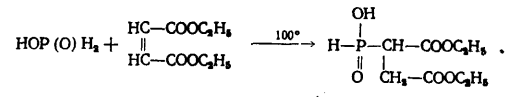
These reactions cna be used to obtain various alkyldichlorophosphines. A convenient procedure consists in initial preparation from an alkene and sodium phosphinate of the monosodium alkyl phosphinate, which is then treated with phosphorus trichloride or thionyl chloride[152]:



The above account shows clearly that all investigators have chosen sodium phosphinate to study the reactivity of salts of phosphinic acid, probably because of its better solubility in various solvents on heating. Only a British Patent[157] chose ammonium phosphinate, which on reaction with divinyl disulphide gave ammonium 3,4-dithiahex-5-enylphosphinate:

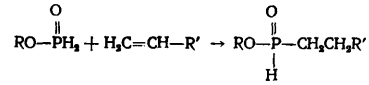


Phosphinic acid reacts with unsaturated compounds to from analogous products[164–167], but the yields are considerably lower, varying in the range 9–40%.[166,167] Reaction occurs with ethyl maleate in the absence of a catalyst to give a 65% yield[168], possibly by an ionic mechanism:



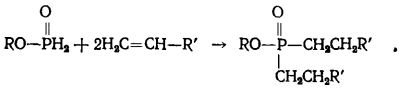
Attempts to catalyse the process with alkali-metal alkoxides or triethylamine did not increase the yield.

Alkyl phosphinates also add to alkenes in the presence of peroxides[76,169]:



R = Alk; R′ = Alk .

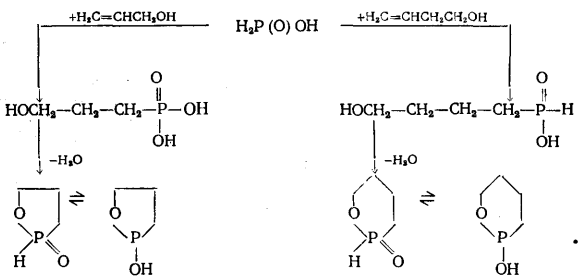
Cyclohexene reacts with greater difficulty. Phosphinic esters are formed with excess of the alkenes at a higher temperature:



The reactions of methyl phosphinate with acrylonitrile and with methyl acrylate follow a similar course; in the latter case the main product is accompanied by a dimethyl phosphonate[170]:

$$CH_3OP(O)H_2 + H_2C{=}CH\text{-}C(O)OCH_3 \rightarrow$$
$$CH_3OP(O)HCH_2CH_2C(O)OCH_3 + (CH_3O)_2P(O)CH_2CH_2C(O)OCH_3 .$$

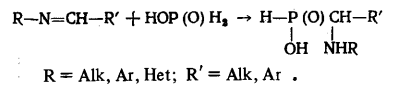
The synthetic possibilities of the reactions of phosphinic acid and its derivatives with unsaturated compounds are confirmed by a publication[161] on the action of allyl alcohols on phosphinates. Aliphatic phosphinic acids containing a hydroxy-group in position 3 or 4 of the alkyl radical, obtained from phosphinates and aliphatic alcohols having a terminal ethylenic bond, undergo cyclisation when heated to 100–150 °C, with formation of 2-oxaphospholan-1-ones and 2-oxaphosphan-1-ones (γ- and δ-phostones):



Owing to the inadequacy of published results it is fairly difficult to compare the reactivities of phosphinates in these reactions. There is no doubt, however, that the use of phosphinate salts instead of the acid itself in reactions with unsaturated compounds is entirely justified. The high yields obtainable are attributable to the greater stability of the salts under the severe conditions of addition at double bonds.

3. Reactions with Azomethines

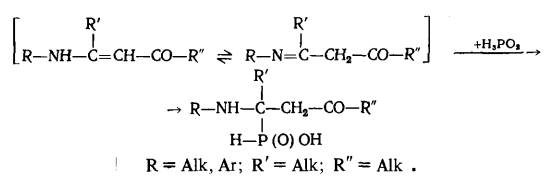
The addition to azomethines of reactants containing an active phosphorus–hydrogen bond provides a method for obtaining aminoalkyl (or aryl)phosphinic acids, interest in which is increasing in view of the physiological activity possessed by compounds of this type[171–176] and their detection in naturally occurring products of biological origin[177–180]. Substituted acids of this type were synthesised from phosphinic acid by Schmidt[3,181,182]. These reactions give good yields under mild conditions, with azomethines obtained from acetone reacting more readily:



R = Alk, Ar, Het; R′ = Alk, Ar .

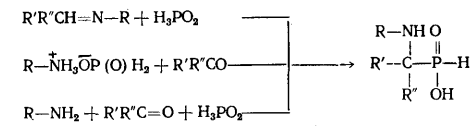
Various Schiff bases obtained from primary amines (aromatic, aliphatic, heterocyclic) and carbonyl compounds (aliphatic and aromatic aldehydes and ketones) have been used[3,182–190].

Certain enamines of β-dicarbonyl compounds react[189]:

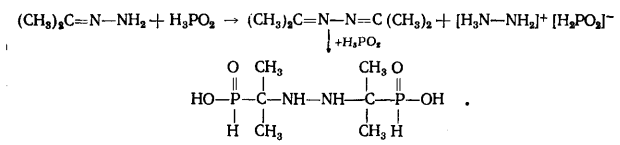


R = Alk, Ar; R′ = Alk; R″ = Alk .

Most of the investigators note[3,67,191] that 1-aminoalkyl(aryl) phosphinic acids can be obtained not only from azomethines but also by other methods, including placing all three components—amine, aldehyde (ketone), and phosphinic acid—together in the reaction vessel, but data on yields are contradictory[67,186]. A third variant—bringing a phosphinate, the amine, and the aldehyde into reaction—has been tested on several examples[3,4,185], but diminished yields of aminophosphinic acids are obtained[185]. Thus *N*-aryl(alkyl)-1-aminoaryl(alkyl)phosphinic acids can be synthesised in three ways:

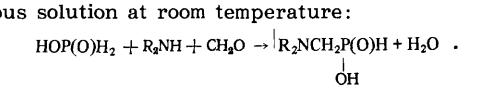


If an unsubstituted hydrazone is used as azomethine, the course of the process is anomalous[67]. Reaction between an equivalent quantity of acetone hydrazone and phosphinic acid gives a quantitative yield of acetone azine and hydrazinium phosphinate:



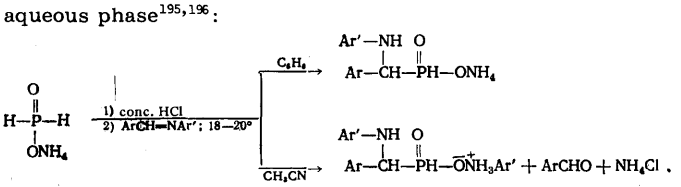
Azines can be obtained also from the hydrazones of benzaldehyde, acetophenone, and butan-2-one. Difunctional amino-acids are formed by the action of phosphinic acid on azines: a diphosphinic acid is obtained in good yield from acetone azine and two equivalents of phosphinic acid.

Secondary amines are more reactive than primary amines[192,193]. Dialkylaminomethylphosphinic acids are formed exothermally from secondary amines, formaldehyde, and phosphinic acid in aqueous solution at room temperature:

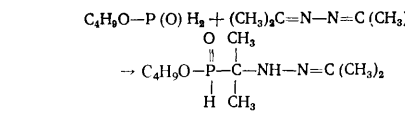


This process, which resembles formally the Mannich reaction, can be more far reaching: with excess of amine and formaldehyde bis(dialkylaminoalkyl)phosphinic acids are formed. With primary amines, however, only phosphinic acids are obtained.

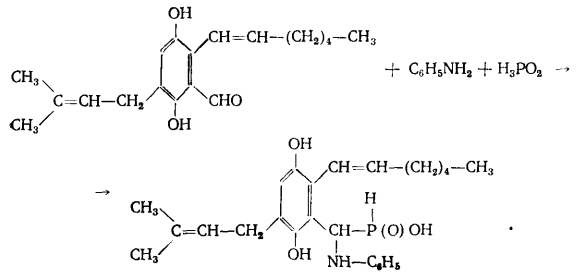
Quite recently phosphinic acid has been replaced by its salts and esters in such reactions. A series of *N*-substituted 1-aminoaralkylphosphinic acids have been obtained from ammonium phosphinate[194]. The latter reacts with azomethines in the presence of an equivalent quantity of hydrochloric acid in benzene and acetonitrile to form arylammonium 1-aryl-1-arylaminomethylphosphinates[195,196]; when benzene is used, ammonium salts of the same acids are formed in the aqueous phase[195,196]:



Treatment of alkyl phosphinates with azines[197,198] yields 1-aminoalkylphosphinic esters. The reaction studied in greatest detail is that between butyl phosphinate and acetone azine, in which heat is evolved and a 1:1 adduct is formed:

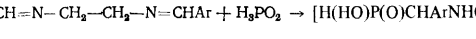


Reactions between phosphinates and azomethines (or their components) have already found practical application. Interest undoubtedly attaches to the selective modification of antibiotics by phosphorus-containing agents with the aim not only of practical application of novel semi-synthetic preparations (the possibility of obtaining forms suitable for injection) but also of their theoretical study, of the effect of introducing phosphorus grouping on the biological properties of the resulting organophosphorus antibiotics. Thus a water-soluble form of the antibacterial antibiotic aspergin has been obtained as 1-*N*-phenylaminoasperginphosphinic acid[15]:



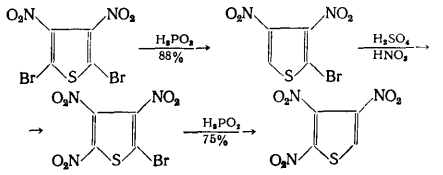
A medical form for parenteral introduction can be obtained by converting the hydrogen form into the sodium salt.

A series of phenothiazinylaminoalkylphosphinic acids have been obtained as potential medicinals[191]. Interesting complexones have been prepared by means of Schiff bases obtainable from ethylenediamine[188]:

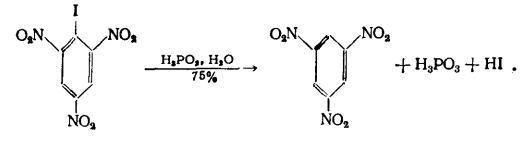


4. Other Reactions of Phosphinates

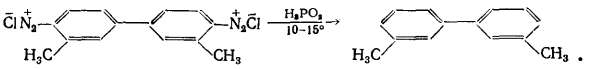
As already noted, the practical application of phosphinates is largely due to their reducing properties[10-12], which are responsible for the use of phosphinic acid in organic synthesis. 2,3,4-Trinitrothiophen can be obtained by means of this acid[199]:



The latter effects reductive elimination also in the formation of trinitrobenzene from picryl iodide[200]:

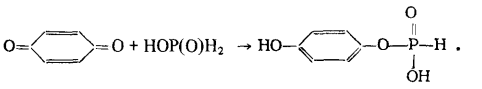


The acid was suggested also for reductive deamination by replacement of a diazonium group by hydrogen[201]:

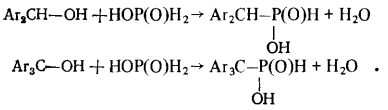


A sixfold excess of 30% phosphinic acid was used to reduce bisdiazotised o-tolidine[202]. The acid has been used also to obtain 2,4,6-tribromobenzoic from *m*-aminobenzoic acid[203].

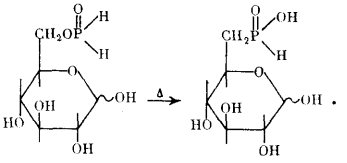
Several studies have been made of the mechanism of the reduction of organic compounds by phosphinates[204-208]. Reduction products—quinhydrone and quinol—are formed by the action of 50% phosphinic acid on *p*-benzoquinone. However, when this reaction is conducted in anhydrous medium or in the presence of a small quantity of water, an addition product—*p*-hydroxyphenyl hydrogen phosphonate—is also formed (in yields up to 46%):[209]



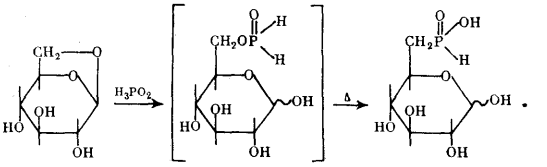
An interesting recent method for obtaining alkylphosphinic acids is the isomerisation of alkyl phosphinates. As early as 1910 Fosse[210], and later other workers[211,212], obtained alkylphosphinic acids by the action of secondary and tertiary arylcarbinols on phosphinic acid in the absence of a catalyst:



However, the mechanism of these reactions was not studied. Nifant'ev, who has detected isomerisation, considers[213] that initial esterification of phosphinic acid is followed by isomerisation of the resulting ester into the substituted phosphinic acid:



When sugars were treated with phosphinic acid, the initially formed phosphinic esters were isolated, and their structure was proved by oxidation to the corresponding phosphates or hydrolysis to the original products. The structure of glucose 6-phosphinate was proved more rigorously by the methods of carbohydrate chemistry. The same compound was obtained from phosphinic acid and levoglycosan[76,214]:



Heating levoglycosan with a mixture of phosphinic acid and sodium phosphinate gives sodium 6-glucophosphinate, whose structure has been confirmed by cross-synthesis[215]. The possibility of such intramolecular rearrangement was further postulated by Plets[216] when investigating the reactions of

sodium phosphinate with methyl iodide and with ethyl chloroacetate:

$$NaOP(O)H_2 + H_2 + CH_3I \xrightarrow{-NaI} CH_3OP(O)H_2 \rightarrow HO-\underset{\displaystyle CH_3}{\underset{|}{P(O)H}}$$

$$NaOP(O)H_2 + ClCH_2COOC_2H_5 \xrightarrow{-NaCl} \rightarrow H_2P(O)-OCH_2COOC_2H_5 \rightarrow \underset{\displaystyle OH}{\underset{|}{HP(O)}}CH_2COOC_2H_5 .$$

Phosphinate salts react vigorously with acetic anhydride. In concentrated media violent reaction occurs with formation of disproportionation products. In extremely dilute solutions (0.2M) high yields of potassium acetylphosphinate have been obtained[217,218]:

$$KOP(O)H_2 + (CH_3CO)_2O \rightarrow \underset{\displaystyle H_3C-C=O}{\underset{|}{KO-P(O)H}} + CH_3COOH .$$

This reaction has been accomplished with various phosphinates—those of sodium, lithium, nickel, barium, and zinc—and other anhydrides of carboxylic acids react similarly. The process probably involves a Michaelis–Arbuzov reaction:

$$H-\underset{\displaystyle OH}{\underset{|}{P}}-OK + (R-\underset{|}{C}=O)_2O \rightarrow \left[\left(R-\underset{\displaystyle O}{\underset{\|}{\overset{\displaystyle OK}{\overset{|}{C}}}}-\overset{+}{P}-H\right)\underset{\displaystyle OH}{\underset{|}{}}R-COO^-\right] \rightarrow R-\underset{\displaystyle O}{\underset{\|}{\overset{\displaystyle OK}{\overset{|}{C}}}}-\underset{\displaystyle O}{\underset{\|}{P}}-H + RCOOH .$$

The aminomethylation of alkyl phosphinates

$$ROP(O)H_2 + (C_2H_5)_2NCH_2X \begin{cases} \rightarrow [(C_2H_5)_2NCH_2]_2P(O)OR + HX \\ \rightarrow (C_2H_5)_2NCH_2P(O)(OR)_2 + HX \end{cases}$$

is of theoretical interest[77]. In the first stage the phosphorus in the phosphinates is probably electrophilic with respect to the amines[76]. The reaction was conducted at 130–160 °C, and nearly always gave a mixture of products containing aminoalkyl-phosphinic and -phosphonic esters and the corresponding amides.

The Todd–Atherton reaction has been successfully extended to phosphinates[68,76,169,219]: alkyl phosphinates react readily with alcohols and tetrachloromethane in the presence of triethylamine. Depending on the proportions of the reactants either phosphonates or phosphates are formed[76,169]:

$$ROP(O)H_2 + CCl_4 + ROH + N(C_2H_5)_3 \begin{cases} \xrightarrow{1:1:1:1} (RO)_2P(O)H \\ \xrightarrow{1:2:2:2} (RO)_3PO \end{cases} .$$

Phosphinates of glycols are converted into cyclic phosphonates:

$$HO-R-O-P(O)H_2 + CCl_4 + N(C_2H_5)_3 \rightarrow R\begin{matrix} O \\ \diagup \\ \diagdown \\ O \end{matrix}P(O)H .$$

If alcohols are replaced by secondary amines, phosphorodiamidates are formed:

$$ROP(O)H_2 + 4HNR'_2 + 2CCl_4 \rightarrow ROP(O)(NR'_2)_2 .$$

The Todd–Atherton reaction has been accomplished also with phosphinic acid[68,219]: thus with tetrachloromethane, triethylamine, and water the acid is converted into phosphorous acid. With tetrachloromethane and aniline the dianilide of phosphoric acid is formed. Aliphatic secondary amines behave similarly. Phosphinic acid on treatment with alcohols, tetrachloromethane, and triethylamine is converted into dialkyl phosphates.

Thus the great activity of phosphinates has permitted their use in many heterolytic and homolytic reactions. Although the range of reactions studied has hitherto been narrowly restricted, the above results demonstrate the wide opportunities open to the use of phosphinates for the preparation of diverse organophosphorus compounds.

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Several publications on the preparation and the chemical properties of phosphinates have appeared while this Review was being prepared for the press. The action of water and hydrogen sulphide on dialkoxyphosphines yields alkyl phosphinates and phosphinothionates respectively[220]. Several inorganic salts of phosphinic acid have been prepared and their physicochemical properties have been studied[221,222].

The thermolysis of *p*-acetylanilinium phosphinate reflects the highly reactive character of the arylammonium salts[223]. A method has been suggested for the phosphorylation of allylcellulose with alkali-metal phosphinates[224]. Ion-exchange resins of polycondensation type, containing phosphorus and nitrogen, have been obtained from various di- and poly-amines, aqueous formaldehyde, and phosphinic acid[225,226]. The condensation of oximes with phosphinic acid yields 1-aminoalkyl-phosphinic and -phosphonic acids[227]. 1,5-Diketones react with phosphinic acid to give hydroxyalkylphosphinic or tetrahydropyranylphosphonic acids and their analogues depending on the structure of the ketone and the acidity of the medium[228–231]. The structure of the reaction product reported in Ref.231 has been refined[228–230]. Several macrocycles[232] and arenediazonium compounds[233] have been reduced with phosphinic acid. Homolytic reactions of phosphinates have been described in a monograph[234].

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