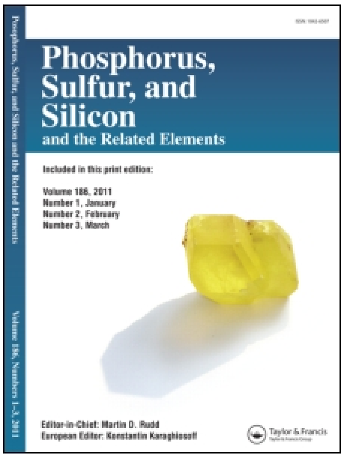

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THE SYNTHESIS OF ORGANOPHOSPHORUS COMPOUNDS DIRECTLY FROM THE ELEMENT

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THE SYNTHESIS OF ORGANOPHOSPHORUS COMPOUNDS DIRECTLY FROM THE ELEMENT

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1 INTRODUCTION

Organophosphorus compounds were first introduced commercially as plasticizers in the 1920's and in succeeding years their use as oil and petrol additives, anti-oxidants, stabilizers for plastics, flame retardants and flotation agents has developed rapidly.[1] All organophosphorus compounds are made from elemental phosphorus, which is converted to phosphine, phosphorus tri and pentachlorides, phosphorus pentoxide or pentasulphide.[2] There are obvious advantages in preparing organophosphorus compounds directly from the element, and in recent years considerable effort has been directed in this area.[3–7]

This has been stimulated by the large scale production of phosphate esters and thio-esters for use in the preparation of insecticides, and the increasing use of organophosphorus compounds in synthesis, particularly the industrial application of the Wittig and related reactions.

The reactions which have been studied fall into three broad categories: (1) alkylation and arylation; (2) reactions under oxidizing conditions; (3) reactions with nucleophiles.

2 ALKYLATION AND ARYLATION OF PHOSPHORUS

Reactions of this type have been widely studied over the years, and were used in some of the earliest direct syntheses of organophosphorus compounds.[8] Petrov and his co-workers[9] have prepared a number of phosphonous dihalides and phosphinous halides, by treatment of white phosphorus with alkyl chlorides, alkyl bromides, or aryl bromides in solution, at temperatures in excess of 250°C.

$$RX + P_4 \rightarrow RPX_2 + R_2PX$$

These authors suggest a free-radical mechanism for the reaction, involving attack by the cleavage products of the alkyl or aryl halide, $R\cdot$ (or $Ar\cdot$) and $X\cdot$, on the P_4 molecule. However, the later stages of the reaction may well involve ionic processes, since Maier's work on the reactions of methyl chloride and of methyl bromide with white phosphorus has shown that high yields of tetramethylphosphonium halides can be obtained by careful control of the reaction temperature and the reaction time.[10]

A number of catalysed vapour-phase alkylations of phosphorus have been reported in the literature, and it would seem that the type and distribution of products depend on reaction conditions and on the nature of the catalyst used. Maier has examined the vapour-phase reactions of red phosphorus with alkyl halides, in the presence of copper,[11] and has shown the major products to be alkylphosphonous dihalides, together with smaller percentages of dialkylphosphinous halides and traces of phosphorus trihalides. Following early work on the uncatalysed reaction of elemental phosphorus with methyl chloride at elevated temperatures,[12a] Gladshtein and his co-workers re-investigated this and other reactions of red phosphorus with alkyl and aralkyl chlorides, in the presence of copper and of cuprous chloride catalysts.[12b, 12c] The vapour-phase reaction of methyl chloride with red phosphorus, in the presence of copper,[12b] was shown to give trimethylphosphine in addition to methylphosphonous dichloride, dimethylphosphinous chloride, and phosphorus trichloride, and a radical mechanism was proposed to account for the observed products. More recently Staendeke has carried out this reaction at 360°C over a charcoal catalyst, in the presence of hydrogen chloride, and reports that in addition to phosphonous and phosphinous chlorides, substantial amounts of dimethylphosphine and trimethylphosphine are produced.[13] These are isolated as their phosphine–hydrogen chloride adducts, by fractional condensation, and are subsequently converted into the free phosphines by treatment with sodium hydroxide solution.

The first example of the preparation of alkylphosphonous dihalides and dialkylphosphinous halides from elemental phosphorus was reported by Emeléus and his co-workers,[14a] who showed that white or red phosphorus reacts with trifluoromethyl iodide according to the following equation.

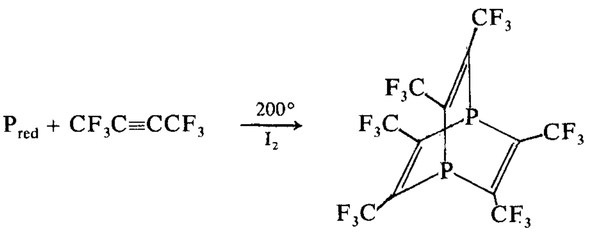
$$P_4 + F_3CI \xrightarrow{200\text{–}220^\circ} (F_3C)_3P + (F_3C)_2PI + F_3CPI_2 + P_2I_4 + PI_3$$

Evidently the products can equilibrate quite readily under the reaction conditions, therefore the individual yields depend on the ratio of the starting materials and on the reaction time. Perfluoropropyl iodide undergoes a similar reaction with red phosphorus[14b] as shown below.

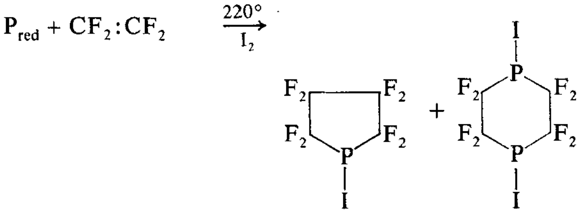
$$n\text{-}C_3F_7I + P_{red} \xrightarrow[8\text{ h}]{230^\circ} n\text{-}C_3F_7PI_2 + (n\text{-}C_3F_7)_2PI$$

Under these conditions the reaction proceeds in 60% yield, based on the iodide, giving a mixture containing the phosphonous di-iodide and the phosphinous iodide in the ratio of 30:70, respectively. It is interesting to note that no trisperfluoropropylphosphine is produced in this reaction even when the temperature is increased to 300°C. Red phosphorus has recently been shown to react with perfluoroalkyl iodides containing more than three carbon atoms.[15] The reactions were carried out at ~230°C, and the resulting mixtures of phosphonous di-iodides and phosphinous iodides have proved useful as lubricating-oil additives.

The related reaction of red phosphorus with hexafluorobut-2-yne, in the presence of iodine, has been investigated by Krespan and his co-workers,[16] and has been shown to give a substituted diphosphabicyclo-octatriene according to the following equation.



A similar reaction, between red phosphorus and tetrafluoroethylene, has been reported to give cyclic fluoroalkyliodophosphines,[17] as shown below.

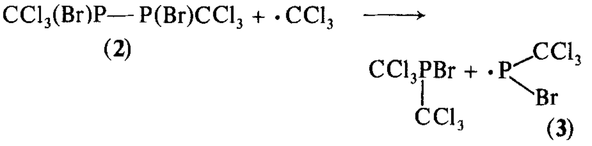


These reactions serve to illustrate how complex organophosphorus compounds, which would be difficult to prepare by conventional methods, can be obtained easily, in a single reaction, from elemental phosphorus.

A vast amount of research has been carried out by Kirsanov and his co-workers, into the reactions of red phosphorus with alkyl halides or alcohols, in the presence of iodine. The first reactions to be investigated were those between red phosphorus and alkyl iodides.[18] The reagents were allowed to react at elevated temperatures, and the reaction mixtures, after being cooled and treated with saturated sodium sulphite solution, were found to give trialkylphosphine oxides in high yield, together with a small percentage of the corresponding dialkylphosphinic acid. For example, trimethyl-, triethyl-, and tributylphosphine oxides were prepared in 54, 56 and 66% yields, respectively, by slow heating of the appropriate alkyl iodide (3 mol) with red phosphorus (1.5 g atom) and a catalytic amount of iodine (0.01 g atom), to 200–220°C in a steel autoclave, followed by treatment of the cooled reaction mixture with sodium sulphite solution. In these early reactions, the nature of the primary products was not elucidated, but more recently,[19] they have been shown to be hexa-alkyliodobiphosphonium pentaiodides $[(R_3PPIR_3)^+I_5^-]$, which are converted quantitatively into the corresponding trialkylphosphine oxides by treatment with sodium hydroxide or sodium sulphite solution. The analogous reactions involving alkyl chlorides[20] and alkyl bromides[20b] have since been investigated, and although the primary products in these reactions are as yet unidentified, they too can be converted into trialkylphosphine oxides by treatment with alkali, although in these cases, small amounts of the corresponding alkylphosphonic and dialkylphosphinic acids are also produced. The presence of the phosphoric acid in the reaction mixture was found to increase the yields of the last two products and the yield of the trialkylphosphine oxide was lowered to between 5 and 15%, depending on the nature of the alkyl group. Alcohols have also been shown to react with red phosphorus, in the presence of iodine,[21] and after treatment with alkali the reaction mixtures yield tertiary phosphine oxides, alkylphosphonic acids, and dialkylphosphinic acids, in much the same way as those from the corresponding reactions with alkyl halides. For example, a mixture of propanol, iodine, and red phosphorus, in the ratio 1:1.2:3, when heated under reflux for 40–44 hr, cooled, treated with 20% sodium hydroxide solution, and extracted with benzene, gave 50.3% tripropylphosphine oxide, while acidification of the alkaline layer gave 32–37% dipropylphosphinic acid. Similarly, reaction with butanol gave 43% tributylphosphine oxide and 45% dibutylphosphinic acid, while reaction with pentanol gave 43% tripentylphosphine oxide and 41% pentylphosphonic acid.

Kirsanov and his co-workers have found that alkyl iodides are capable of reacting with diphosphorus tetraiodide in the same way as with red phosphorus and iodine,[18a] and in view of this observation they conclude that the latter reaction proceeds through formation of P_2I_4, which is subsequently alkylated to give the observed products. If this is the case, then these reactions do not represent direct syntheses of organophosphorus compounds. However, the scheme proposed by the Russian workers has been questioned by Grayson,[2b] who favours a mechanism involving direct alkylation of elemental phosphorus.

The work of Perner, Henglein, and their co-workers provides further examples of reactions involving the alkylation of phosphorus. This group has successfully used γ-irradiation to initiate free-radical reactions of white phosphorus in several organic solvents. For example, trichloromethylphosphonous dichloride (CCl_3PCl_2) is formed on irradiation of a solution of P_4 in carbon tetrachloride at 130°C, while at lower temperatures an interesting variety of red phosphorus is formed, containing a large number of trichloromethyl end groups, which can be converted into trichloromethylphosphonous dibromide by treatment with bromine.[22] In a similar investigation,[23] high yields of cyclohexylphosphonous dichloride and other products were observed when solutions of P_4 in a mixture of carbon tetrachloride and cyclohexane were subjected to γ-irradiation. In this, as in the previous reaction, red phosphorus was formed, containing a large number of radical groups from the solvent, but in later work,[24] where the use of bromoform as a solvent caused a time delay between the formation of the red phosphorus and that of the organophosphorus products, dibromomethylphosphonous dibromide and bis(dibromomethyl)phosphinous bromide, the polymeric material was shown to be a precursor of the low molecular-weight products, rather than simply a side product. When bromotrichloromethane is used as a solvent, however, no red phosphorus is formed,[25] and this has been explained as being due to the low $Cl_3C—Br$ bond energy (49 Kcal/mol), which results in the rapid reaction of intermediates containing four phosphorus atoms, before they are able to undergo condensation reactions to give red phosphorus. The products of this reaction are unusual in that they are substituted diphosphines, and the authors suggest that they are either stable to trichloromethyl radicals or are re-formed after radical attack, according to the following scheme.



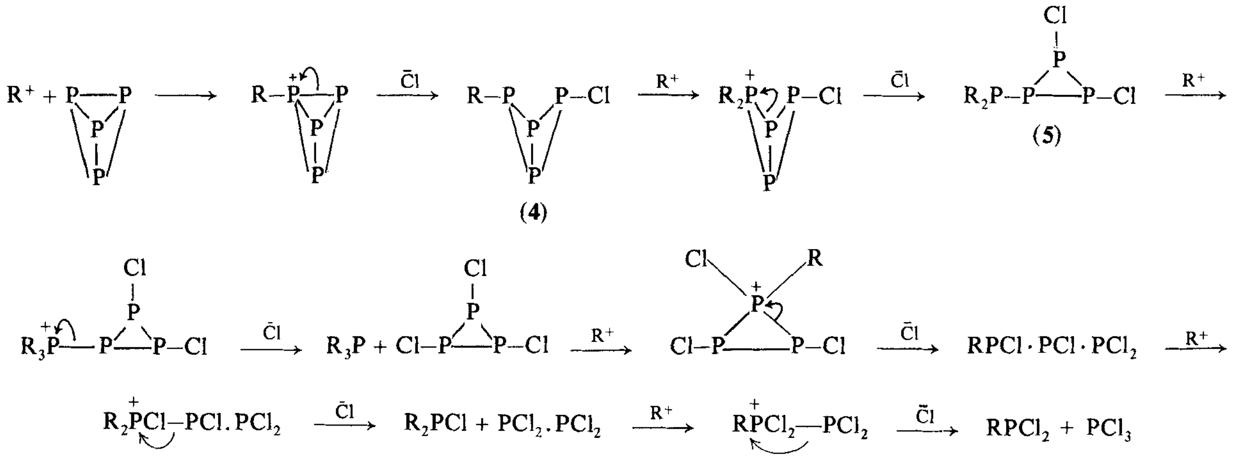
$$\underset{(2)}{CCl_3(Br)P—P(Br)CCl_3} + \cdot CCl_3 \longrightarrow \underset{CCl_3}{\underset{|}{CCl_3PBr}} + \cdot P\begin{smallmatrix} CCl_3 \\ Br \end{smallmatrix} \quad (3)$$

$$(3) + CCl_3Br \longrightarrow CCl_3PBr_2 + \cdot CCl_3$$

$$(CCl_3)_2PBr + CCl_3PBr_2 \longrightarrow (2) + CCl_3Br$$

Tomilov and his co-workers have studied several reactions in which phosphorus is alkylated electrochemically. For example, the electrolysis of a mixture of butyl bromide and white phosphorus in dimethyl formamide (DMF), using butyl bromide in DMF as anolyte, was found to give a mixture of organophosphorus products, including butylphosphine (1.95%), dibutylphosphine (6.35%), tributylphosphine oxide (1.46%), tetrabutyldiphosphine, and tetrabutylcyclotetraphosphine (9.1% jointly),[26] while the use of ethyl iodide in methanol, as catholyte, and methanolic potassium hydroxide solution, as anolyte, gave tetraethylphosphonium iodide, which was isolated as triethylphosphine oxide in 44% yield.[27] Although these reactions are certainly "one-pot" syntheses, it is debatable whether or not they constitute direct syntheses of organophosphorus compounds, since the first step appears to be the electrochemical reduction of P_4, followed by reaction of intermediate lower hydrides of phosphorus, with the alkyl halide. The electrochemical synthesis of organophosphorus compounds from the element has recently been reviewed in the literature.[28]

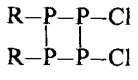
$$RCl + AlCl_3 \longrightarrow R^+[AlCl_4]^-$$



SCHEME 1

Despite the fact that white phosphorus has a molecular structure consisting of a regular tetrahedral arrangement of four phosphorus atoms, each having an unshared pair of electrons, it shows little tendency to react as a nucleophile. The reactions described so far, involving phosphorus and an electrophile have all been shown to proceed by free-radical processes, at least in the initial stages. However, in 1964, two examples of a clear-cut electrophilic reaction were independently reported by Angstadt[29] and by Titov and Gitel.[30] Angstadt investigated the reaction of white phosphorus, in carbon disulphide solution, with *t*-butyl chloride in the presence of aluminium trichloride. The reaction proceeded rapidly at −10°C, but as a result of the work-up procedure the only product isolated was di-*t*-butylphosphinous chloride, which was obtained as a mixture of its oxidation product, di-*t*-butylphosphinic chloride and its hydrolysis product, di-*t*-butylphosphine oxide. The latter workers also investigated the reactions of elemental phosphorus with alkyl chlorides in the presence of aluminium trichloride, and propose the following scheme to account for the products.

Although Scheme 1 is quite sound from an electronic point of view, it is more likely, on the basis of steric considerations that intermediate (**4**) is attacked by a carbonium ion at one of the two equivalent unsubstituted phosphorus atoms, rather than at the site of first substitution, giving the 4-membered cyclic structure shown below, which one would expect to be more stable than the highly strained intermediate (**5**).

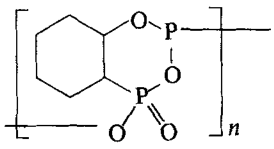


(**6**)

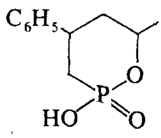
A number of compounds containing four phosphorus atoms in a ring have been shown to be quite stable,[31] and repeated attack by alkyl carbonium ions on intermediate (**6**), according to the processes outlined in Scheme 1 would give rise to exactly the same products as attack on the 3-membered cyclic intermediate (**5**).

3 REACTIONS OF PHOSPHORUS UNDER OXIDIZING CONDITIONS

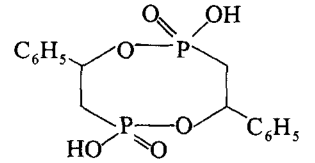
Probably the first observation of the reaction of phosphorus with an olefin and an oxidizing agent was made by Robert Boyle in 1681,[32] when he noticed that the glow accompanying the oxidation of phosphorus in air was not observed with solutions of the element in turpentine. However, it was not until the work of Willstätter and Sonnenfeld,[33] that the reaction was investigated in detail and the products, the so-called "phosphorates", were identified as having the empirical formula, olefin$\cdot P_2O_4$. More recently, Walling and his co-workers[34] have extended this work, showing that the reaction is free-radical in nature, and confirming the presence of both P—C and ester bonds in the product "phosphorates" as proposed by Willstätter and Sonnenfeld. In contrast to the conclusions drawn by the latter authors, however, Walling and his co-workers[34] have shown that the "phosphorates are polymeric anhydrides, containing both trivalent and pentavalent phosphorus". The proposed structure for the cyclohexene product is as shown below, with the nature of the end groups unspecified.



In those cases where the "phosphorate" produced is benzene soluble, additional oxygen is taken up to give an adduct of empirical formula, olefin · P_2O_5, where presumably both phosphorus atoms are at the P(V) level of oxidation. Walling and his co-workers did not investigate reactions involving olefin to phosphorus ratios of greater than 0.5, and in a more recent investigation by Cummins,[35] where ratios as high as 7.7 were used, two additional organophosphorus products were detected. Unlike the "phosphorates" these products were shown to be cyclic phosphonic acid esters, those produced in the reaction of styrene with phosphorus and oxygen having the structures given below.



(7)



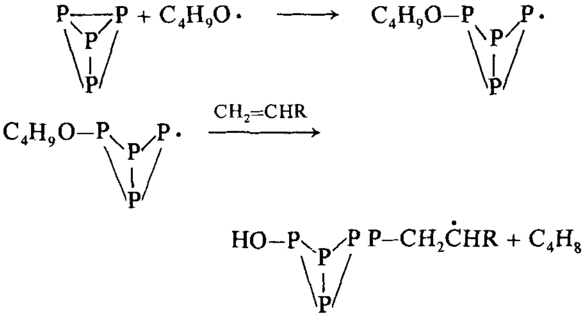
(8)

In reactions with styrene to phosphorus ratios ranging from 2.0 to 7.7, combined yields of (7) and (8) of between 70 and 75% were obtained and the ratio of (7) to (8) was found to increase with the ratio of styrene to phosphorus. Other olefins which give cyclic phosphonic acid esters by a similar reaction include cyclohexene, α-pinene, and 1-octene.

The related, but less efficient reaction of white phosphorus with an olefin and an organic peroxide has been investigated by Garwood and his co-workers.[36] The reaction takes place at 150–160°C giving a viscous yellow mixture of unidentified organophosphorus compounds. With di-*t*-butyl peroxide, the reaction may be represented by Eq. (1), where R is the radical derived from the olefin.

$$n(\text{Olefin}) + P_4 + (t\text{-BuO})_2 \longrightarrow R_nP_4O_2H_2 + 2C_4H_8 \quad (1)$$

A large excess of olefin is required to keep the phosphorus in solution, and with less than a 100% excess, some phosphorus is converted into polymeric red phosphorus solids. Under optimum conditions, the yield of organophosphorus products is ~30%. The authors envisage a mechanism involving initial attack of the *t*-butoxy radical on the P_4 tetrahedron to give an activated phosphorus molecule, which may then lose isobutylene and react with the olefin, as shown below.

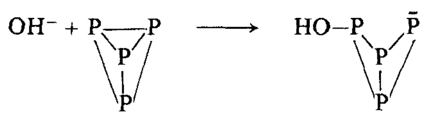


The products exhibit the properties of tertiary phosphines and weak acids, and on oxidation by nitric acid, give a mixture of phosphonic and phosphinic acids, containing only a small proportion of phosphoric acid, indicating that over 90% of the olefin was bonded directly to phosphorus. The reaction is clearly more complex than that involving oxygen, but demonstrates the ease with which phosphorus will add a radical species and undergo chain reactions to give organophosphorus products.

Finally, dialkyl phosphonates are reported to be formed by the introduction of oxygen into a suspension of white phosphorus in an alcohol.[37] The reactions are exothermic and the rate of addition of oxygen should be adjusted so as to keep the temperature of the mixture between 50 and 75°C. The highest yield was obtained with *n*-butanol (79%), but the reaction is reported to be general for alcohols. The reaction of oxygen with white phosphorus, in ethanol, has recently been reinvestigated,[38] and, in addition to diethyl phosphonate, ethyl hydrogen phosphonate, phosphorous acid, and condensed phosphorous acids were detected as products.

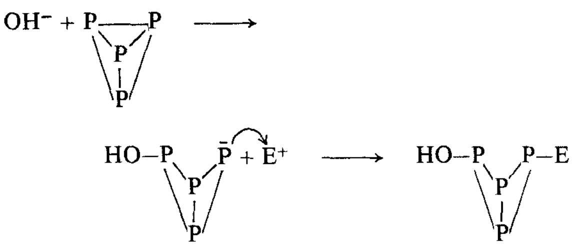
4 REACTION OF PHOSPHORUS WITH NUCLEOPHILES

The reactivity of elemental phosphorus with nucleophiles is illustrated by the well known reaction of white phosphorus with sodium hydroxide solution, which produces phosphine, hydrogen, sodium phosphite, and sodium hypophosphite.[38] Although the mechanism by which this reaction proceeds is not clearly understood, the first step appears to involve attack by the hydroxide anion on the P_4 tetrahedron, resulting in the cleavage of a P—P bond and the formation of a phosphide-type anion as shown below.



(9)

This behaviour suggests that a direct synthesis of an organophosphorus compound could be achieved by treatment of white phosphorus with sodium or potassium hydroxide solution, in the presence of an organic electrophile. In such a reaction, the first step would involve formation of the phosphide-type anion (**9**), which, being a nucleophile itself, could react with the electrophile to form a phosphorus–carbon bond.



(9)

Alternatively, organophosphorus compounds could be prepared by the direct reaction of white phosphorus with organic nucleophiles. A large number of direct syntheses of organophosphorus compounds involving nucleophilic attack on phosphorus have been reported in the literature and both of the methods described above have been exploited.

In 1861, August Wilhelm Hofmann successfully alkylated white phosphorus with ethyl iodide in the liquid phase.[40] The reaction was carried out in the presence of metallic zinc, and so may have been the first example of a nucleophilic reaction involving zinc alkyls. More recently, many examples of the reaction of phosphorus with metal alkyls or metal aryls have been reported. Schumann and Schmidt have investigated the reaction of tetraphenylstannane with elemental phosphorus in a sealed tube, and report that at temperatures above 250°C, the products are triphenylphosphine and tin phosphide,[41] as shown below.

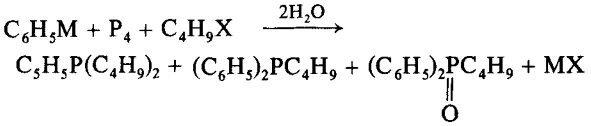
$$3Sn(C_6H_5)_4 + 4P_n \longrightarrow Sn_3P_{n-4} + 4P(C_6H_5)_3$$

They have shown, however, that if the temperature is kept between 235 and 250°C, and the ratio of the reagents is varied, intermediate products of the degradation of phosphorus by phenyl carbanions can be isolated. These intermediate compounds contain tin covalently bonded to phosphorus. Deacon and Parrott report a similar reaction,[42] in which tris-pentafluorophenylphosphine is produced in 70% yield, when elemental phosphorus and bis-pentafluorophenylthallium bromide are heated together in a sealed tube, at 190°C, for 4 days. Evidently this reaction can be used to arylate a number of non-metals besides phosphorus. The preparation of triarylphosphines by reaction of white phosphorus with an aryl halide and metallic magnesium at 200–250°C, has been reported by a group of Russian workers,[43] and presumably the reaction proceeds by nucleophilic attack of the aryl carbanion on phosphorus, as in the previous examples.

The first reactions of this type to be thoroughly investigated, were those reported in 1963 by Rauhut and his co-workers. This group showed that white phosphorus reacts rapidly with phenyl-lithium or with phenylmagnesium bromide in a suitable solvent, at 35–40°C, to give dark red solutions which on hydrolysis give mixtures of phenylphosphines, with the primary phosphine generally predominating.[44a] In its simplest terms the reaction might be expected to conform to the following equation.

$$C_6H_5Li + P_4 \longrightarrow Li_3P + Li_2PC_6H_5 + LiP(C_6H_5)_2 + P(C_6H_5)_3 \quad (2)$$

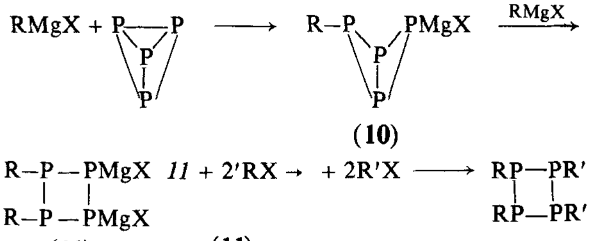
However, hydrolysis of such a mixture would give equal amounts of the primary, secondary, and tertiary phosphines, and would produce an equivalent amount of phosphine, which was not detected. In all of the reactions investigated, substantial amounts of yellow solids were obtained. These solids appeared to be cross-linked organopolyphosphines, and when phenylsodium or tri-isobutylaluminium was used as the organometallic reagent, they were the only products isolated. In view of this, it seems likely that the reaction intermediates are complex lithium phenylpolyphosphides, rather than the simple species shown in equation (2). Reactions of white phosphorus with *n*-butyl-lithium and with phenyl-lithium gave the corresponding primary phosphines in 9 and 40% yields, respectively, while *n*-butyl-magnesium bromide and phenylmagnesium bromide were found to give lower yields of the corresponding products. The organophosphide intermediates were shown to be capable of reacting with a variety of organic electrophiles, including the alkyl halides.[44b] For example, reaction of phenyl-lithium or phenylsodium with phosphorus and a butyl halide, followed by hydrolysis, gave dibutylphenylphosphine and butyldiphenylphosphine as the major products, together with small amounts of butyldiphenylphosphine oxide.



$$C_6H_5M + P_4 + C_4H_9X \xrightarrow{2H_2O} C_5H_5P(C_4H_9)_2 + (C_6H_5)_2PC_4H_9 + (C_6H_5)_2\underset{\underset{O}{\|}}{P}C_4H_9 + MX$$

The reactions were carried out in a suitable solvent at temperatures of about 40°C, and while the yields of individual products were found to vary slightly with conditions, the overall yields (70–80%) were apparently independent of the nature of the alkali metal cation, which is surprising, since straightforward hydrolysis of phenylsodium–phosphorus reaction mixtures was found to give no low molecular-weight products at all. The presence of substituent groups in the phenyl-lithium reagent had little effect on the course of the reaction, but treatment of phosphorus with 1-naphthyl-lithium and butyl bromide gave butyl(1-naphthyl)-phosphine and butylbis(1-naphthyl)phosphine in 35% and 18% yields, respectively. Phosphorus and a butyl halide were found to react similarly with butyl-lithium and with butylsodium giving substantial amounts of dibutylphosphine, although overall yields were lower than in reactions with the corresponding phenyl compounds. On the basis of their observations, Rauhut and his co-workers conclude that the intermediates in these reactions are complex organopolyphosphides, which have variable compositions depending on the reactant ratios. In addition, they suggest that the stability of these intermediates is due to resonance stabilization, and envisage a bonding scheme involving participation by phosphorus *d* orbitals.

In contrast to the behaviour of organolithium and organosodium compounds, butylmagnesium bromide reacts with phosphorus and butyl bromide to give tetrabutylcyclotetraphosphine as the major product. When the reaction is carried out in refluxing tetrahydrofuran, with a reactant ratio of 2 : 1 : 2 ($C_4H_9MgBr : P_4 : C_4H_9Br$), the cyclotetraphosphine is produced in 42% yield, along with a 6% yield of dibutylphosphine, and a trace of tributylphosphine, but when the ratio of Grignard reagent to P_4 is increased, the yield of the cyclic product is reduced. The reaction is though to proceed by the following mechanism.



(10)

(11) (11)

It is likely, however, that intermediates (**10**) and (**11**) can react further with unchanged phosphorus to give more complex phosphides, which are subsequently broken down to give the observed products. This simple, direct synthesis of a tetraalkylcyclotetraphosphine appears to be general for aliphatic Grignard reagents, and $(EtP)_4$ and $(PrP)_4$ have been prepared in comparable yields by this method.[45] However, the reaction of isopropylmagnesium bromide or cyclohexylmagnesium bromide with white phosphorus and the appropriate alkyl bromide is reported to give solid products of composition R_2P_8, where R is an isopropyl or a cyclohexyl group.[46]

More recently, Maier has investigated the reaction of dialkylamines with white phosphorus, in the presence of butyl-lithium.[47] The reaction is carried out in refluxing benzene, and is reported to be complete after 90 min, giving equimolar amounts of lithium dialkylaminophosphides and dilithium alkylaminophosphides, which are useful as catalysts for polymerization reactions.

$$BuLi + P_4 + NHR'R'' \longrightarrow LiP(NR'R'')_2 + Li_2PNR'R'' + BuH$$

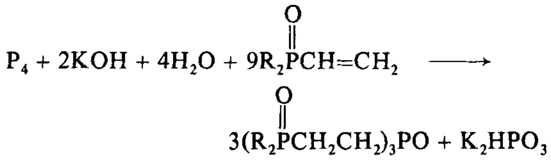
It is interesting to note that although this reaction is closely related to that reported by Rauhut and his co-workers,[44a] the products here are simple ions, rather than complex ones.

As already mentioned, an alternative method of directly synthesizing organophosphorus compounds involves the trapping, by organic electrophiles, of intermediates formed in the reaction of white phosphorus with sodium hydroxide. Early work by Michaelis and Pitsch showed that when phosphorus is treated with sodium hydroxide in aqueous ethanol, hydrogen is evolved and a solution of an unstable dark red intermediate is obtained.[48] Addition of methyl iodide to this solution, followed by oxidation with nitric acid, has been found to give methylphosphonic acid, dimethylphosphinic acid, and trimethylphosphine oxide,[49] indicating that the intermediate behaves as a nucleophile. Rauhut and his co-workers more recently studied the trapping of such intermediates by electrophiles,[50] and have prepared tris(2-cyanoethyl)phosphine oxide in as high as 53% yield, by reaction of white phosphorus with potassium hydroxide and acrylonitrile in ethanol at 0–35°C. The reaction can be expressed by the following equation.

$$P_4 + 2KOH + 4H_2O + 9CH_2{=}CHCN \longrightarrow 3(CNCH_2CH_2)_3PO + K_2HPO_3 \quad (3)$$

An analogous reaction using acrylamide as the organic electrophile gave tris(2-carbamoylethyl)phosphine oxide in 74% yield, under optimum conditions, while the reaction of ethyl acrylate with phosphorus and potassium hydroxide proceeded sluggishly, giving tris(2-carbethoxyethyl)phosphine oxide in only 8% yield, together with a 4% yield of tris(2-carbethoxyethyl)phosphine. The latter compound was probably formed by the base-catalysed addition of phosphine to ethyl acrylate, the phosphine having been produced by the normal phosphorus–hydroxide reaction. From Eq. (3), it can be seen that, at most, only 75% conversion of phosphorus into the phosphine oxide can be achieved in these reactions. Furthermore, the detection of potassium hypophosphite as well as potassium phosphite indicates that the normal phosphorus–hydroxide reaction does occur to some extent, and in practice this will result in even lower yields. Nevertheless, the formation of tris(2-carbamoylethyl)phosphine oxide in 74% yield indicates that the normal reaction can be suppressed almost completely, in the presence of an efficient trapping reagent.

Chisung Wu has recently reported two further examples of this reaction. In the first example diethyl vinylphosphonate is employed as the electrophile, and the reaction produces tris(diethoxyphosphinylethyl)phosphine oxide in high yield.[51a] In the second example, white phosphorus is treated with diethyl- or a diarylvinylphosphine oxide, in the presence of a base, to give the corresponding tertiary phosphine oxide.[51b] These reactions can be represented by Eq. (4), which is analogous to Eq. (3).

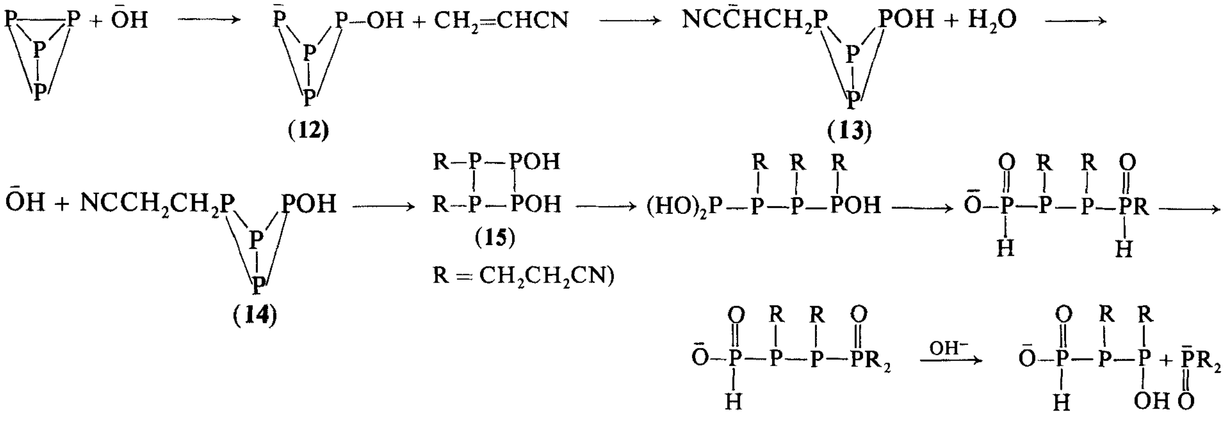


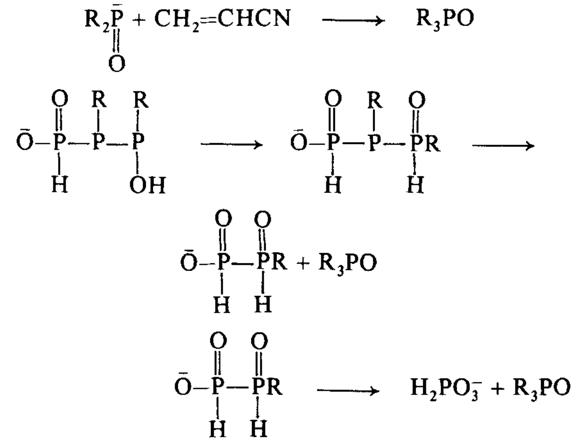
$$P_4 + 2KOH + 4H_2O + 9R_2\overset{\overset{\displaystyle O}{\|}}{P}CH{=}CH_2 \longrightarrow 3(R_2\overset{\overset{\displaystyle O}{\|}}{P}CH_2CH_2)_3PO + K_2HPO_3 \quad (4)$$

R = EtO, Et, or Ar.

Rauhut and his co-workers have shown that a solution of the unstable red compound described by Michaelis and Pitsch is not decolourized by acrylamide or acrylonitrile,[50] therefore they conclude that these compounds must trap an earlier intermediate in the reaction of phosphorus with potassium hydroxide, and propose the following reaction scheme to account for the observed products.

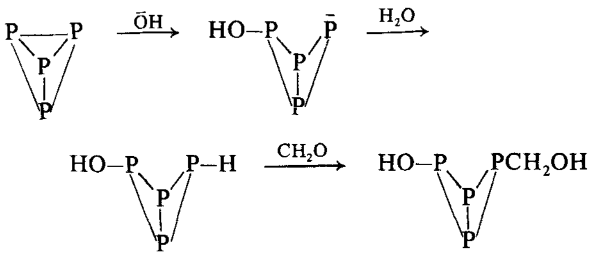
In this mechanism, the trivalent form of intermediates (**12**), (**13**), (**14**), and (**15**) is assumed to be more stable than the pentavalent form. Generally the reverse is true, but if this were the case these intermediates would react, under the conditions used, to give phosphonic or phosphinic acids which were not detected. The unusual stability of the trivalent form



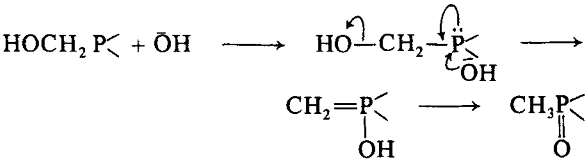


of these intermediates is probably due to the increase in ring strain which would occur as a result of tautomerism to the pentavalent structure.

The related reaction of white phosphorus with paraformaldehyde and aqueous methanolic alkali hydroxide was reported, by Praetzel, to give predominantly bis-hydroxymethylphosphinic acid.[52] However, a more recent investigation of the reaction by Maier[53] has shown the product to be a mixture of organophosphorus compounds, consisting of equal amounts (~30% each) of hydroxymethylphosphonic acid, bis-hydroxymethylphosphinic acid, and hydroxymethyl(methyl)phosphinic acid, together with traces of methylphosphonic acid and tris-hydroxymethylphosphine oxide. Since white phosphorus does not react with aqueous methanolic formaldehyde in the absence of a base, even at the reflux temperature,[54] Maier proposes that the first step involves attack by a hydroxide ion on the P_4 tetrahedron, as in the reactions reported by Rauhut and his co-workers.[50] The resulting phosphide ion might be expected to attack the carbonyl carbon of formaldehyde directly, but Maier suggests that, instead, it reacts with water forming a P–H bond, which then adds formaldehyde to give the hydroxymethyl group, as shown below.



This mechanism is not unreasonable, since formaldehyde has been shown to react with hypophosphorous acid, giving high yields of bis-hydroxymethylphosphinic acid.[55] The formation of products containing a methyl group directly bonded to phosphorus is less easily explained. One possibility is that the CH_3 group comes from the methanol, but this was rejected, since the same products are formed in about the same ratio, even when the reaction is carried out in ethanol. Reduction of the hydroxymethyl group by reaction with formaldehyde was also ruled out, and Maier suggests the following base-catalysed re-arrangement to be the most likely route.



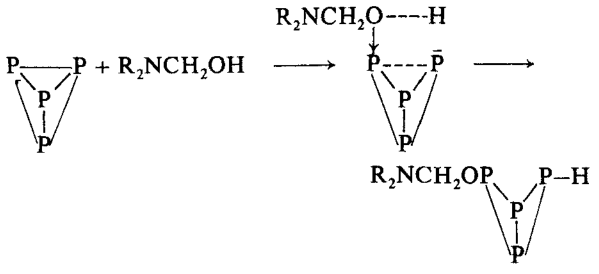
Elemental phosphorus can also react with formaldehyde in the presence of bases other than hydroxide ion, as shown by Maier in his studies of the α-aminoalkylation of white phosphorus.[54,56] In these investigations, white phosphorus was treated with formaldehyde and a dialkylamine, under a variety of conditions, to give dialkylaminomethylphosphonic acid, bis-dialkylaminomethylphosphinic acid, and tris-dialkylaminomethylphosphine oxide. The yield of the various products depends mainly on the ratio of the reactants, the pH, and the solvent used, and tris-dialkylaminomethylphosphine is also produced under some conditions. The reactive species is believed to be an *N*-hydroxymethyldialkylamine, formed by reaction of formaldehyde with the dialkylamine *in situ*, and the overall reaction can be represented by Eq. (5).

$$2P_4 + 18R_2NCH_2OH \longrightarrow R_2NCH_2P(O)(OH)_2 + 4(R_2NCH_2)_2P(O)OH + 2(R_2NCH_2)_3P + (R_2NCH_2)_3PO + 6H_2O \quad (5)$$

In view of the observed products, however, the reaction would seem to correspond more closely to the following equation, than to Eq. (5).

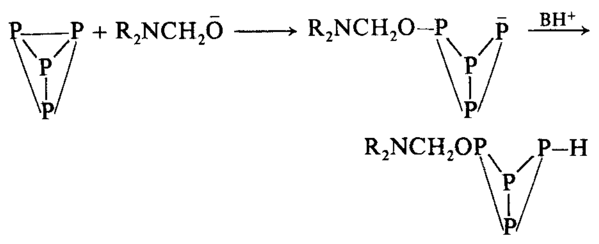
$$2P_4 + 20\ R_2NCH_2OH \longrightarrow R_2NCH_2P(O)(OH)_2 + 2(R_2NCH_2)_2P(O)OH + 5(R_2NCH_2)_3PO + 8H_2O \quad (6)$$

Although the reaction is accelerated by basic catalysts, it proceeds slowly at pH 7, and under these conditions a direct nucleophilic attack by the *N*-hydroxymethyldialkylamine on the P_4 tetrahedron has been postulated.



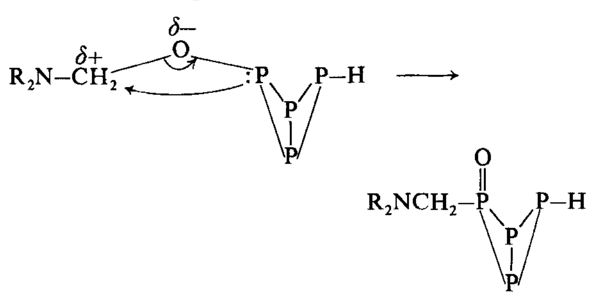
In basic medium, however, the following processes are thought to occur.

$R_2NCH_2OH + B \longrightarrow R_2NCH_2\bar{O} + BH^+$



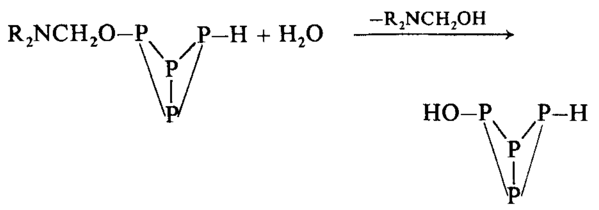
(16)

Maier suggests that, at this point, the unstable intermediate (**16**) may either undergo a Michaelis–Arbusov rearrangement to give intermediate (**17**),



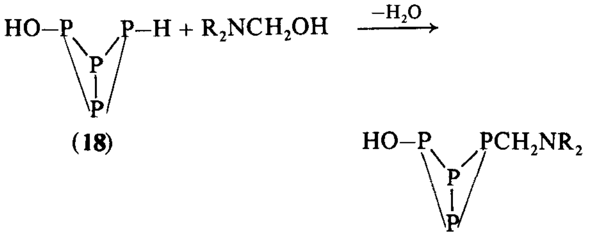
(17)

or may be hydrolysed to give intermediate (**18**).



(18)

In view of the stability of the trivalent form of these cyclic phosphorus intermediates, reported by Rauhut and his co-workers,[50] it seems unlikely that the former process can occur, and Maier, himself, favours the latter process. The final step in the sequence is thought to involve the condensation of intermediate (**18**) with the *N*-hydroxymethyldialkylamine to give intermediate (**19**).

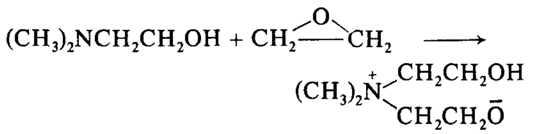


(18) **(19)**

The reaction then proceeds by repetition of the above steps, to give the observed products as shown in Scheme 2, where R′ represents the dialkylaminomethyl group.

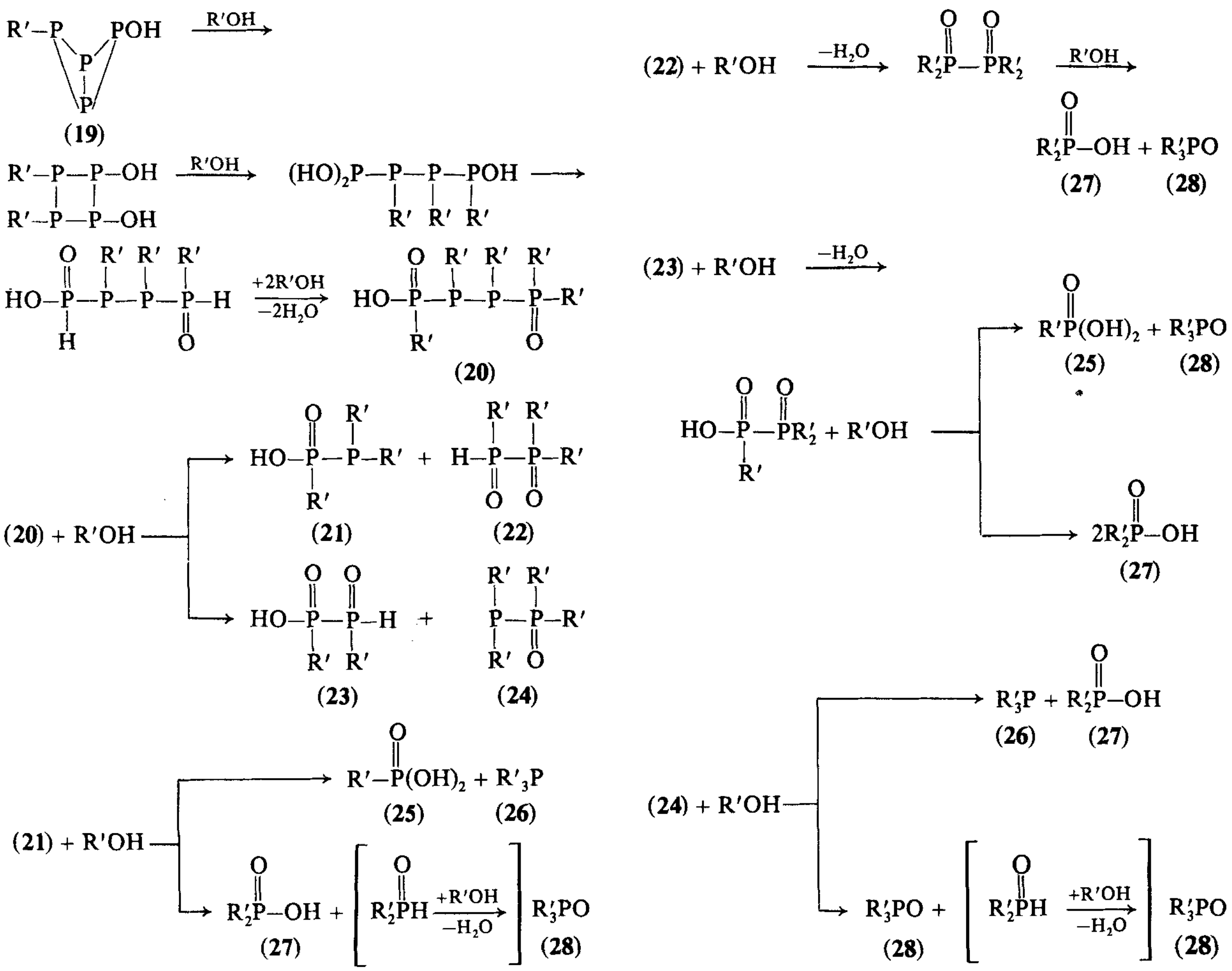
This reaction has been carried out with a variety of dialkylamines, and analogous reactions using an alkylamine as the amine component and formaldehyde or benzaldehyde as the carbonyl component have also been reported.[56b]

Chisung Wu and his co-workers have recently investigated the base-catalysed reaction of elemental phosphorus with a number of alcohol–epoxide mixtures.[57] Potassium alkoxides have been used to initiate these reactions, but *N,N*-dimethylethanolamine was found to be preferable, since it generates alkoxide species, as shown in Eq. (7), and also becomes incorporated into the product, through reaction of its hydroxyl group.



$$(CH_3)_2NCH_2CH_2OH + CH_2\overset{O}{—}CH_2 \longrightarrow (CH_3)_2\overset{+}{N}\begin{matrix}CH_2CH_2OH\\ CH_2CH_2\bar{O}\end{matrix} \quad (7)$$

The reactions were carried out at 70–90°C, and a reactant ratio of 1 g atom of phosphorus : 0.75 mol of epoxide : 0.75 mol of alcohol was employed in order to maintain a fluid, homogenous reaction mixture. Essentially complete conversion of phosphorus into organophosphorus compounds is achieved in these reactions, and the products, which are light yellow oils having high phosphorus contents, are reported to be complex mixtures which resist distillation and separation. Although individual compounds could not be identified by ^{31}P nmr spectroscopy, because of the broad, diffuse nature of the spectra, the following compound types were recognized from their chemical shift values, and their distribution was obtained by approximate integration of peak areas.

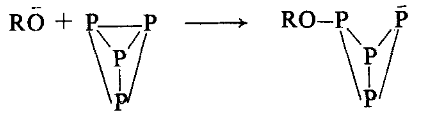


SCHEME 2

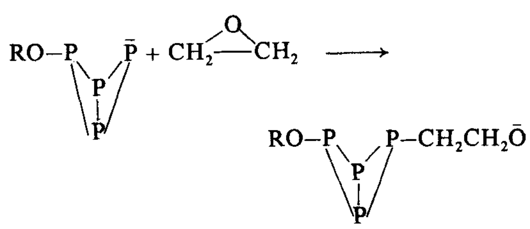
Compound type (R = alkyl group, R′ = alkyl or alkoxy group)	$R(H)P{-}H$	$R'_2P(O){-}H$	$R'_2P(O){-}R'$	$R'_2P{-}OR$
Distribution	7%	33%	42%	18%
Chemical shift	+150 to +160	−10 to −50	−50 to −60	−135 to −190

These reactions clearly proceed by a complex mechanism, but the following processes are thought to be involved.

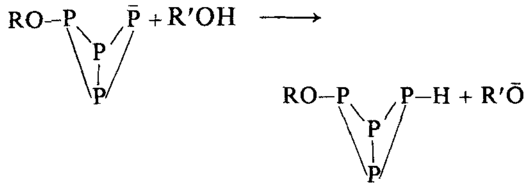
(a)



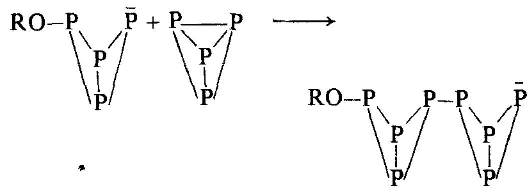
(b)



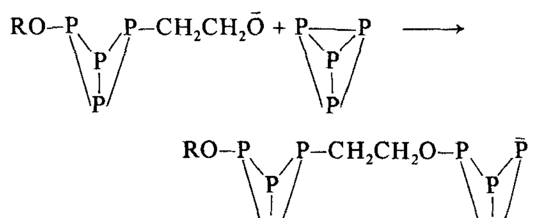
(c)



(d)



(e)



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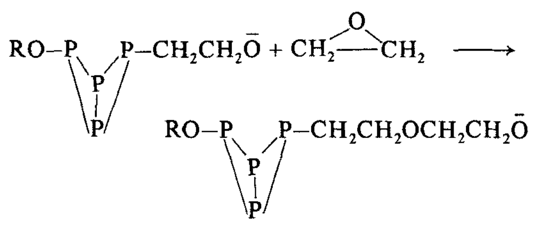
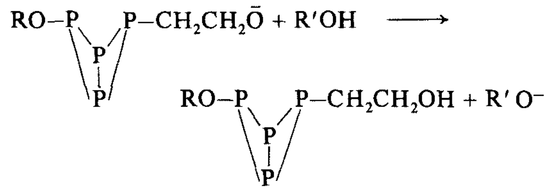


(g)



(h)

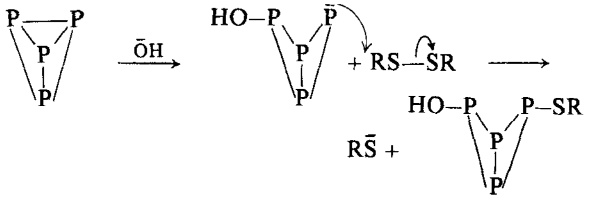
$$R'_2POR \longrightarrow R'_2\overset{\overset{O}{\|}}{P}R$$

The crude mixtures obtained from these reactions were subsequently treated with a formaldehyde reagent to produce colourless viscous mixtures of phosphorus polyols, which are useful as flame retardants for textiles.

Finally, another reaction reported by Chisung Wu, is of considerable preparative importance, since, in contrast to many other base-catalysed reactions of phosphorus, it gives a single organophosphorus product in essentially quantitative yield. The reaction involves white phosphorus and a dialkyl disulphide, and can be represented by the following equation.[58]

$$P_4 + 6RSSR \xrightarrow{B^-} 4(RS)_3P$$

The general procedure adopted by Wu, involved addition of a catalytic amount of 15N potassium hydroxide solution (~1 ml) to a stirred mixture of finely divided phosphorus (1 g atom) and a dialkyl disulphide (1.5 mol), in acetone (500 ml), under nitrogen at room temperature. The reaction is reported to be slightly exothermic, proceeding to completion within 30 min to give the corresponding trialkyl phosphorotrithioite in greater than 90% yield. In other dipolar aprotic solvents, such as acetonitrile, dimethylformamide, or dimethylsulphoxide, the reaction is reported to proceed equally quickly, but in protic solvents such as methanol, or in ethereal solvents such as tetrahydrofuran, it proceeds extremely slowly. The direct synthesis of trialkyl phosphorotrithioites from white phosphorus and dialkyl disulphides has been reported by several groups of workers,[5,59] but in each case the reactions were carried out in the absence of a base, under conditions which would result in homolysis of the disulphide, leading to free-radical processes. In contrast, the reaction reported by Wu is clearly ionic, and is thought to proceed by the following, relatively simple mechanism.



(29)

The phosphide-type anion produced by attack of hydroxide ion on the P_4 tetrahedron is a soft base, according to Pearson's concept of hard and soft acids and bases,[60] and as such would be expected to attack a disulphide readily, cleaving the sulphur–sulphur bond to give intermediate (**29**). The alkanethiolate anion also produced by such a process is itself a nucleophile and can attack elemental phosphorus, or intermediate (**29**), in the same way as hydroxide ion, hence the latter need only be present in catalytic amounts. All the P—P bonds are thus cleaved in a step-wise manner to give the trialkyl phosphorotrithioite in high yield.

This principle can be developed into a general synthetic method involving the simultaneous action of a nucleophile and suitable electrophile on elemental phosphorus. By introducing an electrophile, in particular positive halogen, the highly nucleophilic phosphide ion produced in the initial nucleophilic attack is immediately captured, thus preventing undesirable side reactions which participate in many of these reactions.

Sodium alkoxide reacts with white phosphorus in the presence of tetrachloromethane to give high yields of trialkylphosphite[61] according to the equation,

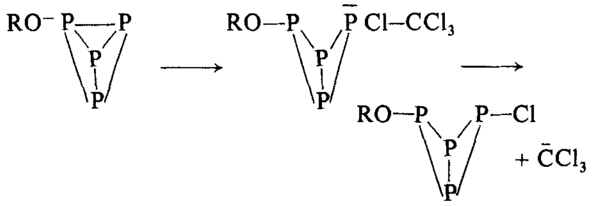
$$P_4 + 6NaOH + 6ROH + 6CCl_4 \longrightarrow 4(RO)_3P + 6CHCl_3 + 6NaCl$$

Side products, particularly dialkyl phosphonates are also produced, but these can be minimized by using an excess of alkoxide. Prolonged reaction also leads to partial conversion of phosphite to phosphate by the well known reaction,

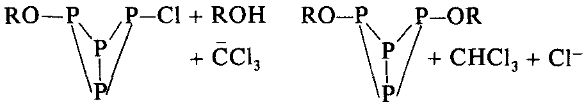
$$\begin{tikzcd}
(RO)_3P + CCl_4 \arrow[d] & \\
(RO)_3\overset{+}{P}Cl + \bar{C}Cl_3 \arrow[r] \arrow[d, "ROH"] & (RO)_3\overset{+}{P}CCl_3 + Cl^- \arrow[d] \\
(RO)_4\overset{+}{P}\,\bar{C}l + CHCl_3 \arrow[d] & (RO)_2\overset{O}{\overset{\|}{P}}CCl_3 + RCl \\
(RO)_3P{=}O + RCl &
\end{tikzcd}$$

Reaction times of the order of 1–3 hr, at room temperature, gave optimum yields of trialkylphosphite with negligible formation of side products.

The mechanism is thought to involve a rate determining attack by alkoxide ions on the phosphorus molecule with rapid reaction of the phosphide with tetrachloromethane to give an intermediate (**30**), which rapidly reacts with alkoxide to give (**31**).

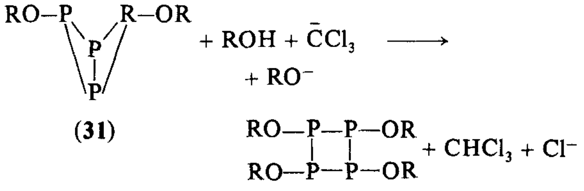


(30)



(31)

Complete conversion to trialkylphosphite can be achieved by a repetition of these processes, with the probably intermediate formation of cyclic tetraphosphites, (**32**),



(31) **(32)**

Phenoxide ions do not react in this way, but thiolate ions give trialkyl thioite. In the presence of 2-equivalents of sodium thiolate high yields of trialkyl phosphorotrithioites, with traces of disulphide and trialkyl triorthoformate are produced by direct reaction between sodium thiolate and tetrachloromethane. The yields of these side products increase as the proportion of sodium thiolate decreases.

$$4NaSR + CCl_4 + RSH \longrightarrow CH(SR)_3 + RSSR + 4NaCl$$

Under these conditions other phosphorus compounds are detected by ^{31}P nmr, in particular diethyl phosphorochloridothioite and diethyl trichloromethylphosphorodithioite.

However, under the optimum conditions, 85–95% conversion of phosphorus to trialkyl phosphorotrithioite is obtained.

REFERENCES

1. J. R. Van Wazer, *Phosphorus and its Compounds* (Interscience, New York, 1961), Vol. II, Chap. 31.
2. A. F. Toy, *Comprehensive Inorganic Chemistry*, 1973, **2**, Chap. 20.
3. M. M. Rauhut, *Topics in Phosphorus Chemistry*, edited by M. Grayson and E. J. Griffith (Interscience, N.Y., 1964), Vol. 1, p. 1.
4. M. Grayson, *Pure Appl. Chem.* **9**(2), 193 (1964).
5. N. G. Feshchenko, *Uspekhi, Khim. Fosfororg. Seraorg. Soedin* No. 2, 89 (1970).
6. L. Maier, *Fortschr. Chem. Forsch.* **19**, 1 (1971).
7. H. Staendeke, *Chem.-Ztg.* **96**(9), 494 (1972).
8. J. M. Crafts and R. Silva, *J. Chem. Soc.* **24**, 629 (1871); O. Masson and J. B. Kirkland, *J. Chem. Soc.* **55**, 135 (1889).

9. K. A Petrov, V. V. Smirnov and V. I. Emel'yanov, *Zhur. obschei Khim.* **31**, 3027 (1961).
10. L. Maier, *Helvetica Chimica Acta* **49**, 2458 (1966).
11. L. Maier, *Helvetica Chimica Acta* **46**, 2026 (1963); *Angew. Chem.* **71**, 574 (1959).
12. (a) B. M. Gladshtein and L. Z. Soborovskii, Russ. P. 130,513 (1960); (b) B. M. Gladshtein, L. N. Shitov, G. B. Kovalev and L. Z. Soborovskii, *Zhur obshchei Khim.* **35**, 1570 (1965); (c) B. M. Gladshtein and L. N. Shitov, *Zhur. obshchei Khim.* **37**, 2586 (1967).
13. H. Staendeke, G.P. 2,116,439 (1972) (*Chem. Abs.* **78**, 16309d (1973)); G.P. 2,255,395 (1974), (*Chem. Abs.* **81**, 49828n (1974)).
14. (a) F. W. Bennett, H. J. Emeléus and R. N. Haszeldine, *J. Chem. Soc.* 1565 (1953); (b) H. J. Emeléus and J. D. Smith, *J. Chem. Soc.* 375 (1959).
15. H. Brecht, G.P. 2,110,769 (1972) (*Chem. Abs.* **78**, 18654m (1973)).
16. C. G. Krespan, B. C. McKusik and T. L. Carins, *J. Amer. Chem. Soc.* **82**, 1515 (1960); C. G. Krespan, *J. Amer. Chem. Soc.* **83**, 3432 (1961).
17. C. G. Krespan and C. M. Langkammerer, *J. Org. Chem.* **27**, 3584 (1962).
18. (a) E. S. Levchenko, Y. V. Piven and A. V. Kirsanov, *Zhur. obshchei Khim.* **30**, 1976 (1960); (*Chem. Abs.* **55**, 6418i (1961); (b) A. V. Kirsanov and N. G. Feshchenko, Russ. P. 149,776 (1962) (*Chem. Abs.* **58**, 11401h (1963); (c) N. G. Feshchenko, T. I. Alekseeva and A. V. Kirsanov, *Zhur. obshchei Khim.* **33**, 1013 (1963) (*Chem. Abs.* **59**, 8782g (1963)).
19. N. G. Feshchenko, T. I. Alekseeva and A. V. Kirsanov, *Zhur. obshchei Khim.* **38**, 545 (1968) (*Chem. Abs.* **69**, 96838c (1968)).
20. (a) L. P. Zhuravleva, M. I. Z'ola, M. G. Suleimanova and A. V. Kirsanov, *Zhur. obshchei Khim.* **38**, 342 (1968) (*Chem. Abs.* **69**, 27484x (1968)); (b) N. G. Feshchenko, A. A. Koval and A. V. Kirsanov, *Zhur. obshchei Khim.* **40**, 2385 (1970).
21. N. G. Feshchenko and A. V. Kirsanov, *Zhur. obshchei Khim.* **36**, 564 (1966) (*Chem. Abs.* **65**, 742b (1966)); N. G. Feshchenko, T. I. Alekseeva, L. F. Irodionova and A. V. Kirsanov, *Zhur. obshchei Khim.* **37**, 473 (1967) (*Chem. Abs.* **67**, 32745w (1967)); N. G. Feshchenko, L. F. Irodionova, O. I. Korol and A. V. Kirsanov, *Zhur. obshchei Khim.* **40**, 773 (1970) (*Chem. Abs.* **73**, 25575m (1970)).
22. D. Perner and A. Henglein, *Z. Naturforsch.* **17b**, 703 (1962).
23. K. D. Asmus, A. Henglein, G. Meissner, and D. Perner, *Z. Naturforsch.* **19b**, 549 (1964).
24. P. Airey, H. Drawe and A. Henglein, *Z. Naturforsch.* **23b**, 916 (1968).
25. P. L. Airey, *Z. Naturforsch.* **24b**, 1393 (1969).
26. L. V. Kaabak, M. I. Kabachnik, A. P. Tomilov and S. L. Varshavskii, *Zhur. obshchei Khim.* **36**, 2060 (1966) (*Chem. Abs.* **66**, 85828m (1967)).
27. L. F. Filimonova, L. V. Kaabak and A. P. Tomilov, *Zhur. obshchei Khim.* **39**, 2174 (1969) (*Chem. Abs.* **72**, 38217a (1970)).
28. A. E. Presnov, A. P. Tomilov, V. K. Promonenkov and M. Ya. Fioshin, *Itogi Nauki, Elektrokhim.* **6**, 293 (1971) (*Chem. Abs.* **77**, 28046h (1972)); A. P. Tomilov, N. E. Khomutov and I. M. Osadchenko, *Encyclopedia of Electrochemistry of the Elements*, edited by A. J. Bard (Marcel Dekker Inc., New York, 1975), Vol. III, p. 34 (*Chem. Abs.* **83**, 138772y (1975)).
29. H. P. Angstadt, *J. Amer. Chem. Soc.* **86**, 5040 (1964).
30. A. I. Titov and P. O. Gitel, *Doklady Akad. Nauk S.S.S.R.* **158**, 1380 (1964) (*Chem. Abs.* **62**, 2791a (1965)).
31. A. H. Cowley and R. P. Pinnell, *Topics in Phosphorus Chemistry*, edited by M. Grayson and E. J. Griffith (Interscience, New York, 1967), Vol. IV, p. 1.
32. R. Boyle, *New Experiments and Observations Made upon the Icy Noctiluca* (London, 1681/2).
33. R. Willstätter and E. Sonnenfeld, *Berflsch. Chem. Ges.* **47**, 2801 (1914).
34. C. Walling, F. R. Stacey, S. E. Jamison and E. S. Huyser, *J. Amer. Chem. Soc.* **80**, 4543, 4546 (1958).
35. R. W. Cummins, *Chem. and Ind.* 918 (1967).
36. W. E. Garwood and L. A. Hamilton, U.S.P. 2,731,458 (1956) (*Chem. Abs.* **50**, 11361g (1956)); W. E. Garwood, L. A. Hamilton and F. M. Seger, *Ind. Eng. Chem.* **52**, 401 (1960).
37. M. L. Ernsberger and J. W. Hill, U.S.P. 2,661,364 (1953) (*Chem. Abs.* **49**, 1774a (1955)).
38. Yoshiki Okamoto and Hiroshi Sakurai, *Yukagaku* **19**, 968 (1970) (*Chem. Abs.* **74**, 12529v (1971)).
39. J. R. Van Wazer, *Phosphorus and Its Compounds* (Interscience, New York, 1958), Vol. I, p. 356.
40. A. W. Hofmann, *Liebigs Ann. Chem. Suppl.* **1**, 1 (1861).
41. H. Schumann and M. Schmidt, *Angew. Chem.* **77**, 1049 (1965).
42. G. B. Deacon and J. C. Parrott, *J. Organometal. Chem.* **17**, 17 (1969); **22**, 287 (1970).
43. L. V. Kaabak, S. L. Varshavskii, M. I. Kabachnik, N. E. Myagkaya and L. A. Koshecchkina, Russ. P. 347,333 (1972) (*Chem. Abs.* **78**, 4358f (1973)).
44. (a) M. M. Rauhut and A. M. Semsel, *J. Org. Chem.* **28**, 471; (b) 473 (1963).
45. A. H. Cowley and R. P. Pinnell, *Inorg. Chem.* **5**, 1463 (1966).
46. H. G. Ang, (cited by B. O. West) *Record Chem. Progr.* **30**, 249, Ref. 10 (1969).
47. L. Maier, G.P. 1,244,180 (1967) (*Chem. Abs.* **67**, 99629e (1967)).
48. A. Michaelis and M. Pitsch, *Berflsch. Chem. Ges.* **32**, 337 (1899); *Liebigs Ann. Chem.* **310**, 45 (1899).
49. V. Auger, *Compt. rend.* **139**, 639 (1904).
50. M. M. Rauhut, R. Bernheimer and A. M. Semsel, *J. Org. Chem.* **28**, 478 (1963).
51. (a) Chisung Wu, U.S.P. 3,420,917 (1969) (*Chem. Abs.* **70**, 58018y (1969)); (b) U.S.P. 3,458,581 (1969) (*Chem. Abs.* **71**, 102007r (1969)).
52. H. E. Praetzel, G.P. 1,249,274 (1967) (*Chem. Abs.* **67**, 109269d (1967)).
53. L. Maier, *Z. Anorg. Chem.* **394**, 117 (1972); U.S.P. 3,776,953 (1973) (*Chem. Abs.* **80**, 48162h (1974)).
54. L. Maier, *Helv. Chim. Acta* **50**, 1723 (1967).
55. L. Maier, *Helv. Chim. Acta* **52**, 827 (1969).
56. (a) L. Maier, *Angew. Chem.* **77**, 549 (1965); (b) *Helv. Chim. Acta* **51**, 1608 (1968).
57. E. J. Boros, W. M. Lanham and Chisung Wu, *Ind. Eng. Chem., Prod. Res. Develop.* **12**(3), 221 (1973).
58. Chisung Wu, *J. Amer. Chem. Soc.* **87**, 2522 (1965).
59. D. R. Stevens and R. S. Spindt, U.S.P. 2,542,370 (1951) (*Chem. Abs.* **45**, 5712g (1951)); M. Scheffler, H. Drawe and A. Henglein, *Z. Naturforsch.* **23b**, 911 (1968).
60. R. G. Pearson and J. Songstad, *J. Amer. Chem. Soc.* **89**, 1827 (1967).
61. C. Brown, R. F. Hudson, G. A. Wartew and H. Coates, *J.C.S. Chem. Comm.* **7** (1978).