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Elemental phosphorus-strong base as a system for the synthesis of organophosphorus compounds

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ABSTRACT. A systematic review is presented on the reactions of elemental phosphorus with organic compounds in the presence of base, proceeding via polyphosphide and polyphosphinite anions. Particular attention has been paid to new effective methods of activating red phosphorus by superbase complexes, formed from alkali metal hydroxides and polar, non-hydroxylic solvents (HMPA, DMSO, DMF, triethylphosphine oxide), by the sodium/liquid ammonia system, or under phase transfer catalysis. The direct phosphorylation of organic halides, activated alkenes, acetylenes and oxiranes is also discussed.

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I. Introduction

Organophosphorus compounds occupy an important place in the chemistry of elementoorganic compounds. Their influence on living organisms is well known,[1] and a wide spectrum of organophosphorus compounds has been prepared for use as extractants,[2,3] antipyretics[4,5] and emulsifiers,[6,7] as fuel additives and in lubricating materials,[8,9] as plasticizers,[10,11] and as biologically active agents for medicinal and agricultural application.[12,13] Triorganophosphines and -phosphine oxides have also been used, and are currently being developed, as effective ligands for complex metal catalysts.[10,14–16]

Organophosphorus compounds with a P–C bond are usually prepared from phosphorus halides or phosphines, which are toxic and ecologically unsuitable for industrial-scale syntheses. Furthermore, it is reported that many important organophosphorus compounds prepared from phosphorus chlorides have been threatened with liquidation because "hydrogen chloride, a by-product, corrodes steel apparatus and leads to the formation of a number of poisonous compounds in the aqueous effluent. For each ton of useful product, around six tons of effluent are produced, the refinement of which is sometimes more costly than that of the product itself".[17]

In view of this, the synthesis of organophosphorus compounds from elemental phosphorus (primarily from non-toxic and non-flammable red phosphorus) has attracted far more interest both from the point of view of the simplicity of the procedures and the fact that organophosphorus compounds can be prepared by this means in one step. The ecological advantages of this methodology also enhances the marketability of organophosphorus compounds in the difficult times which the economy faces.[17]

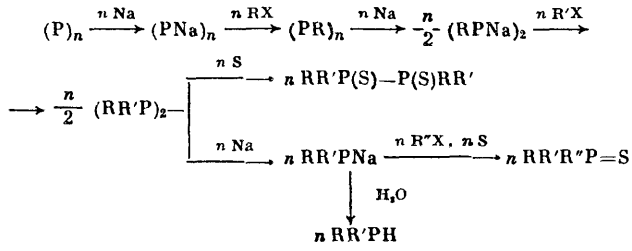
Information published prior to 1979 on the reactions of elemental phosphorus with organic compounds has been covered systematically in five short reviews.[18–22] It is pointed out in these that classical phosphorylation is normally carried out with white phosphorus at high temperatures (200–400 °C), i.e. under conditions for radical initiation.

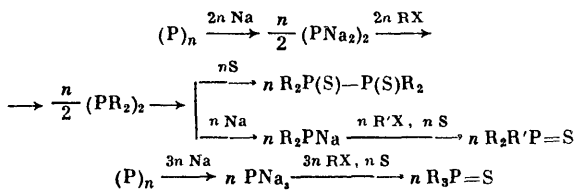
In the present review we have surveyed data on the reactions of elemental phosphorus with electrophilic agents in the presence of strong base. This relates to information published in the last 10–15 years, during which time a number of novel and effective routes to organophosphorus compounds (notably organic phosphines and phosphine oxides) have been developed. Among these new procedures for phosphorylation, much attention has been paid to syntheses with red phosphorus, which may be activated by superbases, such as Na/liquid ammonia,[23–25] alkali metal hydroxide in polar, non-hydroxylic solvent (e.g. HMPA, DMSO),[26–28] or under phase transfer catalysis.[28–30] It should be emphasised that the superbase system, KOH–DMSO (or KOH–HMPA), has already been successfully utilised for direct chalcogenation with elemental sulphur and metallic selenium or tellurium. Here, the superbasic hydroxide ion reacts with the chalcogen to generate the milder, more nucleophilic chalcogen anions, which react subsequently with suitable electrophiles (notably acetylenes).[31–33]

II. Reactions of elemental phosphorus with organic halides in superbasic systems

In 1966, Bogolyubov and Petrov published for the first time a general procedure for carrying out reactions of red phosphorus with organic halides in the presence of the classical superbasic system, Na/liquid ammonia.[23,24] This resulted in the development of new routes to organic phosphines and their derivatives. Depending on the proportion of the reactants, the process takes place with the

participation of polyphosphide anions, according to the following generalised scheme:[23]

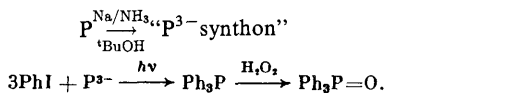




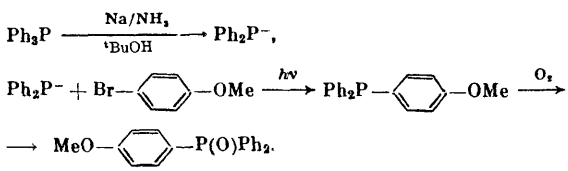
R=Me, Et, $PhCH_2$; X=Cl, Br, I.

The products are obtained in 17–34% yield.

Continuing this theme, the direct phosphorylation of aryl halides with red phosphorus was subsequently carried out with the system, Na/liquid ammonia, under UV-activation.[25] As a result, an effective route to symmetrical and unsymmetrical triarylphosphine oxides has been developed. Thus, triphenylphosphine oxide was obtained in 75% yield from iodobenzene and red phosphorus, followed by oxidation of the intermediate triphenylphosphine with hydrogen peroxide.[25]



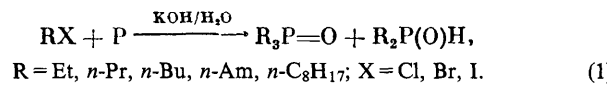
p-Anisyldiphenylphosphine oxide was prepared in 55% yield by treatment of triphenylphosphine with *p*-bromoanisole in the system, Na/liquid ammonia, under irradiation on exposure to air.[25]



The authors of this research[25] did not provide additional supporting evidence in favour of the ion-radical mechanism which they proposed. There was no reference to an earlier finding that there is a noticeable increase in the rate of the reaction of diphenylphosphide[34] and diphenylphosphinite ion[35] with aryl halides on UV-irradiation in the systems, potassium *tert*-butoxide/liquid ammonia and potassium *tert*-butoxide/DMSO.

The same authors[25] also consider that an ion-radical mechanism prevails for the reaction of aryl halides with elemental arsenic and antimony on UV-irradiation in the system, Na/liquid ammonia. The yield of triphenylarsine and triphenylstibine by this procedure was 75% and 40%, respectively. No indication was given by the authors[23–25] of the manner in which they calculated the product yield.

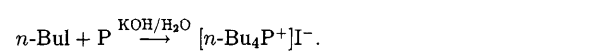
Superbases generated under phase transfer catalysis (50–60% aqueous solution with an organic solvent in the presence of a phase transfer catalyst)[36,37] have been used for the synthesis of trialkylphosphine oxides from alkyl halides and red phosphorus.[28,29,38,39] The reaction also produces a small amount of the corresponding dialkylphosphinous acid.[29]



(1)

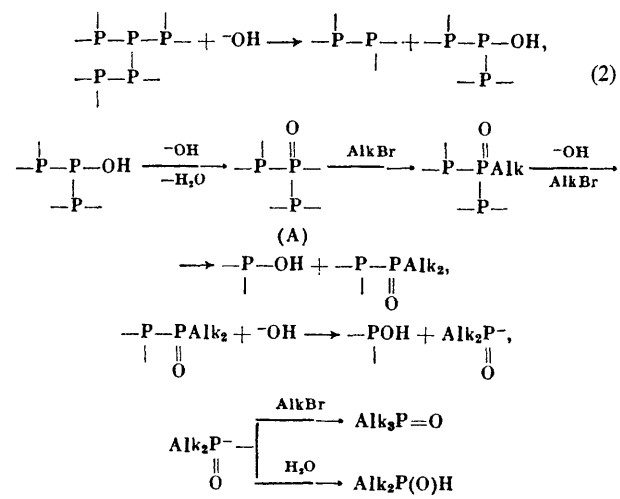
Under optimum conditions (on heating at 93–95 °C for 6–7 h with dioxane as the organic solvent), the yield of trialkylphosphine oxides was 60–65% (based on the alkyl halide).[28]

In studying the above reaction with butyl halides, it was found that butyl bromide was the most suitable substrate. The yield of tributylphosphine oxide was noticeably less with butyl chloride under the same conditions, while butyl iodide reacted with red phosphorus to give a low yield of tetrabutylphosphonium iodide.[29]



It should be stressed that tiralkylphosphines were not detected among the products of reaction (1), even on carrying out the conversion under argon.

Evidently, the interaction of alkyl bromides with the system, P–KOH–H_2O, proceeds with the participation of the polyphosphinite anion (A), formed by cleavage, with hydroxide ion, of a P–P bond of the irregular trimeric phosphorus clusters which unite the red phosphorus macromolecule.[40]



(2)

On heating benzyl chloride with red phosphorus in the system, KOH–DMSO (or KOH–HMPA), at 70–80 °C, tribenzylphosphine oxide (I) was isolated as the main product in 30% yield

(based on benzyl chloride), together with small amounts of tribenzylphosphine (II) and tetrabenzylphosphonium chloride (III).[41]

$$PhCH_2Cl + P \xrightarrow{KOH/DMSO} \underset{(I)}{(PhCH_2)_3P{=}O} + \underset{(II)}{(PhCH_2)_3P} + \underset{(III)}{[(PhCH_2)_4P^+]Cl^-}. \quad (3)$$

The process is thought to involve generation of polyphosphide ions by action of the superbase on red phosphorus, followed by reaction with benzyl chloride. This leads to tribenzylphosphine (II), which is then quaternized with a further molecule of benzyl chloride to give the phosphonium chloride (III) prior to its reaction with base to give the phosphine oxide (I). Toluene, eliminated in the final step of the reaction was identified by g.l.c.[29]

$$P_n + {}^-OH \rightarrow P_m^- + P_k{-}OH,$$

$$P_m^- + 3PhCH_2Cl \longrightarrow (PhCH_2)_3P_m \xrightarrow[-P_{m-1}]{} \underset{(II)}{(PhCH_2)_3P} \xrightarrow{PhCH_2Cl} \underset{(III)}{[(PhCH_2)_4P^+]Cl^-} \xrightarrow{KOH} [(PhCH_2)_4P^+]OH^- \xrightarrow[-PhMe]{} \underset{(I)}{(PhCH_2)_3P{=}O}.$$

Since only traces of dimethyl sulphide were detected during the course of the reaction, it can be assumed that the phosphine oxide (I) is not formed from the corresponding phosphine (II) by oxidation with DMSO.[29]

The selectivity and efficiency of conversion (3) can be increased by carrying out the reaction in the 3-phase system comprising red phosphorus, aqueous KOH, dioxane, and benzyltriethylammonium chloride at 94–96 °C. The yield of the phosphine oxide (I) under these conditions increases to 50% on complete conversion of phosphorus.[28,42]

Heating allyl halides with red phosphorus at 60–65 °C in the system, KOH–H_2O–THF containing benzyltriethylammonium chloride, affords *tris*-(*E*-propen-1-yl)phosphine oxide as well as the expected *tris*(propen-2-yl)phosphine oxide.[28,29,43,44]

$$CH_2{=}CHCH_2X + P \xrightarrow{KOH/H_2O} \underset{35\%}{(E\text{-}MeCH{=}CH)_3P{=}O} + \underset{30\%}{(CH_2{=}CHCH_2)_3P{=}O}$$

X=Cl, Br.

1,1-Dialkoxy-2-bromoethanes also serve as electrophile. Thus, heating these compounds in the system, P–KOH–DMSO, at 70–100 °C in the presence of a small amount of water provides the corresponding *tris*(2,2-dialkoxyethyl)phosphine oxide in up to 15% yield. The products are potentially useful synthons, having three protected aldehyde functions.[45]

$$(RO)_2CHCH_2Br + P \xrightarrow{KOH/H_2O} [(RO)_2CHCH_2]_3P{=}O$$

R = Et, *n*-Bu

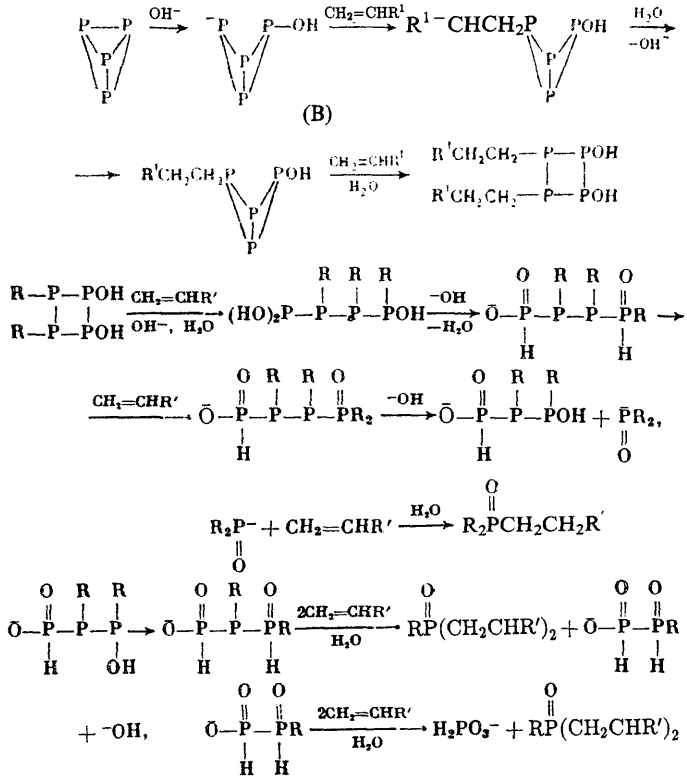
A brief reference has been made to the alkylation of red phosphorus with butyl bromine in the superbasic system, KOH–hydrazine hydrate.[46] When the molar proportion of P : KOH : BuBr is 1 : 12 : 3, reaction proceeds on heating at 80–85 °C, and is reported to lead, not only to tributylphosphine oxide, but also to a small proportion of tributylphosphine. The latter evidently forms by reduction of the phosphine oxide with hydrazine hydrate. Further products were also isolated in 8 and 1.4% yield (based on butyl bromide), but, unfortunately, these were unidentified.

III. Phosphorylation of alkenes with elemental phosphorus in the presence of base

Some interesting results have been obtained by studying the reaction of white phosphorus with acrylonitrile and acrylamide in the presence of KOH.[47] The reaction was conducted at –5 to 35 °C in a system containing an organic solvent (acetonitrile) and 10 N aqueous KOH under an inert atmosphere. The principal products of the reaction were *tris*(2-cyanoethyl)phosphine oxide and *tris*(2-carbamoylethyl)phosphine oxide, the optimum yields of which were 53 and 74%, respectively (based on phosphorus).

$$P_4 + 2KOH + 4H_2O + 9CH_2{=}CHR \rightarrow 3(RCH_2CH_2)_3P{=}O + K_2HPO_3,$$
$$R = CN,\ CONH_2.$$

In the opinion of the authors,[47] reaction is initiated by attack of hydroxide ion on the tetrahedral white phosphorus clusters to give the phosphide anion (B), which then undergoes Michael addition to the activated double bond of the starting alkene:



R=CH_2CH_2R', R'=CN or $CONH_2$.

Subsequently, the same reaction was performed with *N*-alkyl- and *N,N*-dialkyl-acrylamides to give the corresponding *N*-substituted *tris*(2-carbamoylethyl)phosphine oxides in 45–87% yield (based on phosphorus).[48]

$$P_4+2KOH+4H_2O+9CH_2=CHCONR^1R^2\rightarrow$$
$$\rightarrow 3(R^1R^2NCOCH_2CH_2)_3P=O+K_2HPO_3,$$
$$R^1=Me,\ R^2=H\ (45\%);\ R^1=R^2=Et\ (87\%);$$
$$R^1=R^2=CH_2CH=CH_2\ (72\%);\ R^1-R^2=(CH_2)_4\ (75\%);$$
$$R^1-R^2=(CH_2)_5\ (84\%).$$

Vinyldiorganophosphine oxides and sulphides,[48] and dialkyl vinylphosphonates,[49] also undergo Michael addition with phosphide ions (generated from yellow phosphorus and KOH) under mild conditions (25–30 °C) to give the corresponding functionalised phosphine oxide (in 50–100% yield).

$$P_4+KOH+H_2O\xrightarrow{R_2P(X)CH=CH_2}[R_2P(X)CH_2CH_2]_3P=O$$
$$\xrightarrow{(AlkO)_2P(O)CH=CH_2}[(AlkO)_2P(O)CH_2CH_2]_3P=O$$
$$R=Alk,\ Ar;\ X=O,\ S.$$

Recently, it was found that styrene and 4-vinylpyridine may also be phosphorylated with red phosphorus in the system, KOH–DMSO or KOH–HMPA.[50,51] Thus, the phosphorylation of styrene at 75–125 °C affords *tris*(2-phenylethyl)phosphine oxide (IV) in 65% yield (based on styrene) together with a small amount of *bis*(2-phenylethyl)phosohinous acid (V).[28,50]

$$P+PhCH=CH_2\xrightarrow[KOH/DMSO/H_2O]{KOH/HMPA/H_2O}\underset{(IV)}{(PhCH_2CH_2)_3P=O}+$$
$$+\ \underset{(V)}{(PhCH_2CH_2)_2P(O)H}. \qquad (4)$$

For the above reaction, the system, KOH–HMPA–H_2O, is somewhat more effective than the system, KOH–DMSO–H_2O. However, the base generated in the system, 70% aqueous KOH–dioxane– benzyltriethylammonium chloride, is not strong enough to activate the process, only traces of (IV) being detected. Neither the standard radical initiator, azodiisobutyronitrile, nor the radical quencher, hydroquinone, have any effect on the reaction. Evidently, a polyphosphinite anion is involved in the formation of (IV) and (V), i.e. the reaction takes place in the same manner as the previously described phosphorylation of alkyl halides, as outlined in scheme (2).[29]

4-Vinylpyridine reactions in the same way with red (or white) phosphorus in the system, KOH–DMSO–H_2O, leading to *tris*-[2-(4-pyridyl)ethyl]phopshine oxide in 20% yield.[51]



In spite of the lowish yields, the method described above is of preparative value since, at present, there are no other available routes to functionalised phosphine oxides, which are key synthetic intermediates and synthons.

IV. The interaction of elemental phosphorus with alkynes in the presence of superbase

By studying the reactions of phenylacetylene, it was shown for the first time that red phosphorus interacts with acetylenes on heating (at 60–90 °C) in the system, alkali metal hydroxide-polar (non-hydroxylic) solvent (HMPA, DMSO, DMF, Et_3PO), as well as under phase transfer catalysis (aqueous alkali metal hydroxide-organic solvent-phase transfer catalyst). Thus, phenylacetylene affords *tris*(*Z*-styryl)phosphine (VI) in up to 44% yield (based on the alkyne) together with a small amount of *tris*(*Z*-styryl)phosphine oxide (VIII).[26–28,39,44,52–58]

$$PhC\equiv CH+P\xrightarrow{KOH/H_2O}\underset{(VI)}{(Z\text{-}PhCH=CH)_3P}+$$
$$+\ \underset{(VII)}{(Z\text{-}PhCH=CH)_3P=O}.$$

Evidently, reaction involves attack of the triple bond by polyphosphide anion, P_m^- generated from red phosphorus and the superbase.[28]

$$P_n+{}^-OH\rightarrow P_nOH+P_m^-,$$
$$P_m^-+HC\equiv CPh\longrightarrow P_mCH=\bar{C}Ph\xrightarrow[-OH^-]{H_2O}P_mCH=CHPh\xrightarrow[-P_kOH]{-OH}$$
$$\longrightarrow PhCH=CHP_g^-\xrightarrow[H_2O]{PhC\equiv CH}(PhCH=CH)_2P_g\xrightarrow[-P_hOH]{OH^-}$$
$$\longrightarrow (PhCH=CH)_2P_e^-\ \text{etc.}$$

According to ^1H and ^{31}P NMR spectroscopic data, all the styryl groups in (VI) and (VII) are in the *Z*-configuration, i.e. of the four possible stereoisomers, only the *Z,Z,Z*-isomer is formed. This would be anticipated as *trans*-nucleophilic addition to triple bonds in the norm.[28]

For the phosphorylation of phenylacetylene, the 2-phase systems, KOH–DMSO, KOH–Et_3PO and KOH–DMF, and the 3-phase system comprising red phosphorus, 50–70% aqueous KOH and an organic solvent (THF, toluene, dioxane), with or without benzyltriethylammonium chloride,[28] are less effective than the system, KOH–HMPA. Replacement of KOH by NaOH under the same conditions leads to a clear (3-fold) decrease in the yield of (VI).

At the same time, the activity of red phosphorus towards phenylacetylene is enhanced on ultrasonic irradiation in the presence of a strong base. Under these conditions, reaction takes place without external heating, and the yield of (VI) is increased by 50% while the reaction time is reduced to 1 h.[52]

The reaction of phenylacetylene with red phosphorus proceeds equally well under inert atmosphere and on exposure to air. The yield of the phosphine oxide (VII) is always around 2–4%.[28]

Naturally, the question arises: why is it that phenylacetylene affords the corresponding phosphine (VI) almost exclusively, while, under the same conditions, styrene and 4-vinylpyridine afford predominantly the corresponding phosphine oxide? In the original publications,[26,28,50,51] there was no comment on this anomaly. One possible explanation is the competing behaviour of the two different types of P-nucleophile (i.e. the polyphosphide and polyphosphinite anions). With alkynes, the polyphosphide anion is more complementary (according to the principle of hard and soft acid and

base), while the polyphosphinite anion (A) is more complementary with alkenes.

More recently, phosphorylation of acetylene with red phosphorus was carried out under pressure at 105–115 °C in the system, KOH–hydrazine hydrate–aqueous HMPA.[46] Trivinylphosphine was identified in the reaction product by chromato-mass spectrometry. A 10% yield was quoted, but the method by which the yield was calculated was not given. It was not possible to isolate the product nor characterise it further.[46]

V. Reactions of elemental phosphorus with oxygen- and sulphur-containing compounds in the presence of base

By studying the reactions of α-aminoalcohols, Maier was first to demonstrate that white phosphorus reacts with such compounds by an ionic mechanism via intermediate formation of polyphosphide and polyphosphinite ions.[59,60] Almost equal amounts of the corresponding *tris*(dialkylaminomethyl)phosphine oxide (VIII), *bis*(dialkylaminomethyl)phosphinic acid (IX), and dialkylaminomethylphosphonic acid (X) were obtained in a total yield of 90% (based on phosphorus).

$$2P_4+20R_2NCH_2OH \rightarrow \underset{(VIII)}{5(R_2NCH_2)_3P=O}+$$
$$+\underset{(IX)}{2(R_2NCH_2)_2P(O)OH}+\underset{(X)}{R_2NCH_2P(O)(OH)_2}+8H_2O.$$

R_2N = Me_2N, Et_2N, C_4H_8N, $C_5H_{10}N$, $CH_2CH_2OCH_2CH_2N$, $(n\text{-Bu})_2N$, $(cyclo\text{-}C_5H_{11})_2N$.

It was not possible to carry out this reaction with red phosphorus.[60]

Later, a series of publications appeared on the interaction of white phosphorus with alcohols and alkali metal alkoxides in carbon tetrachloride at 50–60 °C under N_2, leading to the formation of trialkyl phosphites as the main product (in 70–80% yield), together with small amounts of trialkyl phosphates and dialkyl alkanephosphonates (in up to 10% yield).[61–66]

$$P_4+ROH+ROM+CCl_4 \rightarrow (RO)_3P+(RO)_3P=O+(RO)_2P(O)R,$$

M – alkali metal, R = Alk.

This reaction involves initial nucleophilic attack of the P–P bond of the phosphorus cluster with alkoxide, as proposed by Brown, et al.[66]

$$P_4+6RO^-+6ROH+6CCl_4 \rightarrow 4(RO)_3P+6CHCl_3+6Cl^-.$$

The reaction of white phosphorus with sodium alkylmercaptides in the presence of the corresponding mercaptan and an excess of CCl_4 proceeds in a similar way at room temperature. Trialkyl trithiophosphites were thus obtained in high yield.[67,68]

$$P_4+6RSH+6RSNa+6CCl_4 \rightarrow 4(RS)_3P+6CHCl_3+6NaCl,$$

R = Et, *n*-Bu.

The corresponding dialkyl disulphides and *tris*(alkylthio)methanes were formed as by-products.

The reaction of white phosphorus with alkali metal phenoxide and CCl_4 in an aprotic dipolar solvent (DMF at 0–100 °C under a dry, inert atmosphere) leads to a mixture of organophosphorus compounds, of which the main component is triphenyl phosphite (70% yield).[69]

$$P_4+PhOM+PhOH+CCl_4 \rightarrow (PhO)_3P+ClCH_2P(OPh)_2+$$
$$+Cl_2CHP(OPh)_2+[(PhO)_2P]_2CH_2,$$

M – alkali metal.

Recently, Ivanov, et al. extended this reaction to other phenols (in the presence of the corresponding phenoxide), and found that the composition and yield of product depends on the acidity of the phenol and the nature of the ring substituent.[70] Phenols with a pK_a in the range 9–11 participate in this reaction.

A number of patents has appeared on the reaction of phosphorus (white or yellow) with alcohols and epoxy compounds in the presence of a catalyst (alkali or alkaline earth hydroxide or alkoxide) at 25–200 °C.[71–76] The products of the reaction have P–H, P–C and P–O linkages in varying proportion, the molecular formula approximating to $(RO)_{3-n}PR'_n$ (where R is an alkyl radical from the alcohol, and R′ = H or a ZOH residue, where Z represents an alkylidene (–C–C–) residue formed by cleavage of the epoxide). These products are potentially useful for the preparation of surface-active compounds and as epoxy resin hardeners.

White phosphorus reacts with alkene oxides in the presence of compounds with an acidic hydrogen and metal alkoxides (or amides) to give phosphorus-containing polyols.[77–79] This reaction was studied in more detail by Ivanov, et al.,[80] who found that a mixture of P_4, propylene oxide, Me_3N and HX (HX = $MeCO_2H$, PhOH, MeC_6H_4OH, H_2O, ^{t}BuOH) in 1 : 5 : 0.8 : 1 proportion leads to the formation of oligomers containing the fragment C–C–P(O)–O as repeating unit.

By studying the reactions of propylene oxide and [2-(vinyloxy)-ethoxy]methyloxirane, it was shown for the first time that epoxides may react with the less toxic, and more convenient, red phosphorus. Phosphorylation proceeds effectively in the 3-phase system comprising red phosphorus, 50% aqueous KOH and an organic solvent (dioxane, toluene or THF) in the presence of benzyltriethylammonium chloride at 60–93 °C. The resulting phosphorus-containing polyols were shown to have structures (XI–XIV) from ^{31}P NMR and IR spectroscopic data, and by elemental analysis.[81,82]

$$P + R^1\text{–}\underset{O}{\triangle}\text{–} \longrightarrow \underset{\underset{R^1}{|}}{R^2_{3-n}P(O)[(CH_2CHO)_mH]_n} \quad (5)$$

(XI)–(XIV)

(XI): R^1=Me, R^2=H, n=2, m=3;

(XII): R^1=Me, R^2=OK, n=2, m=4;

(XIII): $R^1=CH_2=CHO(CH_2)_2OCH_2$, R^2=OK, n=2, m=1;

(XIV): $R^1=CH_2=CHO(CH_2)_2OCH_2$, R^2=OK, n=1, m=4.

As seen with the formation of (XIII) and (XIV), the vinyloxy group remains intact, which further supports the anionic (nucleophilic) character of the reaction.[81] Our finding that butyl vinyl ether remains inert to the above phosphorylation is consistent with this view.

VI. Reactions of elemental phosphorus with organometallic compounds

Carbanions of certain organometallic compounds may also be used to generate polyphosphide anions from elemental phosphorus.[83–91] This was first demonstrated by Rauhut, et al., who studied the interaction of white phosphorus with phenylmagnesium bromide or phenyllithium at 25–40 °C in diethyl ether or THF, followed by treatment with water.[83] Among the products of the reaction, the following were identified: phenylphosphine (in 40% yield based on the conversion of phosphorus); small amounts of diphenyl- and triphenyl-phosphine; and organopolyphosphines, being insoluble, amorphous compounds with a yellow colouration.[83]

$$P_4 \xrightarrow{\text{PhMgBr, PhLi}} \xrightarrow{H_2O} PhPH_2 + Ph_2PH + Ph_3P + Ph_mH_{3-m}P_n,$$

$m=1-3$.

Later, Kaabak, et al. discovered suitable conditions (240–250 °C) for increasing the selectivity and efficiency of this reaction.[84] Thus, triarylphosphines were obtained in 70–83% yield (based on phosphorus) from white phosphorus and arylmagnesium iodides.[84]

$$P_4 + RMgI \xrightarrow{H_2O} R_3P,$$
$$R=Ph,\ 4\text{-}MeC_6H_4.$$

The same authors developed a method of preparing *tris*(*sec*-alkyl)phosphine oxides (in 57–82% yield) by heating white phosphorus with *sec*-alkyl halides and Mg (or Zn) at 120–210 °C, followed by treatment of the mixture with base at 270 °C.[85]

Unsymmetrical tertiary phosphines may be obtained under mild conditions (20–50 °C in an inert organic solvent) by the simultaneous treatment of white phosphorus with an organometallic compound and an alkyl halides.[86,87] The main products from the reaction of white phosphorus with butyl halide and phenyl-lithium or -sodium are dibutylphenyl- and butyldiphenyl-phosphine, obtained in 20–44% yield (based on phosphorus).[86] In certain instances, small amounts (8–11%) of butyldiphenylphosphine oxide were also detected.[86]

$$PhM + P4 + n\text{-}BuHal \xrightarrow{H_2O} PhP(Bu\text{-}n)_2 + Ph_2PBu\text{-}n +$$
$$+\ Ph_2P(O)Bu\text{-}n,$$
$$M=Li, Na;\quad Hal=Cl, Br.$$

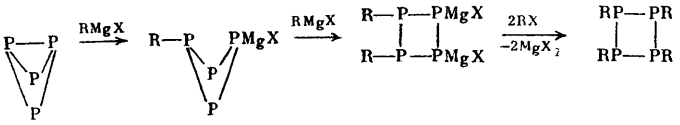
The reaction of white phosphorus with 4-methoxyphenyllithium and butyl bromide proceeds in a similar way, though less efficiently, to give dibutyl(4-methoxyphenyl)phosphine and butyl-*bis*(4-methoxyphenyl)phosphine (in 15 and 20% yield, respectively).[87]

$$MeO\text{-}C_6H_4\text{-}Li + P_4 + n\text{-}BuBr \xrightarrow{H_2O} MeO\text{-}C_6H_4\text{-}P(Bu\text{-}n)_2 +$$
$$+\ (MeO\text{-}C_6H_4\text{-})_2PBu\text{-}n.$$

At the same time, it was found that only trace amounts of the expected di- and tri-butylphosphine were formed by using butylmagnesium bromide as the organometallic compound. The main product of this reaction was tetrabutylcyclotetraphosphine (42% yield).[86]

$$P_4 + 2n\text{-}BuMgBr + 2n\text{-}BuBr \rightarrow \begin{matrix} n\text{-}BuP-PBu\text{-}n \\ | \quad | \\ n\text{-}BuP-PBu\text{-}n \end{matrix}$$

The authors consider that the reaction proceeds as follows:[86]



R = Alk.

Later, it was shown that other tetraalkylcyclotetraphosphines, e.g. $(EtP)_4$ and $(n\text{-}PrP)_4$, were obtainable by this route.[87]

However, the reaction of white phosphorus with isopropylmagnesium bromide or cyclohexylmagnesium bromide and the corresponding alkyl bromide proceeds by a quite different pathway, leading to products of composition R_2P_8 (R = isopropyl, cyclohexyl).[88]

Comparatively recently, unambiguous evidence was provided for the formation of polyphosphide ions from white phosphorus and methyllithium. Thus, organopolyphosphines (XV–XVII) were obtained by quenching intermediate polyphosphide ions with trimethylsilyl chloride or methyl bromide.[89]

$$P_4 + LiMe \rightarrow Li_3P_7 + Li_2P_7Me + LiP_7Me_2 \rightarrow$$
$$\xrightarrow{Me_3SiCl} P_7(SiMe_3)_3 + P_7(SiMe_3)_2Me$$
$$\text{(XV)} \qquad \text{(XVI)}$$
$$\xrightarrow{MeBr} P_7Me_3$$
$$\text{(XVII)}$$

Alkali metal pentaphosphides were also obtained by interaction of white phosphorus with Na (or Li) in diglyme or THF in the presence of a phase transfer catalyst (18-crown-6).[90]

References have been given in the patent literature to the formation of lithium aminophosphides, (XVIII) and (XIX), by heating white phosphorus with butyllithium and dialkylamines in benzene.[91,92] The two products were

$$P_4 + n\text{-}BuLi + R_2NH \rightarrow R_2NPLi_2 + (R_2N)_2PLi,$$
$$\text{(XVIII)} \qquad \text{(XIX)}$$
$$R=Me,\ Et.$$

obtained in quantitative yield.

Attempts to carry out the reaction of organometallic compounds (methylmagnesium iodide and diethylzinc) with red phosphorus met with failure.[40]

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Simple, convenient, and efficient routes to triorganophosphines and -phosphine oxides (including unsaturated derivatives) have been developed, based on the novel activation of red phosphorus by multi-phase superbasic systems (e.g. KOH–HMPA, KOH–DMSO, 50–70% aqueous KOH–organic solvent–phase transfer catalyst).[9,26–30,41–45,50–58,81] This method is currently being developed broadly. In particular, technological aspects of these processes are being improved, and the search continues for suitable electrophiles for redox phosphorylation with red phosphorus.

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