Synthesis of organic phosphines and phosphine oxides from elemental phosphorus and phosphine in the presence of strong bases

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Data on the reactions of elemental phosphorus and phosphine with electrophilic reagents are described systematically and analyzed. These reactions occur in the presence of strong bases and yield primary, secondary, and tertiary phosphines and phosphine oxides.

Key words: elemental phosphorus, phosphine, reactions with electrophilic reagents; superbasic systems; phosphorus-centered nucleophiles; organic phosphines, phosphine oxides.

Introduction

Organic phosphines and phosphine oxides attract the attention of researchers, first of all, as unique ligands for the preparation of effective metal-complex catalysts. In addition, they serve as the basis for creation of extractants for rare earth and transuranium elements, fireproofing compounds, emulsifying agents, and biologically active preparations for medicine and agriculture.[1–3]

However, the absence of facile and convenient methods for the synthesis of phosphines and phosphine oxides hamper broad practical application of these important organophosphorus compounds. To the best of our knowledge, organic phosphines and phosphine oxides are not manufactured on an industrial scale in Russia. The catalogs of foreign companies also offer only a limited range of these compounds.

In this review, we survey and analyze the results of studies (mostly carried out over the last 10—15 years) dealing with the synthesis of primary, secondary, and tertiary phosphines and phosphine oxides using reactions of electrophilic reagents with phosphorus-centered nucleophiles, generated from elemental phosphorus and phosphine in the presence of strong bases. Primary attention is devoted to the new method, developed in our laboratory, for the activation of elemental phosphorus (the least reactive red phosphorus) in heterogeneous highly basic media,[4] such as alkali metal hydroxide—polar nonhydroxylic solvent (the normally used solvents are dimethyl sulfoxide or hexamethylphosphotriamide) or an aqueous solution of alkali metal hydroxide—organic solvent—phase transfer catalyst, and in the alkali metal—tertiary alkanol—NH_3(liq) system. These methods opened up a fundamentally new approach to the formation of a C—P bond and permitted direct phosphorylation of organyl halides, electrophilic alkenes, alkynes, and oxiranes by red phosphorus.[3,5–10]

Synthesis of primary phosphines

A relatively small number of papers dealing with the generation of monophosphide anions from elemental phosphorus and strong bases and the use of this technique in the syntheses of primary phosphines have been published.

It has been reported[11,12] that white phosphorus reacts with metallic sodium in liquid ammonia in the presence of ammonium bromide to give sodium monophosphide, whose treatment with methyl iodide affords methylphosphine in 62% yield (Scheme 1).

Scheme 1

$$P_4 + 12\ Na + 8\ NH_4Br \xrightarrow{NH_3(liq)} 4\ NaPH_2 + 8\ NaBr + 8\ NH_3 \xrightarrow{MeI} MePH_2$$

We found a fundamentally new and a convenient approach to the generation of phosphide anions from red phosphorus on treatment with the metallic Li—NH_3(liq) system in the presence of *tert*-butyl alcohol. This alcohol, which is a soft proton-donating reagent, facilitates the efficient and selective cleavage of the P—P bonds in the macromolecule of red phosphorus. The use of P, Li, and Bu^tOH in a molar ratio of 1 : 3 : 2 leads to the predominant formation of monophosphide anions, whose reactions with organyl halides have resulted in the synthesis of primary phosphines **1** in 72—87% yields (Scheme 2).[7,13,14]

Oxirane can also be used as the electrophile in this reaction; this compound is phosphorylated by the red phosphorus—alkali metal—Bu^tOH system in liquid NH_3 to give 2-hydroxyethylphosphine in 27% yield (not optimized) (Scheme 3).[15]

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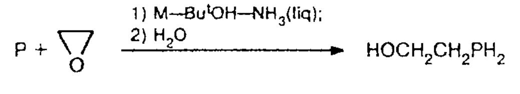
Scheme 2

$$P + 3\,Li + 2\,Bu^tOH \xrightarrow{NH_3(liq)}$$

$$\longrightarrow LiPH_2 + 2\,Bu^tOLi \xrightarrow{RX} \underset{\mathbf{1}}{RPH_2}$$

R = Alk, *cyclo*-Alk, Bn; X = Br, Cl

Scheme 3



M = Li, Na

Phosphine is used in the synthesis of primary phosphines more widely than elemental phosphorus. Systems comprising phosphine and a strong base efficiently phosphorylate organyl halides, alkenes, oxiranes, and thiiranes and allow preparation of primary phosphines of various structures.

Thus primary phosphines **2** were synthesized in 55—87% yield by metallation of phosphine with alkali metal or alkaline earth metal followed by treatment of the resulting phosphide with alkyl halides,[16,17] aminoalkyl halides,[18] or sodium haloalkanoates.[19,20] The reaction is carried out in an organic solvent or in liquid NH_3 using stoichiometric amounts of reagents (Scheme 4).

Scheme 4

$$PH_3 + M \longrightarrow M(PH_2)_n \xrightarrow{RX} \underset{\mathbf{2}}{RPH_2}$$

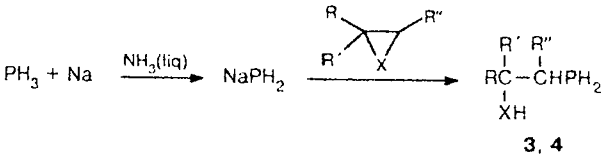
M = Na, *n* = 1; M = Ca, *n* = 2;
R = Me, Et, $CH_2CH{=}CH_2$, $CH_2CH_2NH_2$, $CH_2CH_2NEt_2$, CH_2COONa, CH_2CH_2COONa, CH(Me)COONa, CH(Et)COONa;
X = Cl, Br

However, this approach proved to be inefficient for the synthesis of diorganylphosphines, apparently because it is difficult to obtain disubstituted derivatives upon metallation of phosphine.[1]

Oxiranes[21,22] and thiiranes[23] are phosphorylated by the phosphine—metallic sodium—NH_3(liq) system to give primary phosphines **3** and **4** in 59—73% yields (Scheme 5).

Strong bases such as alkali metal hydroxide—polar nonhydroxylic solvent systems can be used, instead of alkali metals, to generate monophosphide anions from phosphine. Thus treatment of organyl halides with phosphines at an elevated pressure (4.0—7.5 atm) in the system consisting of ~60% aqueous KOH and DMSO afforded primary phosphines 5 (Scheme 6).[24]

Scheme 5



3, 4

3: X = O; R = H, MeC≡C, $Bu^nC{\equiv}C$, $CH_2{=}CH{-}C{\equiv}C$; R′ = Me; R″ = H
4: X = S; R = H, Me; R′ = H; R″ = H, Me

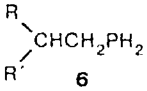
Scheme 6

$$PH_3 + RX \xrightarrow{KOH-DMSO-H_2O} \underset{\mathbf{5}}{RPH_2}$$

R = Me, Et, Bu^n, Bu^t, Bn, $CH_2{=}CHCH_2$; X = Br, Cl

Nucleophilic addition of the phosphine to the C=C bond yielding organic phosphines was first described for alkenes containing strong electron-withdrawing substituents at the sp^2 carbon atom.[25] In particular, 2-cyanoethylphosphine was obtained by this method in 52% yield from acrylonitrile and phosphine in the presence of KOH (pressure 28—32 atm).[25]

Recently we have shown[26,27] that on treatment with superbasic systems, phosphine is capable of adding to the weakly electrophilic double bonds in aryl- and hetarylalkenes (styrene, α-methylstyrene, vinylpyridines) at atmospheric pressure to give, under definite conditions, primary phosphines **6** in 20—24% yields. The process was conducted by slow addition of an alkene to a heated (30—40 °C) suspension of KOH in DMSO with simultaneous vigorous passing of phosphine through the reaction mixture; the phosphine is generated in a separate vessel from red phosphorus and KOH in aqueous dioxane.



$$RR'CHCH_2PH_2$$

6

R = H; R′ = Ph, 4-pyridyl, 2-methyl-5-pyridyl
R = Me; R′ = Ph

The relatively low yields of primary phosphines **6** are due to the fact that this reaction gives the corresponding secondary and tertiary phosphines as the major products.[26,27]

Synthesis of secondary phosphines

Data on the possibility of generating phosphide anions from red phosphorus in the Na—NH_3(liq) system were reported for the first time in 1966.[28] Phosphorylation of alkyl halides under these conditions affords mixtures of organic phosphines and diphosphines. In particular, dialkylphosphines were synthesized in 29—34% yields from red phosphorus and alkyl bromides (Scheme 7).[29]

Scheme 7

$$P_n \xrightarrow{2n\,Na} n/2\,(PNa_2)_2 \xrightarrow{2n\,RBr} n/2\,(PR_2)_2$$

$$R_2P-PR_2 \xrightarrow{2\,Na} 2\,R_2PNa \xrightarrow{H_2O} 2\,R_2PH$$

R = Et, Bu^n

The relatively low yields of the reaction products and the low selectivity of the reaction are apparently due to the insufficient efficiency of cleavage of the P—P bonds in the macromolecule of red phosphorus, resulting in the formation of polyphosphide anions and also phosphides with lower polymerization degrees and higher degrees of substitution.

Recently we have proposed a convenient selective method for the synthesis of secondary phosphines **7** in 52—72% yields by direct reaction of the red phosphorus with organyl halides in the Li—Bu^{t}OH—NH$_3$(liq) system with exactly stoichiometric amounts of the reactants (Scheme 8).[30—32]

Scheme 8

$$P + 3\,Li + Bu^tOH \xrightarrow{NH_3(liq)} Li_2PH + Bu^tOLi \xrightarrow{RX} \underset{\mathbf{7}}{R_2PH}$$

R = Alk, *cyclo*-Alk

The procedure for selective generation of phosphide mono- and dianions from red phosphorus presented in Schemes 2 and 8 was also used in the one-pot synthesis of nonsymmetrical secondary phosphines of type **8** (Scheme 9);[33,34] their yields in this four-step process can be as high as 55%.

Scheme 9

$$P \xrightarrow[2)\,RX]{1)\,3\,Li-2\,Bu^tOH-NH_3(liq);} [RPH_2] \xrightarrow[4)\,R'X]{3)\,M(\rightarrow MNH_2);} \underset{\mathbf{8}}{RR'PH}$$

R = Et, Pr^n; R' = C_7H_{15}; X = Br, Cl

Secondary phosphines can also be prepared using the phosphine—strong base phosphorylating system. Organyl halides and alkenes were introduced into these reactions as electrophilic reagents. For example, heating of organyl halides in a suspension of KOH in DMSO under a pressure of phosphine gave diallyl- and dibutylphosphines.[24]

Recently we have shown that this reaction can also be carried out under atmospheric pressure using the reaction with benzyl chloride as an example; in this case, phosphine is generated from red phosphorus and alkali metal hydroxide in aqueous dioxane and rapidly passed through a KOH—DMSO—H$_2$O suspension heated to 40 °C, and benzyl chloride is simultaneously slowly added to the reaction mixture.[35,36] Under these conditions, the yield of dibenzylphosphine is 50% (Scheme 10).[35]

Scheme 10

$$PH_3 + PhCH_2Cl \xrightarrow{KOH-DMSO-H_2O} (PhCH_2)_2PH$$

The nucleophilic addition of phosphine to acrylonitrile catalyzed by aqueous KOH can be directed, under definite conditions, to predominant formation of bis(2-cyanoethyl)phosphine.[25]

We developed preparation conditions for the selective synthesis of bis(2-arylethyl)- and bis(2-hetarylethyl)phosphines of type **9** from phosphine and weakly electrophilic aryl- and hetarylethenes in the KOH—DMSO system (Scheme 11).[37—40] The process is conducted under mild conditions (45—60 °C, atmospheric pressure) by slow addition of alkene to a suspension of KOH in DMSO with simultaneous intense passing* of the phosphine through the reaction mixture.[37] The yields of phosphines **9** are 60—80%. In the absence of KOH all other factors being the same, the reaction does not occur, which confirms its nucleophilic mechanism.[37]

Scheme 11

$$PH_3 + RR'C{=}CH_2 \xrightarrow{KOH-DMSO-H_2O} \underset{\mathbf{9}}{(RR'CHCH_2)_2PH}$$

R = H; R' = Ph, 4-FC$_6$H$_4$, 2-furyl, 2-thienyl, 4-pyridyl, 2-methyl-5-pyridyl
R = Me; R' = Ph

1-Methyl-2-ethenylpyrrol cannot be involved in the reaction with phosphine in the KOH—DMSO system, which is apparently due to the lower electrophilicity of the double bond in these alkene caused by the electron-donating mesomeric effect of the methylpyrrolyl group.[37]

Synthesis of tertiary phosphines

Before our studies, information on the synthesis of tertiary phosphines from elemental phosphorus in the

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* Phosphine is generated in a separate reactor from red phosphorus and KOH in aqueous dioxane.

presence of bases had been restricted apparently to the data on phosphorylation of halobenzenes by the red phosphorus—Na—NH_3(liq) system with additional activation of the reactants by UV radiation.[41] The resulting triphenylphosphine was oxidized without isolation by hydrogen peroxide to triphenylphosphine oxide, whose yield was 75%.[41]

We found that the red phosphorus—metallic potassium—Bu^tOH—NH_3(liq) system can be successfully used for phosphorylation of aryl- and hetarylethenes, resulting in the selective synthesis of tris(2-arylethyl)- and tris(2-hetarylethyl)phosphines **10** in yields of up to 82% (Scheme 12).[42]

Scheme 12

$$P + 3\,K \xrightarrow[-2\,Bu^tOK]{2\,Bu^tOH-NH_3(liq)} [KPH_2] \xrightarrow[Bu^tOH-NH_3(liq)]{3\,RCH{=}CH_2} (RCH_2CH_2)_3P$$

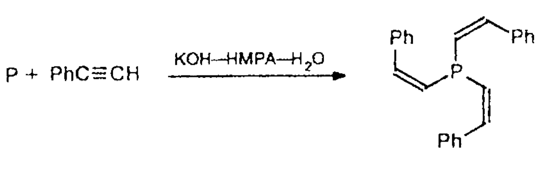
10

R = Ph, 4-FC_6H_4, 2-thienyl

This reaction affords no primary or secondary phosphines even if the alkene is taken in a smaller amount than it is required by the stoichiometry for the preparation of tertiary phosphine.

Using phenylacetylene as an example, we demonstrated for the first time[43,44] that in the system comprising an alkali metal hydroxide and a polar nonhydroxylic solvent (HMPA, DMSO, triethylphosphine oxide), red phosphorus reacts with alkynes at 60—65 °C stereo-, regio-, and chemoselectively giving rise to tris(*Z*-styryl)phosphine in a yield of up to 55% (Scheme 13).[45—49]

Scheme 13



When the reactants are subjected to ultrasonic[46] or mechanochemical[50] treatment, the rate of phosphorylation of phenylacetylene increases, but the stereoselectivity of the process decreases.

The kinetic control of the reaction was confirmed in relation to the thermal (160—165 °C, 7 h) transformation of the *Z,Z,Z*-isomer of tris(2-phenylvinyl)phosphine into its *E,E,E*-isomer *via* the intermediate formation of the corresponding *Z,Z,E*- and *Z,E,E*-isomers.[50]

Before our studies, no data on the possibility of cleavage of the P—P bonds in the molecule of elemental phosphorus by metal acetylenides had been reported. We found that treatment of yellow phosphorus with butyn-1-yllithium in liquid NH_3 [51] or THF [52] results in the formation of butyn-1-ylphosphide and di(butyn-1-yl)phosphide anions, which react with alkyl halides to give approximately equimolar mixtures of dialkylbutyn-1-ylphosphines **11** and alkyldi(butyn-1-yl)phosphines **12** (Scheme 14).[51—53]

Scheme 14

$$P_4 + EtC{\equiv}CLi \longrightarrow [EtC{\equiv}CP^{2-} + (EtC{\equiv}C)_2P^-] \xrightarrow{RX} EtC{\equiv}CPR_2 + (EtC{\equiv}C)_2PR$$

11 **12**

R = Et, Pr^n; X = Br, Cl

The total yield of phosphines **11** and **12** reaches 20%, and there are grounds to hope that optimization of this reaction would result in the development of a convenient procedure for the synthesis of acetylene phosphines.

To the best of our knowledge, no data on the preparation of tertiary phosphines from phosphine and organyl halides under conditions of basic catalysis have been reported in the literature. At the same time, it was shown that nucleophilic addition of phosphine to electrophilic alkenes can be directed at the predominant or exclusive formation of tertiary phosphines.

For example,[25] when phosphine is passed through a solution of KOH in aqueous MeCN and acrylonitrile is added simultaneously at such a velocity as to maintain a slight excess of acrylonitrile with respect to the phosphine in the reaction mixture, tris(2-cyanoethyl)phosphine is formed in 80% yield.

In the 1970s a series of studies was published dealing with the nucleophilic addition of phosphine to dialkyl vinylphosphonates,[54] dialkylvinylphosphine sulfides,[55] and even to a relatively weak electrophile, diphenylvinylphosphine.[56] The process is carried out in boiling THF in the presence of Bu^tOK or in the PhLi—benzene system at 100 °C (closed steel cylinder) and affords functionalized tertiary phosphines **13a—c**, whose yields vary from 24% (**13a**) to 91% (**13c**) (Scheme 15).

Scheme 15

$$PH_3 + R_2P(X)CH{=}CH_2 \xrightarrow{Bu^tOK\ \text{or}\ PhLi} [R_2P(X)CH_2CH_2]_3P$$

13a—c

a: R = Ph, X = LEP*
b: R = Me_2CHO, X = O
c: R = Me, X = S

We developed conditions for the exhaustive aryl(hetaryl)ethylation of phosphine by styrene or vinylpyridines

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* LEP is a lone electron pair.

and synthesized tris(2-phenylethyl)-, tris[2-(4-pyridyl)]ethyl-, and tris[2-(2-methyl-5-pyridyl)]ethylphosphines in 65—76% yields (Scheme 16).[42,57,58] The process is accomplished at 65—98 °C in the KOH—DMSO system.[58]

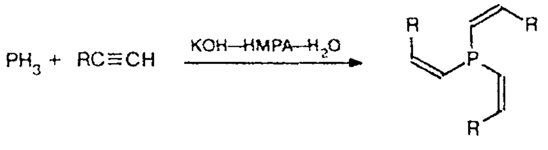
Scheme 16

$$PH_3 + RCH{=}CH_2 \xrightarrow{KOH—DMSO—H_2O} (RCH_2CH_2)_3P$$

R = Ph, 4-pyridyl, 2-methyl-5-pyridyl

Data on the addition of phosphine to triple carbon—carbon bonds are restricted to our recent studies devoted to phosphorylation of aryl- and hetarylacetylenes.[6,59,60] The reaction occurs under mild conditions (55—60 °C, atmospheric pressure) by passing phosphine through a suspension containing substituted acetylene, KOH, and HMPA and gives selectively the *Z,Z,Z*-isomers of tris(2-organylvinyl)phosphines **14** in 60—80% yields (Scheme 17).[60]

Scheme 17



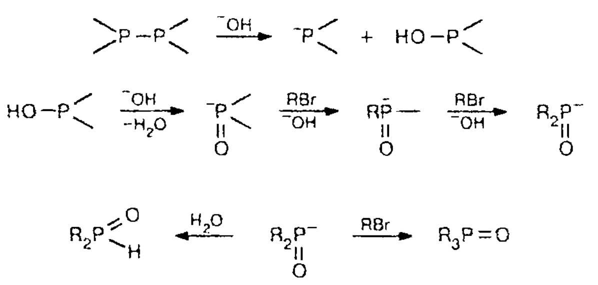
14

R = Ph, 4-FC$_6$H$_4$, 2-furyl, 2-thienyl

Synthesis of secondary phosphine oxides

Recently we reported[61] on the preparation of dialkylphosphine oxides by alkylation of red phosphorus in the presence of a base (yields 14—17%). The reaction is performed by slow addition of alkyl bromide to a suspension of red phosphorus in a mixture of 60% aqueous KOH and dioxane heated to 60—62 °C and containing benzyltriethylammonium chloride (BTEAC) at a P : RBr molar ratio of 1.0 : 0.6. Trialkylphosphine oxides (yields 2—7%) were also identified in the reaction mixture. Since the corresponding dialkyl- and trialkylphosphines are not produced even when this reaction is carried out in an inert atmosphere, it can be assumed that phosphorylation involves phosphinite anions generated from red phosphorus under the action of hydroxide anions (Scheme 18).

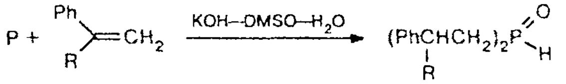
Scheme 18



R = Et, Pr^n

Yet another approach to the selective synthesis of secondary phosphine oxides, described in our previous publication,[62] is based on the reaction of red phosphorus with styrene and α-methylstyrene, which occurs in the KOH—DMSO system at 65—75 °C and at a P : alkene molar ratio of 1.0 : 0.5 and results in the formation of bis(2-phenylethyl)- and bis(2-phenylpropyl)phosphine oxides **15** in yields of up to 20% (not optimized) (Scheme 19).

Scheme 19



15

R = H, Me

To the best of our knowledge, no other methods for the synthesis of secondary phosphine oxides by direct reactions of elemental phosphorus (or phosphine) with electrophiles in the presence of bases have been described in the literature.

Synthesis of tertiary phosphine oxides

The new efficient method for the generation of phosphide and phosphinite anions from red phosphorus under the action of superbasic systems such as a water-organic emulsion of an alkali metal hydroxide in the presence of a phase transfer catalyst or an alkali metal hydroxide in a polar nonhydroxylic solvent has served as the basis for a number of new reactions of red phosphorus with organyl halides occurring with participation of phosphinite anions and yielding tertiary phosphine oxides, difficult to obtain by other methods.[63—69]

Thus trialkyl and tribenzylphosphine oxides are formed in 60—75% yields on treatment of alkyl bromides and benzyl chloride with the system comprising red phosphorus, 50—60% aqueous KOH, dioxane, and BTEAC (Scheme 20).[63—66]

Scheme 20

$$P + RX \xrightarrow{KOH—H_2O} R_3P{=}O$$

R = Alk, Bn; X = Br, Cl

Allyl halides $CH_2{=}CHCH_2X$ (X = Cl, Br) react with red phosphorus under similar conditions to give triallylphosphine oxide and its isomer, tris(*E*-propen-1-yl)phosphine oxide in 30 and 35% yields, respectively (Scheme 21).[67,68]

Scheme 21

$$P + CH_2{=}CHCH_2X \xrightarrow{KOH-H_2O} (CH_2{=}CHCH_2)_3P{=}O + (MeCH{=}CH)_3P{=}O$$

X = Br, Cl

At the same time, phosphorylation of 2-(dialkoxy)ethyl bromides **16** with red phosphorus could be accomplished only under the action of a stronger base,[4] the KOH—DMSO system; this afforded functionalized tris(dialkoxyethyl)phosphine oxides **17** with three protected aldehyde groups (Scheme 22).[69]

Scheme 22

$$P + \underset{\textbf{16}}{(RO)_2CHCH_2Br} \xrightarrow{KOH-DMSO-H_2O} \underset{\textbf{17}}{[(RO)_2CHCH_2]_3P{=}O}$$

R = Et, Bu^n

The first data on the addition of phosphinite anions, generated from white phosphorus on treatment with concentrated aqueous solutions of KOH, to electrophilic alkenes referred to the preparation of tris(2-cyanoethyl)- and tris(2-carbamoylethyl)phosphine oxides from acrylonitrile and acrylamide in an inert atmosphere in 53 and 75% yields, respectively.[70] Later, *N*-alkyl- and *N*,*N*-dialkylacrylamides,[71] vinyldiorganylphosphine oxides and sulfides,[72] as well as ethyl vinylphosphonates[73] were phosphorylated by white and yellow phosphorus, and the corresponding tertiary phosphine oxides were synthesized in moderate to high yields.

Using styrene as an example, we demonstrated for the first time that tertiary phosphine oxides can be obtained from not only white phosphorus,[74] but also from less reactive red phosphorus and weakly electrophilic alkenes in the presence of superbasic systems.[75—77] Thus heating (100—120 °C) of the reactants in the KOH—HMPA system affords tris(2-phenylethyl)phosphine oxide **18a** in 60% yield (Scheme 23).[76]

The red phosphorus—KOH—DMSO system permits also phosphorylation of vinylpyridines to give functionalized tertiary phosphine oxides **18b,c**, whose yields can reach 50% (see Scheme 23).[78—80] Ultrasonic treatment of the reagents accelerates phosphorylation of vinylpyridines.[79,80]

Scheme 23

$$P + RCH{=}CH_2 \xrightarrow[KOH-DMSO-H_2O]{KOH-HMPA-H_2O} \underset{\textbf{18a-c}}{(RCH_2CH_2)_3P{=}O}$$

R = Ph (**a**), 4-pyridyl (**b**), 2-methyl-5-pyridyl (**c**)

* * *

We believe that this review will promote more intense studies dealing with generation of phosphorus-centered nucleophiles from elemental phosphorus and phosphine in the presence of bases and successful use of this technique in organophosphorus synthesis.

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