

Novel general halogen-free methodology for the synthesis of organophosphorus compounds*

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Abstract: The use of novel general halogen-free methodology for the synthesis of phosphines, phosphine chalcogenides, and phosphinic acids from elemental phosphorus and alkenes and alkynes in the superbase suspensions is described.

Keywords: halogen-free phosphorylation with elemental phosphorus; organic synthesis; phosphines; phosphine chalcogenides; phosphinic acids; superbases.

INTRODUCTION

In the last few years, green chemistry, i.e., a scientific direction dealing with the development and modification of environmentally benign chemical processes, has assumed great importance. In particular, special emphasis is placed on the halogen-free methods for the synthesis of organic compounds. It is common knowledge that application of halogen-containing starting materials is accompanied by the formation of large amounts of diverse hazardous unutilized wastes, including dioxins. This is also true for the synthesis of organophosphorus compounds that are conventionally prepared from phosphorus halides (mainly, chlorides) [1] produced by chlorination of elemental phosphorus with chlorine. The emission of chlorine and hydrogen chloride associated with these processes creates severe environmental problems. Besides, the formation of the C–P bond and synthesis of key organophosphorus compounds (organic phosphines, phosphine chalcogenides, phosphinic acids) from phosphorus halides require the application of organometallic compounds as co-reagents that represents some experimental problems such as usage of especially pure anhydrous solvents and dry inert atmosphere, utilization of byproducts [1]. For example, tertiary phosphines, which are the most widely used ligands for metallo-complex catalysts, are still prepared from phosphorus trichloride and Grignard reagents [1,2]. To reach the best yields (about 60–85%) of tertiary phosphines, a considerable excess of Grignard reagent and low temperature (sometimes even down to -78 °C) [1a,2a] while mixing the reactants are required. At the last stage (hydrolytic treatment of the reaction mixture with saturated ammonium chloride solution or aqueous solution of hydrogen chloride), a large amount of byproducts are formed. The industrial synthesis of ubiquitous triphenylphosphine involves the reaction between phosphorus trichloride, chlorobenzene, and sodium metal [3] though the yield of this reaction is not high (44–50 %).

Therefore, the use of elemental phosphorus as alternative phosphorylating reagent for the preparation of organophosphorus compounds represents an urgent R&D challenge [4].

Meanwhile, until recently, only limited efforts were focused on the application of elemental phosphorus in the synthesis of organophosphorus compounds and, no wonder, they did not lead to practi-

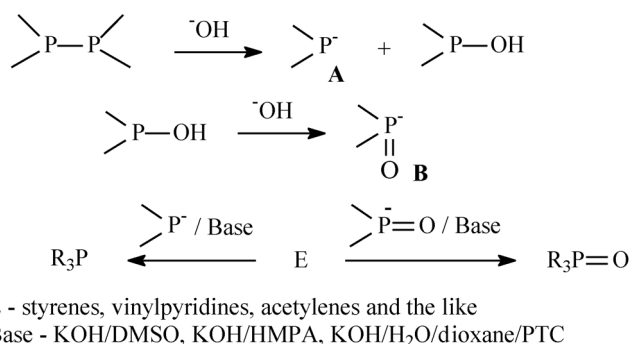
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cally meaningful results. Usually, the activation of elemental phosphorus, especially, red phosphorus, toward the C–P bond formation in the reactions with functional organic compounds required harsh conditions (high temperature and pressure, large amounts of expensive activators, etc.) [1a,b,5].

A more convenient synthetic methodology affording the shortest and environmentally safe routes to important organophosphorus compounds is based on the preparative application of phosphorus-centered nucleophiles originated from elemental phosphorus. The first step in this direction probably belongs to Rauhut [6] who has reported on the addition of phosphinite-anions, generated from white phosphorus under the action of KOH, to strongly electrophilic functional alkenes (acrylonitrile and acrylamide).

More than two decades ago, we started the systematic study of the P–P bond cleavage of red phosphorus macromolecule in heterogeneous highly basic media, such as KOH/polar nonhydroxylic solvent (dimethylsulfoxide, DMSO, or hexamethylphosphoramide, HMPA) or aqueous solution of KOH/organic solvent/phase-transfer catalyst [7]. Highly active P-centered nucleophiles such as polyphosphide-**A** and polyphosphinite-**B** anions thus formed further interact with appropriate electrophile (Scheme 1). This study opened up a fundamentally new approach to the formation of the C–P bond and synthesis of phosphines and phosphine oxides, key objects in the chemistry of organophosphorus compounds. Recently, it has been shown that cross-linked red phosphorus macromolecule can also be disassembled by sulfur-centered nucleophiles in DMSO [8].



Scheme 1 Formation of the C–P bond from elemental phosphorus and electrophiles in superbase systems.

Here, we review the halogen-free syntheses of organic phosphines, phosphine oxides, and phosphinic acids based on this novel concept in organophosphorus chemistry. We focus on the direct reactions of elemental phosphorus (its different modifications) with alkenes and alkynes in the superbase suspensions and emulsions. The synthetic application of a new phosphorylating reagent, namely, a phosphine–hydrogen mixture, generated from red phosphorus in the emulsions KOH/H₂O/organic solvents (dioxane, toluene) [9] is also considered in the review.

PHOSPHORYLATING REAGENTS

The following phosphorylating reagents were used for the formation of the C–P bond by the direct reactions with alkenes and alkynes: commercial red (P_n) or white (P₄) phosphorus, nanocomposites of red phosphorus (nano-P_n) prepared by radiation-induced polymerization (⁶⁰Co γ-radiation) of white phosphorus, phosphine–hydrogen mixture generated from red phosphorus, and alkali metal hydroxide in aqueous–organic systems.

White phosphorus (P₄) represents tetrahedral molecule that results in the ring strain, instability and, as a sequence, high reactivity. In the red phosphorus, one of the P₄ bonds is broken, and one addi-

tional bond is formed with a neighboring tetrahedron to furnish a more chain-like structure. Amorphous red phosphorus exists as a network of atoms that reduces strain and reactivity and gives greater stability. As is known, common amorphous red phosphorus consists of rather large particles with an average size of 40–60 μm [10].

The nanocomposites of red phosphorus (nano- P_n) with carbon, graphite, or organophosphorus inclusions have been obtained by radiation-induced (^{60}Co γ -radiation) polymerization of white phosphorus in benzene at ambient temperature [10,11]. These nanocomposites consist of mainly phosphorus (>80 %) and minor inclusions: carbon (~8–10 %), hydrogen (<1 %), and oxygen (about 10 %). The presence of carbon and hydrogen in the composites indicates to the chemical insertion of benzene molecules or their fractions into the polymeric structure of phosphorus probably by the termination of chains with organic radicals or radical cations produced by benzene under the action of γ -radiation [10,11]. Availability of oxygen in the composites is owing to the oxidation of the most chemically reactive sites (defects) and represented as functional groups with P–O bonds. According to electron microscopy, the nanocomposites contain nanoparticles mainly of 30–50 nm [10,11].

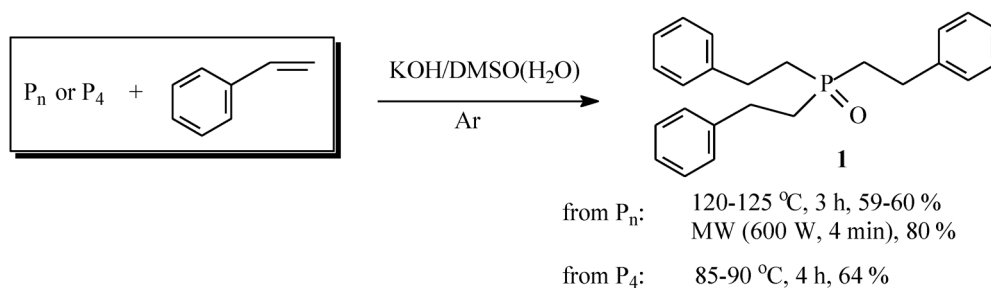
The reactions of elemental phosphorus in the system alkaline (or alkaline-earth) metal/water were intensively studied in the middle of the last century on the example of white phosphorus to produce hypophosphites of alkaline metals. Phosphine, formed in the course of the reaction, was as a rule burnt [12]. We pioneered in the application of novel reagent, phosphine–hydrogen mixture generated from red phosphorus and KOH in aqueous–organic medium (dioxane, toluene) [9]. Chromatographic analysis of the gas mixture has shown that the ratio of phosphine:hydrogen is approximately 55:45 % [13]. The mixture proved to be an efficient phosphinating agent since atom-economic syntheses of primary, secondary, and tertiary phosphines (including functional and unsaturated), based on the addition of phosphine to alkenes [7c,d,g,9] and acetylenes [7c,d,g,9b], were developed.

PHOSPHORYLATION WITH ELEMENTAL PHOSPHORUS

Phosphorylation of alkenes

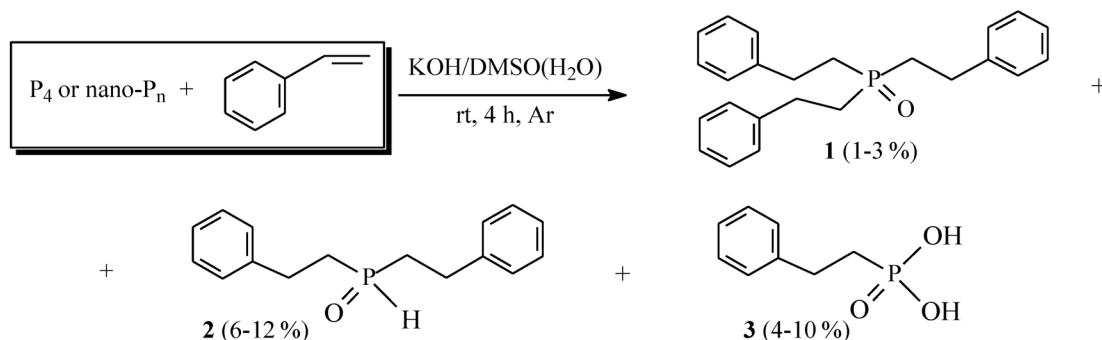
Phosphorylation of styrenes

The application of novel methodology for the superbase-promoted activation of elemental phosphorus turned out to ensure direct phosphorylation of even such weak electrophilic alkenes as styrenes [7a–d,14–16]. Thus, styrene adds phosphorus-centered nucleophiles generated from red or white phosphorus in the system KOH/DMSO (or HMPA) at 85–125 $^{\circ}\text{C}$ in the presence of a small quantity of H_2O (as a proton-transfer agent) to give tris(2-phenethyl)phosphine oxide **1** in good yield (Scheme 2) [14b,f]. The combined action of superbase (KOH/DMSO) and microwave irradiation on the reagents in the course of phosphorylation of styrene with red phosphorus (Scheme 2) allowed selectivity and efficacy of the process to be enhanced [15].



Scheme 2 Reaction of P_n or P_4 with styrene in the KOH/DMSO system under heating or MW irradiation.

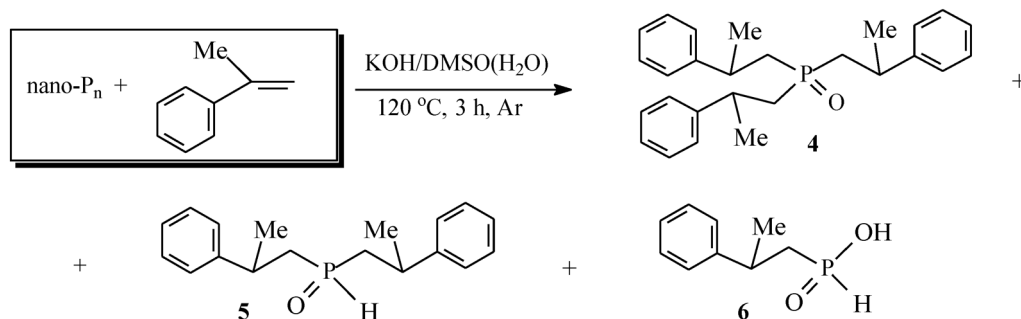
The reaction of styrene with white phosphorus can be accomplished even at room temperature [16b], however, in this case the major reaction products are bis(2-phenethyl)phosphine oxide **2** and phenethylphosphonic acid **3**, the yield of tertiary phosphine oxide **1** being negligible (Scheme 3).



Scheme 3 Reaction of P_4 or nano- P_n with styrene in the KOH/DMSO system at room temperature.

Under these conditions, red phosphorus does not react practically with styrene [16]. At the same time, nanocomposites of red phosphorus (nano- P_n) are more active in this phosphorylation than red phosphorus and react with styrene at room temperature to give phosphine oxides **1**, **2** and phosphonic acid **3** in 11 % total yield (Scheme 3) [16b].

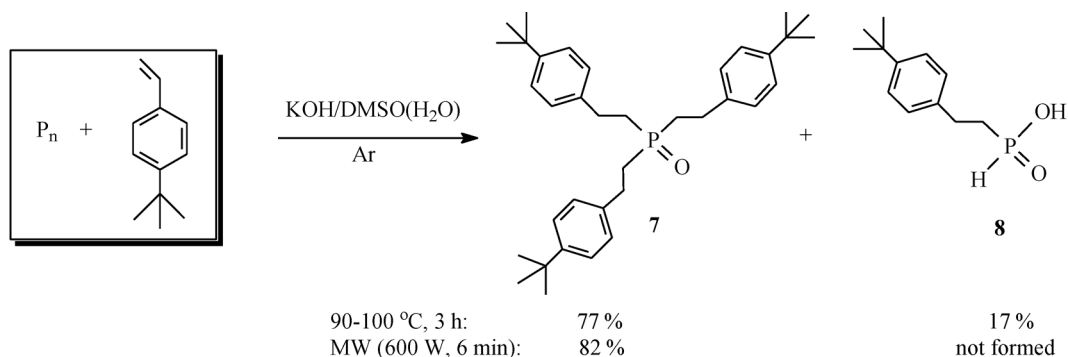
Higher activity of nano- P_n as compared to common red phosphorus was also documented for α -methylstyrene. The latter reacts with nano- P_n at 120 °C in the KOH/DMSO system to produce tertiary **4** and secondary **5** phosphine oxides and phosphonic acid **6** in 95 % total yield (Scheme 4) [10].



Scheme 4 Reaction of nano- P_n with α -methylstyrene in the KOH/DMSO system.

Under analogous conditions, phosphorylation of α -methylstyrene with common red phosphorus proceeds less efficiently though more selectively to give tertiary phosphine oxide **4** in 15 % yield [10].

Even more surprising is the addition of phosphorus-centered nucleophiles generated from elemental phosphorus in the superbases system KOH/DMSO to 1-(*tert*-butyl)-4-vinylbenzene and 4-methoxystyrene. The presence of electron-donating groups in the 4-position of the benzene ring decreases electrophilicity of the double bond of these alkenes and, therefore, their reactivity toward nucleophiles. Nevertheless, we have found that red phosphorus reacts with 1-(*tert*-butyl)-4-vinylbenzene in the KOH/DMSO(H_2O) suspension in the presence of a small amount of hydroquinone as a radical inhibitor to give tris[4-(*tert*-butyl)phenethyl]phosphine oxide **7** and 4-(*tert*-butyl)phenethylphosphonic acid **8** (Scheme 5) [17]. A microwave irradiation promoted version of the reaction delivers (in

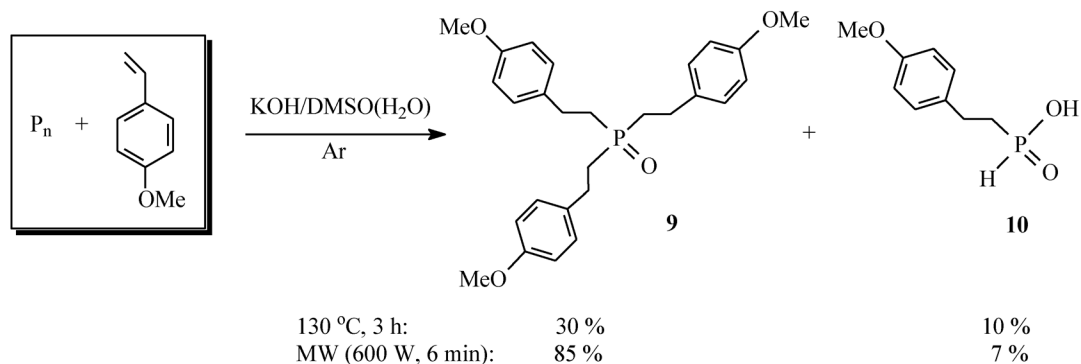


Scheme 5 Reaction of P_n with 1-(*tert*-butyl)-4-vinylbenzene in the KOH/DMSO system under heating or MW irradiation.

6 min) tertiary phosphine oxide **7** as the only product in high yield. Thus, the reaction is more chemoselective and rapid (30 times faster) [17].

Despite the comparable preparative yields of the corresponding tertiary phosphine oxides **1** and **7**, a competitive reaction indicates that *tert*-butylstyrene exerts expectedly lower reactivity than unsubstituted styrene [17].

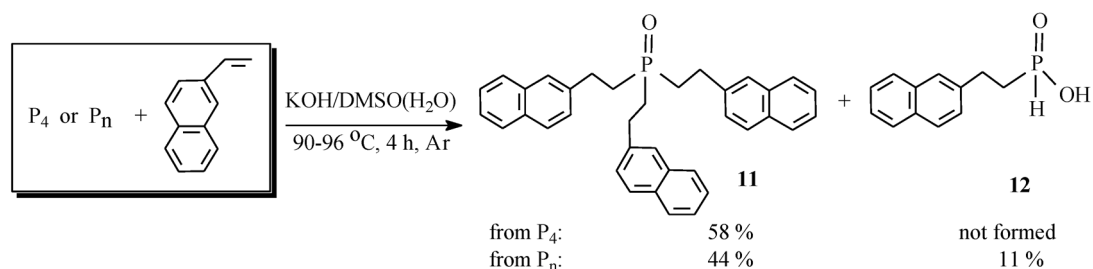
4-Methoxystyrene reacts with red phosphorus in the KOH/DMSO system to give tris[2-(4-methoxyphenyl)ethyl]phosphine oxide **9** and 2-(4-methoxyphenyl)ethylphosphinic acid **10** (Scheme 6) in moderate yields [14f]. Microwave-assisted reaction affords phosphine oxide **9** in high isolated yield (Scheme 6). In addition, this interaction gives a small amount of phosphinic acid **10** [9f].



Scheme 6 Reaction of P_n with 4-methoxystyrene in the KOH/DMSO system under heating or MW irradiation.

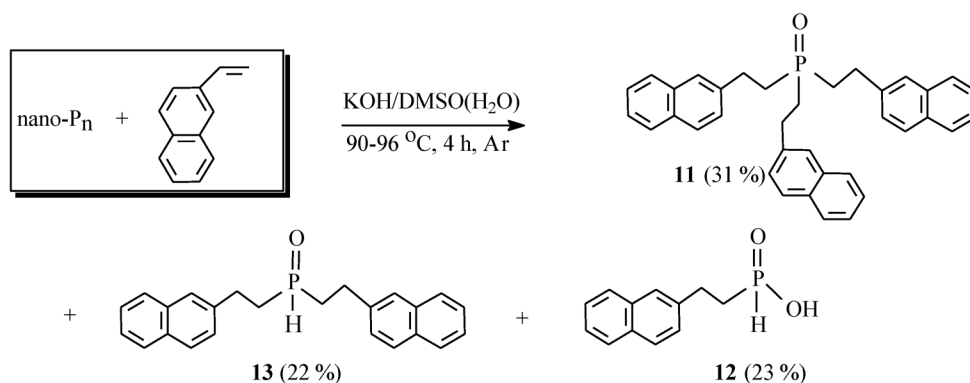
Phosphorylation of 2-vinylnaphthalene

Phosphorus-centered nucleophiles generated from white or red phosphorus in the KOH/DMSO(H_2O) system add to 2-vinylnaphthalene to give tris[2-(2-naphthyl)ethyl]phosphine oxide **11** in good yield (Scheme 7). When red phosphorus (P_n) is used, [2-(2-naphthyl)ethyl]phosphinic acid **12** is also formed in small yield [16,18].



Scheme 7 Reaction of P_4 or P_n with 2-vinylnaphthalene in the KOH/DMSO system.

In the phosphorylation of 2-vinylnaphthalene, red phosphorus nanocomposites (nano- P_n) outperform both P_n and P_4 . The major products of this reaction are tris[2-(2-naphthyl)ethyl]phosphine oxide **11**, bis[2-(2-naphthyl)ethyl]phosphine oxide **13**, and 2-(2-naphthyl)ethylphosphinic acid **12**, their total yield being 76 % (Scheme 8) [16].



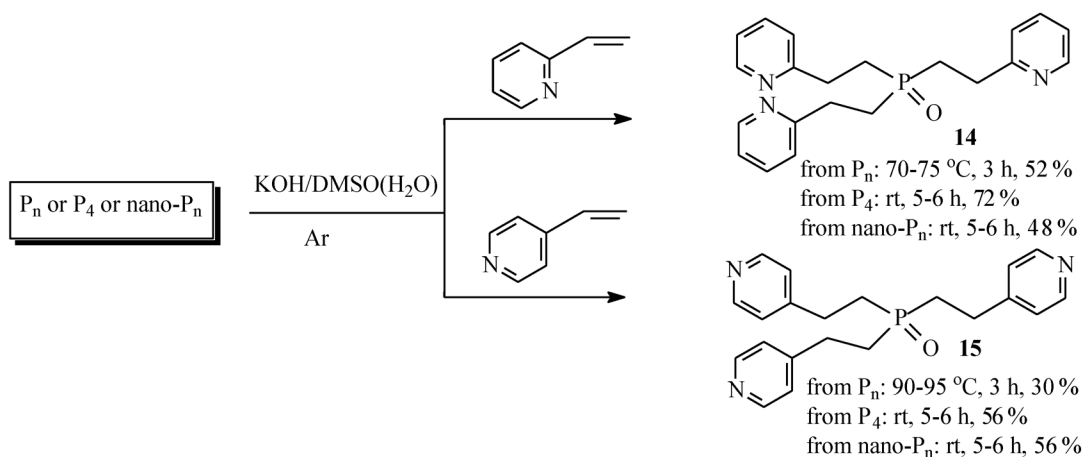
Scheme 8 Reaction of nano- P_n with 2-vinylnaphthalene in the KOH/DMSO system.

Phosphine oxide **11** is a luminophore [16b]. Its luminescence spectrum does not noticeably differ from that of naphthalene. The combination in one molecule of luminescent substituents and phosphine oxide group taking part in specific complex formation with rare-earth elements is a principally new approach to development of liquid and solid scintillators with the required characteristics, e.g., for solving such a basic problem as neutrino detection [19].

Phosphorylation of vinylpyridines

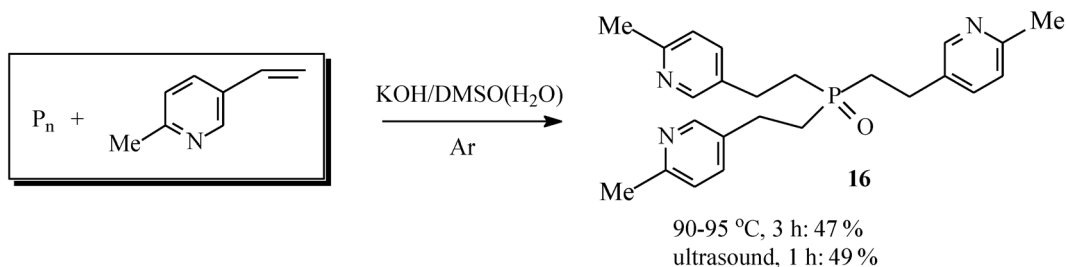
In the phosphorylation, vinylpyridines [20] show a higher reactivity than arylenes. For example, white phosphorus and red phosphorus nanocomposites easily react with 2- or 4-vinylpyridines in the suspension KOH/DMSO(H_2O) even at room temperature to afford tris[2-(2-pyridyl)ethyl]phosphine oxide **14** or tris[2-(4-pyridyl)ethyl]phosphine oxide **15** in up to 72 % yield (Scheme 9) [20d].

The phosphorylation of vinylpyridines with red phosphorus is carried out at higher temperatures (70–95 °C) to give tertiary phosphine oxides **14**, **15** (Scheme 9) in moderate yields [20a–c]. A microwave irradiation promoted version of the reaction (600 W, 2 min) is more rapid [20e].



Scheme 9 Synthesis of tris(2-pyridylethyl)phosphine oxides from elemental phosphorus and 2- or 4-vinylpyridines in the KOH/DMSO system.

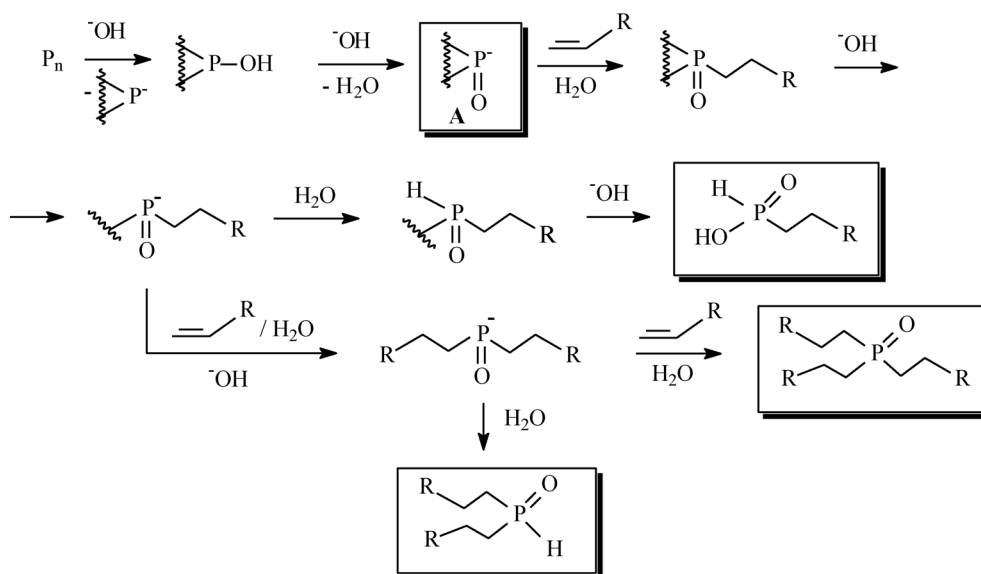
2-Methyl-5-vinylpyridine is also involved in the direct phosphorylation with red phosphorus, the yield of tris[2-(2-methyl-5-pyridyl)ethyl]phosphine oxide **16** being 47 % (Scheme 10) [20b]. Application of an ultrasound activation increases the rate of this phosphorylation [20b].



Scheme 10 Reaction of P_n with 2-methyl-5-vinylpyridine in the KOH/DMSO system.

Plausible scheme of the phosphorylation of aryl(hetaryl)alkenes with elemental phosphorus

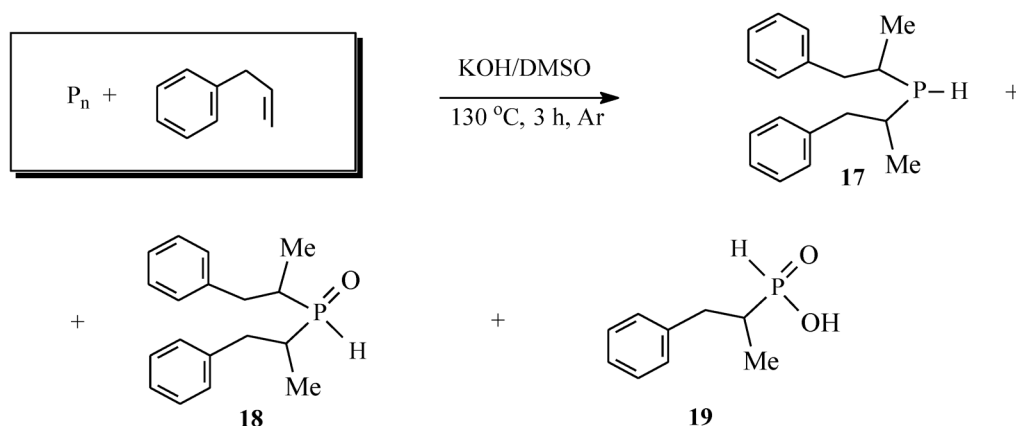
The key steps of the above phosphorylation include the cleavage of elemental phosphorus P–P bond (probably occurring in phosphorus nanoparticles) [17] by hydroxide anions to form highly active *P*-centered nucleophiles and their further addition to the double bond affording the secondary and tertiary phosphine oxides as well as phosphinic acids. The reactions proceed under oxygen-free conditions. Therefore, it is obvious that initial nucleophiles are polyphosphinite anionic nanoclusters **A** (Scheme 11).



Scheme 11 Plausible mechanism of the phosphorylation of aryl(hetaryl)alkenes with elemental phosphorus.

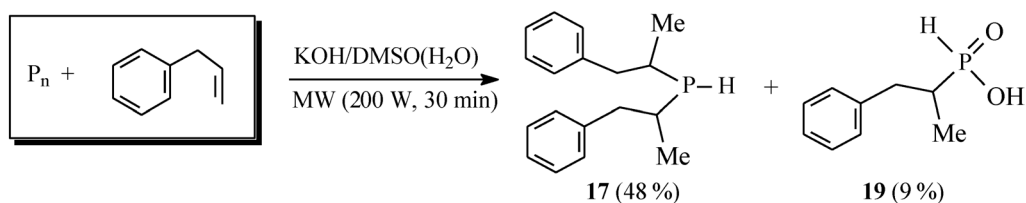
Phosphorylation of allylbenzene

Red phosphorus reacts with allylbenzene in the KOH/DMSO suspension (including ~0.1 mass % of hydroquinone as a radical processes inhibitor) to afford formally Markovnikov adducts, bis(1-phenylprop-2-yl)phosphine **17**, bis(1-phenylprop-2-yl)phosphine oxide **18**, and (1-phenylprop-2-yl)phosphinic acid **19** (Scheme 12). Secondary phosphine oxide **18** and phosphinic acid **19** have been isolated from this mixture in 35 and 32 % yields, respectively [21].



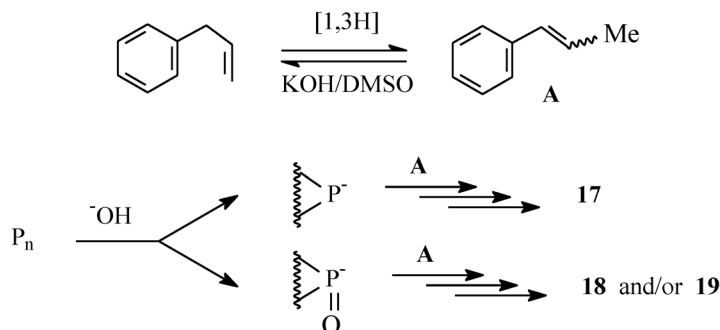
Scheme 12 Reaction of P_n with allylbenzene in the KOH/DMSO system under heating.

Microwave-assisted reaction of red phosphorus with allylbenzene not only shortens the process duration, but affects noticeably its chemoselectivity [21]. Thus, a microwave irradiation promoted version of the reaction gives mainly secondary phosphine **17**. Besides, the reaction delivers phosphinic acid **19** in small yield (Scheme 13).



Scheme 13 Microwave-assisted reaction of P_n with allylbenzene in the KOH/DMSO system.

The authors suppose [21] that in the first stage, owing to [1,3H] isomerization of allylbenzene under the action of the superbase, 1-phenylprop-1-ene **A** is formed. The latter reacts with phosphorus-centered nucleophiles generated by cleavage of the P–P bond in the presence of hydroxide anions. Nucleophilic addition of phosphide- and phosphinite anions to the double bond of **A** results in phosphine **17** and phosphine oxide **18** (or acid **19**), respectively (Scheme 14).



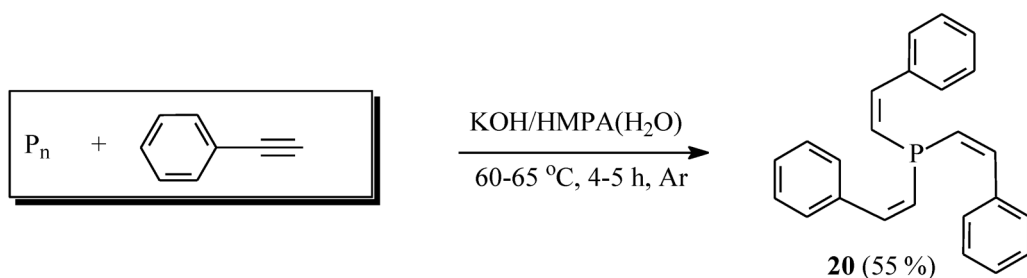
Scheme 14 Plausible mechanism of the phosphorylation of allylbenzene with red phosphorus.

Phosphorylation of alkynes

Aryl(hetaryl)acetylenes are another group of appropriate electrophiles for phosphorus nucleophiles generated from elemental phosphorus in the superbase suspensions. In this case, phosphide-anions turn out to be much more active than phosphinite ions. Thus, phenylacetylene is phosphorylated with red phosphorus in the superbase system alkali metal hydroxide–polar nonhydroxylic solvent (HMPA, DMSO, triethylphosphine oxide) to give chemo-, regio-, and stereoselectively tris(*Z*-styryl)phosphine **20** [7a–d,22] in a yield of up to 55 % (Scheme 15). The corresponding phosphine oxide **21** is formed in trace quantity both in the presence and absence of oxygen.

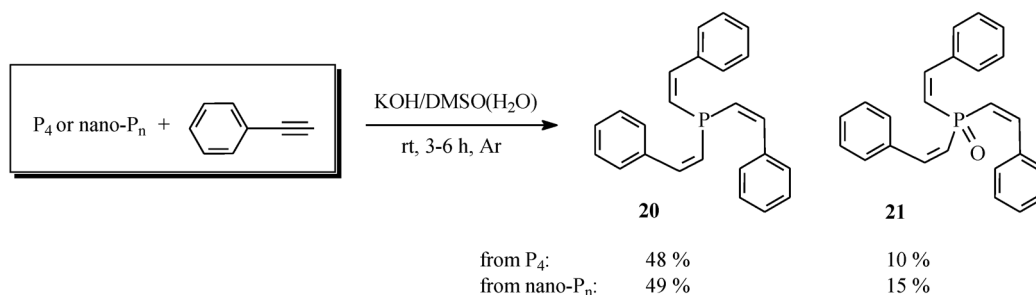
The stereochemistry of the process (*Z,Z,Z*-structure of the product) is in agreement with the well-established *trans*-mode of nucleophilic addition to monosubstituted acetylenes. Kinetic control of the stereochemistry has been confirmed by thermal (165 °C, 7 h) transformation of tris(*Z*-styryl)phosphine to tris(*E*-styryl)phosphine via the consecutive formation of the two other isomers [22c].

Earlier tristyrylphosphine (isomer of an unknown configuration) was prepared through a two-step procedure including synthesis of tristyrylphosphine oxide from phosphorus pentachloride and styrene [23] followed by the reduction of the phosphine oxide [24].



Scheme 15 Chemo-, regio-, and stereoselective synthesis of tris(*Z*-styryl)phosphine from P_n and phenylacetylene in the superbase system.

White phosphorus (P_4) and red phosphorus nanocomposites (nano- P_n) efficiently react with phenylacetylene in the system KOH/DMSO(H_2O) even at room temperature (Scheme 16) to give phosphine **20** and phosphine oxide **21** [25].



Scheme 16 Reaction of P_4 or nano- P_n with phenylacetylene in the KOH/DMSO system.

Tristyrylphosphines of *Z*- and *E*-configuration were easily oxidized to furnish the corresponding tris(*Z*-styryl)- and tris(*E*-styryl)phosphine oxides [22c,26]. The latter turned out to possess “propeller” C_3 -chirality [27].

The reaction of tris(*Z*-styryl)phosphine **20** with $PdCl_2$ (DMF, 90 °C, 15 min, yield 50 %) affords complex $[(Z-PhCH=CH)_3P]_2PdCl_2$ which is shown to be a promising catalyst for the Sonogashira coupling [28]. Easy accessibility of this complex makes it a probable alternative to traditional catalyst $[Ph_3P]_2PdCl_2$ for these type of reactions.

PHOSPHORYLATION WITH PHOSPHINE–HYDROGEN MIXTURE GENERATED FROM RED PHOSPHORUS

Nucleophilic addition of phosphine to alkenes

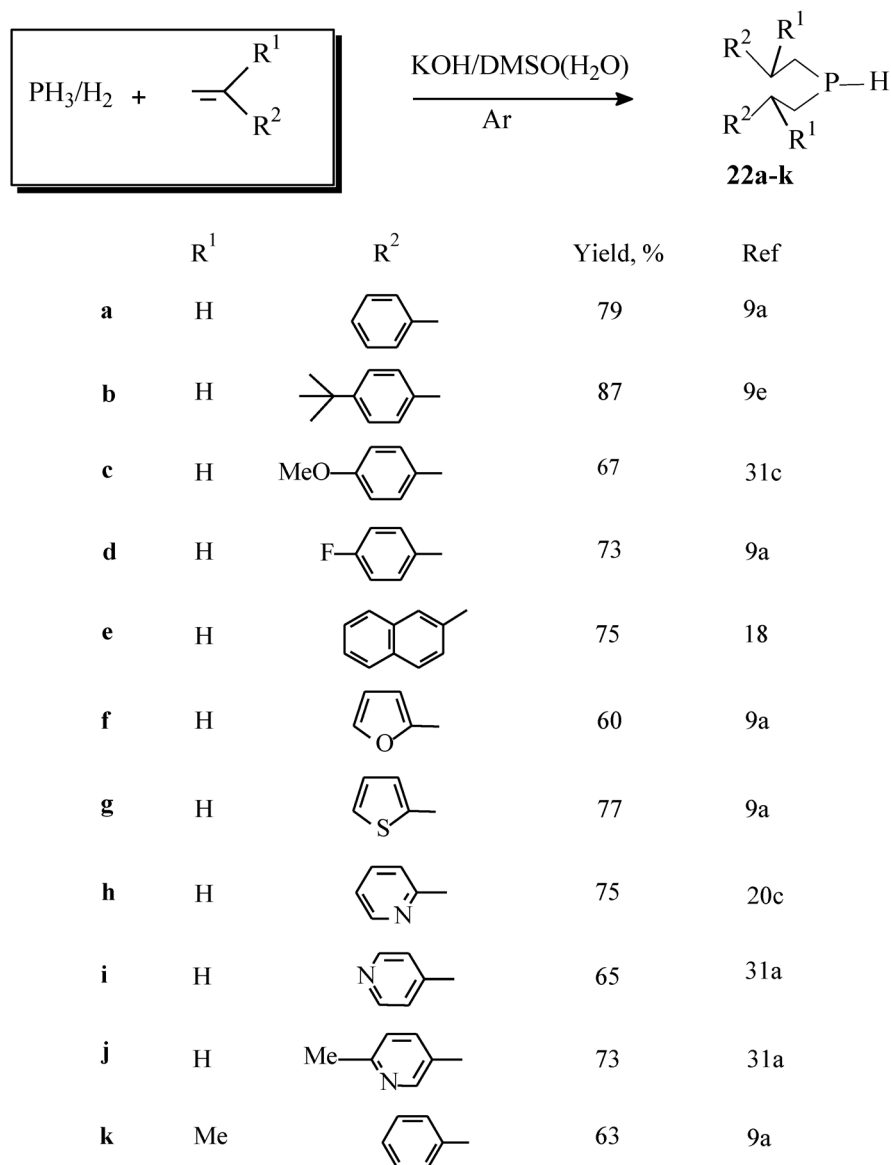
Phosphorylation of aryl- and hetarylalkenes

Nucleophilic addition of phosphine to the double C–C bond in the presence of bases was first described by Rauhut et al. [29] and later by King et al. [30] for the alkenes with strong electron-withdrawing substituents. All these works were discussed in detail in a review [9b].

Later, it has been shown that superbase systems allow hydrophosphination of weakly electrophilic double bonds of aryl- and hetarylethenes with a novel reagent, phosphine–hydrogen mixture generated from red phosphorus and KOH in aqueous-organic medium (dioxane, toluene) [9] and applied without further isolation or purification. The mixture proved to be an efficient phosphinating agent and allowed

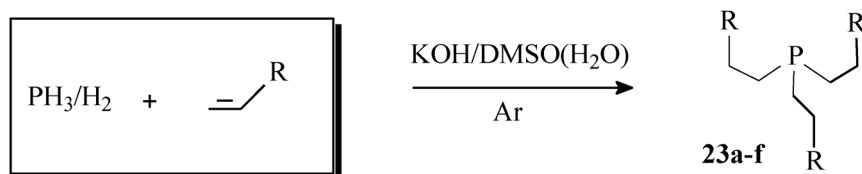
previously unknown or difficult-to-prepare secondary or tertiary phosphines to be synthesized [7c,d,g,9,18,20c,31].

Thus, bis(2-arylethyl)- and bis(2-hetarylethyl)phosphines **22a–k** were selectively prepared (Scheme 17) upon slow addition of alkene to a heated (45–96 °C, atmospheric pressure) KOH/DMSO suspension while passing the phosphine–hydrogen mixture through reaction mixture.



Scheme 17 Synthesis of secondary phosphines from phosphine–hydrogen mixture and aryl(hetaryl)alkenes in the KOH/DMSO system.

Complete and selective aryl(hetaryl)ethylation of phosphine with styrenes and vinylpyridines was accomplished (Scheme 18) at 45–120 °C and atmospheric pressure in the KOH/DMSO system with additional introduction of the alkenes to reaction mixture at the end of the process (after the phosphine



	R	Yield, %	Ref
a		76	31b
b		69	9e
c		80	31c
d		65	20c
e		68	31a
f		70	31a

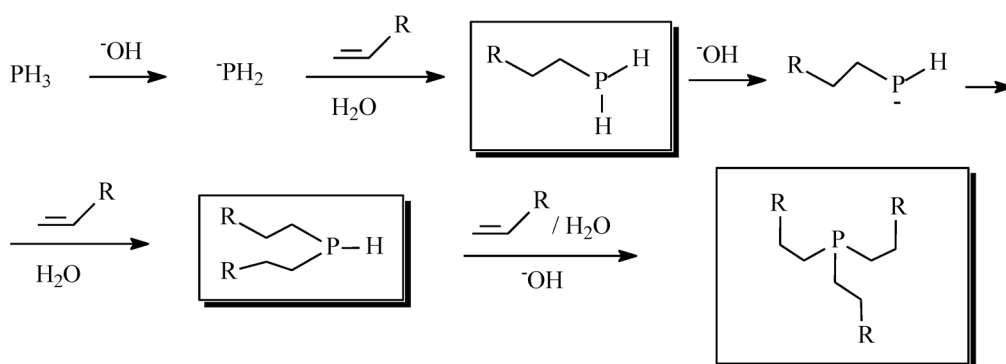
Scheme 18 Synthesis of tertiary phosphines from phosphine–hydrogen mixture and aryl(hetaryl)alkenes in the KOH/DMSO system.

feeding was stopped) to give tris(2-arylethyl)- and tris(2-hetarylethyl)phosphines **23a–f** in 65–80 % yields.

Particular advantages of the above methods are their chemoselectivity and mild conditions (first of all, atmospheric pressure). Previously, phosphine was added to styrene in the presence of a radical initiator under elevated phosphine pressure to give a mixture of primary, secondary, and tertiary phosphines [32].

At lower temperatures (30–40 °C, KOH/DMSO), phosphine generated from red phosphorus and KOH in aqueous-organic medium adds to styrene or vinylpyridines to form the corresponding primary phosphines in 20–24 % yields [31a,33], the major products (up to 60 %) under these conditions remaining diorganophosphines.

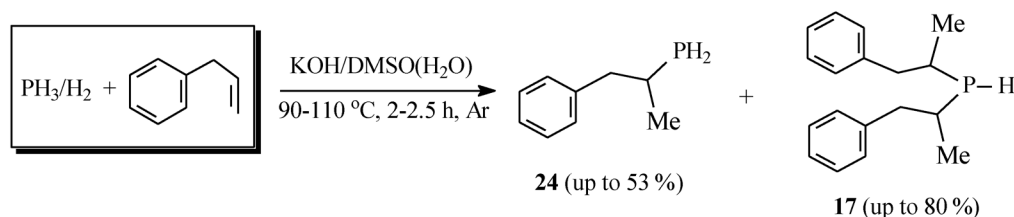
Apparently, the formation of organic phosphines occurs through the phosphination of alkenes with phosphide-anions generated initially from phosphine and further from mono- or diorganophosphines in the KOH/DMSO system (Scheme 19).



Scheme 19 Plausible mechanism of the phosphorylation of aryl(hetaryl)alkenes with phosphine.

Phosphorylation of allylbenzene

Phosphine and allylbenzene under the action of the superbasic catalytic system KOH/DMSO afforded Markovnikov products, namely, (1-phenylprop-2-yl)phosphine **24** and bis(1-phenylprop-2-yl)phosphine **17** (Scheme 20) [34]. The conditions for the target preparation of either phosphine **17** or **24** have been elaborated. Primary phosphine **24** was synthesized in 53 % yield by slow addition of allylbenzene to a suspension of KOH/DMSO at 90 °C under continuous passing a vigorous flow of phosphine–hydrogen mixture through the suspension (the yield of secondary phosphine **17** being 30 %). To attain the addition of phosphine to two molecules of allylbenzene, the reaction was carried out at higher temperatures (90–110 °C), an extra equivalent of allylbenzene being fed after the flow phosphine was ceased. Under these conditions, phosphine **17** was obtained selectively in 80 % yield.



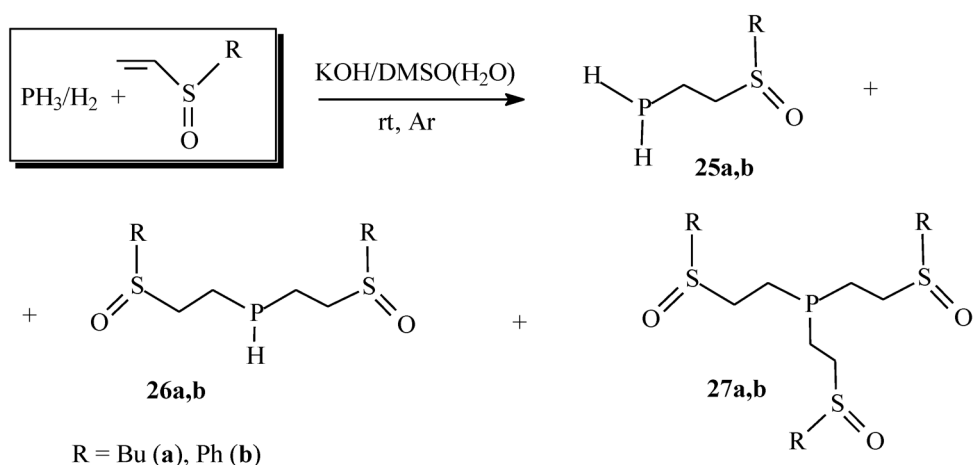
Scheme 20 Reaction of phosphine–hydrogen mixture with allylbenzene in the KOH/DMSO system.

Like in the case of the reaction with red phosphorus, in the first stage, due to [1,3H] isomerization of allylbenzene under the action of the superbases, 1-phenylprop-1-ene is generated. The latter reacts with PH_3 according to a nucleophilic addition mode to give primary phosphine **24** which further interacts with 1-phenylprop-1-ene to produce secondary phosphine **17**.

Phosphorylation of vinylsulfoxides

Nucleophilic addition of phosphine to vinyl sulfoxides in superbasic system KOH/DMSO proceeding at room temperature leads to the formation of all possible phosphines: primary **25**, secondary **26**, and tertiary **27** (Scheme 21) [35].

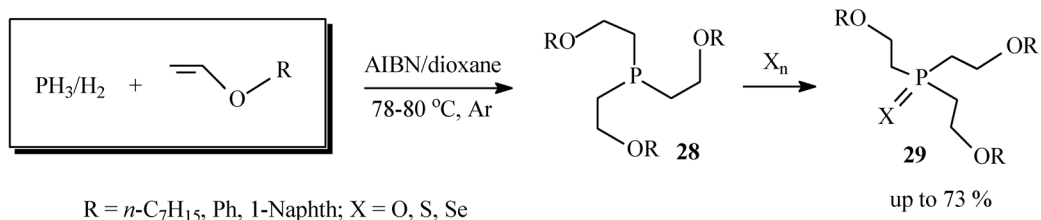
By controlling the conditions of the reaction, it was possible to selectively obtain the secondary phosphine **26a** isolated as the corresponding phosphine oxide (nonoptimized preparative yield of pure product was 35 %).



Scheme 21 Reaction of phosphine–hydrogen mixture with vinylsulfoxides in the KOH/DMSO system.

Radical addition of phosphine to alkenes

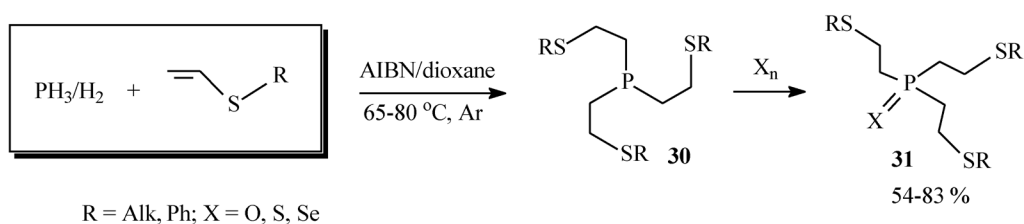
Double bonds of vinyl chalcogenides add phosphine under radical initiation in the anti-Markovnikov mode [9c,32,36]. Thus, phosphine, generated from red phosphorus in the system KOH/H₂O/toluene, reacts with vinyl ethers in the presence of AIBN (atmospheric pressure) to give tris[2-(organyloxy)ethyl]phosphines **28**, which are transformed to the corresponding phosphine chalcogenides **29** (in up to 73 % isolated yield) via the reactions with air oxygen, elemental sulfur, or selenium (Scheme 22) [36a].



Scheme 22 Radical addition of phosphine to vinyl ethers.

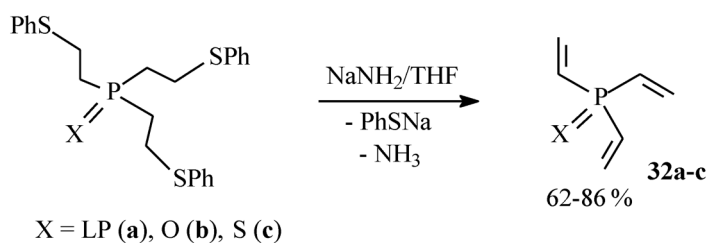
Until our investigation there was only one publication [32] reporting that phosphine added to butyl vinyl ether in the presence of AIBN under pressure 33 atm and heating in autoclave to give a mixture of primary, secondary, and tertiary phosphines.

Likewise, phosphine adds to vinyl sulfides under radical initiation conditions with the formation of tris(2-organythioethyl)phosphines **30** [9c,36b], which are also easily oxidized by air oxygen [9c], elemental sulfur [36b], and selenium [36b] to the corresponding phosphine chalcogenides **31** (Scheme 23).



Scheme 23 Radical addition of phosphine to vinyl sulfides.

The synthesized functional tertiary phosphines and phosphine chalcogenides are convenient intermediates for preparation of, for example, trivinylphosphines and trivinylphosphine chalcogenides. Thus, tris(2-phenylthioethyl)phosphine [36b], -phosphine oxide [37] and -phosphine sulfide [36b] when treated with sodium amide in tetrahydrofuran (THF) (62–64 °C) form trivinylphosphine **32a**, trivinylphosphine oxide **32b**, and trivinylphosphine sulfide **32c** in good yields (Scheme 24).

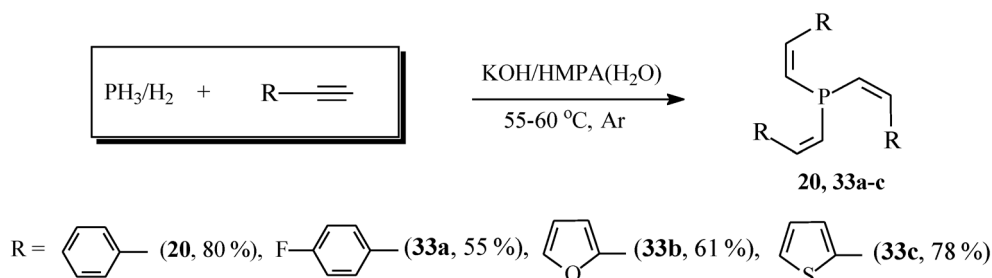


Scheme 24 Synthesis of trivinylphosphine and trivinylphosphine chalcogenides from tris(2-phenylthioethyl) phosphine and its chalcogenides.

Nucleophilic addition of phosphine to alkynes

Phosphine generated in the system $P_n/KOH/H_2O/dioxane$ adds to aryl(hetaryl)acetylenes in the superbase suspension $KOH/HMPA$ under mild conditions (55–60 °C, atmospheric pressure) [38]. Like in the case of elemental phosphorus, the reaction leads to *Z*-isomers of tris[aryl(hetaryl)ethenyl]phosphines **20**, **33a–c** (Scheme 25).

Unlike the addition of phosphide-anions to aryl(hetaryl)alkenes, neither mono- nor diadducts have been detected in the product mixture in this case [7c,g].



Scheme 25 Chemo-, regio-, and stereoselective synthesis of tris(*Z*-styryl)phosphine from phosphine–hydrogen mixture and aryl(hetaryl)acetylenes in the superbase system.

ARYL(HETARYL)ETHYLPHOSPHINES AND -PHOSPHINE CHALCOGENIDES GENERATED BY THE HALOGEN-FREE PROTOCOLS AS REAGENTS IN ORGANOPHOSPHORUS SYNTHESIS

The previously inaccessible primary, secondary, and tertiary phosphines and phosphine chalcogenides, having such rare substituents as aryl(or hetaryl)alkyl, originated from phosphorylation in the system elemental phosphorus/strong bases (now these syntheses are often referred to as the Trofimov–Gusarova reaction [7f,11]), attract growing attention in organic and element-organic syntheses [9d,39–43].

Phosphorylation of alkenes

Secondary phosphines and phosphine chalcogenides add to functional alkenes [9d,39] (vinyl ethers [39a–e], vinyl sulfides [39c,f], vinyl selenides [39f,g], vinyl tellurides [39j], vinyl pyrroles [39h], vinyl imidazoles [39k,l], vinyl pyridines [9d], vinyl sulfoxides [39i], vinyl sulfones [9d]) to afford functionalized tertiary phosphines and phosphine chalcogenides including chiral ones. The additions proceed depending on the conditions and the double bond nature through radical [39a–h,j–l] or nucleophilic [9d,39i] mechanisms.

Phosphorylation of alkynes

Addition of primary and secondary phosphines and phosphine chalcogenides to acetylenes [9d,40] (acetylene [9d,40a], alkyl [9d,40a], aryl- or hetarylacetylenes [40b,c], cyanoacetylenes [40d–g], acylacetylenes [40h,i], alkylthiochloroacetylenes [9d]) occurs as a rule stereoselectively through nucleophilic [40f–i], radical [40a–c], or ion-radical [40d,e] mechanisms to give *Z*-isomers of corresponding mono-adducts.

Phosphorylation of aldehydes

Diverse aldehydes react with bis[2-aryl(or hetaryl)alkyl]phosphine oxides, -sulfides and -selenides under mild catalyst-free conditions to deliver tertiary chiral α -hydroxyphosphine chalcogenides in high or good yields [41].

Novel three-component reactions between secondary phosphines or phosphine selenides, elemental selenium, and bases

Recently, a new general and convenient approach to the preparation of various diselenophosphinates [42] via three-component reactions of secondary phosphines or phosphine selenides with elemental selenium and bases has been developed [42,43]. Alkali metal hydroxides [43a,b], ammonia [43c], amines [43d,e], diamines [43d], and alkaloids [43f] were used as bases. The reactions proceed under mild conditions to afford in high yield hitherto unknown or inaccessible diselenophosphinates, which are [42] unique single-source precursors of semiconducting and magneto-optical nanomaterials, efficient RAFT-agents, as well as the potential building blocks for the synthesis of practically important organophosphorus and organoselenium compounds [42].

CONCLUDING REMARKS

A novel methodology concerning the C–P bond formation using elemental phosphorus/strong bases or phosphine generated in situ from red phosphorus has been discussed. This halogen-free methodology is especially applicable for the phosphorylation of weakly electrophilic alkenes and also alkynes and

represents a new general route to hitherto unknown or inaccessible mono-, di-, or triorganophosphines, phosphine chalcogenides, and phosphinic acids of a great structural diversity. Among a wide range of novel organophosphorus compounds synthesized in the framework of this approach, ligands for design catalytically and biologically prospective metallocomplexes [28,44], flame-retardants [45], extractants of rare-earth, noble and transuranium elements [46], and effective reagents for flotation processes [47] have been found. The new primary and secondary phosphines and phosphine chalcogenides with rare aryl(or hetaryl)alkyl substituents successfully are also used as effective building blocks in the syntheses of diverse functional organophosphorus compounds [39–43].

Thus, thanks to its green background, this halogen-free phosphorylation methodology based on elemental phosphorus is expected to gain ever-growing applications in organophosphorus chemistry, catalysis [28,48], biochemistry [49], hydrometallurgy [46,50] and materials science [42,51].

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