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Elemental phosphorus in strongly basic media as phosphorylating reagent: a dawn of halogen-free 'green' organophosphorus chemistry

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The elemental phosphorus/strong bases systems are gaining a growing attention as halogen-free 'green' phosphorylating reagents enabling a great variety of alkenes, acetylenes, organic halides and oxiranes to be converted in one-pot procedures to inaccessible primary, secondary and tertiary phosphines and phosphine oxides.

The phosphorylation of organic compounds using elemental phosphorus represents one of the most convenient and promising approaches to the C–P bond formation and synthesis of fundamental organophosphorus compounds, particularly, phosphines and phospine oxides. The latter are important objects of diverse branches of chemical science. They are used as ligands to design metallocomplex catalysts for numerous widely applying reactions including those for enantioselective processes.[1] Among them are flame retardants,[2] extractants of rare-earth and transuranium elements,[3] coordinating solvents for the synthesis of conductive nanomaterials,[4] reactive building blocks for organic and organoelement syntheses. Meanwhile, until recently, only limited efforts were focused on application of elemental phosphorus to the synthesis of organophosphorus compounds and, no wonder, they did not lead to practically meaningful results. Usually, the activation of elemental phosphorus, especially, red phosphorus, towards C–P bond formation in the reactions with functional organic compounds required harsh conditions (high temperature and pressure, large amounts of expensive activators, *etc.*).[5] Now in this area growing attention is being paid to an electrochemical method, mainly, for activation of white phosphorus.[6]

A conceptually novel methodology for the activation of elemental phosphorus in heterogeneous highly basic media pioneered at A. E. Favorsky Irkutsk Institute of Chemistry SB RAS two decades ago[7] keeps gaining strength. This study has led to a set of straightforward facile methods for the preparations of diverse phosphines and phosphine oxides,[8] which are currently synthesized from hazardous phosphorus halides and organometallic reagents. Dangerously growing ecological challenges demand urgently to avoid whatever possible the aged halogen-based organophosphorus chemistry.

Presently, the P–P bond cleavage of elemental phosphorus under the action of nucleophiles is being intensively investigated.[9]

Professor Boris A. Trofimov graduated from the Irkutsk State University (ISU) in 1961. He got Candidate (Ph.D.) degree from the ISU in 1964 under Professor M. F. Shostakovsky (a renown pupil of Academician A. E. Favorsky). In 1970, B. A. Trofimov received his Doctor degree from Leningrad State University and headed a Laboratory of the Irkutsk Institute of Organic Chemistry, Academy of Sciences of the USSR (later the A. E. Favorsky Irkutsk Institute of Chemistry, Russian Academy of Sciences), and since 1994 he held the position of the Director of this Institute. In 1990, Professor Trofimov was elected a Corresponding Member of the Academy of Sciences of the USSR, and in 2000 – a Full Member of the Russian Academy of Sciences. He was plenary, invited or guest lecturer in England, Germany, USA, Austria, Denmark, Netherlands, Switzerland, Israel, Japan, France, India, China, Korea, Hungary, Czechoslovakia and Mongolia. Professor Trofimov was awarded the Butlerov Prize of the Russian Academy of Sciences (1997) and honored as a Mendeleev reader (2003). His research interests cover organic and organoelement synthesis based on acetylene; organic chemistry of phosphorus, sulfur, selenium and tellurium; chemistry of heterocyclic compounds; superbases; polymers; new reactions and general methodologies.

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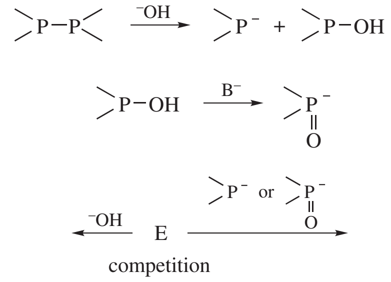
Fundamentally, these investigations substantially complement the existing paradigms of phosphorus chemistry. From synthetic methodology viewpoint, this work paves the shortest and environmentally benign routes to practically important organophosphorus compounds.[1–4] To our knowledge, the preparative application of phosphorus-centered nucleophiles generated by P–P bond cleavage of white phosphorus under the action of charged bases (hydroxide anions) was first mentioned by M. M. Rauhut.[10] Less reactive but non-toxic and safer in handling red phosphorus has been successfully attempted in organophosphorus synthesis by A. A. Petrov and G. M. Bogolyubov[11] and later on by E. Bornancini.[12] They managed to split the P–P bond of this three-dimensional phosphorus modification using the alkali metal/liquid ammonia system.

The communication[7(*a*)] on a direct one-pot synthesis of tristyrylphosphine from phenylacetylene and red phosphorus in the KOH/HMPA superbase system gave rise to systematic application of phosphorus-centered nucleophiles like phosphide and phosphinite anions for the preparation of hardly accessible or hitherto unknown organophosphorus compounds. This concept consists in the generation of phosphorus nucleophiles from elemental phosphorus in superbase media and their simultaneous capture with appropriate electrophiles to form C–P bond in diverse structural surroundings (Scheme 1). The essence of these reactions is a competition between the hydroxide anion and phosphorus nucleophiles (phosphide and phosphinite anions or their nano-sized anionic polyphosphorus precursors) for the electrophile (Scheme 1).



Scheme 1

In this article, we focus on the major features, advantages, peculiarities and prospects of this novel concept in organophosphorus chemistry.

The following phosphorylating systems were proved to be active:

– red (P_n) or white (P_4) phosphorus/MOH (M – alkali metal)/ polar nonhydroxylic solvent (DMSO, HMPA);
– nanocomposites of P_n/MOH/DMSO;
– P_n or P_4/MOH/phase-transfer catalyst;
– P_n/M/NH_3 liquid;
– P_n or P_4/RC≡CM/NH_3 liquid (or THF);
– P_n/MSH/DMSO;
– P_n/MSR (R = organic radical)/DMSO.

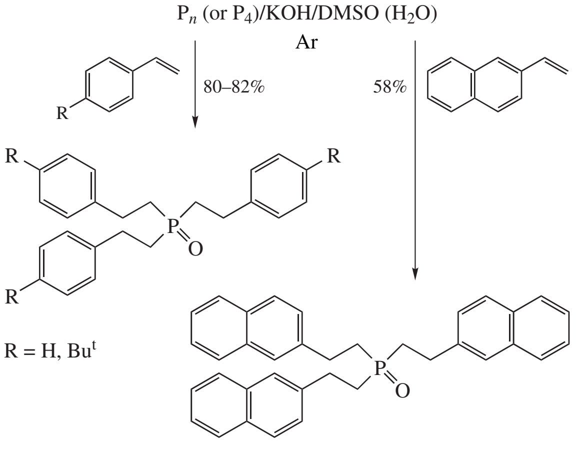
Available alkenes, acetylenes, organic halides, dihaloalkanes, and oxiranes were appropriate electrophiles.

Typical syntheses of phosphines and phosphine oxides performed in the above systems are given below.

Phosphorylation in the elemental phosphorus/MOH/ DMSO (or HMPA) systems

Unexpectedly, an excellent nucleophile/electrophile correspondence was discovered for phosphorus nucleophiles generated from elemental phosphorus in the above systems and weakly electrophilic alkenes like styrenes,[7(*c*),8(*b*),13] 2-vinylnaphthalene[14] and vinylpyridines.[15]

Phosphorylation of styrene,[13(*a*)] *tert*-butylstyrene[13(*d*)] and 2-vinylnaphthalene[14] with the P_n or P_4/KOH/DMSO (or HMPA) systems proceeds at 85–110 °C in the presence of small amount of H_2O (as a proton transfer agent) under argon to give tris(2-phenethyl)-, tris[4-(*tert*-butyl)phenethyl]- and tris[2-(2-naphthyl)ethyl]phosphine oxides in 58–82% yields (Scheme 2).

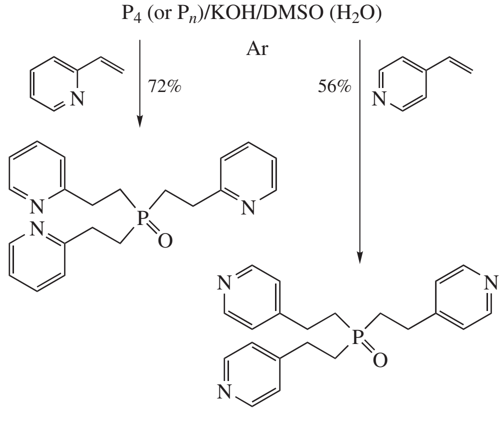


Scheme 2

In these processes, phosphorus nucleophiles win the competition entirely over the hydroxide anion since excess alkenes are almost completely recovered (if used).[13(*a*)]

Under certain conditions, the reaction of red phosphorus with arylethenes can be directed towards the preferable formation of secondary phosphine oxides.[13(*b*),(*c*)]

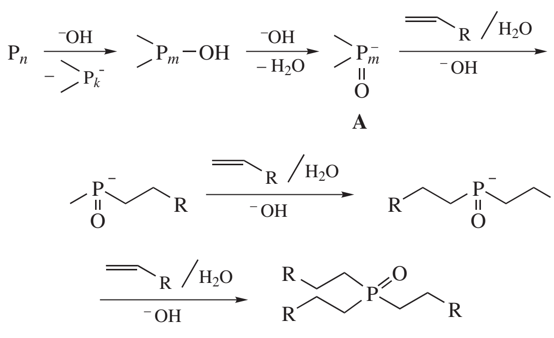
In this phosphorylation, vinylpyridines show a higher reactivity than arylethenes. For example, white phosphorus easily reacts with 2- and 4-vinylpyridines in the KOH/DMSO suspension even at room temperature to afford tris[2-(2-pyridyl)ethyl]phosphine oxide and tris[2-(4-pyridyl)ethyl]phosphine oxide in 72 and 56% yields (Scheme 3).[15(*d*)] The phosphorylation of vinylpyridines with red phosphorus is carried out at a higher temperature (70–95 °C).[15(*a*)–(*c*)]



Scheme 3

The microwave[13(*c*),16] and ultrasonically[15(*b*)] activated phosphorylation of aryl(hetaryl)alkenes with the P_n/KOH/DMSO system is more rapid and, in some cases, results in higher yields.[16(*b*)]

The key steps of the above phosphorylation include the cleavage of elemental phosphorus P–P bond (probably occurring in phosphorus nanoparticles) by hydroxide anions to form highly active P-centered nucleophiles and their further addition to the double bond affording the monoadducts. The reactions proceed under oxygen-free conditions. Therefore, it is obvious that initial nucleophiles are polyphosphinite (nano-sized) anions **A** (Scheme 4).



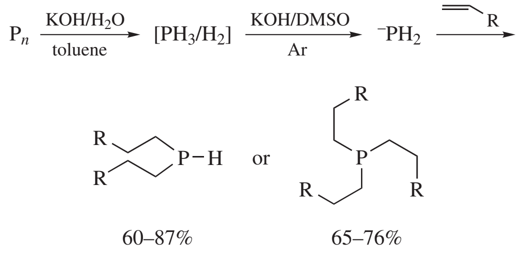
R = Ph, 4-Bu^{t}C$_6$H$_4$, 2-naphthyl, 2-pyridyl, 4-pyridyl

Scheme 4

The final step of this novel cascade reaction, where the key role belongs to the unprecedented polyphosphinite anionic nanocluster addition to the double bond, may be considered as a kind of the Pudovik reaction or, more generally, the Michael addition, though the latter requires strongly electrophilic alkenes, among which styrenes have never been listed.

Apparently, the polyphosphinite nanoclusters **A** (Scheme 4) possess much higher nucleophilicity compared to simple phosphinite anions (O=P$^-$). This inference is experimentally supported by the fact that the model reaction of *tert*-butylstyrene with KH_2PO_2 (the latter and PH_3 are the products of the redox reaction of red phosphorus with KOH) under the same conditions gives only traces of the organophosphorus compounds.[13(d)]

In these cases, DMSO does not act as an oxidizer since under the conditions studied phosphine generated easily together with hydrogen from red phosphorus in KOH/H_2O/toluene (or dioxane) medium[17] adds to aryl(hetaryl)ethenes to furnish the corresponding secondary or tertiary phosphines[14(a),15(c),17,18] in good or high yields (but not phosphine oxides) (Scheme 5).



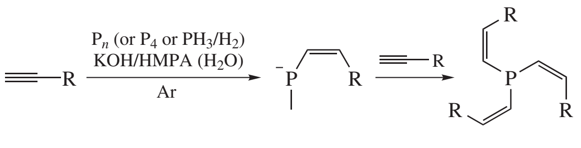
R = Ph, 4-Bu^{t}C$_6$H$_4$, 4-FC$_6$H$_4$, 2-naphthyl,
2-furyl, 2-thienyl, 2-pyridyl, 4-pyridyl

Scheme 5

Actually, these are unusually easy nucleophilic additions to the very weak olefinic electrophiles.

Aryl(hetaryl)acetylenes are another group of electrophiles for which phosphorus nucleophiles generated from elemental phosphorus in the superbase suspension of KOH/HMPA are capable of winning competition over the hydroxide ion.[7(a),8] In this case, phosphide anions are much more active than phosphinite ions. Phosphorylation of aryl(hetaryl)acetylenes with the P_n or P_4 or PH_3/KOH/HMPA systems proceeds under mild conditions (25–65 °C, Ar) to give chemo-, regio- and stereoselectively *Z*-isomers of tris[aryl(hetaryl)ethenyl]phosphines in 55–80% yields[19] (Scheme 6).

Neither mono- nor diadducts have been detected in the product mixture, implying that the intermediate mono- and di[aryl(hetaryl)ethenyl]phosphide anions are much more competitive towards aryl(hetaryl)acetylenes than initial inorganic phosphide anions.



R = Ph, 4-FC$_6$H$_4$, 2-furyl, 2-thienyl 55–80%

Scheme 6

The stereochemistry of the processes [all *Z*-structure of the tertiary aryl(hetaryl)ethenylphosphines] 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.[19(b)]

Phosphorylation in the nanocomposites of red phosphorus/KOH/DMSO system

Recently, it has been shown that elemental phosphorus nanocomposites have enhanced reactivity as compared with common red phosphorus.[20] The nanocomposites of red phosphorus 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 (Scheme 7).[20]

$$P_4 \xrightarrow[C_6H_6]{^{60}\mathrm{Co}\ \gamma\text{-radiation}} \text{Nano-}P_n(\mathrm{C, C{-}P})$$

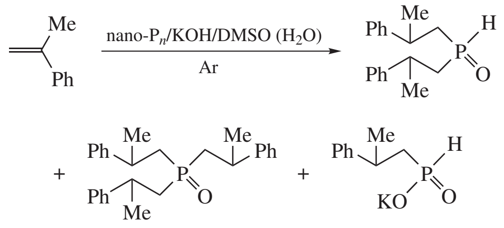
C = carbon, graphite
C–P = organophosphorus compounds

Scheme 7

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.[20] Oxygen is involved in the composites owing to the oxidation of the most chemically reactive sites (defects) and represented as functional groups with phosphorus–oxygen bonds. According to electron microscopy, the nanocomposites contain nanoparticles mainly of 30–50 nm.[20]

In the presence of strong bases, these nanocomposites are more active in phosphorylation of arylethenes than red phosphorus. For instance, the reaction with α-methylstyrene proceeds (120 °C, 3 h) in a KOH/DMSO system to produce secondary and tertiary phosphine oxides and potassium phosphinate in 95% total yield. The conversions of the red phosphorus nanocomposite and α-methylstyrene are almost 100 and 17%, respectively (Scheme 8).[20]

Under analogous conditions, common red phosphorus reacts with the same olefin less efficiently though more selectively to



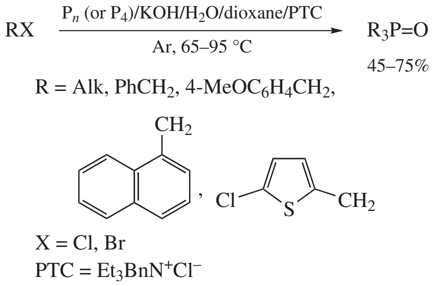
Scheme 8

give tertiary phosphine oxide in 15% yield (the conversions of P_n and the olefin are 82 and 18%, respectively).[20]

Phosphorylation under phase-transfer conditions

The phase-transfer catalysis with strongly basic aqueous solutions is commonly considered to produce superbases.[8(a),(c)] Therefore, this technique can be expected to affect the competition between hydroxide and phosphorus anions generated from base-assisted cleavage of elemental phosphorus in favor of the latter by a better extraction of lipophilic phosphorus anions into the organic phase. This proves to be particularly efficient for electrophiles reactive towards alkali hydroxides like organic halides.

Under phase-transfer conditions, the suspension consisting of red (or white) phosphorus, KOH, dioxane, water, and a phase-transfer catalyst reacts readily with alkyl bromides,[8(b),21] benzyl,[7(b),16(b),22] 4-methoxybenzyl,[23] 1-naphthylmethyl[16(b),24] and 2-chlorothienyl-5-methyl[25] chlorides to give the corresponding tertiary phosphine oxides as major products in a yield up to 75%. In this case, phosphinite anions become more competitive than both hydroxide and phosphide ions (Scheme 9).

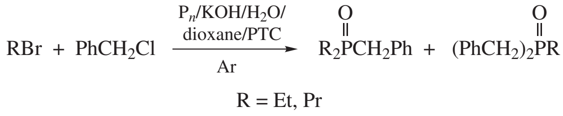


Scheme 9

As mentioned above, the phosphinite anions are ultimate products of the multistep cascade stripping of the polyphosphinite anions (Scheme 4) and their simultaneous alkylation. Therefore, they should also be referred to as the major products of this phosphorylation reaction. The tertiary phosphine oxides are eventually resulted from the Michaelis–Becker alkylation of the secondary phosphinite oxide anions.

Under certain conditions, the reaction of red phosphorus with alkyl halides can be directed towards the preferable formation of secondary phosphine oxides.[16(b),26]

Phase-transfer catalysis has also been employed to synthesize non-symmetric phosphine oxides, which are obtained in 12–17% yields by simultaneous phosphorylation of a mixture of ethyl or propyl bromides and benzyl chloride with red phosphorus, symmetric trialkyl- and tribenzylphosphine oxides being formed in trace amounts (Scheme 10).[27]



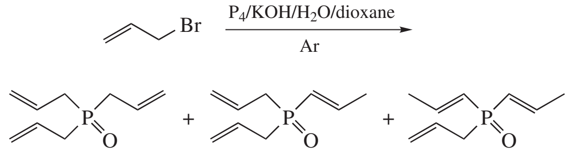
$$RBr + PhCH_2Cl \xrightarrow[Ar]{P_n/KOH/H_2O/\text{dioxane}/PTC} R_2\overset{\overset{\displaystyle O}{\|}}{P}CH_2Ph + (PhCH_2)_2\overset{\overset{\displaystyle O}{\|}}{P}R$$

R = Et, Pr

Scheme 10

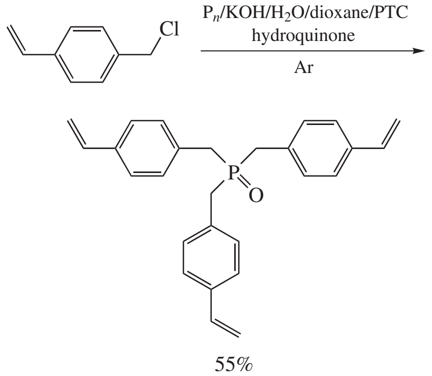
White phosphorus reacts readily with allyl bromide in the KOH/H_2O/dioxane system at room temperature to afford expected tris(propen-2-yl)phosphine oxide as a main product, and also products of its prototropic isomerisation: bis(propen-2-yl)-(*E*-propen-1-yl)phosphine oxide and bis(*E*-propen-1-yl)(propen-2-yl)phosphine oxide, in a total yield of 96%, their molar ratio being 1:0.5:0.1 (Scheme 11).[28]

The phosphorylation of allyl bromide with red phosphorus occurs at a higher temperature (70–75 °C).[29]



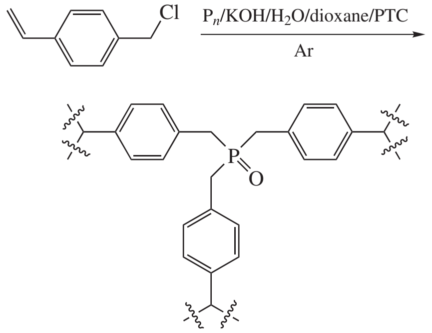
Scheme 11

Red phosphorus reacts with 4-vinylbenzyl chloride chemoselectively to furnish tris(4-vinylbenzyl)phosphine oxide in a good yield.[30] The reaction proceeds in the KOH/H_2O/PTC system at 45–50 °C in the presence of hydroquinone (Scheme 12).



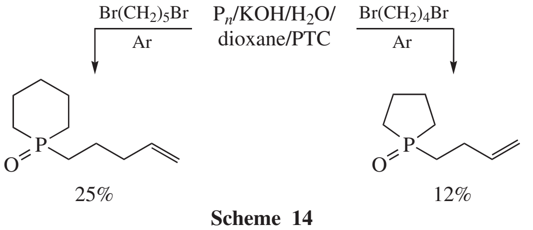
Scheme 12

The performance of this reaction without hydroquinone at 55–60 °C leads to the formation of three-dimensional cross-linked tris(4-vinylbenzyl)phosphine oxide polymer (Scheme 13).[31]



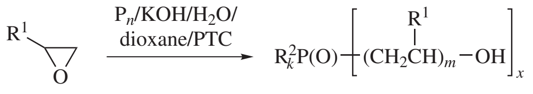
Scheme 13

α,ω-Dibromoalkanes react with the phosphorus nucleophiles produced in the phase-transfer P_n/KOH/H_2O/dioxane/$Et_3BnN^+Cl^-$ system to deliver alkenyl phospholane and phosphorinane oxides in 12–25% yields, due to side elimination processes manifested by the presence of an alkenyl group at the phosphorus atom (Scheme 14).[32] Low yields of the heterocycles are likely due to the competitive interaction of the initial dihaloalkanes with hydroxide ions (in particular, by the dehydrohalogenation).



Scheme 14

Methyl- and [2-(vinyloxy)ethoxy]methyloxiranes are phosphorylated readily with red phosphorus under the conditions of phase-transfer catalysis to give phosphorus-containing polyols (Scheme 15).[33]



R^1 = Me, $CH_2{=}CHO(CH_2)_2OCH_2$
R^2 = H, OH, OK
k = 1, 2; x = 1, 2; m = 3–5

Scheme 15

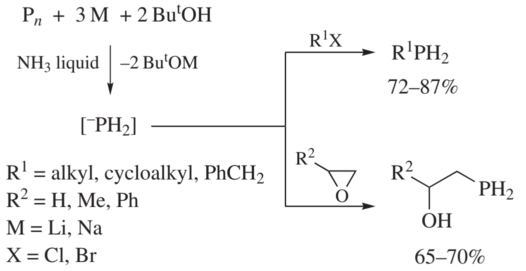
Notably, under the phase-transfer conditions no (or just sluggish) addition of phosphorus nucleophiles to styrenes, vinylpyridines or arylacetylenes occurs, obviously, due to a stronger solvation (hydration) or protonation of the phosphorus anions.[9(b)]

Phosphorylation in the P_n/M/NH_3 liquid systems

The data on the generation of polyphosphide anions from red phosphorus in the Na/NH_3 liquid system were first published in 1966.[11] Under these conditions, phosphorylation of alkyl halides affords a mixture of organic phosphines and diphosphines in 29–34% yields. The moderate yields and selectivity are probably due to lower efficiency of the P–P bonds cleavage in red phosphorus and the formation of polyphosphide anions. Later, it has been reported on phosphorylation of halobenzenes by the P_n/Na/NH_3 liquid system with supplementary UV activation of the reactants.[12] This leads to triphenylphosphine oxide in a good yield.

The use of the modified posphorylating P_n/M/NH_3 liquid/Bu^{t}OH systems opened a new and effective route to primary or secondary phosphines.[34] In these cases, *tert*-butanol drastically assists the fission of the P–P bonds in red phosphorus and formally allows either mono or doubly charged phosphide anions to be selectively generated.[8(c),9(b)]

Thus, at the ratio of reactants P_n/M (Li or Na)/Bu^{t}OH = 1:3:2, monophosphide anions are generated to furnish selectively (in the phosphorylation of organic halides[34(a)] or oxiranes[34(e)]) primary phosphines in up to 87% yield (Scheme 16).



R^1 = alkyl, cycloalkyl, $PhCH_2$
R^2 = H, Me, Ph
M = Li, Na
X = Cl, Br

Scheme 16

When just one equivalent of Bu^{t}OH is employed, with the P_n/Li ratio remaining the same (1:3), doubly charged phosphide anions are then expected to be formed from which dialkylphosphines are selectively obtained by subsequent alkylation in good yield (Scheme 17).[34(b)]

$$P_n + 3\,Li + Bu^tOH \xrightarrow[-Bu^tOLi]{NH_3\ liquid} [^{-2}PH] \xrightarrow{AlkBr} Alk_2PH$$

65–70%

Scheme 17

This is assumed to be one of the most general, efficient and fundamental approach to selective generation of diverse phosphide anions and, consequently, to the syntheses of phosphines of tailor-made structures.

Phosphorylation in the P_n or P_4/RC≡CM/NH_3 liquid (or THF) systems

The phosphorylation of alkyl halides with the P_n or P_4/RC≡CM/NH_3 liquid (or THF) systems leads to a mixture of acetylenic phosphines in 20% total yields.[35] The C_{sp}–P bond formation occurs by the direct cleavage of phosphorus molecules with alkali metal acetylides as nucleophiles (Scheme 18).[35]

$$R^1X \xrightarrow[NH_3\ liquid\ (or\ THF)]{P_4\ (or\ P_n)/R^2C\equiv CM} R^1P(C\equiv CR^2)_2 + R^1_2PC\equiv CR^2$$

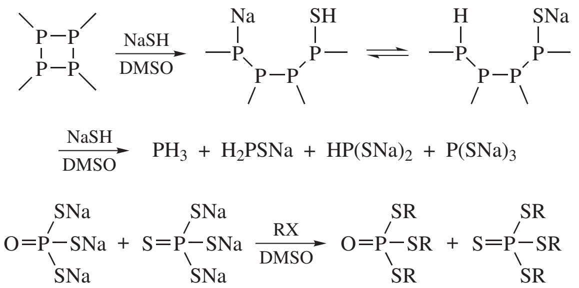
R^1 = alkyl
R^2 = alkyl, Ph
M = Li, Na

Scheme 18

Despite the low yield, this one-pot multicomponent phosphorylation has definitely a preparative meaning since alternative ways to acetylenic phosphines are multi-step and require the use of hazardous phosphorus halides.

Phosphorylation in the P_n/MSR/DMSO systems

Recently, novel prospective reactions of red phosphorus have been discovered.[36] Red phosphorus reacts with NaSH in DMSO (100–116 °C, 4.5 h) *via* redox P–P bond cleavage with hydrosulfide anions to form intermediate species with P–H and P–S bonds, and finally leading to phosphine and trisodium phosphotrithioite. The latter are readily oxidized with air oxygen and elemental sulfur to form *S*,*S*,*S*-trisodium phosphotrithioate and trisodium phosphotetrathioate, respectively. The treatment of the reaction mixture with alkyl halides leads to a ~1:1 mixture of *S*,*S*,*S*-trimethyl phosphorotrithioate and trimethyl phosphorotetrathioate in a total yield of 10% (Scheme 19).[36]



R = alkyl, $PhCH_2$
X = Cl, Br, I

Scheme 19

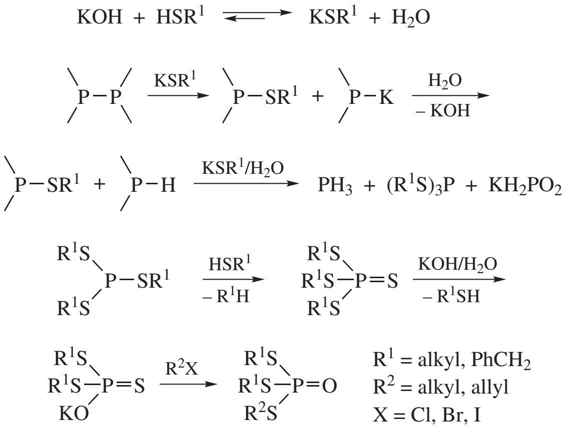
Sulfur-centered nucleophiles produced from thiols in the KOH/DMSO system disassemble (125–128 °C, 4 h) the cross-linked macromolecule of red phosphorus to form finally (in 13–15% yields) potassium *S*,*S*-dialkyl trithiophosphates. The latter are readily alkylated with organic halides to give *S*,*S*,*S*-trialkyl trithiophosphates (Scheme 20).[37]

Thus, the discovered reactions contribute a principally new basic knowledge to the chemistry of phosphorus and open extra possibilities for synthesis of phosphorus-containing compounds from red phosphorus.[36]

Consequences and outlook

The previously inaccessible primary, secondary and tertiary phosphines and phospine oxides, having such rare substituents as aryl(or hetaryl)alkyl, originated from phosphorylation in the elemental phosphorus/strong bases system, attract growing attention in organic and organoelement syntheses.[17,38–41]

H-phosphines and H-phosphine chalcogenides add to functional alkenes[17,38] (vinyl ethers,[38(a)–(e)] vinyl sulfides,[38(c),(f)]



Scheme 20

vinyl selenides,[38(f),(g)] vinyl pyrroles,[38(h)] vinyl pyridines,[17] vinyl sulfoxides,[38(i)] vinyl sulfones[17]), acetylenes[17,39] (acetylene,[17,39(a)] alkyl,[17,39(a)] aryl- or hetarylacetylenes,[39(b),(c)] cyanoacetylenes,[39(d)–(g)] acylacetylenes,[39(h),(i)] alkylthiochloroacetylenes[17]) and aldehydes[40] to afford functionalized phosphines and phosphine chalcogenides including unsaturated and chiral ones. The additions proceed depending on the conditions and the multiple bond nature through radical,[38(a)–(h),39(a)–(c)] nucleophilic[38(i),39(f)–(i),40] or ion-radical[39(d),(e)] mechanisms.

Tertiary phosphine oxides of the above origination bearing benzyl or 5-chloro-2-thienyl radicals react with alkyl, aromatic or heteroaromatic aldehydes under conditions of Wittig–Horner reaction to deliver stereoselectively (in high yields) *E*-isomers of alkenes, stylbenes or their heteroanalogs along with corresponding diorganophosphinic acids.[41]

Among the wide range of novel organophosphorus compounds thus synthesized, ligands for the design of catalytically and biologically prospective metallocomplexes,[1(f),9(d),42] flame-retardants,[2(a)] extractants of rare-earth and transuranium elements[3(d)] and effective reagents for flotation processes[43] have been found.

Thus, the phosphorylation of alkenes, acetylenes, organic halides and oxiranes with the elemental phosphorus/strong bases systems proved to be the most straightforward and well-controlled route to hitherto unknown or inaccessible mono-, di- or triorganophosphines and phosphine oxides of great structural diversity. The synthetic potential and fundamental meaning of this approach is far from being exhausted, and a number of phosphorus organic compounds of new, unusual structure are just waiting to be prepared using the advantages of this concept. New ideas and methodologies concerning the C–P bond formation using elemental phosphorus/strong bases reagents are ready to be further launched from this springboard. Thanks to its ‘green’ background, this halogen-free phosphorylation is expected to gain ever-growing interest in applied organophosphorus chemistry, biochemistry, catalysis, hydrometallurgy and material science.

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