N.K.Gusarova, B.A.Trofimov
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# Organophosphorus chemistry based on elemental phosphorus: advances and horizons

**Nina K. Gusarova, Boris A. Trofimov***

*A.E.Favorsky Irkutsk Institute of Chemistry of the Siberian Branch of the Russian Academy of Sciences, ul. Favorskogo 1, 664033 Irkutsk, Russian Federation*

The results of studies on the application of elemental phosphorus for the synthesis of important organophosphorus compounds are surveyed and summarized. Currently, this trend represents a synthetically, environmentally and technologically attractive alternative to classical organophosphorus chemistry based on toxic and corrosive phosphorus chlorides. Direct phosphination and phosphinylation of organic compounds with elemental phosphorus (discussed in the first part of the review) basically extend the range of available phosphines, phosphine chalcogenides and phosphinic acids and provides further development of their synthetic potential (discussed in the second part of the review). It is shown that the breakthrough in this area is largely due to the discovery of reactions of elemental phosphorus (white and red) with various electrophiles in superbasic suspensions and emulsions derived from alkali metal hydroxides and to the development of electrochemical, electrocatalytic and catalytic activation of white phosphorus.
The bibliography includes 299 references.

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## 1. Introduction

The current state of research on the chlorine-free (*i.e.*, using no environmentally unsafe phosphorus halides) direct formation of the C – P bond based on elemental phosphorus is largely determined by studies summarized in a number of reviews.[1–19] A new method of activation of elemental phosphorus (first of all, red phosphorus) by superbasic reagents and catalytic media (redox cleavage of elemental phosphorus by desolvated hydroxide anion) is successfully developing.[1, 2, 5, 7, 11, 18] The concept of superbasicity formulated by Trofimov *et al.*[20] was defined in the following way: 'By superbasic medium is meant a medium consisting of a strong base and a solvent or a reagent able to specifically bind the cation, thus baring the conjugate anion ...'.[20] According to this concept, superbasicity is a mirror reflection of the superacidity. In other words, a superbase is the complex of a strong ionized base (Brønsted base) with a ligand that specifically interacts with the cation of this base (Lewis base) in a medium that weakly solvates anions (as a rule, in a medium of a polar non-hydroxyl solvent).[21]

Systems are classified as superbases when they have the Hammett acidity function ($H_-$) higher than 18.5,[21] which cannot be generated in hydroxylic solvents (water and alcohols) because of limitations imposed by acidity of the medium.

Among the large diversity of superbasic systems, the KOH – DMSO suspension proved to be most convenient for

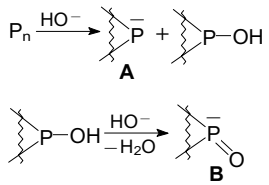
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organic synthesis as the most simple, readily available and versatile.[11, 18, 21 – 33] The upper limit of its basicity is specified by the acidity of DMSO ($pK_a = 35.1$), but usually it does not exceed 32 (on the $H_-$ scale) if no special measures are taken to remove water released upon the formation of potassium methylsulfinylmethide (in minor concentrations).[21]

It is believed[1, 2, 5, 7, 11, 18] that in the KOH – DMSO system, the $P_4$ tetrahedron (white phosphorus) or the three-dimensional supermolecule $P_n$ (red phosphorus) undergoes 'redox disassembly' under the action of activated hydroxide anion to initially give polyphosphide (**A**) and polyphosphinite anions (**B**) (Scheme 1).

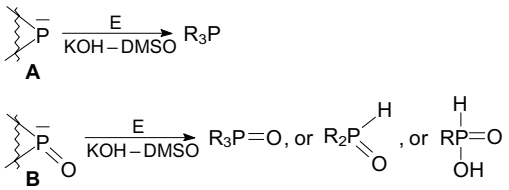
**Scheme 1**




These phosphorus-centred supernucleophiles (in initial steps, possibly, nano-sized ones) react with electrophilic substrates, which finally affords either phosphines (if the competition for the electrophilic centre is won by polyphosphide anions **A**) or phosphine oxides and phosphinic acids (if polyphosphinite anions **B** compete more efficiently). During this redox process, some of the elemental phosphorus is oxidized to hypophosphites and phosphites, while in some cases, side products resulting from further reduction of reactants (phosphine and hydrogen) are formed in minor amounts. This general reaction was used to develop preparative methods for direct phosphination and phosphinylation of electrophiles (alkenes, alkynes, organic halides) and obtain rare, previously unknown or difficult-to-obtain phosphines, phosphine oxides and phosphinic acids (Scheme 2).[1, 2, 5, 7, 11, 18]

Methods of electrochemical,[3, 6, 13 – 17] electrocatalytic[4, 8, 10, 19] and catalytic[9, 12] (by transition metal complexes) activation of white phosphorus are successfully developed in parallel for the synthesis of organophosphorus compounds. In the case of electrochemical activation, white phosphorus is cathodically reduced to phosphide anions, *i.e.*, to the same key intermediates that are formed from elemental phosphorus in superbasic media.

**Scheme 2**




E are alkenes, alkynes, organic halides

The first (major) part of the review considers the achievements over the last 10 – 15 years in the direct phosphination and phosphinylation of electrophiles with elemental phosphorus (red and white) in the presence of superbases and electrochemical and catalytic methods for the formation of C – P bonds from organic compounds and white phosphorus. The benefits, advantages, versatility and limitations of these chlorine-free syntheses of phosphines, phosphine chalcogenides and phosphinic acids based on the above-indicated reactions are analyzed.

The second part of the review, which is logically connected to the first one, is devoted to the development of classical reactions of organophosphorus compounds, mainly the addition of PH compounds to multiple carbon – carbon and carbon – oxygen bonds (Pudovik – Abramov reaction[34 – 38]). We discuss new versions of these reactions (involving conceptually expanded families of secondary phosphines and phosphine chalcogenides) that efficiently proceed without a catalyst and without a solvent. The structural diversity of secondary phosphines and phosphine chalcogenides obtained in this way offers new opportunities for the preparation of functionalized tertiary phosphines, phosphine chalcogenides and their derivatives. The same part of the review presents data on new phosphinylation reactions of azines (pyridines, quinolines, acridines) on treatment with secondary phosphine chalcogenides and electron-deficient acetylenes: tandem vinylation – phosphinylation and chalcogenophosphoryl group substitution for hydrogen in the heteroaromatic ring.

List of abbreviations:
AIBN — azobis(isobutyronitrile);
Bn — benzyl;
Bz — benzoyl;
Cy — cyclohexyl;
Fu — furyl;
HMPA — hexamehylphosphoric triamide;
MW — microwave irradiation;
Naph — naphthyl;
PASE — pot, atom and step economy;
psi — pound per square inch (1 psi = 51.715 mm Hg);
rt — room temperature;
Th — thienyl.

## 2. Phosphination and phosphinylation of organic compounds with elemental phosphorus: formation of C($sp^3$) – P and C($sp^2$) – P bonds

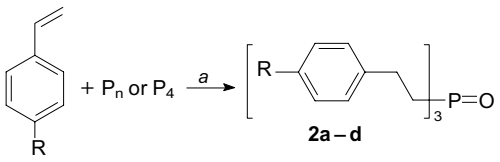
Alkenyl(het)arenes react with elemental phosphorus (red and white) in a KOH – DMSO superbasic suspension to give the corresponding tertiary phosphine oxides and/or phos-

**N.K.Gusarova**. Doctor of Chemical Sciences, Professor, Chief Researcher of the Laboratory of Unsaturated Heteroatomic Compounds at the IrIC SB RAS.
Telephone: +7(3952)42 – 5931, e-mail: gusarova@irioch.irk.ru
**Current research interests**: reactions of elemental phosphorus with unsaturated compounds, arenes and (het)aryl halides in superbasic systems; methods of synthesis of difficult-to-obtain organic phosphines, phosphine oxides and organophosphorus acids; multicomponent reactions of primary or secondary phosphines with elemental chalcogens and organic and inorganic bases; strategy of one-pot atom-economic synthesis of chalcogenophosphinic and -phosphonic acid derivatives.
**B.A.Trofimov**. Academician of the RAS, Doctor of Chemical Sciences, Professor, Head of Research of the IrIC SB RAS.
Telephone: +7(3952)42 – 4411, e-mail: boris_trofimov@irioch.irk.ru
**Current research interests**: organic synthesis based on acetylene and its derivatives (new reactions, general methods, polymers); organic chemistry of phosphorus, sulfur, selenium and tellurium; chemistry of heterocyclic compounds; organic and physical chemistry of vinyl and allenyl ethers, sulfides, polysulfides, selenides, tellurides, phosphines, phosphine oxides and azoles; addition reactions to multiple bonds; superbasic catalysts and reagents.

Translation: Z.P.Svitanko

phinic acids as the major reaction products. The reactions of the starting electrophiles with a phosphine – hydrogen mixture (generated from red phosphorus and KOH) proceed in the KOH – DMSO system and afford organic phosphines. Organophosphorus compounds with the $C(sp^3)-P$ bond were also smoothly synthesized from organic halides and elemental phosphorus under the action of a milder superbasic system: KOH – water – organic solvent (toluene, dioxane) – phase transfer catalyst. In these systems, highly reactive (poorly solvated) anions pass to the organic phase, that is, superbases are generated.[21]

**Scheme 3**



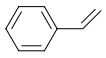
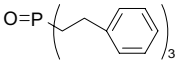
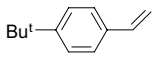
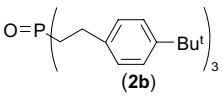
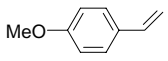
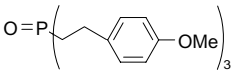
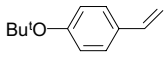
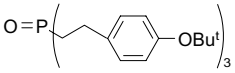
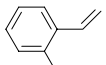
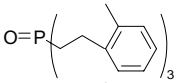
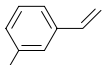
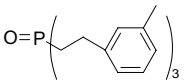
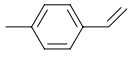
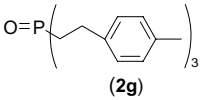
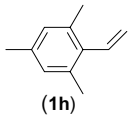
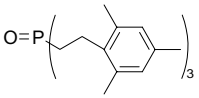

(*a*) KOH – DMSO($H_2O$), argon, 85 – 135 °C, 3 – 4 h;
R = H (**a**), Bu$^t$ (**b**), OMe (**c**), OBu$^t$ (**d**)

## 2.1. Phosphinylation of alkenyl(het)arenes with elemental phosphorus

Styrene (**1a**) and its 4-R-derivatives **1b** – **d** react with elemental phosphorus in the KOH – DMSO system in the presence of minor amounts of water on heating to give anti-Markovnikov tertiary phosphine oxides **2a** – **d** in up to 77% yield (Scheme 3, Table 1).[11, 39 – 42]

The microwave (MW) activation of phosphinylation of styrenes **1a** – **c** sharply (30 – 45-fold) decreases the reaction

**Table 1**. Phosphinylation of styrenes with elemental phosphorus in the KOH/DMSO system (see Schemes 3 and 4).

| Styrene | Phosphorus | $T$/°C or MW (600 W) | Time | Tertiary phosphine oxide | Yield (%) | Ref. |
|---|---|---|---|---|---|---|
|  (**1a**) | $P_n$ | 120 – 125 | 3 h |  (**2a**) | 70 | 11, 39 |
| **1a** | $P_n$ | MW | 4 min | **2a** | 80 | 11 |
| **1a** | $P_4$ | 85 – 90 | 4 h | **2a** | 64 | 11 |
|  (**1b**) | $P_n$ | 90 – 100 | 3 h |  (**2b**) | 77 [a] | 39 |
| **1b** | $P_n$ | MW | 6 min | **2b** | 82 | 39 |
|  (**1c**) | $P_n$ | 135 | 3 h |  (**2c**) | 30 [a] | 40 |
| **1c** | $P_n$ | MW | 6 min | **2c** | 85 [b] | 40 |
|  (**1d**) | $P_n$ | 130 | 3 h |  (**2d**) | 48 [b] | 41 |
|  (**1e**) | $P_n$ | MW | 5 min |  (**2e**) | 45 | 42 |
|  (**1f**) | $P_n$ | MW | 5 min |  (**2f**) | 55 | 42 |
|  (**1g**) | $P_n$ | MW | 5 min |  (**2g**) | 68 | 42 |
|  (**1h**) | $P_n$ | MW | 5 min |  (**2h**) | 40 | 42 |

[a] The corresponding H-phosphinic acids were additionally isolated in 10% – 17% yield.
[b] Apart from tertiary phosphine oxides **2c**,**d**, tertiary phosphines are formed and then oxidized *in situ* to phosphine oxides **2c**,**d**.

time and increases the yield of tertiary phosphine oxides up to 85% (see Table 1).

In some cases, H-phosphinic acids [4-$RC_6H_4CH_2CH_2P(O)(OH)H$] were isolated as side products in up to 17% yield and the corresponding tertiary phosphines $(4\text{-}RC_6H_4CH_2CH_2)_3P$ were identified (see Table 1).

Using the method of competing reactions, it was demonstrated that styrene, as expected, is more reactive than 4-*tert*-butylstyrene, in which the double bond electrophilicity is reduced due to the presence of an electron-donating substituent in the benzene ring. The conversion of styrene over a specified period of time is 89% *versus* 40% for *tert*-butylstyrene.[39] An even lower reactivity in this reaction was found for 4-methoxystyrene:[40] the yield of tertiary phosphine oxide **2c** was only 30% even under more drastic conditions (135 °C, 3 h) (see Table 1). Microwave activation results in the formation of a mixture of phosphine oxide **2c** and the corresponding tertiary phosphine. During workup of the reaction mixture in air, the latter product is readily oxidized, which finally increases the yield of phosphine oxide **2c** to 85% (see Table 1).[40] Heating of 4-*tert*-butoxystyrene in the KOH–DMSO system (130 °C, 3 h) also affords a mixture of tertiary phosphine oxide **2d** and the corresponding tertiary phosphine, which is converted to phosphine oxide **2d** on treatment with aqueous hydrogen peroxide (see Table 1).

This strategy was extended to phosphinylation of 2-, 3- and 4-methylstyrenes **1e**–**g** and 2,4,6-trimethylstyrene **1h**.[42] Tertiary phosphine oxides **2e**–**h** were thus prepared in 40%–68% yields (Scheme 4, see Table 1).[42]

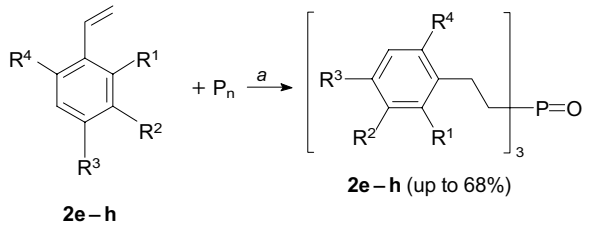
α-Methylstyrene (**3a**) and 4-chloro-α-methylstyrene (**3b**) react with red phosphorus in the KOH–DMSO system (conditions *a*) affording a mixture of tertiary phosphine oxides **4a**,**b** and phosphines **5a**,**b**; treatment of this mixture with aqueous hydrogen peroxide furnishes phosphine oxides **4a**,**b** in 78% and 72% yields, respectively. Also, H-phosphinic acids **6a**,**b** have been isolated from the reaction mixture (Scheme 5).[43]

The microwave-assisted reaction of α-methylstyrenes **3a**,**b** with red phosphorus proceeds chemoselectively over a period of 30 min to give tertiary phosphines **5a**,**b** (Scheme 5, conditions *b*).[43]

A decrease in the microwaving time to 15 min and the use of a lower amount of starting electrophile **3** with respect to red phosphorus and KOH allowed the reaction to be terminated after the formation of secondary phosphines **7a**,**b** (Scheme 5, conditions *c*).[43]

The phosphinylation of 4-methyl-2,4-diphenylpent-1-ene (**8**) (α-methylstyrene dimer) in the $P_n$–KOH–DMSO system in the presence of a minor amount of water on heating (105 °C) followed by acidification of the reaction mixture furnishes (4,4-dimethyl-2,4-diphenylpentyl)phosphinic acid (**9**) (Scheme 6, conditions *a*).[44]

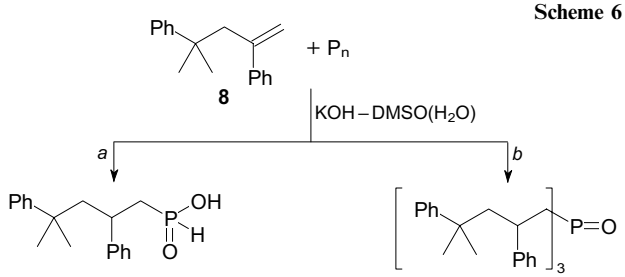
**Scheme 4**




**2e–h** **2e–h** (up to 68%)

(*a*) KOH–DMSO($H_2O$), argon
$R^1$ = Me, $R^2$ = $R^3$ = $R^4$ = H (**e**); $R^1$ = $R^3$ = $R^4$ = H, $R^2$ = Me (**f**);
$R^1$ = $R^2$ = $R^4$ = H, $R^3$ = Me (**g**); $R^1$ = $R^3$ = $R^4$ = Me, $R^2$ = H (**h**)

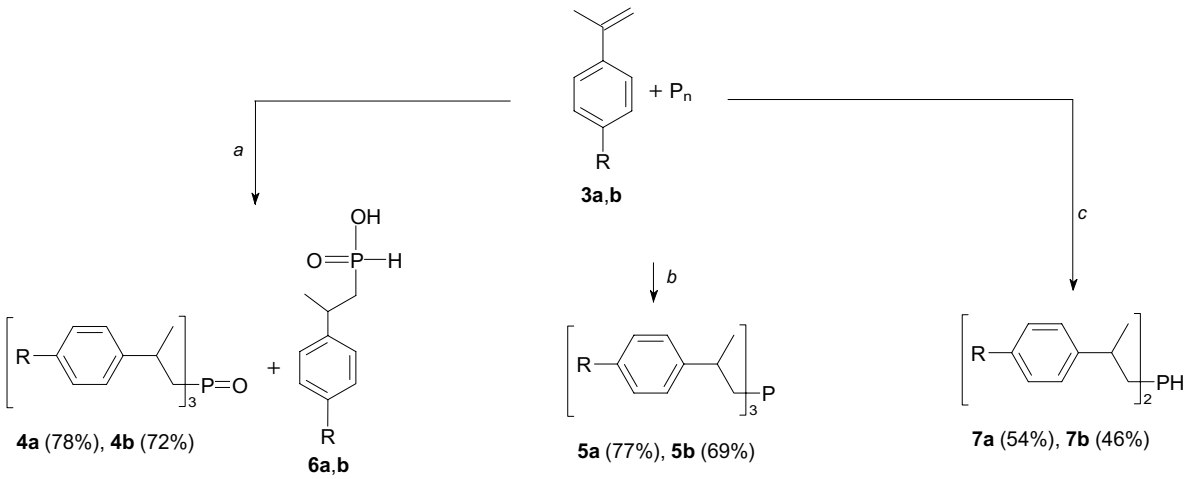
**Scheme 6**




**9** (21%) **10** (38%)

(*a*) 1) argon, 105 °C, 3 h; 2) HCl–$H_2O$, 20–25 °C;
(*b*) 1) MW (15 min); 2) $H_2O_2$–$H_2O$–acetone, 20–25°C, 30 min

**Scheme 5**



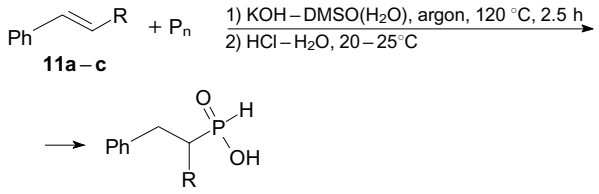

**4a** (78%), **4b** (72%) **6a**,**b** **5a** (77%), **5b** (69%) **7a** (54%), **7b** (46%)

(*a*) 1) KOH–DMSO, argon, 130 °C, 3 h; 2) $H_2O_2$–$H_2O$–acetone, rt; 3) HCl, $H_2O$, rt;
(*b*) KOH–DMSO, MW, 30 min (**3a**,**b** : Pn : KOH ≈ 6 : 10 : 11);
(*c*) KOH–DMSO, MW, 15 min (**3a**,**b** : Pn : KOH ≈ 4 : 10 : 11); rt;
R = H (**a**), Cl (**b**)

Meanwhile, a similar reaction with microwave assistance (100 W, 15 min) afforded a mixture of tris(4,4-dimethyl-2,4-diphenylpentyl)phosphine with the corresponding phosphine oxide (**10**) (Scheme 6, conditions *b*). Compound **10** was isolated in 38% yield after treatment of the crude products with hydrogen peroxide (20 – 25 °C, 30 min).[44]

β-Alkylstyrenes **11a – c** were used as examples to demonstrate[45] that the internal styrenes are also able to react with red phosphorus $P_n$ in a KOH – DMSO suspension to give the $C(sp^3)-P$ bond. Treatment of the reaction mixture with an acid afforded phosphinic acids **12a – c** (Scheme 7).

**Scheme 7**

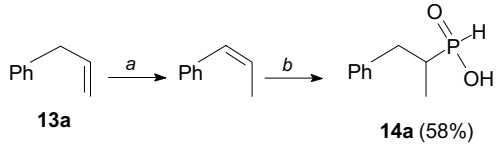



**12a** (40%), **12b** (38%), **12c** (34%)

R = $Pr^n$ (**a**), $Bu^n$ (**b**), n-$C_5H_{11}$ (**c**)

When red phosphorus was heated with allylbenzene **13a** in the KOH – DMSO system, H-phosphinic acid of the same type (**14a**) was also formed as the major product.[46,47] The phosphinylation was preceded by the expected prototropic isomerization of allylbenzene: the resulting β-methylstyrene was isolated from the reaction mixture and identified by $^1H$ NMR spectroscopy (Scheme 8).

**Scheme 8**



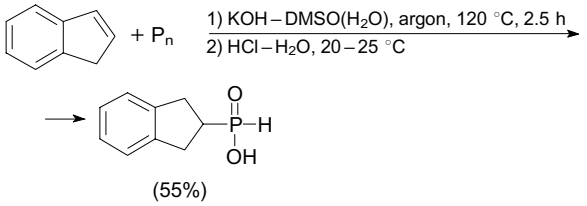

(*a*) KOH – DMSO;
(*b*) 1) $P_n$ – KOH – DMSO, argon, 130 °C, 3 h; 2) HCl – $H_2O$, 20 – 25 °C

Under similar conditions, red phosphorus reacts with substituted allylbenzenes **13b – f** to give H-phosphinic acids **14b – f** in good yields (Scheme 9).[48]

Under microwave activation, polyphosphide anions are involved in this reaction to a larger extent, as indicated by the predominant formation of bis(1-methyl-2-arylethyl)-phosphines **15a – d** in a mixture with minor products **16b – d** (Scheme 9).[46 – 49]

The $P_n$ – KOH – DMSO system proved to be very efficient for phosphinylation of 1*H*-indene (cyclic alkenylarene).[50] The reaction proceeded at 120 °C and yielded 2,3-dihydro-1*H*-inden-2-ylphosphinic acid (Scheme 10).[50]

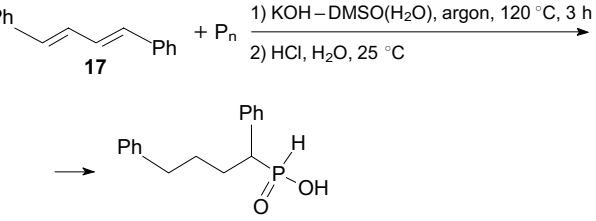
**Scheme 10**




(55%)

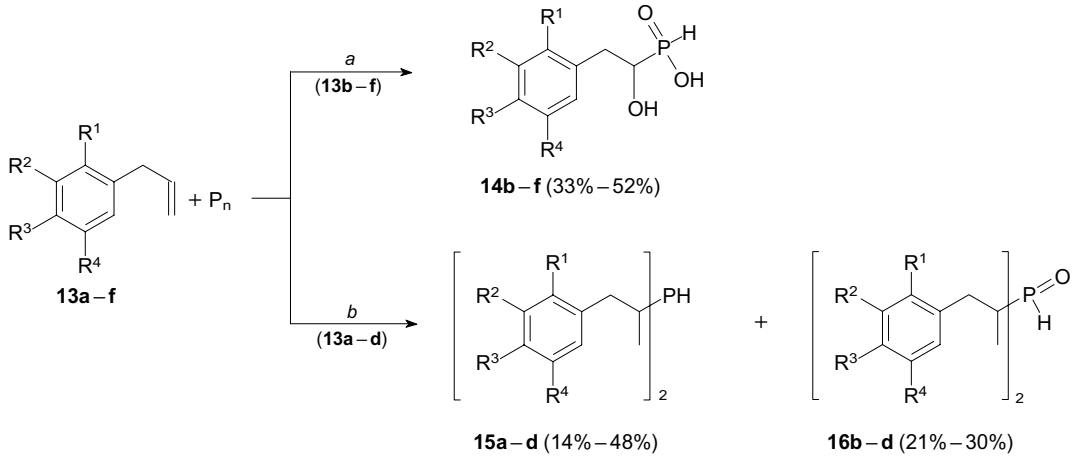
1,4-Diphenylbuta-1,3-diene (**17**) was also allowed to react with red phosphorus.[51] Under conditions similar to those described above, the reaction resulted in the synthesis of 1,4-diphenylbutylphosphinic acid (**18**), *i.e.*, the formation of the $C(sp^3)-P$ bond was accompanied by reduction of the C=C bond (Scheme 11).

**Scheme 11**




**18** (48%)

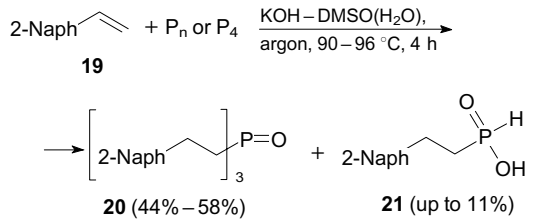
**Scheme 9**




(*a*) 1) KOH – DMSO($H_2O$), argon, 10 5°C, 3 h; 2) HCl – $H_2O$, 20 – 25 °C;
(*b*) KOH – DMSO, MW (200 – 300 W), 30 – 40 min;
$R^1 = R^2 = R^3 = R^4$ (**a**); $R^1$ = OMe, $R^2 = R^3 = R^4$ = H (**b**); $R^1 = R^2$ = OMe, $R^3 = R^4$ = H (**c**); $R^1 = R^4$ = H, $R^2 = R^3$ = OMe (**d**);
$R^1$ = OMe, $R^2$ = Me, $R^3 = R^4$ = H (**e**); $R^1$ = OMe, $R^2 = R^3$ = H, $R^4$ = Me (**f**)

Like styrene, 2-vinylnaphthalene (**19**) also reacts with elemental phosphorus in a KOH–DMSO suspension on heating (90–96 °C, 4 h) to give phosphine oxide **20** as the major product; the product yield is higher (58%) when white phosphorus is used, while in the case of red phosphorus, the yield is 44%. In the latter case, phosphinic acid **21** was also isolated (Scheme 12).[11, 52]

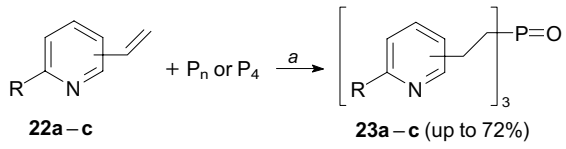
**Scheme 12**




Naph is naphthyl

In relation to vinylpyridines **22a–c**, it was shown that alkenylhetarenes can also be phosphinylated in the $P_n$ (or $P_4$)–KOH–DMSO system to give the corresponding tertiary phosphine oxides **23a–c** (Scheme 13, Table 2).[11, 53]

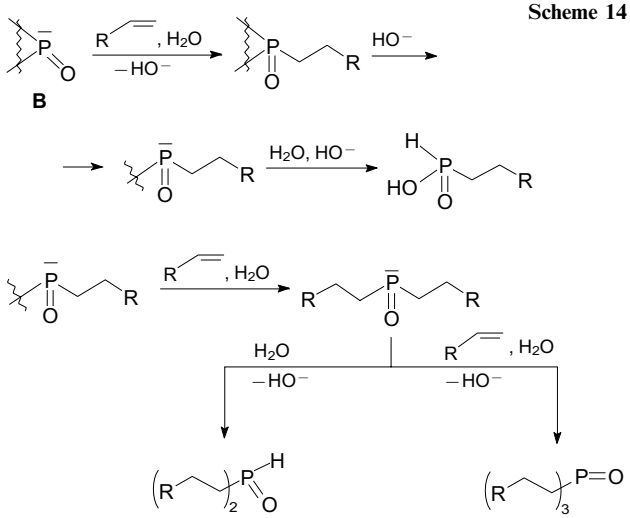
**Scheme 13**




(*a*) KOH–DMSO($H_2O$), argon;
R = H (**a**, **b**), Me (**c**)

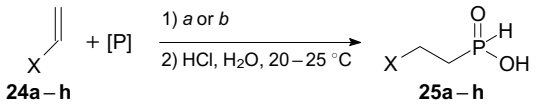
Thus, in the vast majority of cases, phosphinylation of alkenyl(het)arenes with elemental (mainly red) phosphorus in the KOH–DMSO system results in the formation of organic phosphine oxides and H-phosphinic acids. This result indicates that in this case, polyphosphinite anions **B** win the competition with polyphosphide anions **A** for the electrophile. The formation of the C($sp^3$)–P bond in this reaction is usually depicted as shown in Scheme 14.[7, 11]

**Scheme 14**



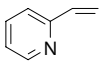
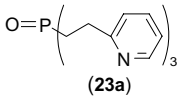
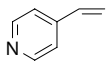
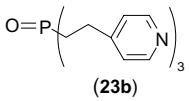
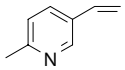
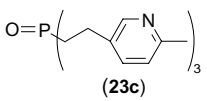

Apparently, phosphinylation of untypical electrophiles such as vinyl sulfides[54] and vinylsilanes[55] with elemental phosphorus in superbasic systems follows a similar mechanism. Indeed, elemental phosphorus (red or white) reacts with alkyl and phenyl sulfides **24a–g** in a KOH–DMSO($H_2O$) suspension on heating to give functionally substituted phosphinic acids **25a–g** (Scheme 15)[54] — promising ligands for transition metal

**Scheme 15**




(*a*) [P] = $P_n$ or $P_4$, KOH–DMSO($H_2O$), argon, 75–120 °C, 2–3 h; **25a–g** (16%–31% yields);
(*b*) [P] = $P_n$, KOH–DMSO($H_2O$), argon, 100 °C, 3 h; **25h** (5%);
X = SR [R = $Pr^n$ (**a**), $Bu^i$ (**b**), $Bu^t$ (**c**), n-$C_5H_{11}$ (**d**), n-$C_7H_{13}$ (**e**), n-$C_8H_{17}$ (**f**), Ph (**g**)], $SiMe_3$ (**h**),

**Table 2**. Phosphinylation of vinylpyridines with elemental phosphorus in the KOH–DMSO system (see Scheme 13).[11, 53]

| Vinylpyridine | Phosphorus | *T*/°C or MW(600 W) | Time | Tertiary phosphine oxide | Yield (%) |
|---|---|---|---|---|---|
|  (**22a**) | $P_n$ | 70–75 | 3 h |  (**23a**) | 52 |
| **22a** | $P_4$ | 20–25 | 5–6 h | **23a** | 72 |
| **22a** | $P_n$ | MW | 2 min | **23a** | 48 [a] |
|  (**22b**) | $P_n$ | 90–95 | 3 h |  (**23b**) | 30 |
| **22b** | $P_4$ | 20–25 | 5–6 h | **23b** | 56 |
|  (**22c**) | $P_n$ | 90–95 | 3 h |  (**23c**) | 47 |

[a] Along with tertiary phosphine oxide **23a**, the corresponding secondary phosphine oxide is formed in 12% yield.

catalysis,[56–59] drug precursors[60–62] and antioxidants.[63–65] However, the yields of the target acids do not exceed 31%.

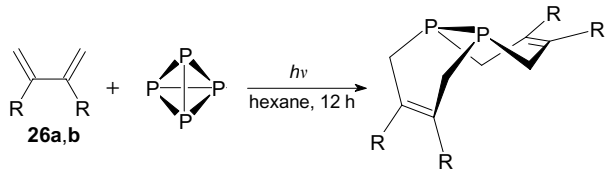
An even lower reactivity in this reaction was found for vinyltrimethylsilane (**24h**), which was converted to 2-(trimethylsilyl)ethylphosphinic acid (**25h**) in 5% yield (Scheme 15, conditions *b*).[55] This low yield of product **25h** was explained by easy cleavage of the C($sp^2$)—Si bond of silane **24h** in a superbasic medium with release of ethylene.

### 2.2. Photochemical phosphination of dienes

The photochemical and catalytic activation of white phosphorus was used for phosphination of 1,3-dienes.[8,66–69]

Photolysis of a solution of $P_4$ and butadienes **26a**,**b** in hexane in an ultraviolet (UV) photoreactor affords diphosphabicycloadducts **27a**,**b** in low yields (Scheme 16).[67]

**Scheme 16**



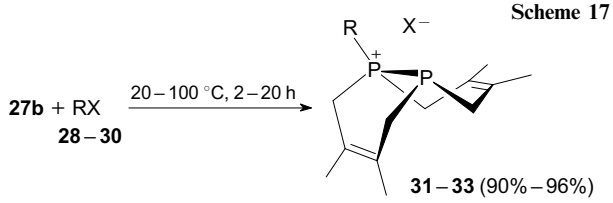

R = H (**a**), Me (**b**)

**27a**,**b** (up to 14%)

Diphosphines **27a**,**b** obtained in this way are efficient ligands for the design of highly desirable metal complexes[70–73] and reactive building blocks for organoelement synthesis.[69]

For example, diphosphine **27b** reacts with alkyl halides **28**–**30** to give the corresponding phosphonium halides **31**–**33** (Scheme 17).[69]

**Scheme 17**




X = I, R = Me (**28**, **31**); X = Br: R = Bn (**29**, **32**), Bu$^t$ (**30**, **33**)

### 2.3. Phosphination of alkenyl(het)arenes with a $PH_3$–$H_2$ mixture

In the last decades, phosphine generated (together with hydrogen) from red phosphorus and a KOH–water–toluene suspension has been successfully used to prepare organic phosphines.[7,11] For example, the slow addition of alkenes **1a**–**c**, **3a**, **19**, **22a**–**c** or **34**–**36** with simultaneous introduction of a phosphine–hydrogen mixture into a heated KOH–DMSO suspension produced [2-(het)arylethyl]phosphines **7a**, **37a**–**j** (Scheme 18, Table 3).[11,52,74–78] Hydrogen contributes to generation of the reductive atmosphere, which prevents the oxidation of organic phosphines.

Exhaustive and selective (het)arylalkylation of phosphine with styrenes **1a**–**c** and vinylpyridines **22a**,**c** is implemented in this system upon the additional introduction of an alkene into the reaction medium after the phosphine–hydrogen flow has been stopped (see Scheme 18). Under the developed conditions (see Table 3), tris(2-arylethyl)- and tris(2-pyridylethyl)phosphines **38a**–**e** were obtained in high yields.[11,74–79]

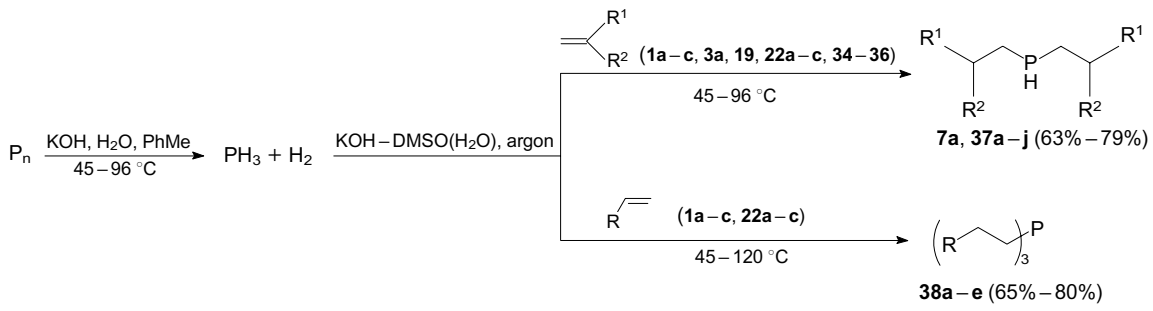
Allylbenzene reacts with a phosphine–hydrogen mixture in the KOH–DMSO system to be converted to Markovnikov adducts — 1-methyl-2-phenylethylphosphine (**39**) and the corresponding secondary phosphine **15a** (Scheme 19).[80] As has already been noted,[46,47] in a superbasic medium, allylbenzene undergoes a prototropic rearrangement to β-methylstyrene, which is phosphinated. Conditions were developed for the selective synthesis of phosphines **39** and **15a** in 53% and 80% yields, respectively.[80]

Fullerene $C_{60}$, which can be roughly conceived as a highly fused molecule composed of dehydrogenated styrene moieties, does not react with a phosphine–hydrogen mixture in the KOH– DMSO system. However, with radical initiation (AIBN), phosphination takes place to give products **40**, which are oxidized when isolated in air to give oligofullerenes **41a**,**b** containing phosphinic and phosphonic acid functional groups (Scheme 20).[81]

It was reported[82–84] that oligomers **41a**,**b** substituted by pharmacophoric phosphine and phosphone groups can be considered as promising precursors of pharmaceuticals. Also, these compounds can be used for the design of special-purpose materials.[85–87]

The synthesis of organophosphorus compounds based on commercial (from gas cylinders) phosphine is also being

**Scheme 18**




**Scheme 19**

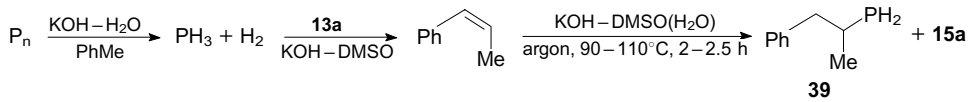
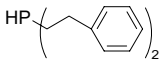
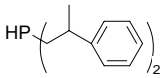
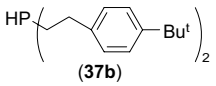
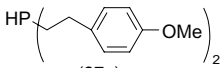
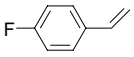
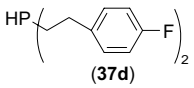
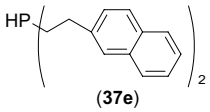
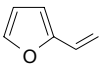
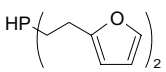
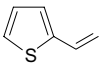
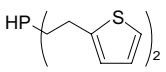
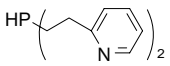
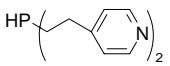
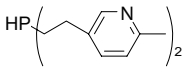
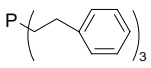
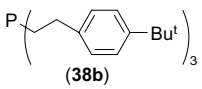
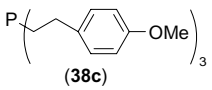
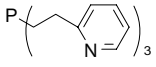
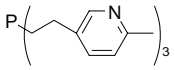
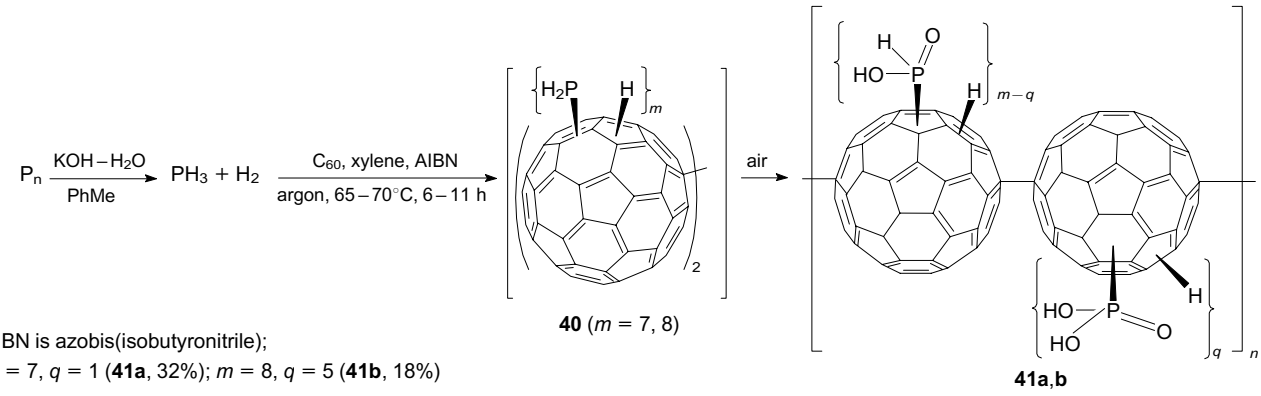


**Table 3**. Synthesis of secondary [a] and tertiary [b] phosphines from (het)arylalkenes and a $PH_3 - H_2$ mixture in the KOH – DMSO system (see Scheme 18).

| Alkene | $T$/°C | Time | Phosphines | Yield (%) | Ref. |
|---|---|---|---|---|---|
| **1a** | 60 – 65 | 2.5 h |  (**37a**) | 79 | 11, 78 |
| **3a** | 60 – 65 | 2.5 h |  (**7a**) | 63 | 11, 78 |
| **1b** | 70 | 3 h |  (**37b**) | 87 | 74 |
| **1c** | 70 | 2 h |  (**37c**) | 67 | 75 |
|  (**34**) | 60 – 65 | 2.5 h |  (**37d**) | 73 | 11, 78 |
| **19** | 90 – 93 | 3.5 h |  (**37e**) | 75 | 52 |
|  (**35**) | 60 – 65 | 2.5 h |  (**37f**) | 60 | 11, 78 |
|  (**36**) | 60 – 65 | 2.5 h |  (**37g**) | 77 | 11, 78 |
| **22a** | 55 – 60 | 3 h |  (**37h**) | 75 | 76 |
| **22b** | 40 – 45 | 3.5 h |  (**37i**) | 65 | 11, 72 |
| **22c** | 60 | 2 h |  (**37j**) | 73 | 11, 77 |
| **1a** | 95 – 98 | 4 h |  (**38a**) | 76 | 79 |
| **1b** | 70 – 120 | 2 h 40 min |  (**38b**) | 69 | 74 |
| **1c** | 70 – 100 | 1 h 40 min |  (**38c**) | 80 | 75 |
| **22a** | 68 – 70 | 3 h |  (**38d**) | 65 | 76 |
| **22c** | 65 – 67 | 2 h |  (**38e**) | 70 | 11, 77 |

[a] Dropwise addition of alkene to a heated KOH – DMSO suspension with simultaneous passing of a phosphine – hydrogen mixture. [b] After heating of alkene in a KOH – DMSO suspension with a flow of phosphine–hydrogen mixture, the flow is stopped, an additional portion of alkene is added and the suspension is heated for additional ~30 min.[11, 74 – 79]

**Scheme 20**




**40** ($m$ = 7, 8)

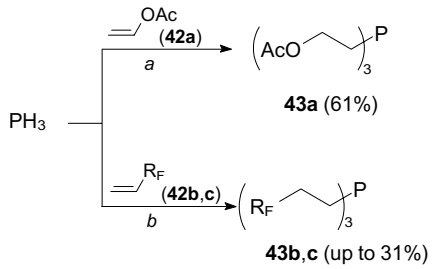
**41a**,**b**

AIBN is azobis(isobutyronitrile);
$m$ = 7, $q$ = 1 (**41a**, 32%); $m$ = 8, $q$ = 5 (**41b**, 18%)

developed.[88–96] In the case of alkenes, phosphination is a radical-initiated reaction.

When phosphine was passed into a toluene solution of vinyl acetate (**42a**) containing AIBN with simultaneous UV irradiation of the reaction mixture, tertiary phosphine **43a** was formed (Scheme 21, conditions *a*).[89] Fluorinated alkenes **42b**,**c** react with phosphine in an autoclave to give tertiary phosphines **43b**,**c** (see Scheme 21, conditions *b*), which were subsequently used to prepare hydrophobic polymeric materials.[90]

**Scheme 21**



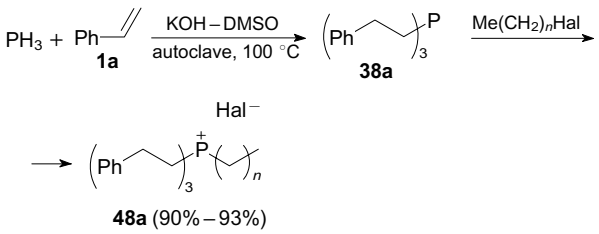

(*a*) AIBN, UV, PhMe, rt, 4 h;
(*b*) AIBN, 70°C, 80 psi, 5–8 h;
**43**: $R_F$ = n-$C_4F_9$ (**b**), $CH_2OC(CF_3)_3$ (**c**)

The radical addition of phosphine to vinylmetallocenes (vinylferrocene **44**, vinyl ruthenocene **45**) results in the formation of a mixture of primary, secondary and tertiary metallocenylethylphosphines **46a**–**c**, **47a**–**c** (Scheme 22).[91,92] Ferrocenyl-substituted phosphines **46a**–**c** were used to obtain efficient metallated phosphonium electrolytes.[91]

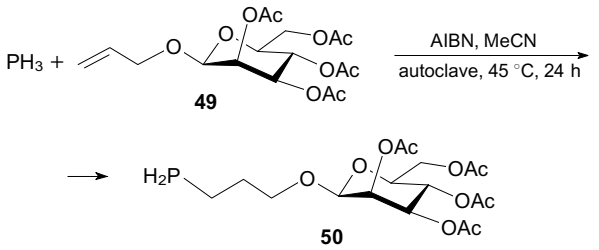
A recent series of patents[93–96] describes the use of phosphine in the targeted synthesis of antibacterial agents. The phosphination was carried out in an autoclave under elevated pressure in the presence of superbases or with radical initiation. The reaction of phosphine with styrene in the KOH–DMSO system afforded tris(2-phenylethyl)-phosphine (**38a**).[93] In essence, this is a modification of a previously reported method for the synthesis of phosphine **38a**[79] (see Scheme 18). However, the latter method is more convenient, as it is conducted under atmospheric pressure, *i.e.*, under safer conditions. According to a patent,[93] phosphonium salts **48** obtained from phosphine **38a** possess antibacterial properties (Scheme 23).

Heating of an allylic tetraacetylmannopyranose derivative (**49**) under a $PH_3$ pressure in the presence of AIBN results in the formation of the corresponding primary phosphine **50** (Scheme 24).[96] Phosphine **50** was employed

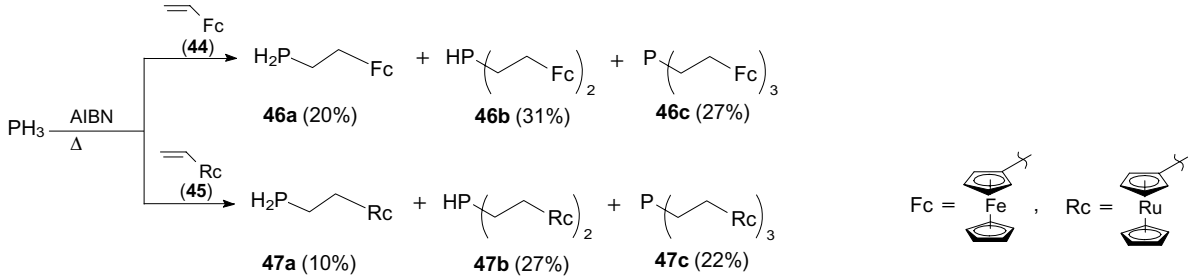
**Scheme 23**




**Scheme 24**




**Scheme 22**

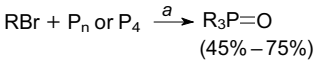


to synthesize functional tertiary phosphine and its phosphonium salts, which exhibit bactericidal properties.[96]

### 2.4. Phosphinylation of alkyl and (het)arylalkyl halides with elemental phosphorus

Superbases generated under phase transfer catalysis[21] also proved to be efficient in the synthesis of tertiary phosphine oxides from elemental phosphorus and organic halides. For example, alkyl bromides react with red and white phosphorus in an aqueous KOH–THF (or dioxane)–phase transfer catalyst (benzyltriethylammonium chloride) system at 65–95 °C to afford good yields of trialkylphosphine oxides,[1,7,97] which are applied as extractants for rare earth elements (Scheme 25).[98]

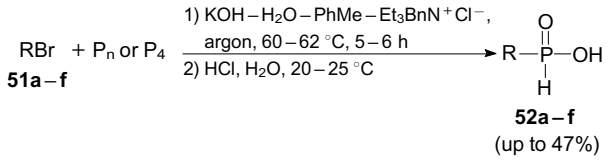
**Scheme 25**




R = Et, n-$C_{12}H_{25}$;
(*a*) KOH–$H_2O$–THF(or dioxane)–$Et_3BnN^+Cl^-$, argon, 65–95 °C

Recently, conditions were developed for the conversion of alkyl bromides **51a–f** and elemental phosphorus to alkylphosphinic acids **52a–f** (Scheme 26).[99] The reaction proceeded towards the predominant formation of these products when conducted in toluene at 60–62 °C and, what is more important, when elemental phosphorus and KOH were taken in an approximately threefold excess over alkyl bromide. The synthesized phosphinic acids **52a–f** are efficient ligands for the design of transition metal catalysts,[100] drug precursors,[101,102] reagents for hydrometallurgy,[103] flame retardants[104,105] and building blocks for the synthesis of organophosphorus compounds.[106–109]

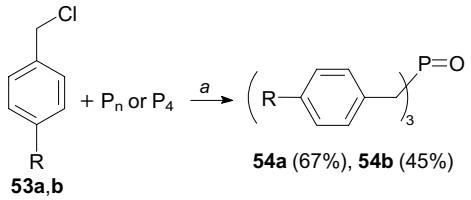
**Scheme 26**




R = $Bu^n$ (**a**), $Bu^t$ (**b**), n-$C_5H_{11}$ (**c**), iso-$C_5H_{11}$ (**d**), n-$C_6H_{13}$ (**e**), n-$C_8H_{17}$ (**f**)

Under phase transfer catalysis, benzyl and 4-methoxybenzyl chlorides **53a**,**b** react with elemental phosphorus to yield the corresponding tertiary phosphine oxides **54a**,**b** in good yields (Scheme 27).[1,7,97,110]

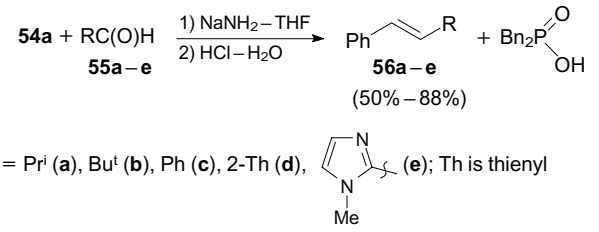
**Scheme 27**




(*a*) KOH, $H_2O$, dioxane, $Et_3BnN^+Cl^-$, argon, 60–90 °C;
R = H (**a**), OMe (**b**)

Tribenzylphosphine oxides prepared by this method substantially expand the scope of stereoselective synthesis of *E*-alkenes by the Wittig–Horner reaction.[111] Heating (60–65 °C) of phosphine oxide **54a** with aldehydes **55a–e** in the $NaNH_2$–THF system furnishes *E*-alkenes **56a–e** in up to 88% yield and dibenzylphosphinic acid (Scheme 28).[111]

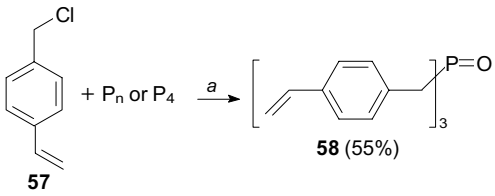
**Scheme 28**




Thus, owing to the use of elemental phosphorus for the preparation of tertiary phosphine oxides, organic synthesis acquires new readily accessible reagents that facilitate stereoselective design of pharmacologically important alkenes such as stilbenes and their analogues containing heterocyclic substituents. Also, organophosphorus chemistry is supplemented by a simple method for the preparation of practically valuable phosphinic acids, in particular, biologically active ones, that were previously difficult to obtain.[112–114]

One more illustration of the stimulating effect of the phosphinylation reaction with elemental phosphorus on the development of organophosphorus chemistry is the convenient chemoselective synthesis of highly reactive polyfunctional tris(4-vinylbenzyl)phosphine oxide[115,116] used as a cross-linking agent for the design of non-combustible polymeric materials.[117] Phosphinylation of 4-vinylbenzyl chloride (**57**) with red phosphorus in the phase transfer system described above yielded phosphine oxide **58**. The carbon–phosphorus bond formation with the participation of the vinyl group of the styrene moiety does not occur under these conditions (Scheme 29).

**Scheme 29**

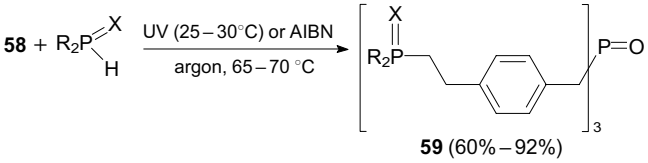



$KOH–H_2O–Et_3BnN^+Cl^-$, hydroquinone, argon, 45–50 °C

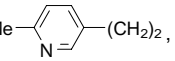
Later, phosphine oxide **58** was successfully used in the synthesis of tetradentate tripodal ligands — first generation dendrimers. Under the action of radical initiators, phosphine oxide **58** reacts with secondary phosphines and phosphine chalcogenides, giving rise to the corresponding anti-Markovnikov triadducts **59** (Scheme 30),[116] which are promising tetradentate tripodal ligands.[118–123]

It is evident that this scheme is far from exhausting the synthetic potential of this highly reactive polyfunctional organophosphorus building block.

**Scheme 30**

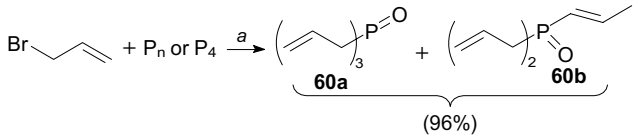



**59** (60% – 92%)

R = Ph, Ph(CH$_2$)$_2$, PhCH(Me)CH$_2$, 2-Fu(CH$_2$)$_2$, , 4-MeOC$_6$H$_4$(CH$_2$)$_2$, 4-Bu$^t$C$_6$H$_4$(CH$_2$)$_2$,
X = lone pair, S, Se; Fu is furyl

The reaction of allyl bromide with elemental phosphorus is easily implemented in the KOH – H$_2$O – dioxane system even in the absence of a phase transfer catalyst (apparently, this role is performed by tetraallylphosphonium bromide generated in the reaction) and gives triallylphosphine oxide **60a** and product **60b**, resulting from its prototropic isomerization (Scheme 31).[1, 7, 97] The total yield of compounds **60a**,**b** is nearly quantitative. The mixture of phosphine oxides **60a**,**b** was proposed as an efficient additive for nonferrous metal flotation.[124]

**Scheme 31**



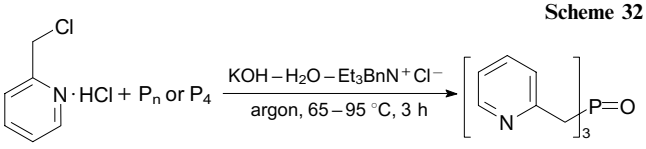

**60a** **60b**

(96%)

(*a*) KOH – H$_2$O – dioxane, argon, 20 – 75 °C

Superbases generated in the KOH – H$_2$O – PhMe – Et$_3$BnN$^+$Cl$^-$ system proved to be suitable for the synthesis of tris(2-picolyl)phosphine oxide (**61**) from elemental phosphorus and 2-picolyl chloride (65 – 95 °C, 3 h). The latter is formed *in situ* under the reaction conditions as a result of alkaline hydrolysis by the starting 2-(chloromethyl)pyridine hydrochloride (Scheme 32).[125]

**Scheme 32**

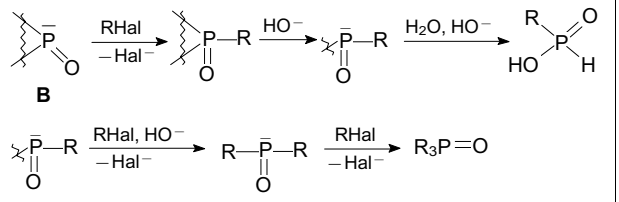



**61** (up to 50%)

The developed synthesis of tri(picolyl)phosphine oxide **61** favourably compares with the known multistep syntheses from phosphorus chlorides and organometallic compounds.[126, 127] This opens up new prospects for further development of the chemistry of tri(picolyl)phosphine oxide and its derivatives — efficient ligands for the design of valuable metal complexes.[128 – 132]

Analysis of the above data on the phosphinylation of alkyl and (het)arylalkyl halides with elemental phosphorus conducted using phase transfer catalysts and resulting mainly in tertiary phosphine oxides or H-phosphinic acids[99] indicates that the C(sp$^3$) – P bond is formed in these reactions wih the participation of the polyphosphinite anions **B** (Scheme 33).[7, 99, 110, 115, 116, 125]

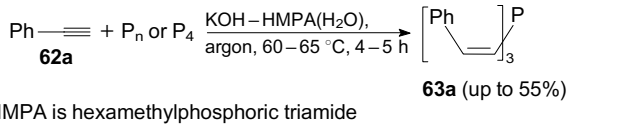
**Scheme 33**




## 2.5. Phosphination of acetylenes

Direct phosphination of acetylenes with elemental phosphorus was first implemented for phenylacetylene (**62a**), which reacts with red or white phosphorus in the KOH – hexamethylphosphoric triamide (HMPA) superbasic system with chemo-, regio- and stereoselective formation of tris(*Z*-styryl)phosphine (**63a**) in up to 55% yield (Scheme 34).[133] The stereochemical outcome of this reaction (*Z*,*Z*,*Z*-structure of phosphine **63a**) is in line with the classical rule of *trans*-nucleophilic addition to monosubstituted acetylenes.

**Scheme 34**



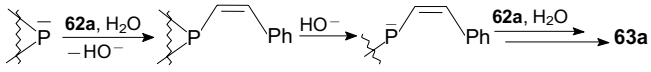

**62a**

**63a** (up to 55%)

HMPA is hexamethylphosphoric triamide

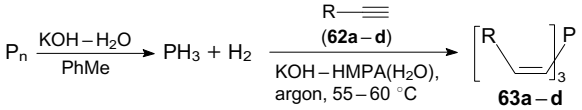
The formation of the C(sp$^2$) – P bond upon phosphination of phenylacetylene indicates that in this case, polyphosphide anions **A** win the competition for the electrophile (Scheme 35).[7, 11]

**Scheme 35**




An alternative synthetic route to tristyrylphosphines **63a** – **d** is the phosphination under similar conditions of (het)arylacetylenes **62a** – **d** with a phosphine – hydrogen mixture prepared in dosed amounts from red phosphorus in an aqueous alkaline medium (Scheme 36).[1, 134]

**Scheme 36**



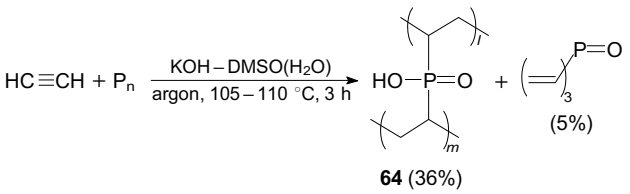

**63a** – **d**

R = Ph (80%), 4-FC$_6$H$_4$ (55%), 2-Fu (61%), 2-Th (78%)

The synthesized tertiary phosphines **63a** – **d** are promising ligands for metal complexes. They were used to prepare palladium complexes,[135] which exhibited, in particular, pronounced catalytic activity in the Sonogashira reaction,[136] and complexes of platinum,[135] rhodium,[137] erbium and ytterbium.[138]

When acetylene is passed through a heated (105 – 110 °C) red phosphorus – KOH – DMSO suspension, the reaction gives divinylphosphinic acid polymer **64** as the

**Scheme 37**

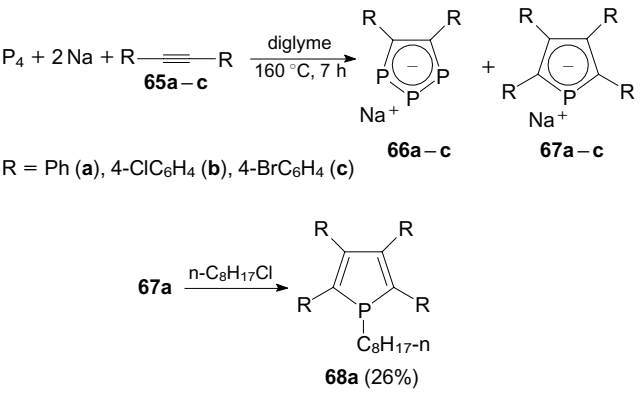



major product; trivinylphosphine oxide is also identified in the reaction mixture (Scheme 37).[139]

Polydivinylphosphinic acid **64** is an efficient flame retardant and can be used as an active plasticizing agent in the preparation of non-flammable polymers.[139]

The activation of white phosphorus by alkali metals in polyether solutions is an efficiently developing trend.[3,13,140–147] The polyphosphide anions generated in this way are used to synthesize organophosphorus products. Refluxing diarylacetylenes **65a–c** in the $P_4$–Na–diglyme–dibenzo-18-crown-6 ether system affords sodium phospholides **66a–c** and **67a–c** (Scheme 38).[146,147] They react with octyl chloride to be converted to phospholes **68** (exemplified by monophospholide **67a**, see Scheme 38).[147]

**Scheme 38**



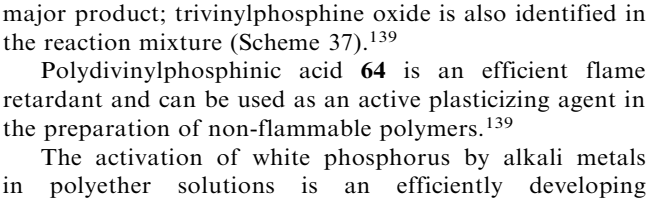

## 2.6. Phosphination of haloarenes

Currently, triphenylphosphine is the most widely used tertiary phosphine, which serves most often as a ligand for metal complexes,[148–155] a component of catalytic systems,[156–159] and a building block for organic synthesis.[160–164] Triphenylphosphine is also employed for stabilization of nanoparticles[165] for medical purposes.[166]

The conventional methods for the preparation of $Ph_3P$ from phosphorus halides (most often, $PCl_3$) and organometallic compounds (PhMgHal, $Bu^nLi$) or sodium metal[167–169] have obvious drawbacks and do not comply with current environmental requirements.

Methods for $Ph_3P$ synthesis by phosphination of halobenzenes with elemental phosphorus are also known. Among them, mention should first be made of reactions proceeding upon electrochemical and/or catalytic activation.[3,6,13,14,16,17,170–173] Researchers of Academician Sinyashin's school[16,17,171] obtained triphenylphosphine in a high yield from white phosphorus and halobenzenes by an electrochemical procedure using a Pt, Ni or glassic carbon cathode and a sacrificial anode (Mg, Zn or Al). The reaction proceeded in DMF at 25–50 °C and a current density of 4–8 mA $cm^{-2}$ (Scheme 39).

**Scheme 39**



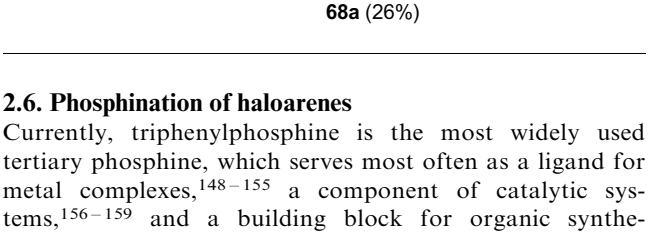

Direct phosphination of bromobenzene with white phosphorus was also accomplished in the presence of a large amount (a fivefold molar excess over elemental phosphorus) of the $Ti(NBu^tAr)_3$ complex, which was fully consumed during the reaction to give the corresponding bromide (Scheme 40).[172]

**Scheme 40**



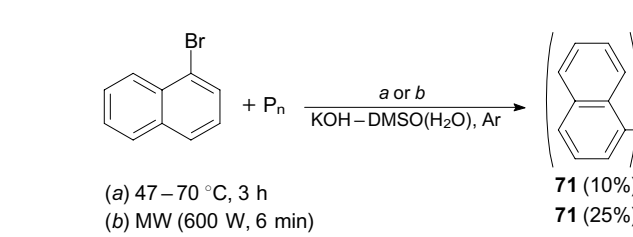

Recently, a process was reported for chemoselective phosphination of fluoroalkylaryl iodides with white phosphorus using samarium bromide as a reducing agent.[173] For instance, 3,5-bis(perfluorohexyl)iodobenzene **69** reacts with white phosphorus in the presence of excess samarium bromide in THF on cooling (down to −35 °C) or at room temperature giving functional polyfluorine-containing triphenylphosphine **70** in 41% yield (Scheme 41).[173]

**Scheme 41**




The KOH–DMSO type superbase was used, for the first time, for the formation of the $C(sp^2)$–P bond by the reaction of 1-bromonaphthalene with red phosphorus[174] or with a phosphine–hydrogen mixture generated from red phosphorus.[175–177] Heating (47–70 °C, 3 h) of 1-bromonaphthalene in a red phosphorus–KOH–DMSO suspension furnishes tris(1-naphthyl)phosphine (**71**) and 1-naphthylphosphinic acid (**72**) (Scheme 42).[174] Under these con-

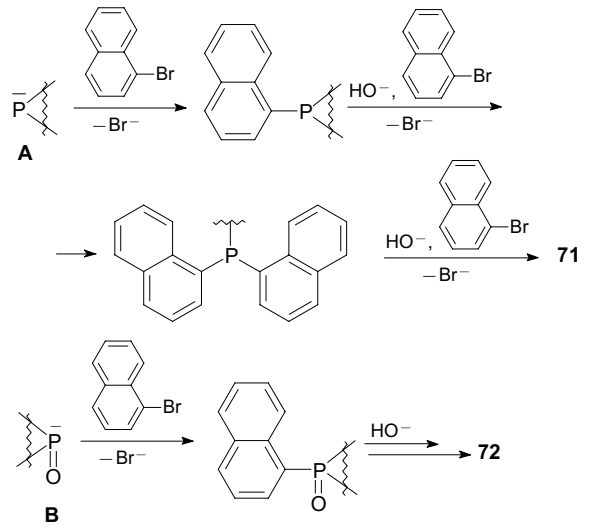
**Scheme 42**



ditions, a marked amount of naphthalene, resulting from reduction of 1-bromonaphthalene, is also detected in the reaction mixture. The efficiency and chemoselectivity of phosphination of 1-bromonaphthalene were increased and tertiary phosphine **71** was obtained in 25% yield when the reactants were activated by microwave irradiation (see Scheme 42).

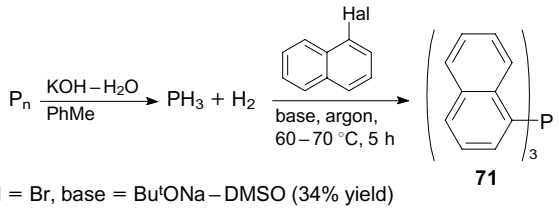
A pathway towards phosphine **71** and phosphinic acid **72** involving the participation of the polyphosphide and polyphosphinite anions was proposed (Scheme 43).[174]

**Scheme 43**




In a more potent superbasic system (Bu$^t$ONa – DMSO), the phosphine–hydrogen mixture reacts with 1-bromonaphthalene to give trinaphthylphosphine **71** in 34% yield.[177] This reaction with 1-chloronaphthalene was accomplished in the Bu$^t$OK – DMSO system, with the yield of phosphine **71** being 32% (Scheme 44).[176]

**Scheme 44**




Hal = Br, base = Bu$^t$ONa – DMSO (34% yield)
Hal = Cl, base = Bu$^t$OK – DMSO (32%)

According to EPR and UV spectroscopy data, phosphination of 1-bromonaphthalene with a phosphine – hydrogen mixture follows the $S_{RN}1$ radical nucleophilic substitution mechanism.[175]

Previously, phosphine **71** was prepared in 20% – 30% yields from 1-bromonaphthalene, $PCl_3$ and Li metal (or Bu$^n$Li).[178, 179] The synthesis of this product from red phosphorus (the most facile and environmentally benign procedure) extends the applicability of phosphines with bulky substituents in the chemistry of metal complexes.[180 – 187] Phosphine **71** synthesized in this way[174, 176] has already been used to obtain mononuclear catalytically active palladacycles and Cu$^I$-based luminescent complexes.[176] In addition, this phosphine catalyzes cross-coupling of phenylacetylenes with iodobenzenes.[178]

9-Bromoanthracene (**73a**) reacts with red phosphorus in the KOH – DMSO system without a palladium catalyst to be converted to anthracen-9-ylphosphinic acid (**74**) in 10% yield (Scheme 45, conditions *a*).[188] In addition, anthracene **73b** and 9,10-dihydroanthracene (**75**), resulting from the reduction of the starting bromide **73a**, were isolated from the reaction mixture.

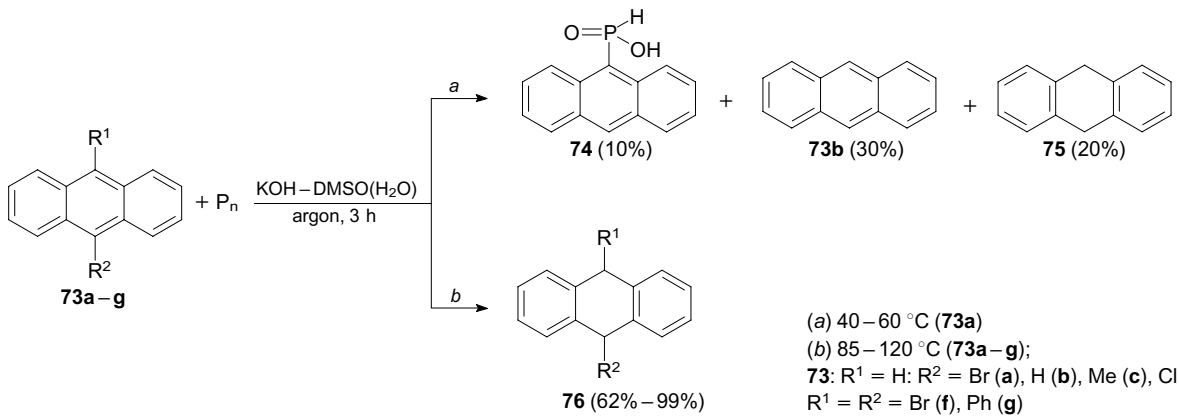
At higher temperature (85 – 120 °C), anthracene **73b** and its 9,10-substituted analogues **73a**, **c** – **g** are regioselectively reduced by this system to 9,10-dihydroanthracenes **76** in high yields (see Scheme 45, conditions *b*).[189]

The reduction of anthracenes is the subject of numerous publications.[190 – 193] This is done *via* a reaction in a hydrogen atmosphere under pressures up to 100 atm[194, 195] using transition metal catalysts.[196, 197] The main goal is to selectively prepare 9,10-dihydro isomers, which are widely used as mild hydrogen donors (in petrochemistry),[198, 199] fluorescent chemosensors,[200, 201] drug precursors,[202] *etc*. The regioselective reduction of anthracene and its substituted derivatives with red phosphorus in the KOH – DMSO($H_2O$) system is the most convenient and efficient method for the synthesis of 9,10-dihydroanthracenes.[189]

## 2.7. Phosphination of halohetarenes

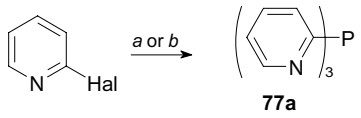
Phosphination of halohetarenes with elemental phosphorus was successfully performed in relation to halopyridines. Using the KOH – DMSO system, the reaction of 2-bromopyridine with red and white phosphorus was performed for the first time, resulting in the synthesis of tris(2-pyridyl)phosphine (**77a**),[203] an efficient tetradentate tripodal ligand[203 – 207] and a useful intermediate for the design of innovative materials.[208 – 210] The phosphination of 2-bromopyridine takes place at elevated temperature (100 °C for

**Scheme 45**




(*a*) 40 – 60 °C (**73a**)
(*b*) 85 – 120 °C (**73a** – **g**);
**73**: $R^1$ = H: $R^2$ = Br (**a**), H (**b**), Me (**c**), Cl (**d**), Br (**e**), $R^1$ = $R^2$ = Br (**f**), Ph (**g**)

**Scheme 46**



**77a**

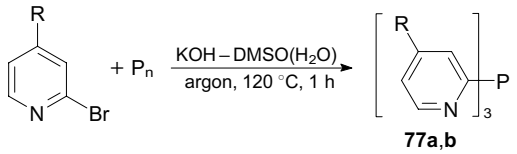
(*a*) (Hal = Br) — $P_n$ or $P_4$, KOH–DMSO($H_2O$), argon, 75–100 °C, 3 h (yield up to 62%);
(*b*) (Hal = Cl) — $P_n$, KOH–DMSO, argon, 125 °C, 2 h (70%)

$P_n$, 75 °C for $P_4$), with the yields of tris(pyridyl)phosphine **77a** being 62% and 50%, respectively (Scheme 46).[203]

An efficient method was developed for the synthesis of phosphine **77a** from red phosphorus and more readily available 2-chloropyridine (see Scheme 46, conditions *b*).[211,212]

More recently, the conditions of direct phosphination of 2-pyridyl halides with elemental phosphorus[211,212] were utilized without significant changes for the preparation of both unsubstituted (**77a**) and substituted (**77b**) phosphines (Scheme 47).[213]

**Scheme 47**

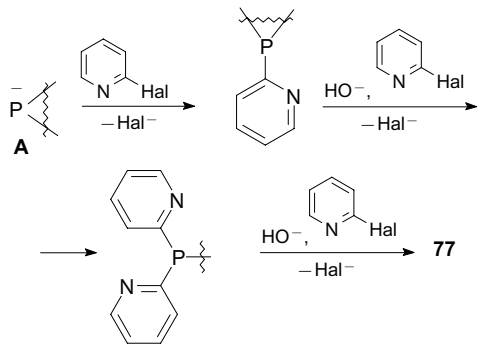


**77a**,**b**

R = H (**a**, 86%), Me (**b**, 82%)

According to experimental data and quantum chemical calculations, nucleophilic substitution in 2-halopyridines with halogen (Cl, Br) displacement by polyphosphide anions **A** proceeds as depicted in Scheme 48.[211]

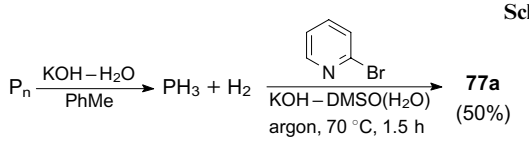
**Scheme 48**



2-Halopyridines also react with phosphine in the KOH–DMSO system.[214,215] When a phosphine–hydrogen mixture is passed through a 2-bromopyridine–KOH–DMSO suspension heated to 70 °C, tris(pyridyl)-phosphine **77a** is formed (Scheme 49). However, the product yield is lower than those attained in the methods described above (see Schemes 46, 47).[215]

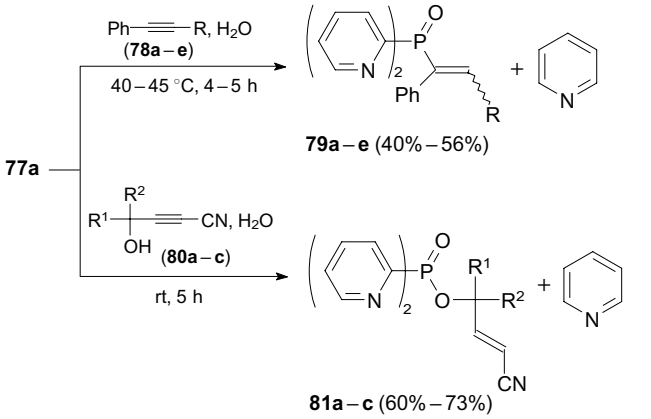
The developed method for the synthesis of phosphine **77a** using elemental phosphorus[203,211] favourably compares with the previously known syntheses of this phosphine from phosphorus trichloride, 2-bromopyridine and organolithium or -magnesium compounds[216–218] and, hence, contributes to further vigorous development of the chemistry of organophosphorus pyridine derivatives.[214,219–223] In particular, tris(pyridyl)phosphine **77a** was used to synthesize luminescent copper[224] and silver[225,226] complexes, iron complexes with magnetic properties,[213] catalytically active transition metal complexes[227,228] and hybrid bismuth complexes.[229] Phosphine **77a** is also used in organoelement synthesis as a reactive building block.[230–232]

**Scheme 49**



Original three-component non-catalytic reactions between tris(pyridyl)phosphine **77a**, electron-deficient acetylenes **78a–e** and water were discovered. The reactions led to functionalized vinyldi(pyridyl)phosphine oxides **79a–e** in good yields (Scheme 50).[230,231]

**Scheme 50**

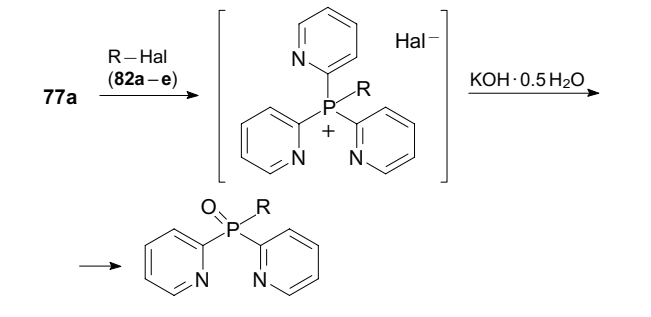


**78**, **79**: R = Bz (**a**), 2-FuC(O) (**b**), 2-ThC(O) (**c**), 3-PyC(O) (**d**), CN (**e**);
**80**, **81**: $R^1 = R^2$ = Me (**a**); $R^1$ = Et, $R^2$ = Me (**b**);
$R^1–R^2 = (CH_2)_5$ (**c**)

The reaction of tris(pyridyl)phosphine **77a** with cyanopropargyl alcohols **80a–c** readily proceeds even at room temperature giving disubstituted esters of dipyridylphosphinic acid **81a–c** (see Scheme 50).[231]

The successive treatment of phosphine **77a** with alkyl iodides **82a–c** (24–70 °C, 0.5–1 h) or arylmethyl chlorides **82d**,**e** (140 °C, 1–1.5 h) and cleavage of the resulting phosphonium salts with potassium hydroxide produced alkyl(arylalkyl)dipyridylphosphine oxides **83a–e** in high yields (Scheme 51).[232]

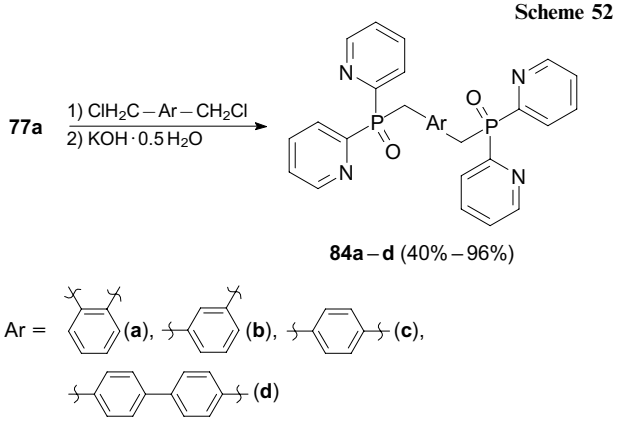
**Scheme 51**



**83a–e** (63%–96%)

R = Me (**a**), Et (**b**), $Bu^n$ (**c**), Bn (**d**), (1-Naph)$CH_2$ (**e**);
Hal = I (**82a–c**), Cl (**82d**,**e**)

**Scheme 52**




The use of organic dichlorides in this reaction afforded bis(dipyridylphosphine oxides) **84a – d** (Scheme 52).[232]

Dipyridylphosphine oxides **83** served for the synthesis of photoluminescent binuclear $Cu^{I}$ complexes, promising intermediates for the design of optoelectronic devices.[233]

It should be emphasized that studies of the above-described transformations of tris(pyridyl)phosphine **77a** (see Schemes 50 – 52) illustrating new trends in the chemistry of this organophosphorus reagent and ligand, which was difficult to prepare until recently, became possible only after the development of its direct one-step synthesis from 2-halopyridines and elemental phosphorus.[211, 212] Owing to this, tris(pyridyl)phosphine **77a** is currently as readily accessible as triphenylphosphine.

## 3. Development of the chemistry of phosphines and phosphine chalcogenides

The chemistry of organic phosphines and phosphine chalcogenides, basic organophosphorus compounds, has been traditionally studied and developed for phenyl-, diphenyl- and triphenylphosphines and their chalcogenides prepared from phosphorus halides and oganometallic compounds. New direct approaches to the formation of C – P bonds with participation of elemental phosphorus opened up previously unknown opportunities for further progress of the chemistry of organic phosphines and their derivatives. Considerable expansion of the class of secondary phosphines and phosphine chalcogenides by new available derivatives is now helpful for further elaboration and in-depth study of the classical Pudovik – Abramov reactions[34 – 38] — hydrophosphination and hydrophosphinylation of various unsaturated compounds. New versions of these reactions were found, *e.g.*, the possibility to conduct them without a catalyst and without a solvent and, in some cases, an unexpected change in the reaction pathway. As a rule, these versions ensure high yields of functionalized (in particular, by rare substituents) tertiary phosphines and phosphine chalcogenides and comply with the pot, atom and step economy (PASE) paradigm.

A new trend in this research area is the conduction of three-component reactions of secondary phosphine chalcogenides with azines and electron-deficient acetylenes, resulting in phosphinylated *N*-vinylpyridines and quinolines and products of nucleophilic displacement of hydrogen in the heteroaomatic ring by chalcogenophosphoryl anions (new types of $S_N^H Ar$ reaction).

### 3.1. Non-catalyzed addition of secondary phosphines and phosphine chalcogenides to alkenes and alkynes

The hydrophosphination and hydrophosphinylation of alkenes and alkynes with H-phosphines and their chalcogenides is a convenient atom-economic pathway to diverse compounds with C – P bonds. Usually these reactions proceed in the presence of bases, transition metal catalysts or radical initiators in organic solvents.[5, 11, 234 – 237] Recently, while considering the reaction of diphenylphosphine with styrene, Alonso *et al.*[238] demonstrated that alkene hydrophosphination can be successfully carried out without a catalyst and without an organic solvent. Heating of a mixture of these reactants gives anti-Markovnikov adduct **85** in a yield of 82% (Scheme 53). Remarkably, this reaction conducted in a solvent (DMSO, DMF, toluene) is much less efficient: the yield of adduct **85** in 24 h does not exceed 19% (Scheme 53). Later, this reaction was performed for other alkyl- and (het)arylalkenes.[239, 240]

**Scheme 53**

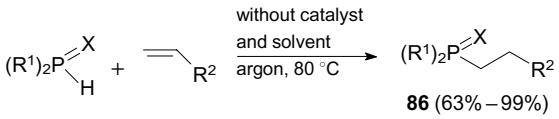



| Solvent | Time /h | Yield of **85** (%) |
|---|---|---|
| – | 4 | 82 |
| DMF | 24 | 19 |
| PhMe | 24 | 13 |
| DMSO | 24 | 7 |
| EtOH | 24 | 0 |

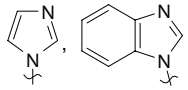
It is worth noting that non-catalyzed reactions of secondary phosphine chalcogenides with various alkenes proceed efficiently only without a solvent (reactions in solutions barely occur without a catalyst).[241 – 248]

Secondary phosphine sulfides and phosphine selenides add to aliphatic (hetero)aromatic and some functionalized alkenes on heating to give anti-Markovnikov products, tertiary phosphine chalcogenides **86**, in high yields (Scheme 54).[241, 242, 244, 246]

**Scheme 54**



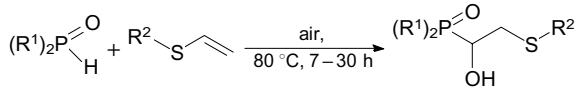

$R^1$ = Ph, $Ph(CH_2)_2$, 4-$ClC_6H_4(CH_2)_2$, 4-$Bu^tC_6H_4(CH_2)_2$, 2-$Py(CH_2)_2$, 2-$Fu(CH_2)_2$;

$R^2$ = n-$C_5H_{11}$, CN, $CH_2OH$, $OBu^n$, SEt, S($C_7H_{15}$-n), SPh, Se($C_5H_{11}$-n), $SiMe_3$, Ph, $C_6H_4Bu^t$-4, ; X = S, Se

Under these conditions, secondary phosphine oxides do not react with aliphatic and (hetero)aromatic alkenes, which is attributable to higher dissociation energy of the P – H bond compared to that for analogous phosphine sulfides and phosphine selenides.[249]

However, heating of secondary phosphine oxides with vinyl sulfides in air unexpectedly resulted in the formation of hydroxysulfanylethylphosphine oxides **87** — oxidized

**Scheme 55**



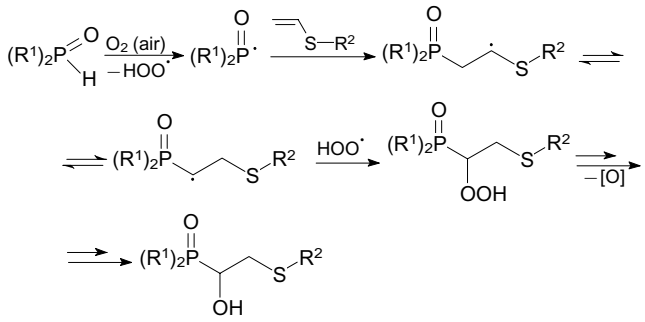

**87** (70%–93%)

$R^1$ = 4-$MeC_6H_4(CH_2)_2$, 4-$Bu^tC_6H_4(CH_2)_2$, 4-$ClC_6H_4(CH_2)_2$, $Ph(CH_2)_2$, 2-$Fu(CH_2)_2$, Ph; $R^2$ = Alk, Ph

rearranged adducts of aerobic hydrophosphinylation of vinyl sulfides (Scheme 55).[243]

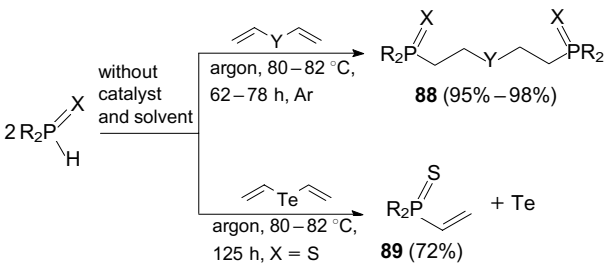
Apparently, the discovered oxidative rearrangement proceeds according to Scheme 56, which includes the initial generation of hydroperoxyl and phosphinoyl radicals from secondary phosphine oxides and air oxygen.[243]

**Scheme 56**




Non-catalyzed reactions of secondary phosphine sulfides and phosphine selenides with divinyl chalcogenides have been studied;[245] in the case of divinyl sulfide and selenide, the reactions lead to a nearly quantitative formation of anti-Markovnikov diadducts **88**, which are unique stabilizing solvents for the design of nano-sized semiconductor materials (Scheme 57).[250–252] Under the same conditions, divinyl telluride acts as a vinylating agent with respect to secondary phosphine sulfides, which are thus converted to vinylphosphine sulfides **89** (see Scheme 57). This is accompanied by evolution of an equivalent amount of tellurium metal.[245]

**Scheme 57**



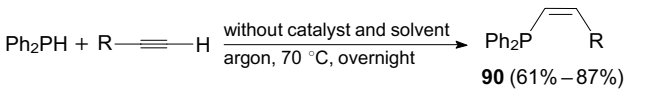

**88** (95%–98%)

**89** (72%)

R = Ph, $Ph(CH_2)_2$; X, Y = S, Se

In relation to diphenylphosphine and terminal alkyl- and arylacetylenes, it was shown that triple bonds can be successfully hydrophosphinated without catalysts and solvents, which gives *Z*-alkenyldiphenylphosphines **90** in high yields (Scheme 58).[240]

**Scheme 58**

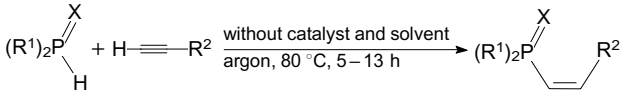



**90** (61%–87%)

R = n-$C_6H_{13}$, Cy, Ph, 4-$MeOC_6H_4$, 4-$Me_2NC_6H_4$; Cy is cyclohexyl

Secondary phosphine chalcogenides also efficiently react with various acetylenes under similar conditions, which results in the regio- and stereoselective formation of *Z*-isomers of β-monoadducts **91** (Scheme 59).[253]

**Scheme 59**



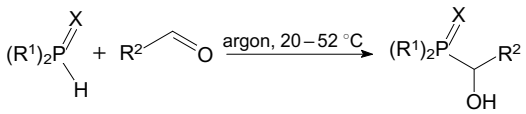

**91** (60%–94%)

$R^1$ = Ph, $Ph(CH_2)_2$, 2-$Fu(CH_2)_2$;
$R^2$ = n-$C_6H_{13}$, Ph, $C_6H_4Me$-4, $CH_2OH$, $C(OH)Me_2$, $CO_2Me$, $SiMe_3$;
X = S, Se

## 3.2. Hydrophosphinylation of aldehydes

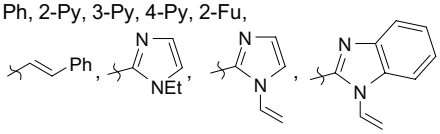
Over the last two decades, particular interest has been attracted by non-catalyzed reactions of secondary phosphine chalcogenides with aldehydes of various structures, which occur, most often, in organic solvents under mild conditions. Tertiary hydroxymethylphosphine chalcogenides **92** were obtained in these reactions in high yields (Scheme 60).[254–270] The elimination of a solvent from the reaction medium, with all other conditions being the same, markedly decreases the reaction time and, in some cases, increases the efficiency (Scheme 60).[270]

**Scheme 60**




**92**

$R^1$ = ArAlk, HetArAlk, Ar; X = O, S, Se;
$R^2$ = Ph, 2-Py, 3-Py, 4-Py, 2-Fu,



| Solvent | Time /h | Yield of **92** (%) |
|---|---|---|
| – | 0.1–5 | 96–98 |
| THF | 0.8–84 | 75–98 |
| 1,4-dioxane | 1–24 | 82–99 |
| PhH | 2 | 42 |
| $CH_2Cl_2$ | 24 | 77–99 |

The developed conditions (20–52 °C, without a catalyst and a solvent) comply with the green and click chemistry requirements and make it possible to easily obtain tertiary α-hydroxy-substituted phosphine chalcogenides **92** — promising ligands for transition metal catalysts,[271] flame retardants,[272] drug precursors[273] and building blocks for organic synhesis, in particular, for the preparation of polyfunctional vinyl ethers.[274]

### 3.3. Tandem reactions of secondary phosphine chalcogenides with azines and electron-deficient acetylenes

#### 3.3.1. Vinylation – phosphinylation or phosphinylation of pyridines

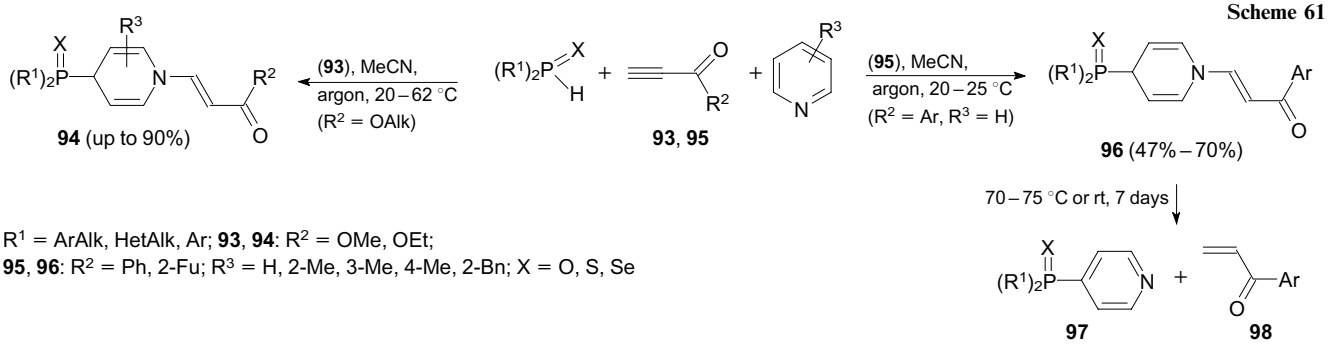
Secondary phosphine chalcogenides react with alkyl propiolates **93** and pyridine and its derivatives under mild conditions according to the vinylation – phosphinylation pathway without a catalyst to give (*E*)-*N*-vinyl-4-chalcogenophosphoryl-1,4-dihydropyridines **94** in up to 90% yields and with high stereo-, regio- and chemoselectivity (Scheme 61).[275 – 277]

A similar three-component reaction is also easily implemented between secondary phosphine chalcogenides, terminal acylacetylenes **95** and pyridine, giving rise to (*E*)-*N*-acylvinyl-4-chalcogenophosphoryl-1,4-dihydropyridines **96** (see Scheme 61).[278] However, unlike *N*-vinyldihydropyridines **94**, these products are unstable: on heating (70 – 75 °C) or during storage under ambient conditions (7 days), they are completely aromatized to 4-(chalcogenophosphoryl)pyridines **97** with elimination of (*E*)-acylalkenes **98**.[278]

In the presence of internal acylacetylenes **99**, pyridines undergo regioselective cross-coupling with secondary phosphine chalcogenides giving rise to 4-(chalcogenophosphoryl)pyridines **97**.[278] This reaction is a new type of nucleophilic substitution in the heteroaromatic ring ($S_N^H$Ar) in which electron-deficient acetylenes **99** act as oxidants, being stereoselectively reduced to the corresponding *E*-alkenes **100** (Scheme 62). [278] The expected phosphinylated *N*-acylvinyl-1,4-dihydropyridines of type **96** were not detected in the reaction mixture.

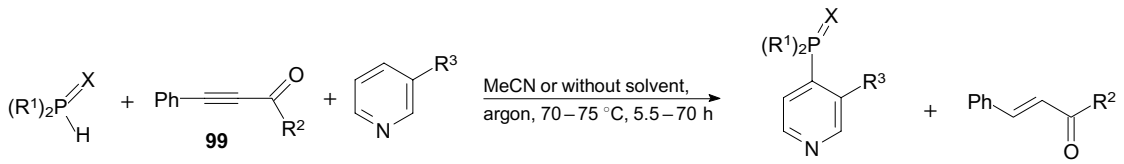
A scheme proposed for the reaction of pyridines with electron-deficient acetylenes **93**, **95** and **99** and secondary phosphine chalcogenides[275 – 278] includes nucleophilic attack by pyridine on the triple bond and formation of zwitter-ions **C** – **E** with the carbanion centre in the *trans*-position relative to the nitrogen atom. Subsequently zwitterion **E** is neutralized by the proton of the secondary phosphine chalcogenide, and the phosphorus-centred anion thus formed attacks position 4 of pyridinium cation **F**. In the

**Scheme 61**



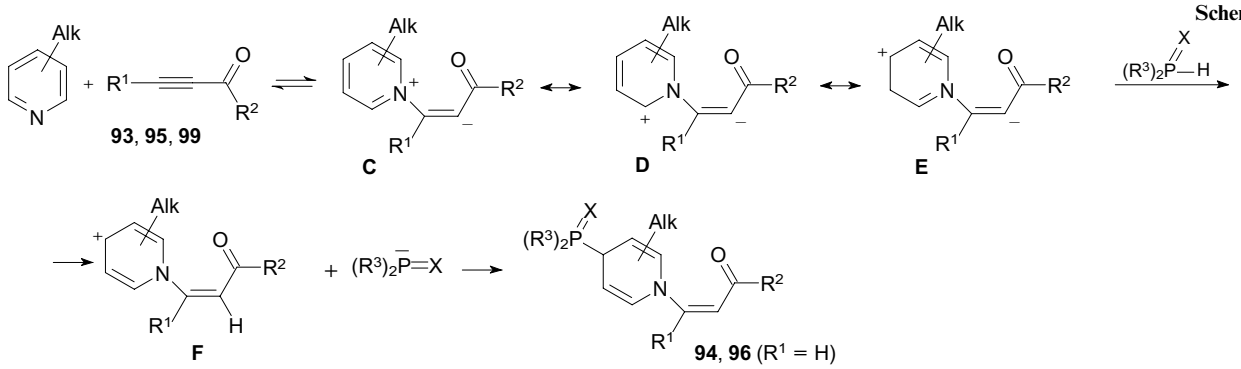

R$^1$ = ArAlk, HetAlk, Ar; **93**, **94**: R$^2$ = OMe, OEt;
**95**, **96**: R$^2$ = Ph, 2-Fu; R$^3$ = H, 2-Me, 3-Me, 4-Me, 2-Bn; X = O, S, Se

**Scheme 62**

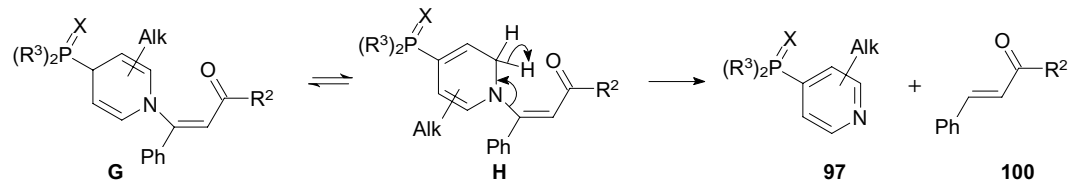



R$^1$ = Ph, Ph(CH$_2$)$_2$, 4-ClC$_6$H$_4$(CH$_2$)$_2$, PhCH(Me)CH$_2$; R$^2$ = Me, Et, Ph, 2-Fu; R$^3$ = H, Me; X = O, S, Se

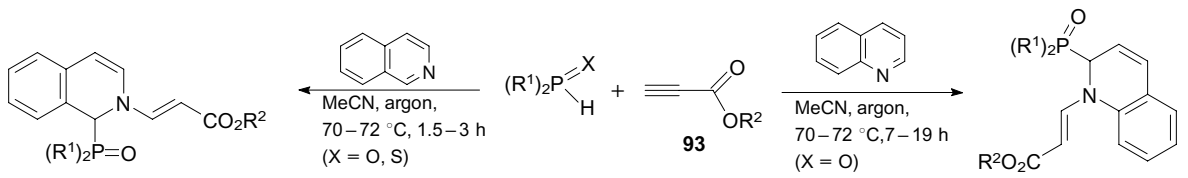
**Scheme 63**




**Scheme 64**



**Scheme 65**




**102** (82 – 93%) $R^1$ = Ph, $Ph(CH_2)_2$; $R^2$ = Me, Et **101** (up to 75%)

case of terminal acetylenes **93** and **95** ($R^1$ = H), this gives functionalized 1,4-dihydropyridines **94** and **96** (Scheme 63).[275 – 277]

Meanwhile, when internal acetylenes **99** are used ($R^1$ = Ph, see Scheme 63), the reaction does not stop after the formation of the corresponding 1,4-dihydropyridines **G**, but proceeds further with elimination of chalcones **100** from prototropically isomerized intermediate **H** to give cross-coupling products **97** (Scheme 64).[278]

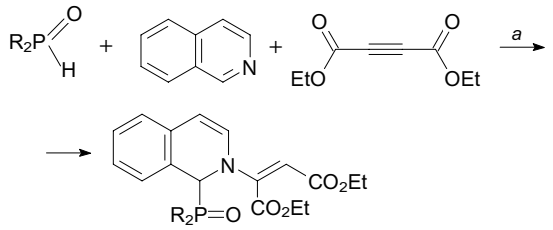
### 3.3.2. Vinylation – phosphinylation of quinolines

Quinoline, like pyridines, reacts with alkyl propiolates **93** and secondary phosphine oxides according to the *N*-vinylation – *C*-phosphinylation pathway giving rise to (*E*)-*N*-vinyl-1,2-dihydroquinolines **101** with a phosphoryl substituent in position 2 of the quinoline ring. The reaction takes place upon heating, with the yields of 1,2-dihydroquinoline **101** varying from moderate (35% – 45%) to good (61% – 75%) (Scheme 65).[279]

In the case of isoquinoline, this reaction proceeds faster and is more efficient: the yield of *C*(1)-phosphinylated (*E*)-*N*-vinyl-1,2-dihydroisoquinolines **102** reaches 82% – 93%.

Using the reaction of diethyl acetylenedicarboxylate and secondary phosphine oxides, it was shown that isoquinoline readily undergoes the *N*-vinylation and *C*(1)-phosphinylation reaction with not only terminal, but also internal acetylenes. As a result, polyfunctionalized (*E*)-*N*-ethenyl-1,2-dihydroisoquinolines **103** were synthesized in good yields (Scheme 66).[279]

**Scheme 66**



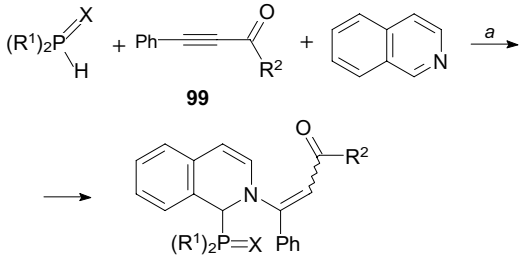
**103** (60% – 74%)

(*a*) MeCN, argon, 70 – 72 °C, 1.5 h;
R = Ph, $Ph(CH_2)_2$

Non-catalyzed regio- and stereoselective three-component reactions of secondary phosphine oxides with quinolines or isoquinolines and acylacetylenes **95** were found to efficiently proceed at room temperature to give the corresponding phosphinylated (*E*)-*N*-acylvinyl-1,2-dihydroquinolines **104** or 1,2-dihydroisoquinolins **105** (Scheme 67).[280]

Isoquinoline undergoes the vinylation – phosphinylation tandem reaction with internal acylacetylenes **99** and secondary phosphine chalcogenides under more drastic conditions, giving phosphinylated *N*-ethenyl-1,2-dihydroisoquinolines **106** in good yields (Scheme 68).[280]

**Scheme 68**

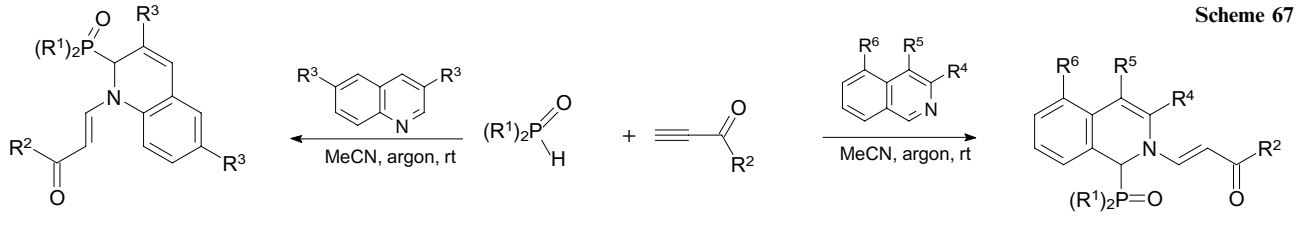


**106** (51% – 66%)

(*a*) MeCN, argon, 70 – 75 °C, 45 – 72 h;
$R^1$ = $Ph(CH_2)_2$, 4-$ClC_6H_4(CH_2)_2$, $PhCH(Me)CH_2$; $R^2$ = Ph, 2-Fu;
X = O, S

The considered tandem reactions of secondary phosphine chalcogenides with azines and electron-deficient acetylenes are general. Their benefits include mild reaction conditions, the absence of a catalyst, strict stereo-, regio- and chemoselectivity and valuable products — functionalized phosphinylated *N*-vinyldihydroazines, which are promising drug precursors.[281 – 284] Of particular value is the non-catalyzed direct cross-coupling of azines with secondary phosphine chalcogenides induced by electron-deficient acetylenes, which simultaneously act as internal oxidants. 4-Chalcogenophosphorylpyridines synthesized in this way are efficient ligands for metal complexes for various purposes.[276, 285 – 287]

**Scheme 67**



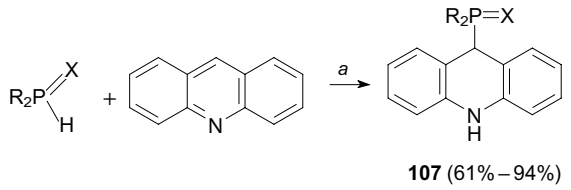

**104** (60% – 80%) **105** (65% – 91%)

$R^1$ = Ph, $Ph(CH_2)_2$, 4-$ClC_6H_4(CH_2)_2$, $PhCH(Me)CH_2$; $R^2$ = Ph, 2-Fu; $R^3$ = H, Me, OMe; $R^4$ = H, Me; $R^5$ = H, Br; $R^6$ = H, $NO_2$

### 3.4. Phosphinylation of acridine

Unlike pyridines and quinolines, acridine does not react with secondary phosphine chalcogenides and electron-deficient acetylenes through the phosphinylation – vinylation (see Scheme 61) or oxidative cross-coupling pathway ($S_N^HAr$ reaction) (see Scheme 62). It was found that without a catalyst, acridine adds secondary phosphine chalcogenides both in the presence and in the absence of electron-deficient acetylenes with the regioselective formation of 9-chalcogenophosphoryl-9,10-dihydroacridines **107** in high yields (Scheme 69).[288, 289]

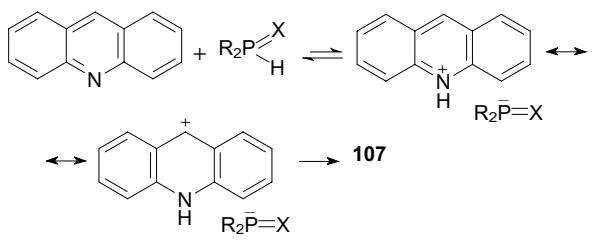
**Scheme 69**




(*a*) MeCN or without solvent, argon, 70 – 75 °C, 1 – 30 h;
R = Ph, $Ph(CH_2)_2$, 4-$ClC_6H_4(CH_2)_2$, $PhCH(Me)CH_2$; X = O, S, Se

The inability of acridine to undergo a one-step $S_N^HAr$ reaction in the presence of electron-deficient acetylenes is explained by the steric factor: the proton formed upon dissociation of secondary phosphine chalcogenide easily surpasses bulky electron-deficient acetylene in the competition for the nitrogen lone pair. After that, the formed conjugated acridinium cation adds chalcogenophosphoryl anion to position 9 of the acridine ring, which gives adducts **107** (Scheme 70).[288, 289]

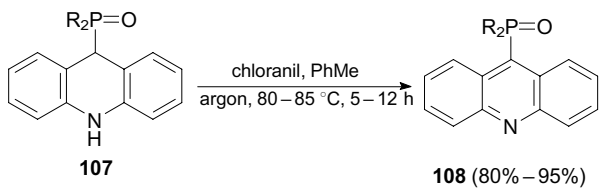
**Scheme 70**




In this case, the $S_N^HAr$ reaction ends in the oxidation of dihydroacridines **107** with chloranil yielding the corresponding aromatic derivatives **108** (Scheme 71).

The synthesized dihydroacridines **107**, acridines **108** and their derivatives could be used in pharmaceutics,[290, 291] catalysis [292, 293] and optoelectronics.[294, 295]

**Scheme 71**

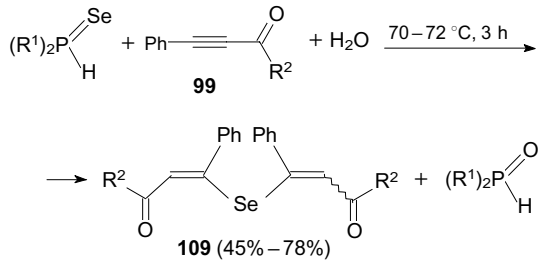



R = Ph, $Ph(CH_2)_2$, 4-$ClC_6H_4(CH_2)_2$, $PhCH(Me)CH_2$

### 3.5. Secondary phosphine selenides as selenylating reagents

Secondary phosphine selenides proved to be active selenylating reagents with respect to electron-deficient acetylenes.[296] Bis(2-acylvinyl) selenides **109** (*Z*,*Z*- and *E*,*Z*-isomers) were obtained by the reaction of secondary phosphine selenides with acylphenylacetylenes **99** without a catalyst in water (Scheme 72). The corresponding secondary phosphine oxides were identified in the reaction mixture. In the absence of water, this reaction does not occur.

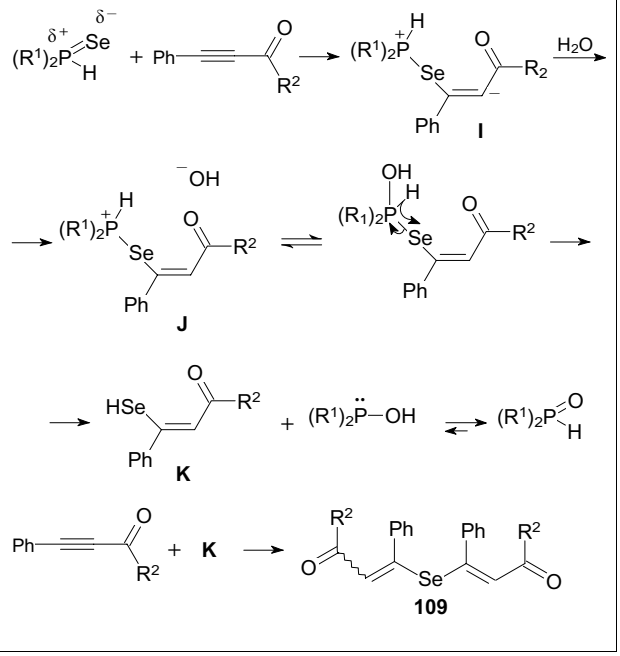
**Scheme 72**




$R^1$ = Ph, $Ph(CH_2)_2$; $R^2$ = Me, Et, Ph, 2-Fu

The pathway towards divinyl selenides **109** includes nucleophilic addition of secondary phosphine selenide to the triple bond of acylacetylene (with selenium atom acting as the nucleophile). The carbanionic centre of the resulting zwitter-ion **I** is neutralized by the water proton, and the hydroxide anion thus released adds to the positive charge on the phosphorus atom to give phosphorane **J**, which then degrades into secondary phosphine oxide and vinylselenol **K**. The latter adds to a second acylacetylene molecule to give bis(2-acylvinyl) selenides **109** (Scheme 73).[296]

**Scheme 73**




The described unusual non-catalyzed transfer of the selenium atom from secondary phosphine selenides to acylacetylenes is a new method for carbon – selenium bond formation, which opens up a way to the synthesis of bis(ketovinyl) selenides **109**, which are potential precursors

of selenium-containing drugs,[297] ligands for transition metal catalysts [298] and materials for microelectronics.[298, 299]

## 4. Conclusion

The prospects and implementation of the advantages of chlorine-free direct reactions of C–P bond formation using elemental phosphorus activated by superbases or *via* electrochemical or catalytic methods imply the development of research along the following lines:

— expanding the range and increase in the activity and selectivity of superbasic catalytic suspensions (dynamic systems, which include molecular solutions, nano-sized particles and submicron- and micron-sized crystals, bases and polyphosphide and polyphosphinite anions possessing the properties of supernucleophiles);

— increasing efficiency of the involvement of elemental phosphorus into the C–P bond formation by means of reduction of the oxidized products (hypophosphites and phosphites);

— development of fundamentally new catalytic superbase–reducing agent compositions (internal $PH_3$–$H_2$ or external one);

— further investigation of the electrochemical activation of white phosphorus with the goal of development of an environmentally benign and industrially adaptable method for the C–P bond formation; as applied to halobenzenes, this may contribute to the development of an industrial synthesis of triphenylphosphine, an important organophosphorus product.

Since the reactions of electrophiles with elemental phosphorus in superbasic systems are, most often, accompanied by generation of a phosphine–hydrogen mixture, this opens up the possibility for development of new processes for C–P bond formation by utilization of this accessible and easily dosable source of phosphine.

So far, there are no implemented controlled syntheses of organic phosphines, phosphine oxides and phosphinic acids of a specified structure based on direct phosphinylation of electrophilic substrates by elemental phosphorus with variable alkali metal cations and complex forming ligands — key components of multiphase superbasic systems.

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