

Nucleophilic and free-radical additions of phosphines and phosphine chalcogenides to alkenes and alkynes

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Dedicated to Professor E. Lukevics on the occasion of his 70th anniversary

Abstract

Nucleophilic and free-radical additions of phosphines and phosphine chalcogenides to alkenes and alkynes are discussed. The bibliography includes 169 references.

Keywords: Phosphines, phosphine chalcogenides, alkenes, alkynes, addition

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1. Introduction

Addition of phosphines and phosphine chalcogenides to double and triple carbon-carbon bonds represents a convenient and atom-economic approach to C–P bond formation and synthesis of functional phosphines and phosphine chalcogenides.¹⁻⁴ These compounds are important objects in the chemistry of organophosphorus compounds and widely applied as ligands for advanced catalysts (including those for enantioselective processes⁵⁻¹¹), flame retardants,^{12, 13} extractants of rare earth and transuranic elements,¹⁴ building blocks and starting materials for the preparation of biologically active compounds for medicine and agriculture.¹⁵⁻¹⁸ Over the recent years, a lot of research has been devoted to addition reactions of P-H reagents to multiple carbon-carbon bonds, catalyzed by metal complexes, and, as a result, numerous synthetic methods have been developed (for example, see the reviews¹⁹⁻²³). Meanwhile, hydrophosphination of alkenes and alkynes under base-catalyzed or free-radical conditions (*i.e.*, under “green chemistry” conditions) often appears to be competitive, let alone ecologically safer, and sometimes experimentally even more advantageous.

In this review, we survey and analyze results of the investigations concerning the heavy metal-free additions of phosphines and phosphine chalcogenides, containing a P-H function, to multiple carbon-carbon bonds. The attention is focused on the work of the last 10 years, relating to synthesis of functional phosphines and phosphine chalcogenides through reactions of phosphine, primary and secondary phosphines, phosphine oxides and sulfides with substituted alkenes and alkynes. For this period a number of new or earlier inaccessible P-H species became readily available owing to the methodology for the activation of elemental phosphorus in heterogeneous strongly basic media^{24, 25} developed in late 80-s²⁶⁻³¹ (now often referred to as the Trofimov-Gusarova reaction^{32, 33}). This new approach to the C–P bond formation allows one to carry out direct phosphorylations of organohalides, dihaloalkanes, electrophilic alkenes, acetylenes and oxiranes with elemental phosphorus to afford diverse primary, secondary and tertiary phosphines and phosphine chalcogenides, including functionalized and unsaturated ones.³⁴⁻³⁸ Some of the P-H compounds derived from these reactions turned out to be rewarding addends for nucleophilic and free-radical additions to multiple bonds, thus further unfolding the field.

2. Addition of phosphines and phosphine chalcogenides to alkenes

Electrophilic addition of such P-H addends as phosphines and their chalcogenides to unsaturated compounds is not as extensively studied as their nucleophilic and free-radical additions. Among scarce examples of these reactions^{4, 39-41} phosphine was reported to react with alkenes in the presence of acids under pressure (60-90°C, 30-47 atm) to give mostly primary Markovnikov phosphines.³⁹ Secondary phosphines add to alkyl vinyl ethers in the presence of acids (CF₃COOH, 130°C) to form Markovnikov adducts.^{40, 41}

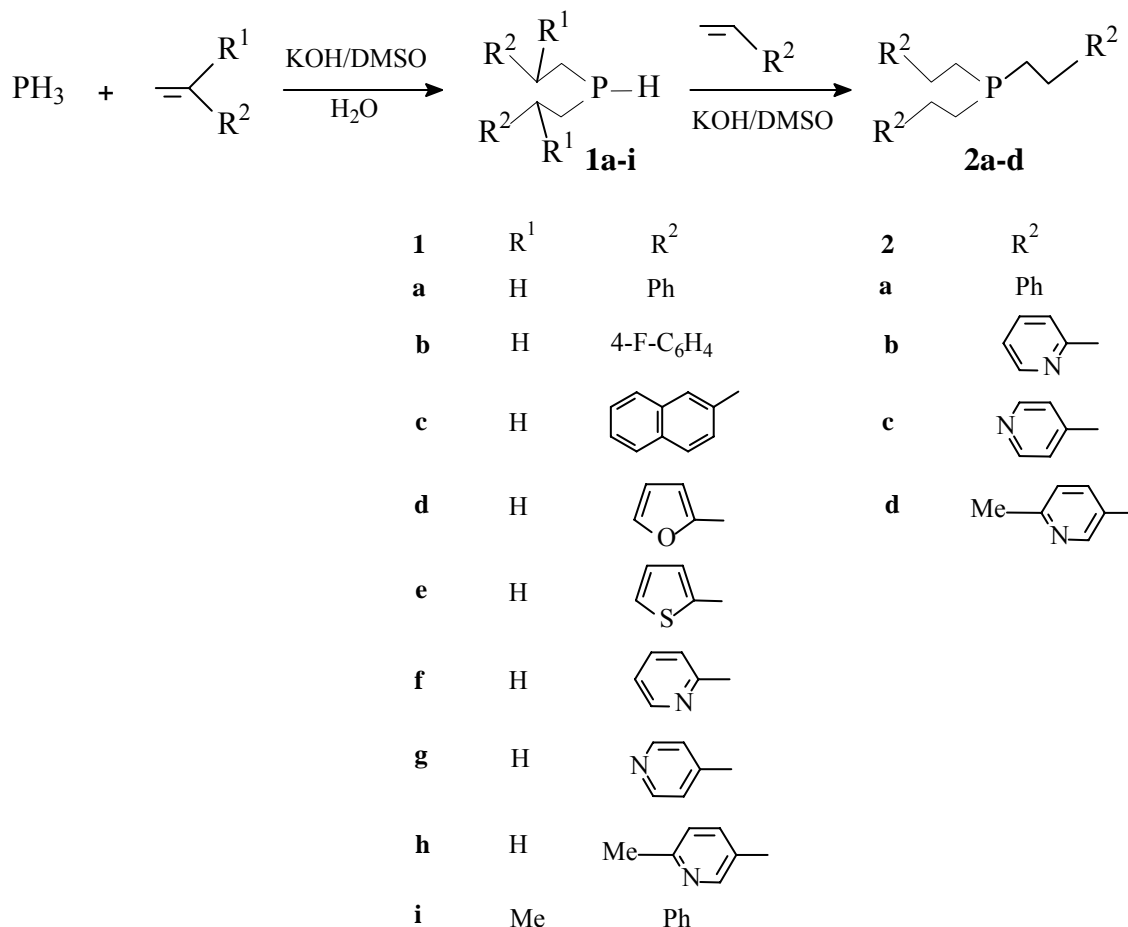
Therefore, we limit the review mostly with recent strides in the base-catalyzed and free-radical additions of phosphines and phosphine chalcogenides, yet recently uncommon addends, to the double and triple carbon-carbon bonds.

2.1 Nucleophilic addition of phosphines and phosphine chalcogenides to alkenes

2.1.1 Phosphine. Nucleophilic addition of phosphine to the double carbon-carbon bond in the presence of bases was first described by Rauhut *et al.*^{42, 43} and later by King *et al.*⁴⁴⁻⁵² for the alkenes with strong electron-withdrawing substituents. All these works are discussed in detail in a review.⁴

Later,^{53, 54} it has been shown that superbasic systems allows hydrophosphination of weakly electrophilic double bonds of aryl- and hetarylethenes with phosphine to synthesize previously unknown or difficult-to-prepare secondary or tertiary phosphines.⁵³⁻⁶¹ In these processes, instead of pure phosphine, a phosphine-hydrogen mixture generated from red phosphorus suspensions in organic solvents (dioxane, toluene) under the action of aqueous KOH⁵³ (or NaOH) was used. Phosphine thus obtained was successfully utilized in hydrophosphination reactions without further isolation or purification.⁵³⁻⁶¹

Thus, bis(2-arylethyl)- and bis(2-hetarylethyl)phosphines (**1a-i**) were selectively synthesized (Scheme 1) in 60-80% yield upon slow addition of alkene to a heated (45-60°C) KOH-DMSO suspension while passing the phosphine-hydrogen mixture through reaction mixture.^{53, 54, 56-58, 60, 61} Complete and selective aryl(hetaryl)ethylation of phosphine with styrene and vinylpyridines was accomplished (Scheme 1) at 95-98°C and 67-70°C, correspondingly, in the KOH-DMSO system with additional introduction of the alkenes to reaction mixture at the end of the process (after the phosphine feeding was stopped) to give tris(2-phenylethyl)- (**2a**) and tris(2-pyridylethyl)phosphines (**2b-d**) in 65-76% yield.⁵⁸⁻⁶⁰



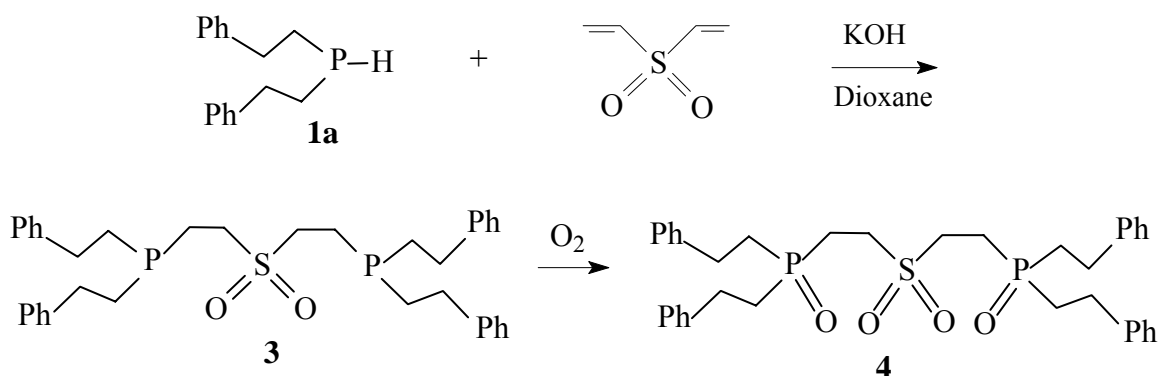
Scheme 1

At a lower temperature (30-40°C) corresponding primary phosphines are formed in 20-24% yield. Still, the major products (up to 60%) under these conditions remain diorganylphosphines.^{55, 58}

2.1.2 Primary and secondary phosphines and phosphine chalcogenides. Unlike PH₃, which requires a base catalyst for its addition even to strongly electrophilic alkenes,⁴²⁻⁵² primary and secondary phosphines⁶²⁻⁶⁵ and phosphine oxides⁶⁶⁻⁷⁰ are capable of adding to electron-deficient alkenes (nitroethenes,⁶⁴ fluorosulfonylene,⁶⁵ acrylonitriles,^{62, 63} organylacrylates,^{62, 69, 70} vinylphosphine oxides⁶⁶⁻⁶⁸) without catalyst, thus providing an atom-economic and ecologically benign synthetic route to various functionalized phosphines and phosphine oxides. Phosphine oxides bearing unsaturated alkenyl and alkynyl radicals are more active in these processes.^{69, 70} Noticeably, the non-catalyzed addition of secondary phosphine oxides and phosphine sulfides to acrolein and its derivatives proceeds at the carbonyl group with the double bond remained intact to give corresponding unsaturated hydroxyl-containing tertiary phosphine oxides and sulfides.^{71, 72}

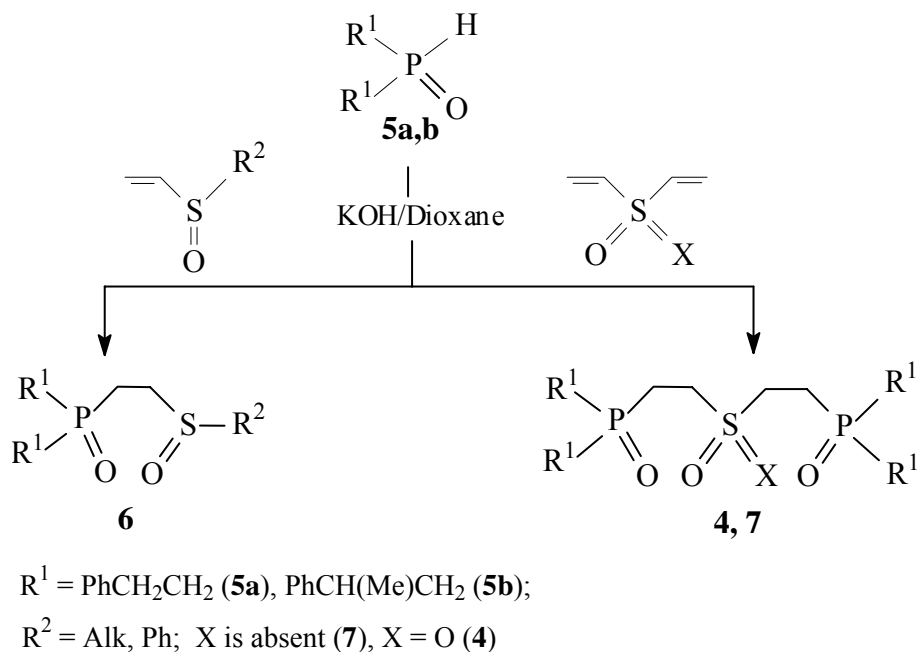
In the presence of bases addition of organic phosphines^{47-52, 65, 73-77} and phosphine oxides^{68, 78-90} to electron-deficient double bonds results mainly in corresponding tertiary phosphines and phosphine oxides in 27-93% yield.

Phosphine **3** and phosphine oxide **4** were synthesized through hydrophosphination of divinylsulfone (Scheme 2) under mild conditions (room temperature, KOH-dioxane) in high yield.⁸⁸



Scheme 2

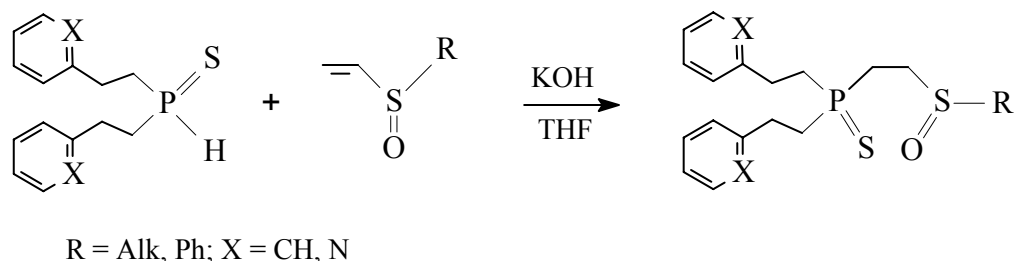
Under analogous conditions, secondary bis(2-phenylethyl)- and bis(2-phenylpropyl)phosphine oxides (**5a,b**) react with vinylsulfoxides,⁸⁹ divinylsulfoxide⁹⁰ and divinylsulfone⁸⁸ to form corresponding functionalized tertiary phosphine oxides **6** or diphosphine oxides **4, 7** in high yield (Scheme 3).



Scheme 3

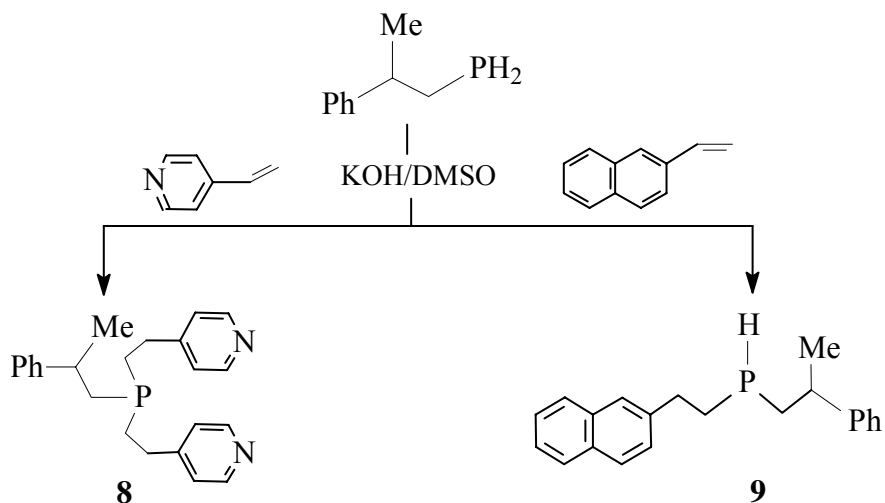
At a higher temperature (over 50°C), along with the adducts **4**, **6**, **7**, the reaction also gives diorganylvinylphosphine oxides as a result of desulfinylation or desulfonylation of the addition products.⁸⁸⁻⁹⁰

Recently, first examples of facile hydrothiophosphorylation of organyl vinyl sulfoxides were described.⁹¹ Nucleophilic addition of secondary phosphine sulfides to organyl vinyl sulfoxides (KOH-THF, room temperature) proceeds chemo- and regioselectively to give corresponding bis(2-organylethyl)[2-(organylsulfinyl)ethyl]phosphine sulfides in high isolated yield (Scheme 4).



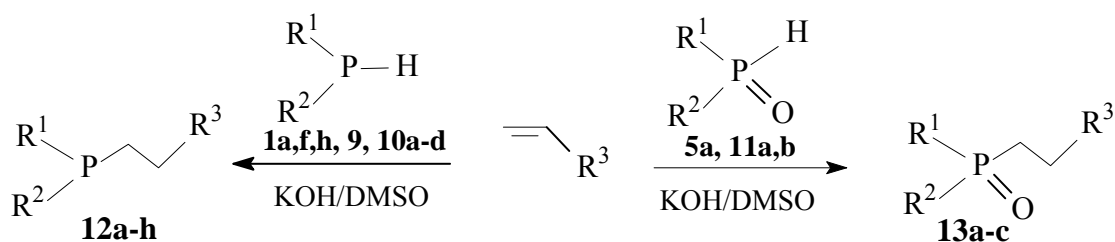
Scheme 4

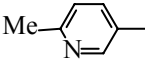
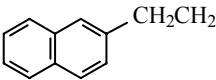
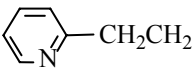
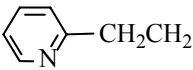
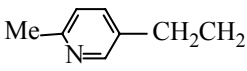
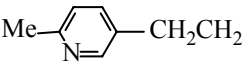
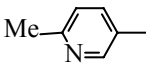
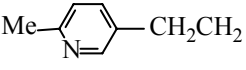
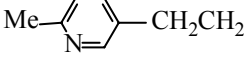
Hydrophosphination and hydrophosphorylation of such weakly electrophilic alkenes as styrene,⁹²⁻⁹⁴ 2-vinylnaphthalene⁶¹ and vinylpyridines⁹⁴ became possible due to superbase catalytic systems. Thus, 2-phenylpropylphosphine reacts with 4-vinylpyridine⁹⁴ in a KOH-DMSO suspension to give corresponding tertiary phosphine **8** with chiral carbon (Scheme 5). In the case of the reaction of 2-phenylpropylphosphine with sterically hindered 2-vinylnaphthalene, the process stops at the stage of the formation of secondary phosphine **9** (Scheme 5).⁶¹



Scheme 5

Under similar conditions, secondary phosphines **1a,f,h, 9**, diphenyl-, bis(3-fluorophenyl)-, bis(4-fluorophenyl), bis(3-trifluoromethylphenyl)phosphines (**10a-d**), as well as phosphine oxide **5a**, diphenyl- and bis[2-(2-methyl-5-pyridyl)ethyl]phosphine oxides (**11a,b**) add to styrene,^{60, 61, 92-94} and vinylpyridines⁹⁴ to form 2-aryl- and 2-pyridylethyl-diorganylphosphines **12a-h** or phosphine oxides **13a-c** (the yields are 47-95%) (Scheme 6), prospective building blocks for design of complex-forming luminophores,^{32, 38} *P,N*-chelating ligands³⁷ and flame retardants.^{13, 33}



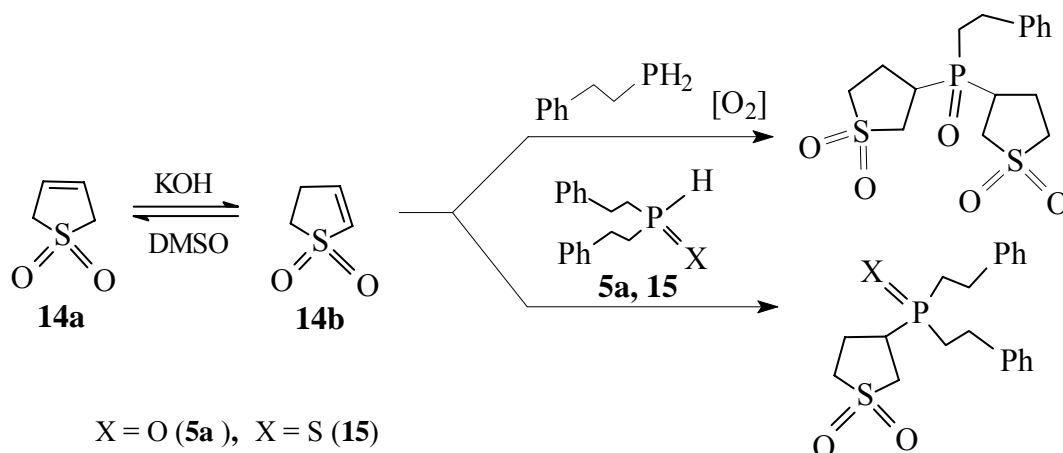
Compound	R ¹	R ²	R ³	Ref
12a	Ph	Ph	Ph	93
12b	3-F-C ₆ H ₄	3-F-C ₆ H ₄	Ph	92
12c	4-F-C ₆ H ₄	4-F-C ₆ H ₄	Ph	92
12d	3-CF ₃ -C ₆ H ₄	3-CF ₃ -C ₆ H ₄	Ph	92
12e	PhCH ₂ CH ₂	PhCH ₂ CH ₂		94
12f	PhCH(Me)CH ₂		Ph	61
12g			Ph	60
12h			Ph	94
13a	Ph	Ph	Ph	93
13b	PhCH ₂ CH ₂	PhCH ₂ CH ₂		94
13c			Ph	94

Scheme 6

Later, another superbase, *t*-BuOK-DMSO, was used for hydrophosphination and hydrophosphorylation of alkenes.^{86, 87} The authors successfully reproduced the reactions with styrene,⁹²⁻⁹⁴ vinylpyridines⁹⁴ and vinyl-diphenylphosphine,⁴⁷ and extended the set of alkenes over vinyl-triphenylsilane⁸⁶, 1-vinylimidazole (in the *t*-BuOK-toluene system)⁹⁵ and vinylphenylsulfide.⁸⁶ The latter two reactions are, to the best of our knowledge, the first

examples of nucleophilic addition to such electron-rich double bonds. Unfortunately, the paper⁸⁶ does not contain any data proving the structures of the compounds obtained.

The system KOH-DMSO also allowed the reaction of 3-thiolen-1,1-dioxide (**14a**) with primary phosphines⁹⁶ and secondary phosphine chalcogenides **5a**, **15**^{97, 98} to be carry out. The corresponding adducts were synthesized in high yield. Without KOH or under radical conditions [65°C, 6 h, azabisobutyronitrile (AIBN)], neither hydrophosphination nor hydrophosphorylation occurs, thus confirming the nucleophilic character of this addition, which, presumably, proceeds *via* the formation of intermediate 2-thiolen-1,1-dioxide (**14b**) (Scheme 7).^{97, 98}

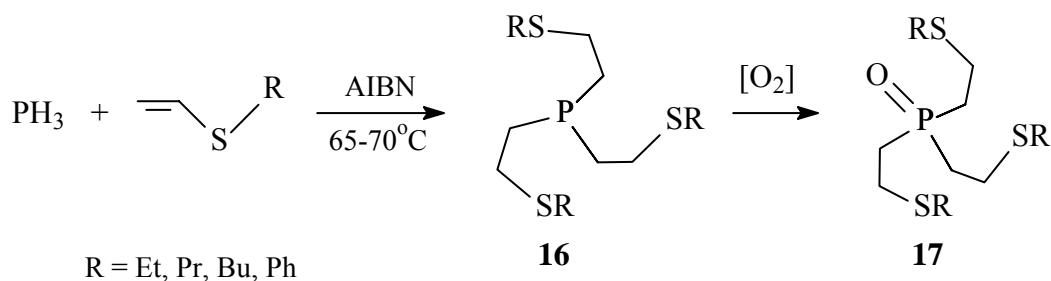


Scheme 7

2.2 Radical addition of phosphines and phosphine chalcogenides to alkenes

2.2.1 Phosphine. Addition of phosphine to alkenes under radical conditions (organic peroxides, AIBN, UV irradiation) was published mainly as patents and discussed in a review.⁴ Representative recent investigations are the synthesis of limonene-derived chiral phosphines⁹⁹ and polyfunctional tertiary phosphines and phosphine oxides from vinylsulfides.¹⁰⁰ The use of phosphine-hydrogen mixture⁵³ generated *in situ* from elemental phosphorus in the latter case demonstrates applicability of this available phosphorylating reagent also for free-radical addition reactions.¹⁰⁰

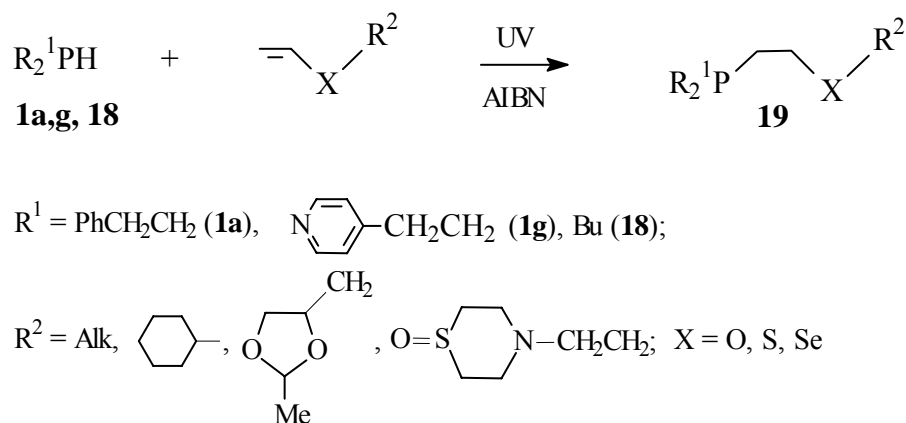
Thus, the phosphine-hydrogen mixture generated from red phosphorus in the system KOH-toluene-H₂O, reacts readily with vinyl sulfides under free-radical conditions (dioxane, AIBN, 65-70°C, atmospheric pressure) to give regioselectively anti-Markovnikov adducts, tris[2-(organylthio)ethyl]phosphines (**16**) (Scheme 8).¹⁰⁰ The latter easily oxidize by air during their isolation and purification on Al₂O₃ giving a 56-83% yield of tris[2-(organylthio)ethyl]phosphine oxides (**17**) (Scheme 8).



Scheme 8

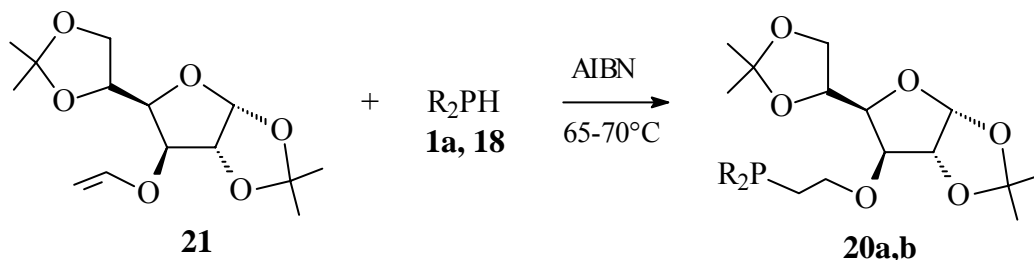
2.2.2 Primary and secondary phosphines. Addition of primary and secondary phosphines to alkenes (linear unsubstituted alkenes¹⁰¹ with terminal double bonds and, less often, internal ones, as well as cycloalkenes,¹⁰¹ aryl- and hetarylalkenes,^{101, 102} dienes,¹⁰¹ vinyl^{40, 41, 101} and divinyl¹⁰³ ethers, vinylsulfides,^{104, 105} vinyl phosphines,^{106, 107} unsaturated organohalides,¹⁰⁸ acrylic acid derivatives^{101, 109} *etc*) under free-radical conditions is widely used in organophosphorus synthesis.¹¹⁰ This pathway allows one to obtain phosphines with hydrophilic substituents,^{62, 101, 102, 109, 111, 112} including water-soluble phosphines, di- and polyphosphines,^{106, 107, 113} polydentate *P,N*-,^{62, 101, 102, 107, 111, 114} *P,O*-,^{62, 101-103, 111} *P,S*-,^{104, 105, 107} *P,Se*-,¹⁰⁵ and *P,Si*-^{115, 116} ligands.

Hydrophosphination of vinyl ethers,⁴¹ vinyl sulfides¹⁰⁵ and vinyl selenides¹⁰⁵ with secondary phosphines **1a,g, 18**, prepared from elemental phosphorus and electrophiles in superbase systems,^{53, 117} readily proceeds under UV irradiation or in the presence of AIBN at 65-70°C to form the corresponding phosphines **19** (Scheme 9) in nearly quantitative yields.^{41, 105}



Scheme 9

Novel optically active polyfunctional tertiary phosphines **20a,b** have been synthesized in high yield by the hydrophosphination of chiral vinyl ether **21** (prepared from diacetone-*D*-glucose and acetylene) with secondary phosphines **1a, 18**, proceeding regiospecifically in the presence of AIBN at 65-70°C (Scheme 10).¹¹⁸



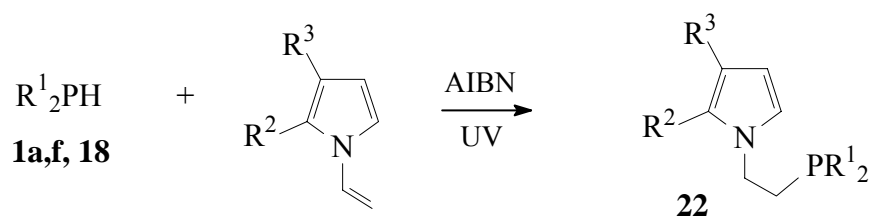
R = Bu (**18, 20a**), PhCH₂CH₂ (**1a, 20b**)

Scheme 10

With air or elemental sulfur the phosphines **20a,b** quantitatively oxidize to the corresponding phosphine oxides or phosphine sulfides, respectively.¹¹⁸ Polydentate phosphines, phosphine oxides and phosphine sulfides thus obtained, containing protected hydroxy functionalized tetrahydrofuran and dioxolane moieties, are promising chelating ligands for metal complex catalysts for asymmetric synthesis.

Recently, first examples of the hydrophosphinations of available^{24, 25} *N*-vinyl- and *N*-isopropenylpyrroles have been reported.^{119, 120}

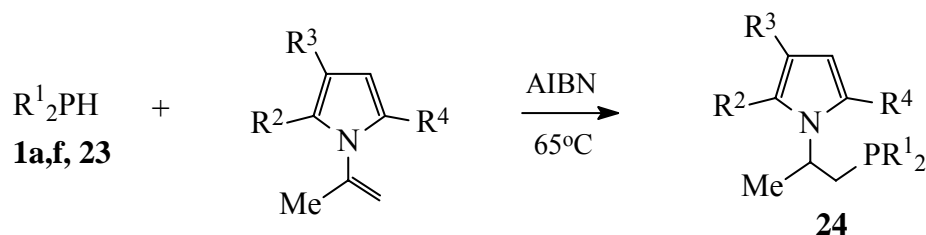
Secondary phosphines **1a,f, 18** add to *N*-vinylpyrroles regio- and chemospecifically in the presence of AIBN at 65-70°C or under UV irradiation to form almost quantitatively the corresponding tertiary diorganyl-2-(1-pyrrolyl)ethylphosphines (**22**) (Scheme 11),¹¹⁹ prospective polydentate *P,N*-ligands.^{87, 121-123}



R^1 = Bu (**18**), PhCH₂CH₂ (**1a**), 2-PyCH₂CH₂ (**1f**); R^2 = Pr, R^3 = Et; R^2, R^3 = (CH₂)₄

Scheme 11

Free-radical addition of secondary phosphines **1a,f, 23** to 1-isopropenylpyrroles (AIBN, 65°C) also proceeds with 100% regioselectivity to give diorganyl-2-(1-pyrrolyl)propylphosphines (**24**) in 89-92% isolated yields (Scheme 12).¹²⁰



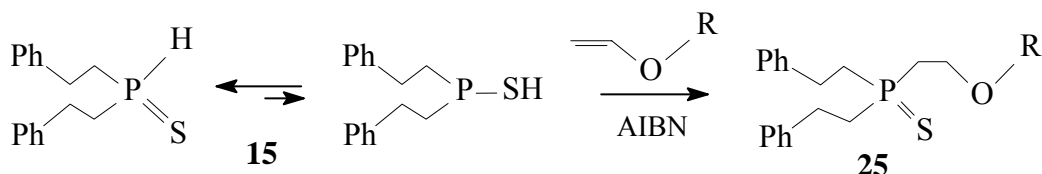
$R^1 = PhCH_2CH_2$ (**1a**), 2-Py CH_2CH_2 (**1f**), $PhCH_2$ (**23**);

$R^2 = R^3 = Me, R^4 = H$; $R^2, R^3 = (CH_2)_4, R^4 = Me$; $R^2, R^3 = (CH)_4, R^4 = H$

Scheme 12

2.2.3 Secondary phosphine chalcogenides. Hydrophosphorylation^{79, 124-130} and hydrothiophosphorylation¹³¹⁻¹³⁵ of alkenes proceeding under radical initiation and giving anti-Markovnikov adducts are scarcely studied.

Recently, chemo- and regiospecific synthesis of 2-alkoxyethyl(di-2-phenylethyl)phosphine sulfides **25** in practically quantitative yield (92-98%) was realized by hydrothiophosphorylation of alkyl vinyl ethers with *P,S*-ambident¹³⁶ bis(2-phenylethyl)phosphine sulfide (**15**) in the presence of AIBN ($60-65^\circ C$, 5 h, THF) (Scheme 13).¹³⁴

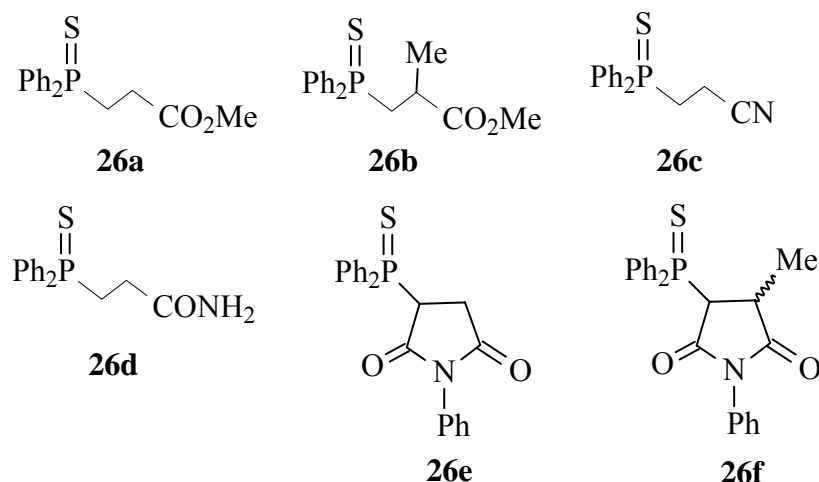


$R = Et, Bu, i-Bu$

Scheme 13

The chemo- and regioselective addition of secondary phosphine sulfides to alkyl vinyl ethers contributes to better understanding the reactivity of the both classes of compounds and offers a facile straightforward route to potent cocatalysts and "hemilabile" ligands¹³⁷ (e.g., triphenylphosphine sulfide is more effective ligand for palladium-catalyzed bisalkoxycarbonylation of olefins than triphenylphosphine¹³⁸).

Later, free-radical addition of diphenylphosphine sulfide to butyl vinyl ether was realized using Et_3B/O_2 as the initiator.¹³⁵ Apart from alkenes with electron-rich double bonds, the authors also used a set of alkenes with electron-poor double bonds to prepare phosphine sulfides **26** (Scheme 14).



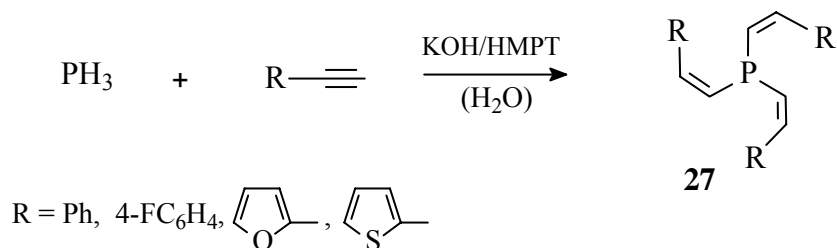
Scheme 14

3. Nucleophilic addition of phosphines and phosphine chalcogenides to alkynes

Addition of P-H reagents to acetylenes^{4, 47, 93, 101, 109, 139-163} is a convenient and atom-economic method of the C–P bond formation and the simplest route to unsaturated phosphines. At the same time, this field still remains poorly explored and existing publications are mostly related to nucleophilic addition of phosphines and phosphine chalcogenides.^{4, 47, 93, 139-142, 144, 146-149, 151-153, 155-163}

3.1 Phosphine

The data on the addition of phosphine to the triple carbon-carbon bond are limited to reports concerning phosphorylation of aryl- and hetarylalkynes in the presence of superbase.^{4, 153, 155} The reaction proceeds under mild conditions (55-60°C, atmospheric pressure) upon passing phosphine-hydrogen mixture generated from red phosphorus and potassium hydroxide in aqueous dioxane through the reaction mixture to give stereoselectively tris(*Z*-2-organylethenyl)phosphines (**27**) in 60-80% yields (Scheme 15).^{153, 155} The stereodirection of these reactions agrees with the common *trans*-addition scheme.^{25, 34}

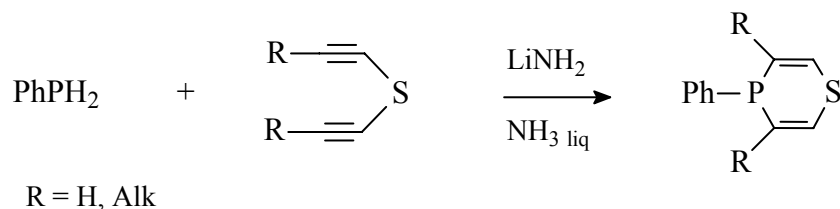


Scheme 15

3.2 Primary phosphines

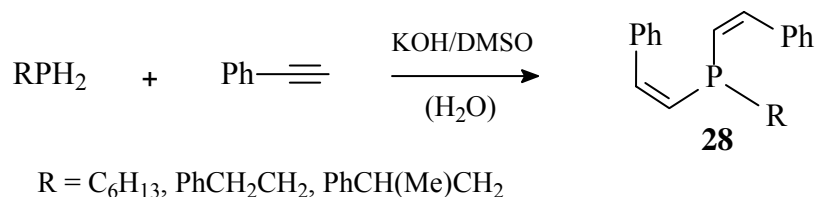
Similarly to phosphine, primary phosphines react with acetylenes according to the nucleophilic monoaddition mechanism to form *Z*-ethenylphosphines. With weakly electrophilic acetylenes, these reactions, as a rule, require strong bases to proceed.

Phenylphosphine reacts with di(alkynyl)sulfides under the action of base system $\text{LiNH}_2\text{-NH}_3$ to afford 4-phenyl-4*H*-1,4-thiaphosphinines (Scheme 16).¹⁴⁴



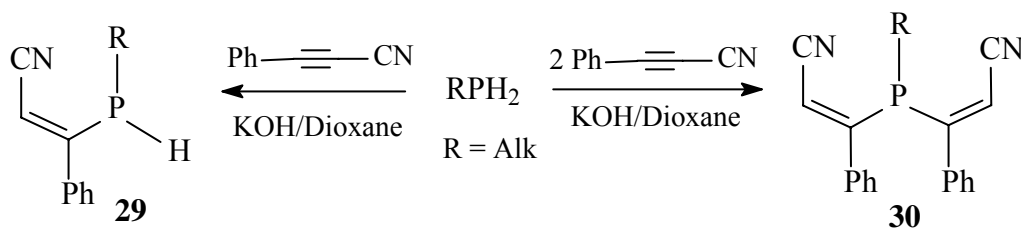
Scheme 16

Primary alkyl- and arylalkylphosphines add to phenylacetylene in the KOH-DMSO suspension (60°C, 1-4 h) giving predominantly or exclusively *Z,Z*-isomers of bis(2-phenylethenyl)organylphosphines (**28**) (Scheme 17) in good yield (up to 81%).¹⁵⁹



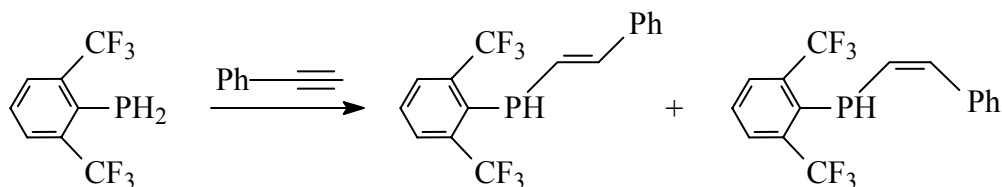
Scheme 17

Activated phenylcyanoacetylene reacts with alkylphosphines under milder conditions (KOH-dioxane suspension, 20-22°C) to afford, depending on the reactant ratio, either secondary **29** or tertiary **30** phosphines of *Z*-configuration in the yield of 70-91% (Scheme 18).¹⁶⁰ According to ESR and UV data, the addition involves a single electron transfer.¹⁶⁰



Scheme 18

Organic phosphines were also reported to be capable of adding to arylacetylenes without catalyst, but a high temperature (over 100°C) and long reaction time were required.^{140, 141, 151} Thus, reaction of 2,6-bis(trifluoromethyl)phenyl]phosphine with phenylacetylene (100-110°C, 40 h) gave *E*- and *Z*-isomers of secondary [2,6-bis(trifluoromethyl)phenyl](styryl)phosphine in a ratio of 3/2 (59% yield) (Scheme 19).¹⁵¹



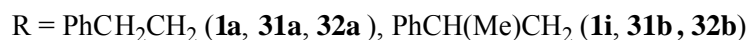
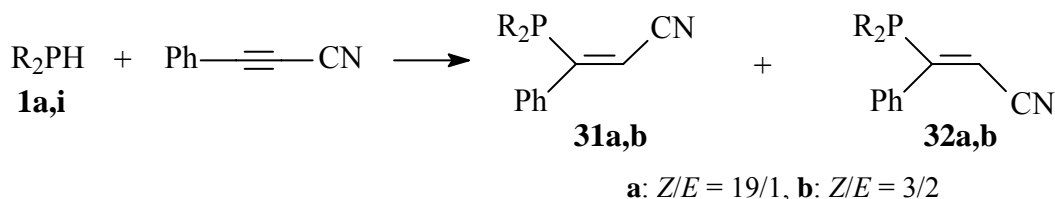
Scheme 19

3.3 Secondary phosphines

Unlike primary phosphines, secondary phosphines add to acetylenes with strong electron-withdrawing substituents (cyanoacetylene,¹⁴⁶ phenylcyanoacetylene,^{157, 160} 4-hydroxy-4-methyl-2-pentynenitrile,^{160, 162} methyl 2-propynoate,¹⁴⁷ hexafluoro-2-butyne¹³⁹) without catalysts.

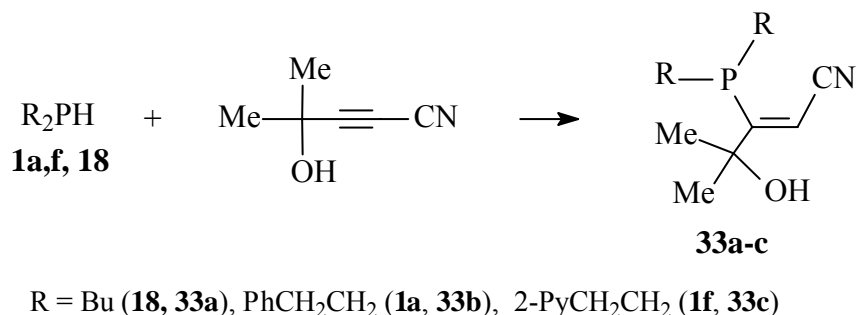
Dialkylphosphines react with cyanoacetylene to afford exclusively or predominantly *Z*-isomers of the corresponding alkenes $\text{Alk}_2\text{PCH}=\text{CHCN}$.¹⁴⁶

The reaction of bis(2-phenylethyl)- and bis(2-phenylpropyl)phosphines (**1a,i**) with phenylcyanoacetylene proceeds with the same stereodirection to give mainly monoadducts **31a,b**,¹⁵⁷ though in the case of **1i** a considerable amount of *E*-isomer **32b** is formed (Scheme 20) that is explained by the competition of *trans*- and *cis*-addition to triple bond owing to steric hindrance. According to ESR and UV data, the reaction involves a single electron transfer.¹⁵⁷



Scheme 20

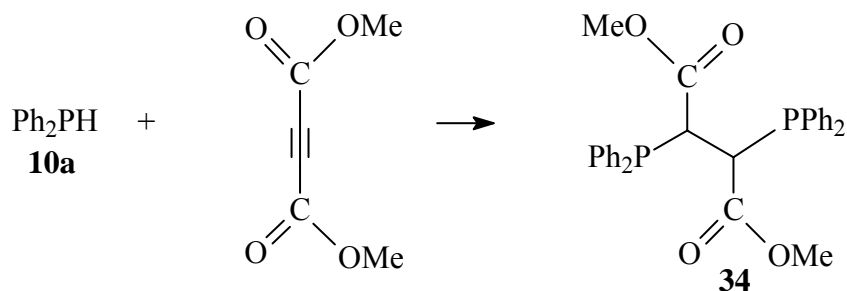
An easy stereocontrolled access to functionalized tertiary phosphines **33** of *Z*-configuration proves to be the addition of dibutyl-, bis(2-phenylethyl)- and bis[2-(2-pyridyl)ethyl]phosphines (**18**, **1a,f**) to 4-hydroxy-4-methyl-2-pentynenitrile (Scheme 21).^{160, 162}



Scheme 21

Only *E*-isomers of ethenylphosphines $\text{Alk}_2\text{PCH}=\text{CHCO}_2\text{Me}$ are formed in the reaction of dialkylphosphines with methyl 2-propynoate.¹⁴⁷ Authors explain this fact by easy isomerization of the intermediate carbanion.

Non-catalyzed interaction of diphenylphosphine (**10a**) with dimethyl 2-butynedioate reveals the effect of second strong electron-withdrawing group, which activates double bond of the intermediate monoadduct. As a result, the reaction affords the saturated α,β -diadduct **34** (Scheme 22).¹⁴²



Scheme 22

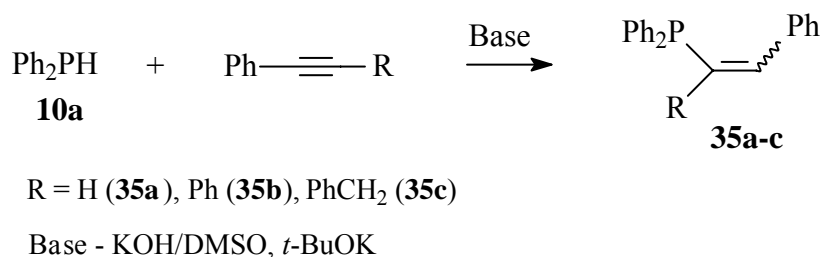
These reactions of phosphines with activated acetylenes (Schemes 19-22) represent a new general atom-economic approach to the synthesis of versatile reactive building blocks for organic synthesis and prospective polydentate and amphiphilic ligands for design of metal complex catalysts.^{77, 164}

With weakly electrophilic acetylenes, addition of secondary phosphines requires strong bases or high temperature to proceed.

Prolonged heating (100°C, 4 days) of diphenylphosphine and diphenylacetylene afforded *E*-isomer of the corresponding monoadduct $\text{Ph}_2\text{PC}(\text{Ph})=\text{CHPh}$.¹⁴¹ It seems that the formation of *E*-isomers in this addition¹⁴¹ as well as in the reaction presented in Scheme 19¹⁵¹ is thermodynamically controlled, *i.e.*, under the reaction conditions *Z*-adduct isomerizes to the *E*-form.

Diphenylphosphine with diphenyl(ethynyl)phosphine $\text{Ph}_2\text{PC}\equiv\text{CH}$ in the presence of PhLi furnishes $E\text{-Ph}_2\text{PCH}=\text{CHPh}_2$ in a 72% yield.⁴⁷ The E -isomer is likely to be formed owing to sterical factors.

Diphenylphosphine (**10a**) adds to arylacetylenes in the presence of strong bases giving arylolefinylphosphines **35** of unknown configuration (Scheme 23).^{93, 148} From the $^3J_{\text{HP}}$ coupling,¹⁴⁸ one may assume¹⁶⁵ that the compound **35c** is a Z -isomer.



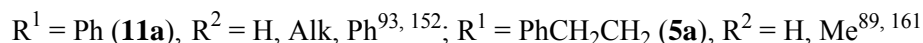
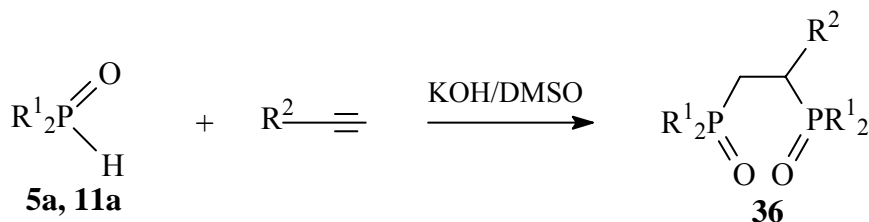
Scheme 23

Later, reaction of diphenylphosphine with diarylacetylenes $\text{RC}\equiv\text{CR}^1$ ($\text{R} = \text{Ph}$, $\text{R}^1 = \text{Ph}$, o -tolyl, m -tolyl or 2-biphenyl; $\text{R} = m$ -tolyl, $\text{R}^1 = o$ -tolyl, m -tolyl) was studied in detail.^{149, 156} In the system $t\text{-BuOK}$ -THF the reaction yields monoadducts $\text{Ph}_2\text{PC}(\text{R})=\text{CHR}^1$ and/or diphosphines $\text{Ph}_2\text{PCH}(\text{R})\text{CH}(\text{R}^1)\text{PPh}_2$ in a ratio that depends on the reactants ratio and nature of the substituent structure.^{149, 156}

3.4 Secondary phosphine chalcogenides

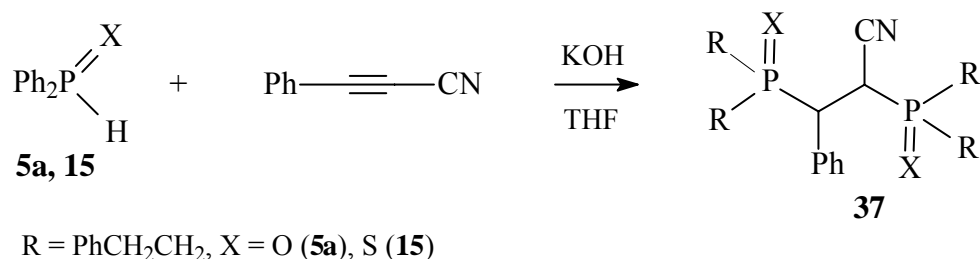
Addition of secondary phosphine chalcogenides to acetylenes^{89, 93, 152, 161, 163} proceeding in the presence of base catalysts usually results in double addition products. Presumably, this occurs due to the strong electron-withdrawing character of phosphoryl or thiophosphoryl group, which activates double bond of monoadducts toward addition of the second phosphine chalcogenide molecule.

Unsubstituted acetylene, as well as alkyl- and arylacetylenes add secondary phosphine oxides in the superbase system KOH-DMSO to give diphosphine oxides **36** (Scheme 24).^{89, 93, 152, 161}



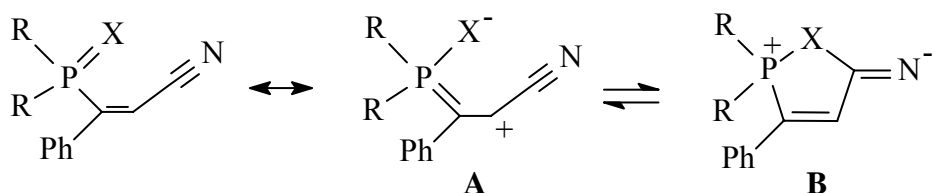
Scheme 24

Recently, there was found that the reaction of phenylcyanoacetylene with secondary phosphine oxide **5a** and sulfide **15** proceeds under milder conditions (KOH-THF, 22-62°C) forming unexpected α,β -diadducts **37** (Scheme 25).¹⁶³



Scheme 25

Unusual here is the second stage of the process, addition of phosphine chalcogenides to the α -position of intermediate acrylonitrile system. Apparently, this occurs due to the competing electron-withdrawing effect of the added phosphoryl group, which changes the polarization of the double bond contributing the zwitterionic forms **A** and **B** (Scheme 26).

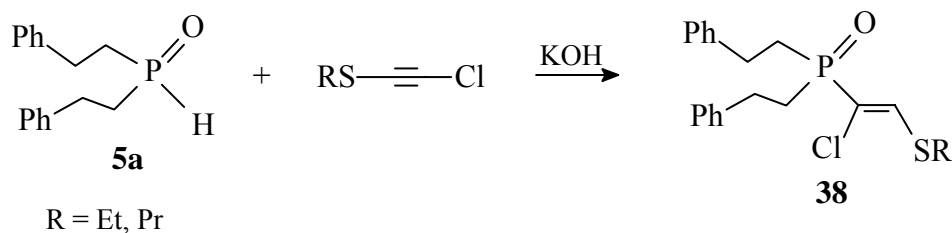


Scheme 26

Perhaps, this pathway is the only one also because the alternative addition to the β -carbon is sterically hindered.

α,β -Acetylenic aldehydes, namely 3-(trialkylsilyl)-, 3-(trialkylgermyl)-2-propynals as well as 2-propynal react with secondary phosphine oxides under mild conditions (-10 to 22°C) by carbonyl group only to give corresponding tertiary phosphine oxides in quantitative yield.¹⁶⁶

Haloacetylenes are usually prone to nucleophilic substitution reactions.¹⁶⁷⁻¹⁶⁹ However, bis(2-phenylethyl)phosphine oxide (**5a**) was found to add to alkylthio(chloro)acetylenes (dioxane, 20-22°C) in the presence of equimolar amount of KOH to form regio- and stereoselectively 1-chloro-2-(alkylthio)vinyl(diphenylethyl)phosphine oxides (**38**) (Scheme 27) of *Z*-configuration (the yield is 78-85%).¹⁵⁸



Scheme 27

4. Conclusions

In conclusion, nucleophilic and free-radical additions of now readily available phosphines and their chalcogenides to alkenes and alkynes are attracting increasing attention as heavy-metal free and atom-economic syntheses of valuable, and otherwise inaccessible, functionalized phosphines and phosphine chalcogenides.

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