Green Chemistry

PAPER

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Cite this: *Green Chem.*, 2016, **18**, 4896

Catalyst- and solvent-free hydrophosphination and multicomponent hydrothiophosphination of alkenes and alkynes†

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Received 30th March 2016,
Accepted 24th May 2016

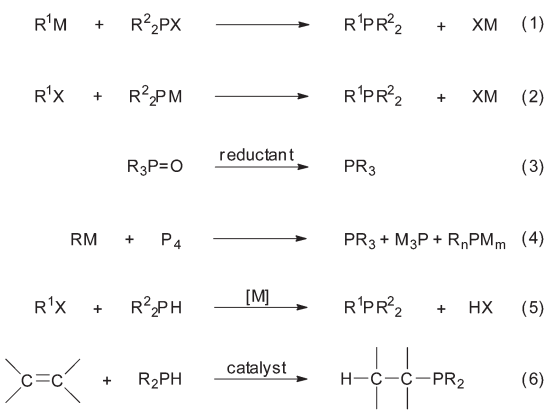
DOI: 10.1039/c6gc00903d

www.rsc.org/greenchem

The hydrophosphination of carbon–carbon multiple bonds has been generally performed under acid, base or metal catalysis in different solvents. Herein, alkyl and alkenyl tertiary phosphines are obtained by the addition of diphenylphosphine to alkenes and alkynes, respectively, in the absence of a solvent and a catalyst. In the presence of elemental sulfur, the corresponding alkyl and alkenyl tertiary phosphine sulfides are synthesized in a three-component process. These simple methods, which meet most of the principles of Green Chemistry, are highly regioselective towards the anti-Markovnikov products and diastereoselective towards the *Z* alkenyl phosphines. The mechanistic aspects of the reactions are also tackled and the efficiency of the latter is compared with that of the catalytic methods.

Introduction

The deployment of phosphorus compounds in industry has become widespread because of their manifold applications.[1] Nowadays, many chemical, agrochemical and pharmaceutical substances containing phosphorus are routinely produced to control some natural or human-triggered processes and to upgrade the quality of our lives. Research laboratories also make extensive use of organophosphorus compounds, particularly as ligands for homogeneous, heterogeneous and asymmetric catalysis,[2a–i] but also as organocatalysts.[2j,k] Metal–phosphine complexes with anticancer activity is another field of recent interest aimed at developing substitutes for the current platinum drugs.[3] Tertiary phosphines can be synthesized using different procedures (Scheme 1), such as (a) the displacement of a good leaving group on a phosphine by an organometallic reagent (eqn (1)), (b) the reaction of a metal phosphide with an organic electrophile (eqn (2)), (c) the reduction of a phosphorus halide or oxide (eqn (3)), (d) from elemental phosphorus (eqn (4)) and (e) by phosphination (*i.e.*, the metal-catalysed cross-coupling of aryl halides or triflates with P–H bonds; eqn (5)).[4]



Scheme 1 Some general methods for tertiary phosphine synthesis; M = metal, X = leaving group; n = 2, m = 1 and n = 1, m = 2.

Modern chemical research and production must advance on the basis of sustainable and environmentally benign practices.[5] In this vein, the hydrophosphination of unsaturated compounds (*i.e.*, alkenes and alkynes) appears as the most straightforward approach to form C–P bonds from readily accessible starting materials (Scheme 1, eqn (6));[6] maximum atom economy is attained with no by-product formation.

Closely related to phosphines are the phosphine sulfides,[7] a type of compound with multiple applications in different disciplines. Among others, phosphine sulfides have been utilized

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†Electronic supplementary information (ESI) available: Experimental procedures, compound characterisation, NMR spectra, kinetic graphics and X-ray data. CCDC 1468810 and 1437629. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c6gc00903d

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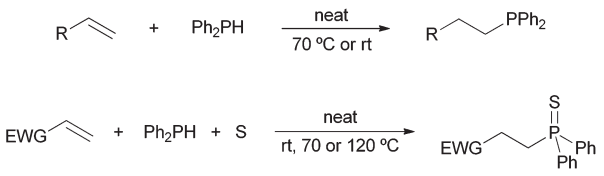


Scheme 2 Solvent- and catalyst-free hydrophosphination[22a] and hydrothiophosphination[22b] of alkenes; EWG = electron-withdrawing group.

in anion-selective electrodes,[8] lanthanide extraction from a nitrate medium,[9] as sensor fluorescent materials for metal ions of environmental concern,[10] as anchor units for single molecule junctions,[11] in polymer chemistry,[12] and as ligands for gold,[13] catalysis[14] and asymmetric synthesis.[15] Base-promoted[16] and free-radical[17] initiated addition of secondary phosphine sulfides to alkenes (or alkynes)[7] are the most practiced methods to prepare tertiary phosphine sulfides. The reaction of secondary phosphine sulfides with carbonyl compounds can provide tertiary α-hydroxy phosphine sulfides.[7] The transformation of pre-formed tertiary phosphines into the corresponding sulfides can be readily accomplished by reaction with sulphur; in this case, however, hazardous solvents such as benzene, chloroform and dichloromethane are required.[7] More recently, Trofimov *et al.* reported the one-pot synthesis of tertiary phosphine sulfides from styrenes, red phosphorus and elemental sulfur in a superbasic system containing hydroquinone under microwave irradiation.[18] In addition to these, transition-metal catalyzed procedures have recently been published.[19]

On the other hand, both solvent-free reactions[20] and catalyst-free organic synthesis[21] notably simplify the reaction mixtures and experimentally, at the same time reduce the amount of waste which, in turn, depletes the environmental impact.

By virtue of our current interest in phosphorus chemistry,[22] we found out that tertiary phosphines can be obtained in a very straightforward manner by addition of secondary phosphines to carbon–carbon double bonds under solvent- and catalyst-free conditions.[22a] Moreover, under these conditions but in the presence of sulfur, α,β-unsaturated carbonyl compounds have been converted into the corresponding β-substituted tertiary phosphine sulfide derivatives through a three-component approach (Scheme 2).[22b] Our intention is to present herein a comprehensive study on the substrate scope and mechanism of these environmentally friendly protocols, including the hydrophosphination and multicomponent hydrothiophosphination of alkenes and alkynes.

Results and discussion

Alkene hydrophosphination

Originally, alkene hydrophosphination[6] was induced by base catalysis or radical activation to form the anti-Markovnikov products,[6c] whereas the Markovnikov counterparts were better obtained by acid treatment.[23] More advantageous were, however, the methodologies based on catalysis by metal[6] complexes, such as those of platinum,[24] lanthanides,[25] alkaline-earth metals,[25e,f,26] nickel,[27] palladium[27] or iron.[28] Of particular interest is the catalytic asymmetric hydrophosphination of certain substrates, which was achieved by the use of chiral organopalladium(II) complexes.[29] Not only metal complexes but also metal salts of copper[30] or iron[31] have been utilized as catalysts in alkene hydrophosphination. With the exception of the Pd- and Ni-catalysed hydrophosphination of vinyl ethers,[27c,d] the aforementioned methodologies afford the anti-Markovnikov products.

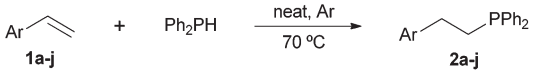
In spite of the higher selectivity achieved by metal catalysis, most of its applications in alkene hydrophosphination does not meet some of the stringent criteria demanded for green and sustainable production because of the use of non-reusable precious metals or noxious solvents (*e.g.*, benzene). In addition, transition metals can accelerate the undesired phosphine oxidation to the phosphine oxide. Ideally, this reaction should be conducted under metal-free and neutral conditions, with the latter also preventing side-reactions and use of aqueous work-up (which can favour oxidation). To the best of our knowledge, Gaumont's group was the first to report the uncatalysed hydrophosphination of alkenes: phosphine–borane complexes were added to inactivated alkenes under neutral conditions followed by either conventional or microwave heating.[32]

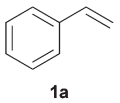
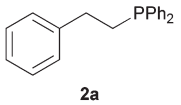
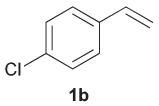
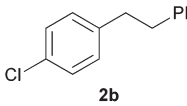
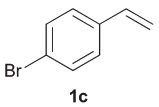
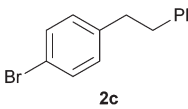
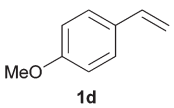
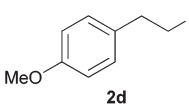
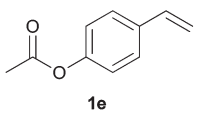
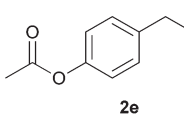
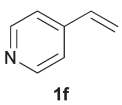
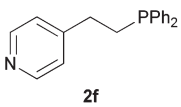
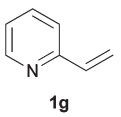
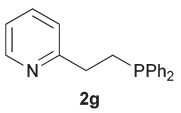
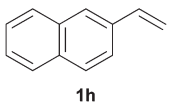
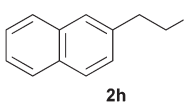
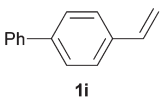
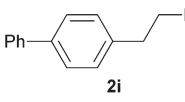
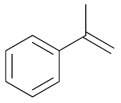
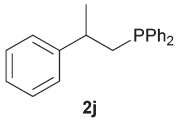
Following our recent discovery on the uncatalysed addition of secondary phosphines to carbon–carbon double bonds under solvent-free conditions,[22a] we expanded this practice to the addition of diphenylphosphine to a wide range of alkenes, including not only styrenes but also α,β-unsaturated carbonyl compounds and inactivated alkenes (Tables 1–3). All reactions were executed under an inert atmosphere of argon.

As regards styrenes, the simplest one (**1a**) reacted the fastest and resulted in good yield. *p*-Halostyrenes (**1b** and **1c**), *p*-methoxy- and *p*-acetoxystyrene (**1d** and **1e**, respectively) behaved similarly in terms of yield (around 85%), with a shorter reaction time for **2d**. This hydrophosphination was also appropriate for vinyl pyridines (**1f** and **1g**), permitting the synthesis of the P,N-bidentate ligand pyphos (**2g**), used in homogeneous transition-metal catalysis.[33] Other vinyl aromatics, such as 2-vinylnaphthalene (**1h**) and 4-vinyl-1,1′-biphenyl (**1i**) were transformed into the tertiary phosphines in high yields. Furthermore, the standard conditions were also effectual for the less reactive 1,1-disubstituted alkene isopropenyl benzene (**1j**). We must underline that all products **2a–2j** were produced with exclusively anti-Markovnikov regioselectivity.

We next explored the diphenylphosphine addition to α,β-unsaturated carbonyl and related compounds (Table 2). These substrates can be considered more activated alkenes than the aforesaid styrenes and, hence, more reactive under milder conditions. Indeed, most of the starting alkenes (except **1l** and **1q**) experienced hydrophosphination at room temperature (7–12 h); alternatively, the reaction times could be decreased (1–3 h) by warming at 70 °C with comparable yields

Table 1 Hydrophosphination of styrenes[a]

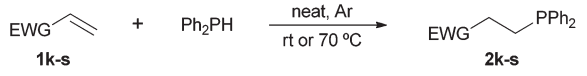


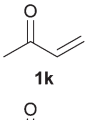
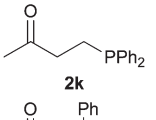
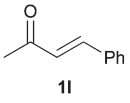
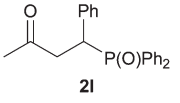
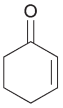
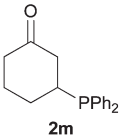
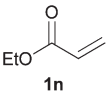
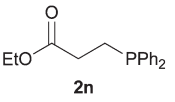
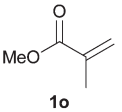
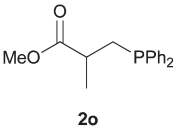
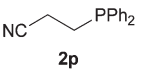
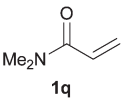
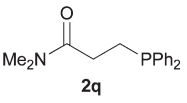
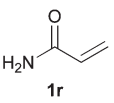
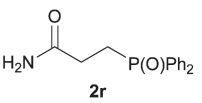
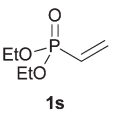
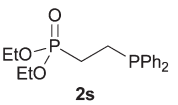
Starting alkene	Product	Yield[b] (%)
 1a	 2a	82[c]
 1b	 2b	85
 1c	 2c	82
 1d	 2d	88[d]
 1e	 2e	85[d]
 1f	 2f	74
 1g	 2g	80
 1h	 2h	91
 1i	 2i	90
 1j	 2j	79

[a] Alkene **1** (0.5 mmol) and Ph_2PH (0.5 mmol) at 70 °C under Ar, 16 h (unless otherwise stated). [b] Isolated yield. [c] Reaction time = 4 h. [d] Reaction time = 8 h.

(see **1k**, **1n** and **1p**). Diverse functional groups were compatible with these conditions, whereby the synthesis of β-diphenylphosphino ketones (**1k–1m**), esters (**1n** and **1o**), nitrile (**1p**), amides (**1q** and **1r**) and phosphonate (**1s**) was carried out in good yields; products **2l** and **2r** were isolated as the phosphine oxides due to easy oxidation of the phosphine precursors when exposed to air. It is worth noting that the platinum-catalysed[24] addition of diphenylphosphine to acrylonitrile (**1p**) can instead be effectuated in the absence of a catalyst at room temperature.

Table 2 Hydrophosphination of activated alkenes[a]

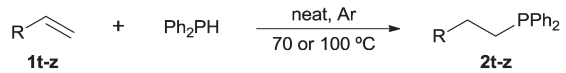


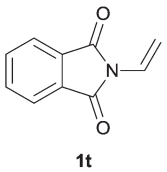
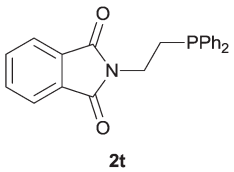
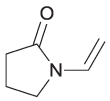
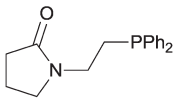
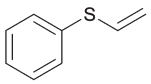
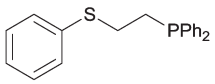
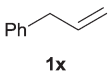
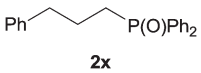
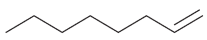
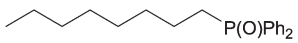
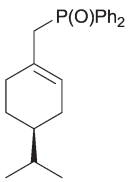
Starting alkene	*t*/*T*	Product	Yield[b] (%)
 1k	7 h/rt, 1 h/70 °C	 2k	70
 1l	12 h/70 °C	 2l	69
 1m	2 h/rt	 2m	83
 1n	7 h/rt, 3 h/70 °C	 2n	77
 1o	12 h/rt	 2o	75
 1p	7 h/rt, 3 h/70 °C	 2p	81
 1q	12 h/70 °C	 2q	70
 1r	12 h/rt	 2r	75
 1s	12 h/rt	 2s	71

[a] Alkene **1** (0.5 mmol) and Ph_2PH (0.5 mmol) at rt or 70 °C under Ar. [b] Isolated yield.

Heteroatom-bonded vinyl compounds, such as *N*-vinylphthalimide (**1t**), *N*-vinylpyrrolidin-2-one (**1u**) and phenyl vinyl sulfide (**1v**) gave the expected (diphenylphosphino)ethyl heteroatom products under the conventional conditions (70 °C) (Table 3). Compound **2v** is a P,S-bidentate ligand also employed in catalysis.[34] The usefulness of this protocol was validated by its exploitation in the hydrophosphination of inactivated alkenes such as allylbenzene (**1x**) and oct-1-ene (**1y**). The anti-Markovnivov regioselectivity was consistent with the trend displayed by all the substrates in Tables 1–3. Still, the tertiary phosphines originated from **1x** and **1y** were susceptible to oxidation and were isolated as the phosphine oxides **2x** and **2y**, respectively. It was gratifying to verify that the hydrophosphination of (–)-β-pinene (**1z**) followed an anti-Markovnivov addition and involved the opening of the cyclo-

Table 3 Hydrophosphination of Het-vinyl compounds and inactivated alkenes[a]



Starting alkene	Product	Yield[b] (%)
 1t	 2t	70
 1u	 2u	78
 1v	 2v	85
 1x	 2x	85
 1y	 2y	70
 1z	 2z	75

[a] Alkene **1** (0.5 mmol) and Ph_2PH (0.5 mmol) at 70 °C (**1t–v**) or 100 °C (**1x–z**) under Ar, 16–24 h. [b] Isolated yield.

butane ring to supply the enantiomerically pure *p*-menth-1-ene derived phosphine oxide **2z**. An unmistakable assignment of the structure was done by X-ray crystallographic analysis (Fig. 1).[35]

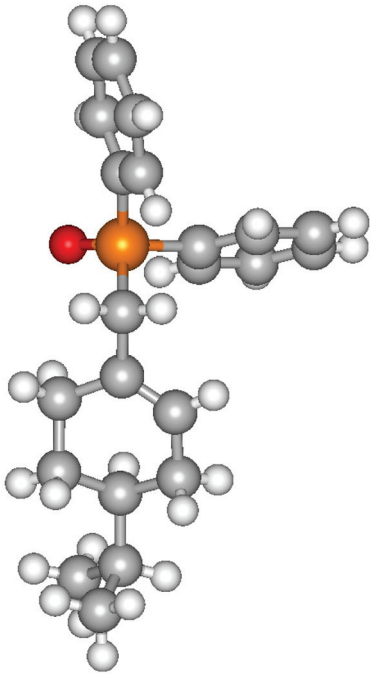


Fig. 1 X-ray crystallographic structure of phosphine oxide **2z**.

Alkene hydrothiophosphination

Apart from the base-promoted[16] and free-radical[17] initiated addition of secondary phosphine sulfides to alkenes, and related to the title topic, is the recent synthesis of tertiary phosphine sulfides by addition of secondary phosphine sulfides to alkenes in the absence of a solvent and catalyst.[36a,b] Reactions were performed at 80 °C under an inert atmosphere to give the anti-Markovnikov products.

In a previous study,[22b] we evidenced that alkene hydrothiophosphination could be achieved through a three-component approach involving the alkene, diphenylphosphine and sulfur, under solvent- and catalyst-free conditions in air. This is an advantageous strategy not only from the environmental point of view, but also because it circumvents the preparation of the secondary phosphine sulfide, which is generated *in situ*.[36c] Only α,β-unsaturated carbonyl compounds were covered in that preliminary study; the results obtained for other alkenes, either activated or not activated, are depicted in Table 4.

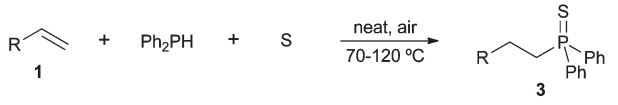
A variety of electron-neutral, -rich and -deficient styrenes underwent the hydrothiophosphination reaction at 70 °C in air; the corresponding products (**3a**, **3b**, **3aa**, **3e** and **3ab**) were obtained in moderate-to-excellent isolated yields (Table 4). Likewise, styrenes bearing N and S atoms, as well as allylbenzene, were successfully converted into phosphine sulfides (**3f**, **3g**, **3v** and **3x**). It is worth noting that the process was highly regioselective, giving rise in all cases to the anti-Markovnikov products. The same conditions were applicable to aliphatic substrates, such as oct-1-ene (**1y**) and 3,4-dihydro-2*H*-pyran (**1ac**). Despite the lack of regioselectivity observed for oct-1-ene, both regioisomers (**3y** and **3y′**) could be separated by chromatography in reasonable yields, as a result of the quantitative reaction conversion. In contrast, the hydrothiophosphination of 3,4-dihydro-2*H*-pyran (**1ac**) led to a single regioisomer (**3ac**), derived from the addition of P to the α-O carbon atom.

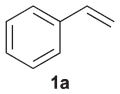
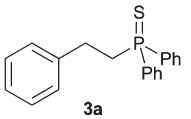
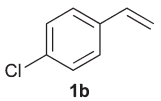
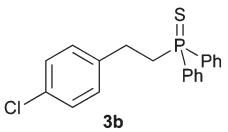
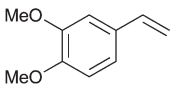
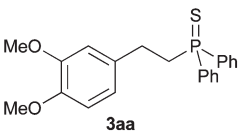
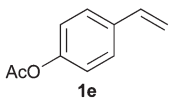
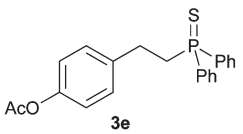
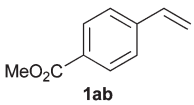
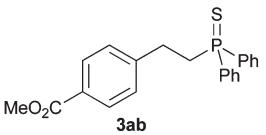
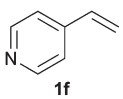
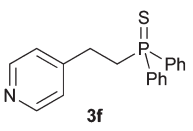
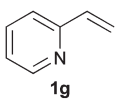
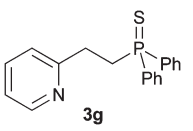
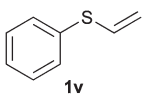
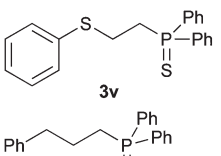
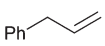
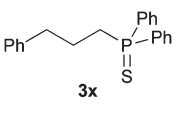
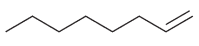
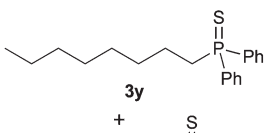
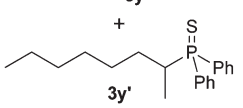
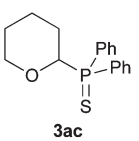
Alkyne hydrophosphination

Comparatively, alkyne hydrophosphination has been much less studied than alkene hydrophosphination. Beletskaya *et al.* reported, for the first time, the hydrophosphination of alkynes catalyzed by palladium and nickel complexes; interestingly, depending on the metal used the α- or β-adduct was mainly formed, with predominant *syn* addition.[37] Other metal complexes or salts (*i.e.*, Yb, Pd, Ni, Cu, Ca, Fe and Y) have been deployed for the same purpose with variable selectivity.[25e,38]

In our preliminary communication,[22a] we observed that phenylacetylene could also undergo diphenylphosphine

Table 4 Alkene hydrothiophosphination[a]

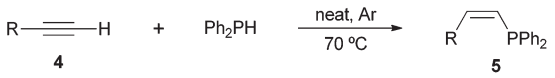


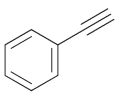
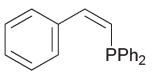
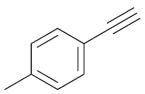
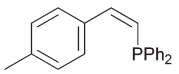
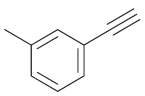
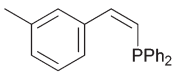
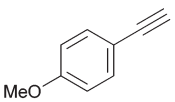
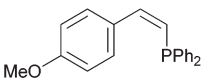
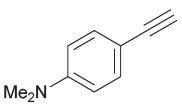
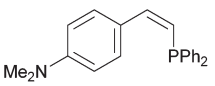
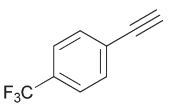
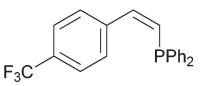
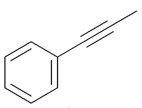
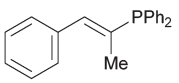
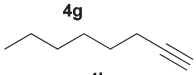
Starting alkene	Product	Yield[b] (%)
 1a	 3a	97
 1b	 3b	72
 1aa	 3aa	87
 1e	 3e	65[c]
 1ab	 3ab	97
 1f	 3f	90
 1g	 3g	95
 1v	 3v	80
 1x	 3x	67[c]
 1y	 3y	45
	+  3y'	55
 1ac	 3ac	60[d]

[a] Alkene **1** (0.5 mmol), Ph_2PH (0.5 mmol) and S (0.5 mmol) at 70 °C in air, overnight. [b] Isolated yield. [c] Reaction at 120 °C. [d] Reaction at 100 °C.

addition under solvent- and catalyst-free conditions. A variety of alkynes has been subjected to this simple procedure to produce vinylphosphines in a regio- and stereoselective manner (Table 5).

Table 5 Alkyne hydrophosphination[a]

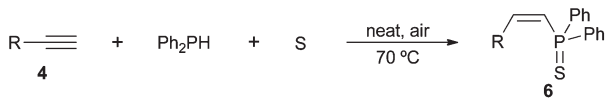


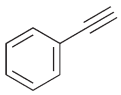
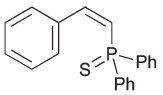
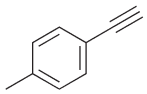
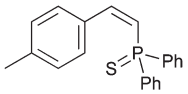
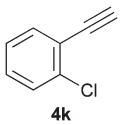
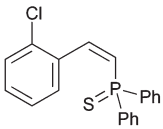
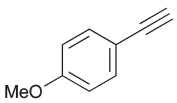
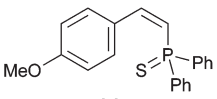
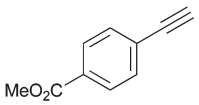
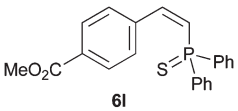
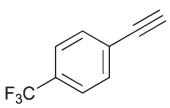
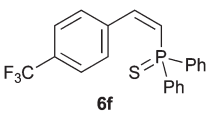
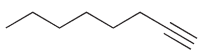
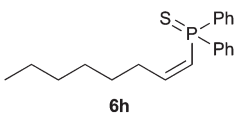
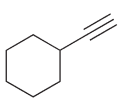
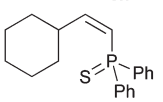
Starting alkyne	Product	Yield[b] (%)
 4a	 5a	80[c]
 4b	 5b	73
 4c	 5c	88
 4d	 5d	86
 4e	 5e	87
 4f	 5f	13[d]
 4g	 5g	64[e]
 4h	5h	62[f]
4i	5i	61[g]
4j	5j	60

[a] Alkyne **4** (0.5 mmol) and Ph_2PH (0.5 mmol) at 70 °C under argon, overnight. [b] Isolated yield. [c] As a 95 : 5 *Z*/*E* diastereomeric mixture. [d] GLC yield. [e] As a 90 : 10 *E*/*Z* diastereomeric mixture. [f] As a 97 : 3 *Z*/*E* diastereomeric mixture. [g] Yield of the major diastereoisomer, isolated from a 60 : 40 *Z*/*E* diastereomeric mixture.

Electron-neutral and -rich arylacetylenes reacted nicely with diphenylphosphine at 70 °C yielding the expected anti-Markovnikov alkenylphosphines (**5a–5e**) as *Z* diastereoisomers.[39] Converse behaviour was observed for arylacetylenes bearing electron-withdrawing substituents (*e.g.*, **4f**), which were reluctant to react under the same conditions. When methyl(phenyl) acetylene (**4g**) was subjected to the standard reaction conditions, the corresponding vinylphosphine was formed as a 90 : 10 *E*/*Z* diastereomeric mixture, with opposite regioselectivity to that reported with a calcium complex.[38d] Besides arylacetylenes, aliphatic alkynes also experienced hydrophosphination. The alkyl-chain alkyne **4h** was converted into the phosphine **5h** with a high degree of stereocontrol (97 : 3 *Z*/*E* ratio), whereas the tertiary phosphines resulting from the cyclohexyl derivatives **4i** and **4j** were prone to rapid oxidation, being obtained as the phosphine oxides **5i** and **5j**, respectively. A 60 : 40 *Z*/*E* ratio was recorded for **5i**, though the major *Z* isomer could be isolated in moderate yield. Different outcome arose for the hydroxyl derivative **5j**, with absolute control of both the regio- and the stereochemistry.

Table 6 Alkyne hydrothiophosphination[a]



Starting alkyne	Product	Yield[b] (%)
 4a	 6a	96
 4b	 6b	78
 4k	 6k	93
 4d	 6d	90
 4l	 6l	92
 4f	 6f	30
 4h	 6h	90
 4i	 6i	60

[a] Alkyne **4** (0.5 mmol), Ph_2PH (0.5 mmol) and S (0.5 mmol) at 70 °C in air, overnight. [b] Isolated yield.

Alkyne hydrothiophosphination

Trofimov *et al.* have recently extended their addition of preformed secondary phosphine sulfides to alkenes, under catalyst- and solvent-free conditions, to alkynes, giving the tertiary anti-Markovnikov alkenylphosphine sulfides with *Z* stereochemistry.[40] With a more straightforward approach in hand, and based on our previously reported three-component alkene hydrothiophosphination,[22b] hydrothiophosphination was undertaken for a series of alkynes (Table 6). The standard reaction conditions, in air, were applied to obtain alkenylphosphine sulfides in high yields from diphenylphosphine, sulfur and phenylacetylenes bearing electron-neutral, -donating and -withdrawing substituents (**4a**, **4b**, **4d**, **4k** and **4l**). As occurred in the alkyne hydrophosphination, the hydrothiophosphination of 4-trifluoromethyl(phenyl)acetylene was difficult, giving the expected product **6f** in low yield. The same conditions were suitable for aliphatic alkynes, either linear-alkyl or cycloalkyl-substituted ones (**4h** and **4i**).

It must be pointed out that all the alkenylphosphine sulfides were synthesised as single anti-Markovnikov regioisomers and *Z* stereoisomers. The stereochemistry of the alkyne hydrothiophosphination and, therefore, that of the alkyne hydrophosphination was unequivocally established by X-ray crystallographic analysis of alkenylphosphine sulfide **6a** (Fig. 2).[41]

Mechanistic aspects

Koenig *et al.* concluded that the radical or ionic mechanism of addition of organophosphorus compounds containing a labile P–H bond to alkenes and alkynes was dependent on the nature of the unsaturated substrate (activated or inactivated),

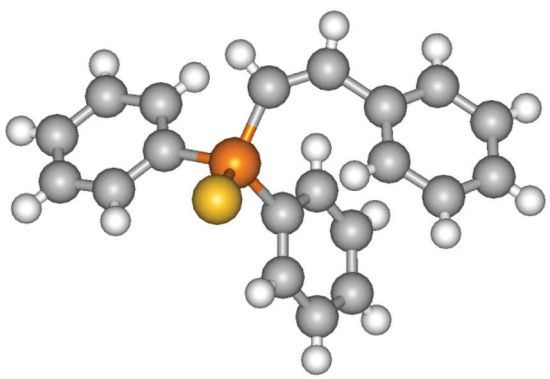
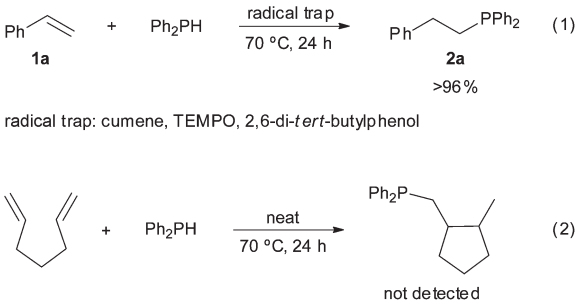


Fig. 2 X-ray crystallographic structure of phosphine sulfide **6a**.

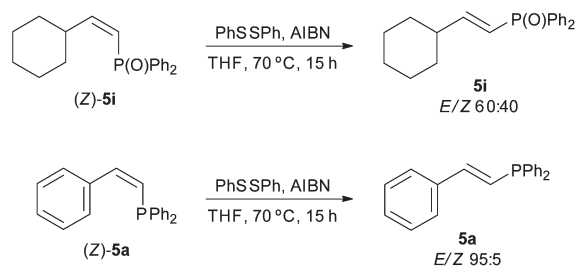


Scheme 3 Experiments demonstrating the radical-free addition of diphenylphosphine to alkenes.

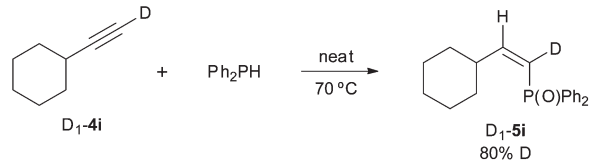
the nature of the organophosphorus compound (with P–H, O=P–H or S=P–H bonds) and the mode of activation (dry alkaline medium, alkaline medium/classical heating, US irradiation, alkaline medium/US irradiation, radical initiator/classical heating or photochemical irradiation).[42]

In order to gain an insight into the reaction mechanism, the hydrophosphination of styrene was performed in the presence of radical traps, such as cumene, TEMPO or 2,6-di-*tert*-butylphenol [Scheme 3, eqn (1)]. All reactions proceeded with >96% conversion and products derived from the radical traps and diphenylphosphinyl radicals were not detected. These results, together with the fact that the addition of diphenylphosphine to hepta-1,6-diene did not yield the corresponding cyclopentane derivative [Scheme 3, eqn (2)],[43] point to a radical-free process. This hypothesis is consistent with the *Z* to *E* isomerisation observed for alkenylphosphine derivatives **5a** and **5i** under radical conditions (Scheme 4); that is, the thermodynamic *E* isomers, instead of the *Z* counterparts, should be largely formed if the hydrophosphination was driven by radicals. It must be highlighted that *E*/*Z* equilibration did not occur when the alkenyl phosphines **5a** and **5i** were subjected to prolonged heating either in the absence or presence of iodine.

A series of deuterium-labelling experiments have provided additional evidence on the reaction course. The addition of diphenylphosphine to deuterated cyclohexylacetylene D_1-**4i** gave the *Z* α-deuteriovinylphosphine oxide D_1-**5i** with 80% D incorporation. This essay ratifies the *anti*-addition of the P–H



Scheme 4 Radical-promoted *Z*/*E* isomerisation of alkenyl phosphine derivatives.



Scheme 5 Deuterium-labelling experiments in the hydrophosphination of **4i**.

bond across the carbon–carbon triple bond which, apparently, can involve some H/D scrambling (Scheme 5).

We also compared the rate of addition of Ph_2PH to styrene at 70 °C with that of Ph_2PD (Fig. 3). A kinetic isotopic effect was manifested, which was especially dramatic in the range 0–50 min (induction period for Ph_2PD) and points to the cleavage of the P–H bond as being the rate-determining step of the reaction.

The effect of the stoichiometry of the reactants was also investigated for the addition of diphenylphosphine to styrene, in this case, in the range 10–60 min (Fig. 4). It is clear that, with respect to a 1 : 1 stoichiometric ratio, the excess of styrene has a negligible effect on the formation of **2a**, whereas an excess of diphenylphosphine speeds up its formation (*e.g.*, >5-fold at 10 min by doubling the amount of diphenylphosphine).

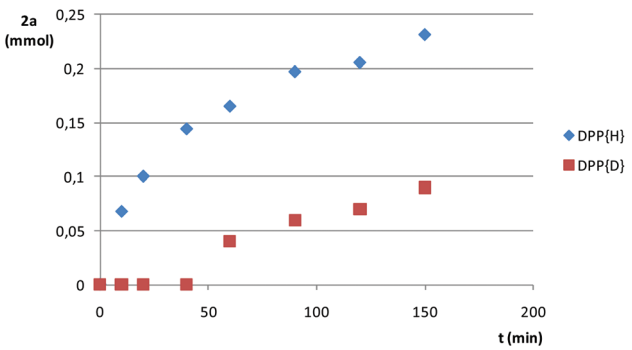


Fig. 3 Kinetic profiles for the reaction of styrene (**1a**) with protio- and deuteriodiphenylphosphine, DPP{H} and DPP{D}, respectively, at 70 °C under Ar.

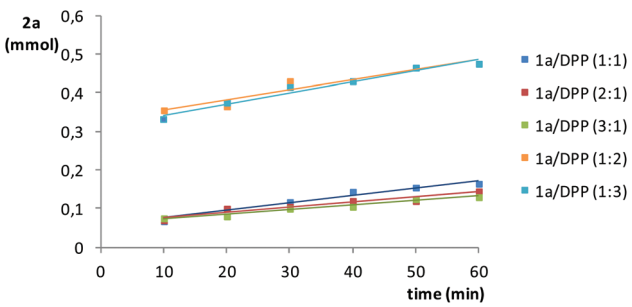


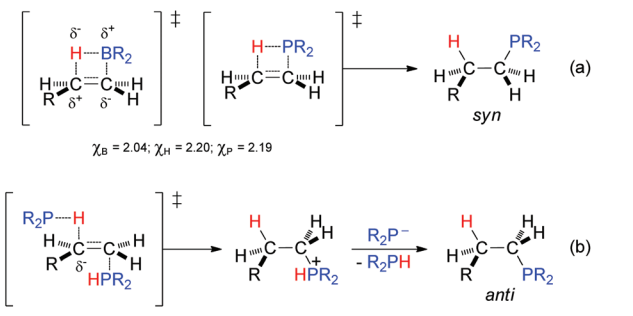
Fig. 4 Effect of the styrene (**1a**)/diphenylphosphine (DPP) ratio on the formation of **2a** in the 10–60 min range, at 70 °C under Ar. The amount of **2a** is referenced to the limiting substrate.

This effect was expected to be more prominent at shorter reaction times.[44] Larger amounts of diphenylphosphine (*e.g.*, 1 : 3 ratio) were shown to be unproductive with respect to the 1 : 2 ratio, displaying a very similar trend.

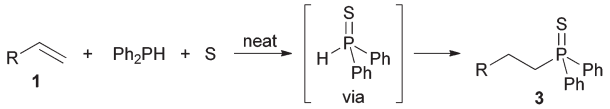
Considering the close electronegativities of P (χ_P = 2.19) and H (χ_H = 2.20), in principle it might be presumed that the anti-Markovnikov regioselectivity for the hydrophosphination (particularly, that of inactivated substrates) is primarily governed by steric factors rather than by electronic factors. In this context, substrates leading to more sterically hindered products, such as stilbene of diphenylacetylene, reacted sluggishly with diphenylphosphine either in the presence or absence of sulfur. A hydroboration-type model, in which the P–H bond is added through a four-membered ring transition state must be disregarded because (a) the B–H bond (χ_B = 2.04) is more polarized than the P–H bond and this circumstance works in the same direction as the steric factor in the former, and (b) the hydroboration is *syn* whereas the hydrophosphination is *anti* [Scheme 6, eqn (a)].

The above experiments and considerations lend weight to the argument that the hydrophosphination reaction follows an ionic pathway with *anti*-addition, where each of the P and H atoms emerges from two different phosphine molecules. The ability of tertiary phosphines to act as nucleophilic catalysts in the addition to alkenes (especially, α,β-unsaturated carbonyl compounds) is well known.[45] Therefore, it seems reasonable to propose that one phosphine molecule has a nucleophilic role, by addition to the terminal carbon atom of the alkene, while a second molecule behaves as the electrophilic partner through its hydrogen atom [Scheme 6, eqn (b)].

With the proposed transition state model, electronic factors also come into play as the negative charge density developed in the transition state is especially stabilised at the benzylic position (*e.g.*, in the styrenes) as well as at the α-position with respect to heteroatoms (in Het-vinyl substrates) and carbonyl groups (in α,β-unsaturated carbonyl compounds). In the case of 3,4-dihydro-2*H*-pyran (**1ac**), with a near symmetric carbon–carbon double bond, electronic factors seem to prevail with the addition of the P atom to the most electrophilic α-C atom (Table 4). Further support for the interpretation made of the hydrophosphination comes from the addition of Ph_2PH to



Scheme 6 Mechanistic proposals for the hydrophosphination of carbon–carbon double bonds following (a) a *syn* addition (hydroboration-type model) and (b) an *anti* addition.



Scheme 7 Diphenylphosphine sulfide as an intermediate in the three-component synthesis of alkylphosphine sulfides.

β-pinene (**1z**): the formation of the ring-opened product **2z** (Table 3) seems more feasible if two molecules of diphenylphosphine are implicated in the reaction.

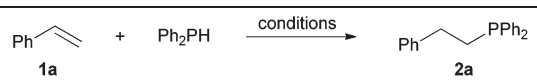
Concerning the three-component syntheses of alkyl and alkenyl phosphine sulfides, we earlier confirmed that *in situ* formation of diphenylphosphine sulfide comes off prior to the addition (Scheme 7).[22b]

Comparison with other catalysts

Although an array of effective catalysts has been designed for the hydrophosphination of alkenes, some operating even at room temperature, in practice, the results do not differ so much from those attained in the absence of a solvent and a catalyst (Table 7). Moreover, most of these results are based on NMR conversions (instead of isolated yields) and small-scale reactions performed in NMR tubes, which curtail the potential scope of the method. Similarly, the usage of an excess of the starting alkene in some of the methods has a negative effect on the *E*-factor.

Similar comments can be extended to the hydrophosphination of alkynes, in this case exemplified by the addition of diphenylphosphine to phenylacetylene (Table 8). The vinyl phosphine **5a** can be obtained without a catalyst and a solvent, not only in good isolated yield but also in the highest *E*/*Z* diastereoselectivity (entry 6). Taking into account different parameters (catalyst, solvent, temperature, time, yield and selectivity), together with the simplicity of the procedure, we

Table 7 Addition of diphenylphosphine to styrene

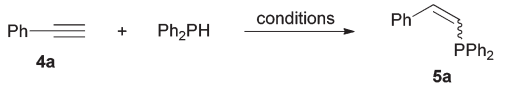


1a **2a**

Entry	Catalyst (mol%)	Solvent	*T* (°C)	Time (h)	Yield[a] (%)
1[46]	*t*-BuOK (20)	DMSO	rt	1	83
2[27b]	$Ni[P(OEt)_3]_4$ (5)	C_6H_6[b]	130	20	92
3[26a]	Ca-amide complex (10)	C_6H_6	75	20	64[c] (95)[d]
4[30]	$Cu(OTf)_2$·PhMe (10)	Dioxane-d_8	100	18–24	83
5[31]	$FeCl_2$ (30)	MeCN	60	12	87[e]
6[25e]	Ca-amide complex (2)	C_6D_6	25	3	(100)[d]
7[25f]	Ba-amide complex (2)	C_6D_6	60	0.4	(>96)[d]
8[25g]	Yb(II) complex (1)	C_6D_6	60	4	(92)[d]
9[28]	Fe(III) complex (0.5)	MeCN[f]	rt	24	89
10	None	None	70	4	82[g]

[a] Isolated yield unless otherwise stated; conversion in parentheses. [b] 2.0 equiv. of styrene; 1 equiv. of Et_3N. [c] Isolated yield of the phosphine oxide. [d] Conversion determined by NMR. [e] Isolated as the borane complex. [f] 1.82 equiv. of alkene. [g] This work.

Table 8 Addition of diphenylphosphine to phenylacetylene



4a 5a

Entry	Catalyst (mol%)	Solvent	T (°C)	Time	Yield[a] (%)
1[37]	$Pd(PPh_3)_4$ (1.2)	MeCN	130	18 h	95[b] (86/14)
2[38a]	Yb-imine complex (5)	THF	rt	5 min	>99[c] (24/76)
3[25e]	Ca-amide complex (5)	C_6D_6	75	38 h	78[d] (76/24)
4[25e]	Yb-amide complex (5)	C_6D_6	75	38 h	91[d] (10/90)
5[38f]	Y complex (2)	C_6D_6	70	72 h	100[d] (42/58)
6	None	None	70	10	80[e] (95/5)

[a] Z/E ratio in parenthesis. [b] ^{31}P NMR yield. [c] GC yield of the phosphine oxide. [d] Conversion determined by NMR. [e] This work; isolated yield.

can state that this approach towards the addition of the P–H bond to alkenes and alkynes distinctly outperforms others based on catalytic approaches.

Conclusions

For decades, the addition of the P–H bond across multiple carbon–carbon bonds has been associated with activation by bases, acids, radicals or metals. We have demonstrated that tertiary phosphines can be readily prepared by thermal treatment of secondary phosphines and alkenes in the absence of solvents and catalysts, under an inert atmosphere. This method is applicable to α,β-unsaturated carbonyl compounds, styrenes, *N*- and *S*-vinyl compounds, as well as inactivated alkenes. The process is highly regioselective producing the tertiary phosphines in an anti-Markovnikov fashion. Alkynes undergo the same type of addition to furnish anti-Markovnikov alkenyl phosphines with *Z* stereoselectivity.

Furthermore, by introducing elemental sulfur into the reaction mixture in air, alkyl and alkenyl phosphine sulfides can be readily synthesised through a one-pot three-component approach in a regio- and stereoselective manner. Compelling experimental evidence suggests an ionic-type anti addition reaction mechanism governed by steric and electronic effects different from that of the alkene/alkyne hydroboration.

These methods are in agreement with some of the twelve principles introduced by Anastas *et al.*,[5a] namely: (a) waste is prevented because of no by-product formation, (b) high atom economy, as all the starting materials are incorporated into the final products, (c) unnecessary use of solvents, (d) some reactions proceed at room temperature and most of them at 70 °C, (e) unnecessary derivatisation (the secondary phosphine sulfides are generated *in situ*) and (f) neither stoichiometric nor catalytic reagents are employed because the processes are catalyst free. In addition to this, similar or better results are obtained with respect to the catalytic methods.

In short, this study supports the statements by Sheldon that "the best catalyst is no catalyst" and "the best solvent is no solvent".[47]

Experimental

General procedure for the hydrophosphination of alkenes 1

All reactions were performed using tubes in a multi-reactor system under argon. Diphenylphosphine (0.5 mmol, 87 μL) and alkene (**1**, 0.5 mmol) were stirred during the specified time at room temperature, 70 or 100 °C (Tables 1–3). The progress of the reaction was monitored by TLC and/or GLC until total or steady conversion was achieved. The resulting mixture was dissolved in EtOAc (20 mL) followed by the addition of silica gel and removal of the excess of solvent *in vacuo*. The reaction crude absorbed on silica gel was subjected to column chromatography (silica gel, hexane/EtOAc) to give the pure tertiary phosphines **2**. The phosphine oxides **2x**, **2y** and **2z** were purified by preparative chromatography (silica gel, hexane/EtOAc).

General procedure for the hydrothiophosphination of alkenes 1

All reactions were performed using tubes in a multi-reactor system under air. Diphenylphosphine (0.5 mmol, 87 μL), alkene (**1**, 0.5 mmol) and elemental sulfur (0.5 mmol, 16.0 mg) were stirred at 70, 100 or 120 °C overnight (Table 4). The progress of the reaction was monitored by TLC and/or GLC until total or steady conversion was achieved. The resulting mixture was dissolved in EtOAc (20 mL) followed by the addition of silica gel and removal of the excess of solvent *in vacuo*. The reaction crude absorbed on silica gel was subjected to column chromatography (silica gel, hexane/EtOAc) to give the pure tertiary phosphine sulfides **3**. Compounds **3b**, **3e**, **3n** and **3y** were purified by preparative chromatography (silica gel, hexane/EtOAc).

General procedure for the hydrophosphination of alkynes 4

All reactions were performed using tubes in a multi-reactor system under argon. Diphenylphosphine (0.5 mmol, 87 μL) and alkyne (**4**, 0.5 mmol) were stirred at 70 °C overnight (Table 5). The progress of the reaction was monitored by TLC and/or GLC until total or steady conversion was achieved. The resulting mixture was dissolved in EtOAc (20 mL) followed by the addition of silica gel and removal of the excess of solvent *in vacuo*. The reaction crude absorbed on silica gel was subjected to column chromatography (silica gel, hexane/EtOAc) to give the pure alkenyl phosphines **5**.

General procedure for the hydrothiophosphination of alkynes 4

All reactions were performed using tubes in a multi-reactor system under air. Diphenylphosphine (0.5 mmol, 87 μL), alkyne (**4**, 0.5 mmol) and elemental sulfur (0.5 mmol, 16.0 mg) were stirred at 70 °C overnight (Table 6). The progress of the reaction was monitored by TLC and/or GLC until total or steady conversion was achieved. The resulting mixture was dissolved in EtOAc (20 mL) followed by the addition of silica gel and removal of the excess of solvent *in vacuo*. The reaction crude absorbed on silica gel was subjected to column chrom-

atography (silica gel, hexane/EtOAc) to give the pure alkenyl phosphine sulfides **6**.

Acknowledgements

This work was generously supported by the Spanish Ministerio de Economía y Competitividad (MINECO; CTQ2011-24151). Y. M. and I. M.-G. acknowledge the Instituto de Síntesis Orgánica (ISO) of the Universidad de Alicante for the grants. M. J. G.-S. Thanks the ISO and the Generalitat Valenciana (grant no. APOTIP/2015/014) for financial support.

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