EurJOC
European Journal of Organic Chemistry

FULL PAPER

DOI: 10.1002/ejoc.201301786

Facile Non-Catalyzed Synthesis of Tertiary Phosphine Sulfides by Regioselective Addition of Secondary Phosphine Sulfides to Alkenes

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Keywords: Synthetic methods / Green chemistry / Alkenes / Phosphorylation / Regioselectivity

An atom-economic green synthesis of tertiary phsophine sulfides has been developed based on catalyst- and solvent-free addition of secondary phosphine sulfides to diverse terminal and internal alkenes (hept-1-ene, cyclohexene, styrenes, allyl alcohol, vinyl ethers, vinyl sulfides, vinyltrimethylsilane, 1-vinylimidazoles, vinyl acetate). The reaction proceeds under mild conditions (80 °C, without solvent, 4–45 h) to afford chemo- and regioselectively the corresponding anti-Markovnikov adducts in excellent to quantitative yields (50–99 %).

Introduction

The tertiary phosphine sulfides continue to attract significant attention from researchers. Currently, these important organophosphorus compounds find widespread application as extractants for noble metals and radionuclides,[1] excellent ligands and pre-ligands for metal complex catalysts,[2] efficient precursors and capping agents for the preparation of metal sulfide nanoparticles[3] as well as reagents for organic synthesis.[4] In addition, tertiary phosphine sulfides have been offered as modifiers for rubbers and resins,[5] chemical sensitizers in photographic materials,[6] additives to lubricating oils, and as electrolytes.[7]

A number of synthetically useful reactions leading to tertiary phosphine sulfides have been described.[8] However, from the viewpoint of green chemistry, the most ideal route to tertiary phosphine sulfides is direct atom-economic addition of secondary phosphine sulfides across the C=C bonds of alkenes. Usually, activation of the P–H bonds within secondary phosphine sulfides in the above process requires the utilization of strong basic catalysts or radical initiators.[9] For instance, the nucleophilic addition of secondary phosphine sulfides to vinyl sulfoxides[10] or vinyl sulfones (including divinyl sulfoxide and -sulfone[11] as well as 2-sulfolene[12]) has been carried out in the presence of KOH (50–100 mol-%, THF) to give anti-Markovnikov adducts in high yields. The radical addition of secondary phosphine sulfides to alkenes has received significantly greater attention. Upon UV-irradiation or in the presence of initiators such as AIBN or in Et_3B/O_2 systems, this reaction proceeds in an anti-Markovnikov manner to give rise to diverse tertiary phosphine sulfides, as a rule, in high yields.[9] A variety of electron-rich (vinyl ethers,[13] vinyl sulfides,[14] vinyl selenides[15] and tellurides,[16] styrene,[17] 1-vinylimadazoles,[18] diketene[19]) and electron-poor (methyl methacrylate, acrylonitrile, acrylamide and *N*-phenylmaleimide)[17] alkenes can serve as unsaturated substrates. Subsequently, this approach has been extended to the synthesis of branched di-,[20] tri-[21] and tetraphosphine sulfides[22] from the corresponding alkenes.

In addition, there is a series of studies devoted to transition metal-catalyzed (Pd, Ni, Fe, Cu, etc.) additions of various P–H addends (mainly, H-phosphonates, secondary phosphines and their oxides) to C=C and C≡C bonds.[23] Although these reactions afford the target adducts in good yields, the application of expensive noble metal-based catalytic systems is necessary.

The main disadvantage of the aforementioned methodology for the synthesis of tertiary phosphine sulfides is the application of basic and free-radical conditions, which are often not compatible with the functionalized molecules. In addition, harmful organic solvents (e.g. THF, 1,4-dioxane) and free-radical initiators (e.g. toxic AIBN or pyrophoric Et_3B) or metal-based catalysts are required for the above reactions. Avoiding the use of the catalysts, initiators and solvents in syntheses of tertiary phosphine sulfides is highly desirable also from an environmental safety viewpoint. An uncatalyzed solvent-free protocol meets the modern requirements of green chemistry.[24] In line with this thinking, the regioselective addition of secondary phosphine-boranes and H-phosphinates to alkenes[25] or alkynes[26] in the absence of solvents and catalysts has been accomplished.

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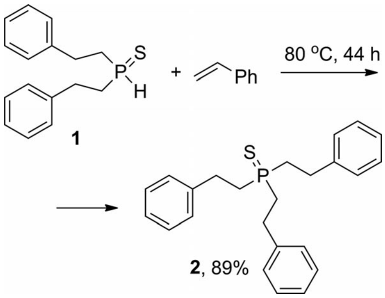
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201301786.

In this paper we report the facile and convenient green route toward tertiary phosphine sulfides based on the addition of secondary phosphine sulfides to alkenes, proceeding under catalyst- and solvent-free conditions.

Results and Discussion

Serendipitously, we found that secondary phosphine sulfide **1**, without any catalyst and solvent, easily (80 °C, 44 h, inert atmosphere) adds to styrene to give tertiary phosphine sulfide **2** in 89% yield (Scheme 1). Remarkably, the reaction proceeds strictly regioselectively as an anti-Markovnikov addition; no alternative isomer has been detectable in the reaction mixture on the basis of ^{1}H and ^{31}P NMR studies. The equimolar ratio of reactants is close to optimal although excess styrene does not affect the course of the reaction.



Scheme 1. Addition of secondary phosphine sulfide **1** to styrene under catalyst- and solvent-free conditions.

To extend the application and demonstrate a substrate scope for this efficient protocol, we have tested the reaction of diverse secondary phosphine sulfides with a series of alkenes. As seen in Table 1, various terminal and internal alkenes (including functionalized ones) successfully participate in the reaction to give only anti-Markovnikov adducts in 50–99% yields. The product yields depend upon the electronic and steric properties of the alkenes. Expectedly, terminal alkenes appeared to be more reactive than internal ones. For example, the reaction of diphenylphosphine sulfide (**3**) with hept-1-ene (**7**) or allyl alcohol (**10**) for 12 h provided desired products in 70–84% isolated yields (Table 1, Entries 1 and 4), whereas cyclohexene (**8**) or β-propylstyrene (**9**) showed lower reactivity under the same conditions (Table 1, Entries 2 and 3). Among the terminal alkenes, vinyl ethers (Table 1, Entries 6–9), vinyl sulfides (Table 1, Entries 10–16) and vinyltrimethylsilane (Table 1, Entry 17) displayed higher reactivity than 1-vinylimidazoles (Table 1, Entries 18 and 19), not to mention styrene (Scheme 1) and 4-*tert*-butoxystyrene (Table 1, Entry 5). It should be noted that the reactive functional groups, (e.g. OH, $SiMe_3$, OAc and imidazole) within alkenes **10**, **14**, **18**–**20** tolerate the reaction conditions. Among the secondary phosphine sulfides, diphenylphosphine sulfide (**3**) is the most reactive (cf. Table 1, Entry 14 with Entries 12 and 13) presumably due to the lower energy necessary for P–H bond cleavage.

Eventually, using the example of secondary phosphine sulfide **1** and vinyl sulfide **17**, we discovered that the reaction proceeds also at room temperature. However, even after a long reaction time (72 h), the conversion of the initial compounds is only 60%.

Regarding the mechanism of this non-catalyzed addition, at the moment it is difficult to draw reliable conclusions. Using the example of phosphine sulfide **3** and its reaction with alkene **17** (Table 1, Entry 14), we have shown that the addition reaction proceeds in the dark with the same efficiency as in the presence of light. Furthermore, the addition of a radical inhibitor such as TEMPO and hydroquinone (5–10 mol-%) does not affect the reaction course. It is quite possible that different reaction mechanisms are specific for each alkene group. So, it is known that the styrenes,[9] vinyl sulfides[9,27] and 1-vinylimidazoles[28] react with H-phosphines and H-phosphine chalcogenides not only under the conditions of radical initiation but also in the presence of basic catalysts to afford the anti-Markovnikov adducts, whereas the reactions of nucleophilic addition of PH-addends to alkenes **7**–**10** and vinyl ethers have not been described.

The synthetic utility and efficiency of the disclosed protocol is further demonstrated by the fact that alkynes can also react with secondary phosphine sulfides under catalyst- and solvent-free conditions. For example, phenylacetylene adds phosphine sulfide **3** chemo-, regio- and stereoselectively at 80 °C (5 h) to produce corresponding anti-Markovnikov adduct **22** in 94% isolated yield with a *Z*/*E* ratio of 95:5.

The synthesized products were fully characterized by ^{1}H, ^{13}C, ^{31}P NMR and IR spectroscopy. Moreover, molecular structures of phosphine sulfides **2** and **21h** were established by single-crystal X-ray diffraction analysis (Figure 1, Figure 2).[29]

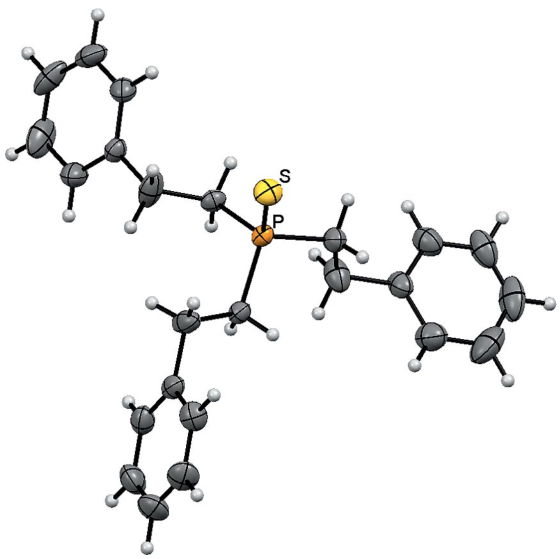
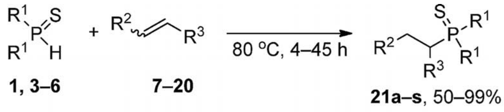


Figure 1. ORTEP plot of the phosphine sulfide **2** at 25% thermal ellipsoid probability.

Table 1. Synthesis of tertiary phosphine sulfides **21a**–**s**.[a]



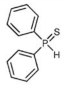
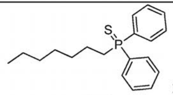
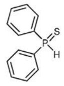
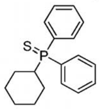
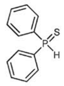
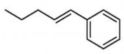
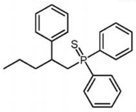
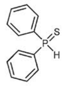
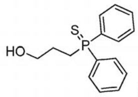
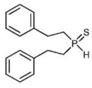
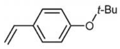
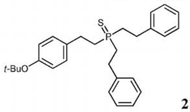
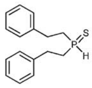
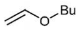
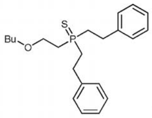
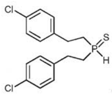
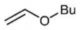
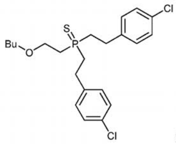
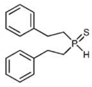
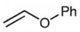
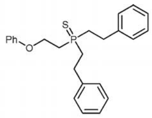
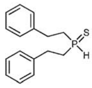
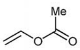
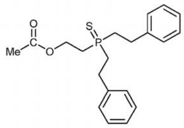
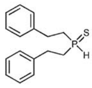
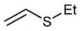
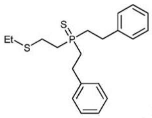
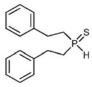
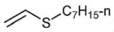
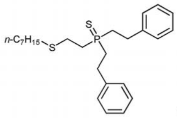
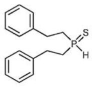
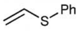
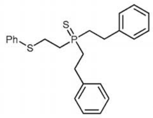
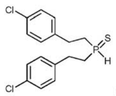
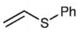
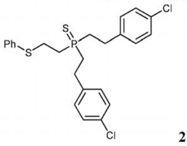
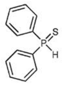
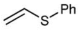
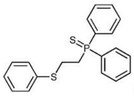
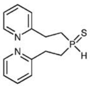
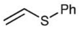
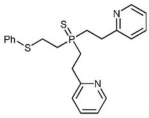
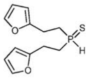
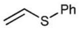
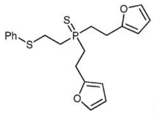
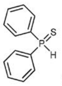
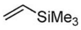
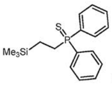
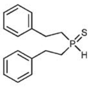
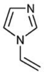
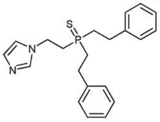
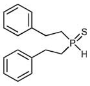
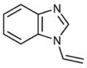
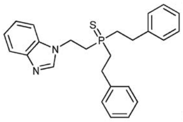
Entry	Secondary phosphine sulphide	Alkene	Reaction time [h]	Product	NMR yield [%][b]	Yield [%][c]
1	 **3**	 **7**	12	 **21a**	78	70
2	 **3**	 **8**	45	 **21b**	65	50
3	 **3**	 **9**	30	 **21c**	67	63
4	 **3**	 **10**	12	 **21d**	87	84
5	 **1**	 **11**	40	 **21e**	90	86
6	 **1**	 **12**	5	 **21f**	~ 100	98
7	 **4**	 **12**	6	 **21g**	93	90
8	 **1**	 **13**	6	 **21h**	99	97
9	 **1**	 **14**	4	 **21i**	≈ 100	98
10	 **1**	 **15**	5	 **21j**	98	96
11	 **1**	 **16**	7	 **21k**	99	97
12	 **1**	 **17**	7	 **21l**	≈ 100	99
13	 **4**	 **17**	5	 **21m**	95	91

Table 1. *(Continued)*.

Entry	Secondary phosphine sulphide	Alkene	Reaction time [h]	Product	NMR yield [%][b]	Yield [%][c]
14	 3	 17	4	 21n	≈ 100 (99)[d]	98 (94)[d]
15	 5	 17	9	 21o	86	80
16	 6	 17	6	 21p	95	93
17	 3	 18	5	 21q	85	80
18	 1	 19	10	 21r	95	93
19	 1	 20	12	 21s	95	91

[a] Reaction conditions: secondary phosphine sulfides **1**, **3**–**6** (1 mmol), alkenes **7**–**20** (1 mmol), 80 °C, inert atmosphere, stirring. [b] Yields based on ^{31}P NMR spectra of the crude reaction mixture. [c] Isolated yields. [d] Yields refer to experiments carried out in dark conditions.

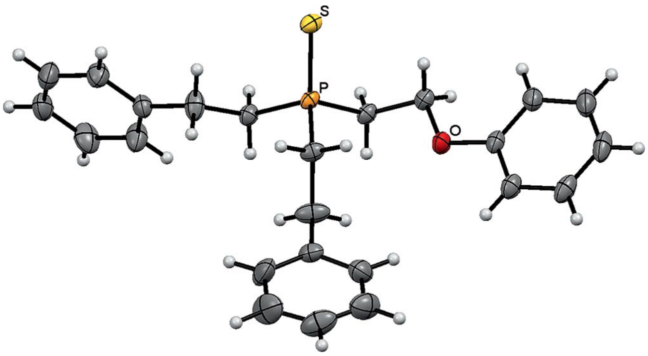
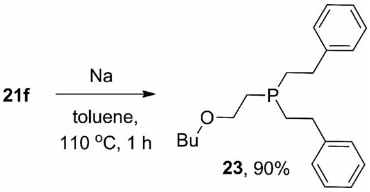


Figure 2. ORTEP plot of the phosphine sulfide **21h** at 25% thermal ellipsoid probability.

The synthesized tertiary phosphine sulfides can be successfully converted into the corresponding phosphines. We found that reduction of phosphine sulfide **21f** by treatment with sodium metal in toluene (110 °C, 1 h) furnishes to phosphine **23** in 90% yield (Scheme 2).



Scheme 2. Reduction of phosphine sulfide **21f** with sodium.

Conclusions

To summarize, a facile, green and high-yielding protocol for the addition of secondary phosphine sulfides to a series of alkenes under mild catalyst- and solvent-free conditions has been developed. The reaction selectively proceeds in an anti-Markovnikov fashion to form tertiary phosphine sulfides bearing diverse functional groups. These products are promising ligands for the construction of metal complexes, prospective metal extracting agents and building blocks in organic synthesis.

Experimental Section

General: All reactions were carried out under an argon atmosphere. Secondary phosphine sulfides **1**, **3**–**6** were synthesized by oxidation of the corresponding phosphines with powdered sulfur. The initial phosphines were prepared from the corresponding styrenes or 2-vinylfurane and red phosphorus as described in the literature.[30] Diphenylphosphine was purchased from Aldrich. Hept-1-ene, cyclohexene, styrene, 4-*tert*-buthoxystyrene, allyl alcohol, vinyltrimethylsilane and vinyl acetate are all commercially available products (Aldrich, Alfa Aesar). Vinyl ethers **12**, **13**, vinyl sulfides **15**–**17**

and 1-vinylimidazoles **19**, **20** were prepared by direct vinylation of the corresponding alcohols, thiols and imidazoles with acetylene.[31] The ^{1}H, ^{13}C, ^{31}P NMR spectra were recorded with a Bruker DPX 400 and Bruker AV-400 spectrometers (400.13, 100.62 and 161.98 MHz, respectively) at ambient temperature (23–25 °C) using $CDCl_3$ solutions. Chemical shifts were reported in δ (ppm) relative to $CDCl_3$ (^{1}H, ^{13}C) as an internal standard or H_3PO_4 (^{31}P) as an external standard. IR-FT spectra were obtained with a Bruker Vertex 70 spectrometer. Microanalyses were performed using a Flash EA 1112 elemental analyzer. Melting points (uncorrected) were determined with a "Stuart" apparatus.

General Procedure for Synthesis of Tertiary Phosphine Sulfides: A mixture of secondary phosphine sulfides **1**, **3**–**6** (1.0 mmol) and alkenes **7**–**20** (1.0 mmol) was stirred at 80 °C for 4–45 h (depending on reactant structures) under an argon atmosphere. The reaction was monitored by ^{31}P NMR following the disappearance of the signal corresponding to the starting phosphine sulfide (δ_P = 20–23 ppm) and simultaneous appearance of a new signal at 46–48 ppm, corresponding to tertiary phosphine sulfides **2**, **21a**–**s**. After completion of the reaction, the crude product was purified by flash chromatography (neutral alumina, hexane/Et_2O, 1:1 mixture as eluent) to give compounds **2**, **21a**–**s** in 50–99% yields.

Supporting Information (see footnote on the first page of this article): Synthetic procedures, spectroscopic data for the synthesized compounds, NMR spectra and crystallographic data for compounds **2** and **21h**.

Acknowledgments

This work was supported by the President of the Russian Federation (program for the support of leading scientific schools, grant number NSh-156.2014.3).

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[29] The crystal data for compounds **2** and **21h** are summarized in Supporting Information. CCDC-969346 (for **2**), and CCDC-970458 (for **21h**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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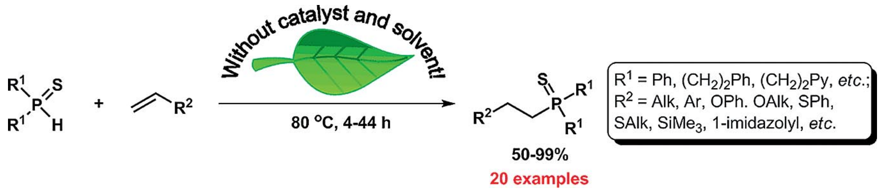
Received: November 30, 2013

Green Synthesis



Secondary phosphine sulfides easily add to diverse terminal and internal alkenes (hept-1-ene, cyclohexene, styrenes, allyl alcohol, vinyl ethers, vinyl sulfides, vinyltrimethylsilane, 1-vinylimidazoles, vinyl acetate) under catalyst- and solvent-free conditions at 80 °C (4–44 h) to afford the corresponding anti-Markovnikov adducts in good to excellent yields (50–99 %).

S. F. Malysheva, N. K. Gusarova, A. V. Artem'ev, N. A. Belogorlova, A. I. Albanov, T. N. Borodina, V. I. Smirnov, B. A. Trofimov* 1–7

Facile Non-Catalyzed Synthesis of Tertiary Phosphine Sulfides by Regioselective Addition of Secondary Phosphine Sulfides to Alkenes

Keywords: Synthetic methods / Green chemistry / Alkenes / Phosphorylation / Regioselectivity