Atom-economic synthesis of tertiary 2-alkoxyethylphosphine sulfides

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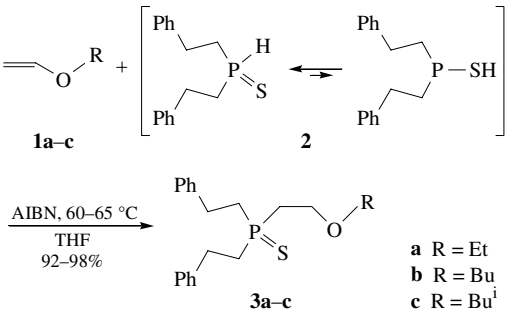
Secondary phosphine sulfides react chemo- and regiospecifically with alkyl vinyl ethers under radical conditions in the anti-Markovnikov mode giving corresponding tertiary phosphine sulfides in high yield.

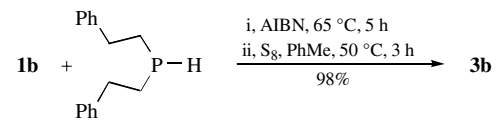
Reactions of PH acids with alkenes represent one of the most convenient approaches to C–P bond formation and continue to attract attention as an efficient method for the synthesis of phosphines and their derivatives, including asymmetrical and functional ones. Addition of phosphines to double carbon–carbon bonds (including those of vinyl ethers)[1] can proceed under radical conditions[1,2] or under the action of acidic[1] or basic[3] catalysts or metal complexes.[4] At the same time, data concerning the hydrothiophosphorylation of alkenes are scarce. Thus, diorganylphosphine sulfides were reported to react with alkenes[5] and triethoxyvinylsilane[6] in the presence of azaisobutyronitrile (AIBN) giving anti-Markovnikov adducts. There was also a brief communication describing the base-catalysed addition of secondary phosphine sulfides to acrylonitrile. However, no experimental details were given and reaction products were neither isolated nor characterised.[7]

In this work, to obtain new information on the addition of PH acids to alkenes and to extend the synthetic potential of this reaction, we studied the hydrothiophosphorylation of alkyl vinyl ethers **1a–c** with secondary phosphine sulfide **2**. The reaction was found to proceed in the presence of AIBN under mild conditions (60–65 °C, 5 h, THF) with chemo- and regiospecific formation of bis(2-phenethyl)(2-alkoxyethyl)phosphine sulfides **3a–c** in 92–98% yield (method A).†



Scheme 1

The structure of phosphine sulfides **3a–c** was confirmed using NMR (^{1}H, ^{13}C, ^{31}P) and IR spectroscopy, as well as by an independent synthesis of compound **3b** according to Scheme 2 (method B).‡



Scheme 2

Thus, the chemo- and regioselective addition of P,S-ambident secondary phosphine sulfides to alkyl vinyl ethers contributes to understanding the reactivity of these compounds and offers a facile straightforward atom-economic route to products **3**, which are potent special solvents, cocatalysts,[8] 'hemilabile' ligands[9] (for example, triphenylphosphine sulfide is a more effective ligand for palladium-catalysed bisalkoxycarbonylation of olefines than triphenylphosphine[10]), and complex-forming agents.[11]

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† *General procedure for the preparation of compounds* **3a–c** *(method A).*

A mixture of secondary phosphine sulfide **2** (0.41 g, 1.5 mmol), ether **1a** (0.11 g, 1.5 mmol) and AIBN (5 mg) in 5 ml of THF was stirred at 60–65 °C for 5 h under argon in a glass vial sealed with a rubber septum and equipped with a small Teflon stirring bar. The solvent was then removed under reduced pressure. The crude product was purified by column chromatography (Al_2O_3, eluent: chloroform–acetone, 5:1; column height, 90 mm; diameter, 12 mm) to give 0.51 g (98%) of **3a** as a honey-like product.

Phosphine sulfides **3b**,**c** (honey-like products) were prepared in the same way in 92 and 97% yields, respectively.

^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on a Bruker DPX 400 (400.13, 101.61 and 161.98 MHz, respectively) spectrometer. IR spectra were measured on a Bruker IFS-25 spectrometer in a microlayer.

Bis(2-phenethyl)(2-ethoxyethyl)phosphine sulfide **3a**. ^{1}H NMR ($CDCl_3$) δ: 7.32–7.25 (m, 10H, Ph), 3.85 and 3.80 (2dd, 2H, CH_2OEt, $^3J_{HH}$ = = $^3J_{PH}$ 6.4 Hz), 3.53 (q, 2H, CH_2Me, $^3J_{HH}$ 7.1 Hz), 3.07–2.96 (m, 4H, CH_2Ph), 2.33–2.15 (m, 6H, CH_2P), 1.22 (t, 3H, Me). ^{13}C NMR ($CDCl_3$) δ: 140.88 (d, C_{ipso}, $^3J_{PC}$ 14.7 Hz), 128.78 (C_m), 128.36 (C_o), 126.56 (C_p), 66.71 (CH_2Me), 64.50 (d, CH_2OEt, $^2J_{PC}$ 3.9 Hz), 33.71 (d, $2CH_2P$, $^1J_{PC}$ 48.0 Hz), 32.13 (d, CH_2P, $^1J_{PC}$ 49.3 Hz), 28.71 (d, CH_2Ph, $^2J_{PC}$ 3.0 Hz), 17.03 (Me). ^{31}P NMR ($CDCl_3$) δ: 47.4 (s). IR (ν/cm^{-1}): 600 (P=S). Found (%): C, 69.31; H, 7.89; P, 8.89; S, 9.30. Calc. for $C_{20}H_{27}OPS$ (%): C, 69.33; H, 7.85; P, 8.94; S, 9.26.

Bis(2-phenethyl)(2-butoxyethyl)phosphine sulfide **3b**. ^{1}H NMR ($CDCl_3$) δ: 7.29–7.21 (m, 10H, Ph), 3.80 and 3.76 (2dd, 2H, CH_2OBu, $^3J_{HH}$ = = $^3J_{PH}$ 5.9 Hz), 3.43 (dd, 2H, CH_2Pr, $^3J_{HH}$ 6.6 Hz), 2.99–2.93 (m, 4H, CH_2Ph), 2.28–2.11 (m, 6H, CH_2P), 1.52 (m, 2H, CH_2Et), 1.33 (m, 2H, CH_2Me), 0.89 (t, 3H, Me, $^3J_{HH}$ 7.4 Hz). ^{13}C NMR ($CDCl_3$) δ: 140.41 (d, C_{ipso}, $^3J_{PC}$ 14.2 Hz), 128.36 (C_m), 127.94 (C_o), 126.15 (C_p), 70.86 (CH_2Pr), 64.36 (CH_2OBu, $^2J_{PC}$ 3.9 Hz), 33.27 (d, $2CH_2P$, $^1J_{PC}$ 48.0 Hz), 31.46 (CH_2Et), 31.45 (d, CH_2P, $^1J_{PC}$ 49.7 Hz), 28.70 (CH_2Ph, $^2J_{PC}$ 2.7 Hz), 19.13 (CH_2Me), 13.56 (Me). ^{31}P NMR ($CDCl_3$) δ: 47.9 (s). IR (ν/cm^{-1}): 601 (P=S). Found (%): C, 70.51; H, 8.31; P, 8.25; S, 8.53. Calc. for $C_{22}H_{31}OPS$ (%): C, 70.55; H, 8.34; P, 8.27; S, 8.56.

Bis(2-phenethyl)(2-isobutoxyethyl)phosphine sulfide **3c**. ^{1}H NMR ($CDCl_3$) δ: 7.28–7.19 (m, 10H, Ph), 3.78 and 3.73 (2dd, 2H, CH_2OBu^i, $^3J_{HH}$ = $^3J_{PH}$ 6.1 Hz), 3.18 (d, 2H, CH_2Pr^i, $^3J_{HH}$ 6.6 Hz), 2.98–2.91 (m, 4H, CH_2Ph), 2.29–2.12 (m, 6H, CH_2P), 1.82 (m, 1H, CH), 0.86 (d, 6H, Me, $^3J_{HH}$ 6.7 Hz). ^{13}C NMR ($CDCl_3$) δ: 140.60 (d, C_{ipso}, $^3J_{PC}$ 14.4 Hz), 128.63 (C_m), 128.21 (C_o), 126.32 (C_p), 78.31 (OCH_2Pr^i), 64.45 (CH_2OBu^i, $^2J_{PC}$ 3.5 Hz), 33.52 (d, $2CH_2P$, $^1J_{PC}$ 48.6 Hz), 31.75 (CH_2P, $^1J_{PC}$ 49.8 Hz), 28.58 (d, CH_2Ph, $^2J_{PC}$ 2.6 Hz), 28.37 (CH), 19.39 (Me). ^{31}P NMR ($CDCl_3$) δ: 48.2 (s). IR (ν/cm^{-1}): 601 (P=S). Found (%): C, 70.54; H, 8.32; P, 8.23; S, 8.54. Calc. for $C_{22}H_{31}OPS$ (%): C, 70.55; H, 8.34; P, 8.27; S, 8.56.

‡ *Synthesis of compound* **3b** (method B).

A mixture of bis(2-phenethyl)phosphine (0.31 g, 1.3 mmol) and ether **1b** (0.13 g, 1.3 mmol) was heated at 65 °C in the presence of AIBN (4 mg) in a sealed ampoule for 5 h to give bis(2-phenethyl)(2-butoxyethyl)phosphine, whose ^{1}H and ^{31}P NMR spectra corresponded to published data.[1(a)] Toluene (4 ml) and elemental sulfur (0.06 g, 1.8 mmol) were successively added to the product obtained. The reaction mixture was heated at 50 °C for 3 h; then, the solvent was removed under reduced pressure. The residue was dissolved in diethyl ether, and unreacted sulfur was filtered off. Removal of the ether gave 0.47 g (98%) of **3b** as a honey-like product.

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