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Free-radical addition of phosphine to vinyl ethers: atom-economic synthesis of tris(2-organyloxyethyl)phosphines and their derivatives

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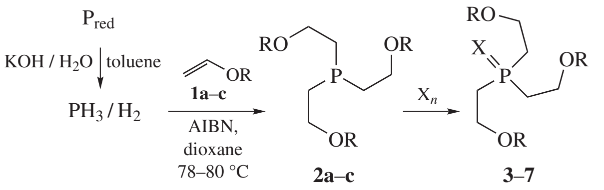
Phosphine, generated from red phosphorus in the system KOH–H_2O–toluene, reacts with vinyl ethers under radical initiation (AIBN, dioxane, 78–80 °C, atmospheric pressure) to give tris(2-organyloxyethyl)phosphines, which are transformed to the corresponding phosphine chalcogenides (in up to 73% isolated yield) *via* the reactions with air oxygen, elemental sulfur or selenium.

Organic phosphines and phosphine chalcogenides are widely used in the synthesis of metal complexes,[1] extractants of noble, rare-earth and transuranic elements,[2] precursors and special solvents for the preparation of conductive nanomaterials,[3] flame retardants[4] and building blocks for the design of diverse organophosphorus compounds.[5] Currently, a particular emphasis is placed on functional phosphines and phosphine chalcogenides. For instance, phosphines bearing ether moieties[6] are effective chelating ligands for the design of metal complex catalysts which are used for ring-opening metathesis polymerization of norbornene,[7] carbonylation of methanol,[8] hydroformylation of styrene.[9] A conventional method for synthesis of such functional phosphines is based on the reaction of alkali metal phosphides with 1,2-chlororganyloxyethanes.[7–10]

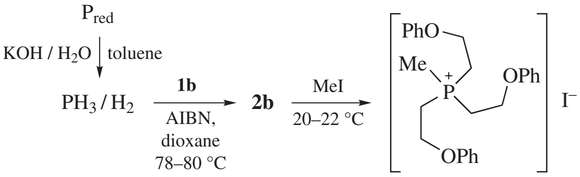
The most convenient, atom-economic and environmentally benign approach to such compounds is addition of PH reactants[11] to vinyl ethers, that has been demonstrated on the example of secondary phosphines and phosphine chalcogenides.[12] Phosphine, PH_3, is one of the most available and efficient phosphinating agents since a feasible method for its generation from elemental phosphorus and potassium hydroxide in aqueous-organic systems has been developed.[13] This allowed one to carry out atom-economic syntheses of primary, secondary and tertiary phosphines (including functional and unsaturated), based on the addition of phosphine to alkenes[11,13] and acetylenes.[11] At the same time, to the best of our knowledge, there is only one publication[14] reporting that phosphine adds to butyl vinyl ether in the presence of AIBN under heating in autoclave (33 atm) to give a mixture of primary, secondary and tertiary phosphines.

Table 1 Reaction of PH_3 with vinyl ethers.



Entry	CH_2=CH–OR	R	Phosphine[a]	X	Phosphine chalcogenide, yield[b] (%)
1	**1a**	C_7H_{15}	**2a**	O	**3**, 36[c]
2	**1b**	Ph	**2b**	O	**4**, 60
3	**1b**	Ph	**2b**	S	**5**, 73
4	**1b**	Ph	**2b**	Se	**6**, 56
5	**1c**	1-naphthyl	**2c**	O	**7**, 54

[a] Identified in the reaction mixture by ^{31}P NMR. [b] Yield of isolated product. [c] Along with phosphine oxide **3**, the product contains small amount of bis(2-heptyloxyethyl)phosphine oxide (yield, 5%).



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Scheme 1

Here we report on the convenient atom-economic synthesis of tertiary phosphines (isolated as the corresponding phosphine chalcogenides or phosphonium salts) based on radical addition of phosphine to vinyl ethers under atmospheric pressure. The reaction proceeds upon passing phosphine, generated as a phosphine–hydrogen mixture from red phosphorus and potassium hydroxide in aqueous-toluene medium,[13] through a solution of vinyl ethers **1a–c** in dioxane heated to 78–80 °C in the presence of AIBN. To achieve the complete organyloxyethylation of phosphine, vinyl ethers are introduced into the reaction vessel by two portions: the first one (two thirds) is placed into the flask at the initial reaction stage, while the remaining portion is added after the phosphine feeding is stopped. Under these conditions,[†] the major reaction products are the corresponding tris(2-organyloxyethyl)phosphines **2a–c** (identified in the reaction mixture by

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[†] The ^{1}H, ^{31}P and ^{77}Se NMR spectra were recorded on a Bruker DPX 400 spectrometer (400.13, 161.98 and 76.31 MHz, respectively). The yields were calculated with an allowance for the conversion of the vinyl ether. The phosphine–hydrogen mixture (PH_3/H_2, ~1:1) was generated[13] in a separate flask by dropwise addition of 50% aqueous solution of KOH (150 g) to a mixture of red phosphorus (30 g) in 100 ml of toluene at 70–75 °C. The gas mixture was passed through a washing bottle containing mixture of KOH (10 g), H_2O (10 g) and 15 ml of DMSO (for scavenging of flammable diphosphine) and further through the reaction flask, all connections of equipment were made gas-tight, the outlet of the reaction flask was connected with two washing bottles containing aqueous solutions of $CuSO_4$ (to catch residual phosphine). Thus, only small amounts of hazardous phosphine diluted with hydrogen was present in the system at every moment, so the synthesis was safe.

the ^{31}P NMR peaks at –40.3 to –38.5 ppm). The latter are transformed by the reactions with air oxygen, elemental sulfur or selenium to give tris(2-organyloxyethyl)phosphine chalcogenides **3**–**7** (Table 1).[†]

When iodomethane was used as a 'trap' for phosphine **2b**, methyl[tris(2-phenyloxyethyl)]phosphonium iodide **8** was obtained in 61% yield (Scheme 1).[†]

Thus, the reaction of phosphine with vinyl ethers, proceeding under mild conditions (atmospheric pressure, AIBN) represents a convenient approach to the atom-economic synthesis of new functional tertiary phosphines with an ether moiety and their derivatives, prospective hemilabile ligands for metal complex catalysis.

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Tris(2-organyloxyethyl)phosphines **2a**–**c** *(general procedure).* A solution of AIBN (0.065 g) in dioxane (25 ml) contained in the reaction flask, was blown with argon and saturated with phosphine–hydrogen mixture. To the solution obtained, vinyl ether **1** (8.3 mmol) in 5 ml of dioxane was added dropwise over 1 h at 78–80 °C, while bubbling phosphine at a rate of 15 ml min^{-1}, with the following heating (78–80 °C) of the reaction mixture for additional 4 h upon passing phosphine. The phosphine feeding was stopped, the system was blown with argon, then 0.033 g of AIBN was introduced and a solution of vinyl ether **1** (4.2 mmol) in 3 ml of dioxane was added dropwise over 10 min into the reaction mixture, which was then stirred at 78–80 °C for additional 2 h (for **1a**), 1.5 h (for **1b**) or 3 h (for **1c**). The reaction mixtures containing only or predominately tertiary phosphines **2a**–**c** (^{31}P NMR data, δ: –38.5, –39.8, –40.3, respectively) were then used (without isolation) for the preparation of phosphine chalcogenides **3**–**7** and phosphonium iodide **8**.

Tris(2-organyloxyethyl)phosphine oxides **3**–**5** *(general procedure)*. The reaction mixture, containing phosphine **2**, was blown with air and allowed to stay for 2 days, then dioxane and unreacted vinyl ether were removed under reduced pressure, the residue was washed with diethyl ether (1 ml) and dried *in vacuo*.

Tris(2-heptyloxyethyl)phosphine oxide **3**. A product (0.65 g), containing according to the ^{31}P NMR, phosphine oxide **3** and bis(2-heptyloxyethyl)phosphine oxide [δ_P 28.1 (d, $^1J_{PH}$ 462.2 Hz)] in the molar ratio of 5:1 was obtained. Yields are 36% and 5%, respectively (conversion of vinyl ether **1a** is 80%), yellowish oil. ^{1}H NMR (CDCl$_3$) δ: 0.87 (t, 9H, Me, $^3J_{HH}$ 6.9 Hz), 1.19–1.50 (m, 30H, CH$_2$), 2.04 (m, 6H, CH$_2$P), 3.31 and 3.64 (2m, 12H, CH$_2$O). ^{31}P NMR (CDCl$_3$) δ: 46.9.

Tris(2-phenyloxyethyl)phosphine oxide **4**. Yield 0.55 g (60%, conversion of vinyl ether **1b** is 53%), white powder, mp 139–140 °C. ^{1}H NMR (CDCl$_3$) δ: 2.50 (m, 6H, CH$_2$P), 4.43 (m, 6H, CH$_2$O), 6.80–7.40 (m, 15H, Ph). ^{31}P NMR (CDCl$_3$) δ: 44.9. Found (%): C, 70.52; H, 6.93; P, 7.45. Calc. for $C_{24}H_{27}O_4P$ (%): C, 70.23; H, 6.63; P, 7.55.

Tris[2-(1-naphthyloxy)ethyl]phosphine oxide **5**. Yield 0.33 g (54%, conversion of vinyl ether **1c** is 26%). A paraffin-like yellowish product. ^{1}H NMR (CDCl$_3$) δ: 2.77 (m, 6H, CH$_2$P), 4.63 (m, 6H, CH$_2$O), 6.77–8.26 (m, 21H, naphthyl). ^{31}P NMR (CDCl$_3$) δ: 44.6. Found (%): C, 76.83; H, 5.90; P, 5.81. Calc. for $C_{36}H_{33}O_4P$ (%): C, 77.13; H, 5.93; P, 5.52.

Tris(2-phenyloxyethyl)phosphine sulfide **6**. To the reaction mixture, containing phosphine **2b**, a solution of 0.13 g (4.1 mmol) of elemental sulfur in 2 ml of benzene was added and the mixture was stirred at ambient temperature for 1.5 h, then the solvents and unreacted vinyl ether **1b** (conversion 44%) were removed under reduced pressure, the residue was washed with ethanol (1 ml) and dried *in vacuo* to give a paraffin-like yellowish product. Yield 0.57 g (73%). ^{1}H NMR (CDCl$_3$) δ: 2.55 (m, 6H, CH$_2$P), 4.42 (m, 6H, CH$_2$O), 6.81–7.31 (m, 15H, Ph). ^{31}P NMR (CDCl$_3$) δ: 46.9. Found (%): C, 67.29; H, 6.25; P, 6.96; S, 7.81. Calc. for $C_{24}H_{27}O_3PS$ (%): C, 67.59; H, 6.38; P, 7.26; S, 7.52.

Tris(2-phenoxyethyl)phosphine selenide **7**. To the reaction mixture containing phosphine **2b**, elemental selenium (0.33 g, 4.2 mmol) was added and the mixture was stirred at 65–66 °C for 2 h and left overnight. Then unreacted selenium was filtered off, dioxane and unreacted vinyl ether **1b** (conversion 61%) were removed under reduced pressure, the residue was washed with ethanol (1 ml) and dried *in vacuo* to afford a yellowish oil. Yield 0.67 g (56%). ^{1}H NMR (CDCl$_3$) δ: 2.69 (m, 6H, CH$_2$P), 4.45 (m, 6H, CH$_2$O), 6.80–7.38 (m, 15H, Ph). ^{31}P NMR (CDCl$_3$) δ: 35.2. ^{77}Se NMR (CDCl$_3$) δ: –392.2 (d, $^1J_{SeP}$ 723.7 Hz). Found (%): C, 60.79; H, 5.95; P, 6.24; Se, 16.38. Calc. for $C_{24}H_{27}O_3PSe$ (%): C, 60.89; H, 5.75; P, 6.54; Se, 16.68.

Methyl[tris(2-phenoxyethyl)]phosphonium iodide **8**. To the reaction mixture containing phosphine **2b**, a solution of 1.2 g (8.45 mmol) of iodomethane in 5 ml of dioxane was added dropwise for 5 min and the mixture was left overnight. Then dioxane and unreacted vinyl ether **1b** (conversion 64%) were removed under reduced pressure, the residue was washed with diethyl ether (1 ml) and dried *in vacuo* to afford a yellowish oil. Yield 0.87 g (61%). ^{1}H NMR (CDCl$_3$) δ: 2.38 (d, 3H, Me, $^2J_{HP}$ 14.3 Hz), 3.37 (m, 6H, CH$_2$P), 4.52 (m, 6H, CH$_2$O), 6.81–7.37 (m, 15H, Ph). ^{31}P NMR (CDCl$_3$) δ: 33.2. Found (%): C, 56.18; H, 5.94; I, 23.81; P, 5.84. Calc. for $C_{25}H_{30}IO_3P$ (%): C, 55.98; H, 5.64; I, 23.66; P, 5.77.