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Nucleophilic additon of phosphine to 1-(*tert*-butyl)-4-vinylbenzene: a short-cut to bulky secondary and tertiary phosphines and their chalcogenides

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Phosphine readily adds to 1-(*tert*-butyl)-4-vinylbenzene in the KOH–DMSO system (70–120 °C, 3 h, atmospheric pressure) to form bis[4-(*tert*-butyl)phenethyl]phosphine and tris[4-(*tert*-butyl)phenethyl]phosphine, which are further oxidized to corresponding phosphine oxides, sulfides and selenides.

Organic phosphines and phosphine chalcogenides are widely used as ligands for metal-complex catalysts.[1] Among such ligands, bulky phosphines and phosphine chalcogenides are of special importance. They are employed as building blocks to design new catalytic systems for activation of cross-coupling reactions,[2(*a*)–(*c*)] amination,[2(*d*),(*e*)] cyanation,[2(*f*)] silylation,[2(*g*),(*h*)] hydroboration of vinylarenes,[2(*i*)] arylation of ketones,[2(*j*)] reactions of cyclization,[2(*k*)] dimerization,[2(*l*)] trimerization,[2(*m*)] and polymerization[2(*n*),(*o*)] of unsaturated compounds, *etc*.

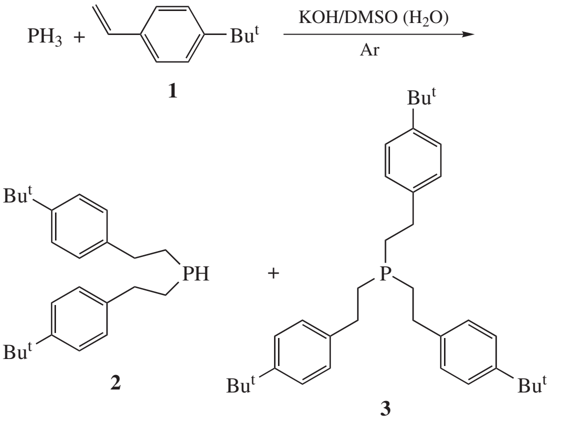
As a rule, the bulky phosphines and phosphine chalcogenides are synthesized from hazardous phosphorus halides and organometallic reagents. An alternative and convenient approach to the C–P bond formation is the reactions of PH addends with alkenes.[3] The simplest available[4] PH addend is phosphine (PH_3). However, this alternative is not systematically elaborated, though a few addition reactions of phosphine to multiple C–C bonds have been published.[3(*d*),5]

This paper reports a facile atom-economic one-pot method for the synthesis of secondary and tertiary phosphines and phosphine chalcogenides bearing bulky sterically hindered *tert*-butylphenyl substituents. Here, the method is exemplified by the nucleophilic addition of phosphine to 1-(*tert*-butyl)-4-vinylbenzene in the KOH–DMSO system. The investigation of the reaction is also of basic importance both for organophosphorus and alkene chemistry. Indeed, the addition of PH nucleophiles to arylalkenes is unusual and, to our knowledge, is described only for styrene, α-methyl- and α-phenylstyrene.[3(*d*),6] Under specially forced superbasic conditions (the sodium naphthalenide–TMEDA–THF system), a CH acid (2-methylpropanoic) seems to be the only nucleophile capable of adding to styrene.[7]

As far as the electron donating substituents in the benzene ring should slow down the nucleophilic addition to the double bond of vinylbenzene, a possibility of the reaction of phosphine with 1-(*tert*-butyl)-4-vinylbenzene is far from to be obvious.

We have found that phosphine[†] reacts with 1-(*tert*-butyl)-4-vinylbenzene **1** in a KOH–DMSO suspension in the presence of a small quantity of H_2O at 70–120 °C for 3 h to give bis[4-(*tert*-butyl)phenethyl]phosphine **2** and tris[4-(*tert*-butyl)phenethyl]phosphine **3** (Scheme 1).

In the absence of KOH no reaction occurs. This fact confirms a nucleophilic mechanism of addition, which is presumed to be through the phosphide anions, formed from phosphine under the action of the superbase KOH–DMSO system.



Scheme 1

Conditions for selective preparation of phosphines **2** or **3** have been elaborated. Secondary phosphine **2** has been synthesized in 87% yield by slow addition of styrene **1** to a suspension of KOH–DMSO (~2 wt% H_2O from total weight of the reaction mixture styrene–KOH–DMSO) heated to 70 °C with simultaneous vigorous passing of a phosphine stream through the suspension.[‡] Exhausting and selective 4-*tert*-butylphenylation of phosphine occurs at 70–120 °C in the KOH–DMSO system in the presence of H_2O (1.5 wt%) under additional introduction of styrene **1** (~ one third from the total weight) to the reaction

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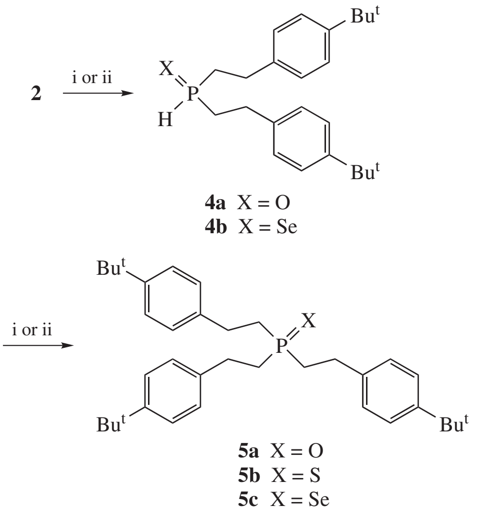
[†] *Preparation of phosphine*. Red phosphorus (15.5 g, 500 mmol) and toluene (50 ml) were placed in a 500-ml conical three-necked flask fitted with a gas inlet, combined with a pressure-equalizing dropping funnel, a magnetic stirrer, a reflux condenser, and a combination of outlet. An aqueous solution of 50 wt% KOH (50 g, 893 mmol) was added in the dropping funnel. The flask was connected, *via* a washing bottle [containing a mixture of aqueous KOH (50%) and DMSO] with a 200-ml four-necked flask containing KOH–DMSO–H_2O. This second flask was equipped with an efficient mechanical stirrer, a combination of gas-inlet tube and a dropping funnel containing a mixture of the styrene **1** and DMSO, and a combination of gas-outlet and thermometer. The outlet of the flask was connected with another washing bottle containing an aqueous solution of $CuSO_4$ (for trapping unreacted phosphine and converting it into cupric phosphide). The contents of the first flask were refluxed to ~60–70 °C, those of the second flask, to 70 °C.

The rate of this addition was adjusted so that PH_3 was evolved at a rate of 45–50 bubbles per min. 10 min after the evolution of PH_3 began, the addition of the styrene–DMSO mixture was started.



4a X = O
4b X = Se

5a X = O
5b X = S
5c X = Se

Scheme 2 *Reagents and conditions*: i, aqueous H_2O_2 (36%), acetone, 50 °C, 2 h; ii, S_8 or Se, toluene, Ar, 60 °C, 2 h.

mixture after completion of phosphine feeding. These conditions allow phosphine **3** to be prepared in 69% yield.§

Note that, under radical conditions (60–65 °C, AIBN, dioxane), phosphine adds to styrene **1** non-selectively to form a mixture of corresponding primary, secondary and tertiary phosphines in low yields.

Phosphines **2**, **3** react smoothly with an aqueous solution of H_2O_2, elemental sulfur and selenium in toluene to give corresponding secondary **4a**,**b** and tertiary **5a**–**c** phosphine chalcogenides in high yields (Scheme 2).¶

Thus, the reaction of phosphine with styrene **1** is a convenient approach to the synthesis of secondary and tertiary phosphine and phosphine chalcogenides with bulky sterically hindered *tert*-butylphenyl moieties, possible ligands for the design of the special metal complex catalysts,[1] as well as intermediates and coordinating solvents for the preparation of conductive nanomaterials.[8]

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2008.09.011.

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‡ *Preparation of bis[4-(*tert*-butyl)phenethyl]phosphine* **2**. A solution of styrene **1** (8.3 g, 51.8 mmol) in DMSO (5 ml) was added dropwise for 2 h to a suspension of KOH (10 g, 178.6 mmol), DMSO (40 ml) and water (1.5 ml), blown through argon and saturated with phosphine, at 70 °C under stirring and continuous bubbling of phosphine. The reaction mixture was additionally heated (70 °C) for 1 h in the flow of phosphine, and then the phosphine feeding was stopped. The mixture was blown through argon, cooled, diluted with water and extracted with benzene. The benzene extract was washed with water, dried over K_2CO_3, benzene was distilled, and the residue was fractionated in a vacuum to recover 2.1 g of styrene **1** (75% conversion). The residue was washed with hexane (10 ml) and dried in a vacuum to furnish 6 g (87%, calculated with conversion **1**) of phosphine **2**.

The ^{1}H, ^{13}C, ^{31}P and ^{77}Se NMR spectra were recorded on a Bruker DPX 400 spectrometer (400.13, 100.61, 161.98 and 76.31 MHz, respectively).

For **2**: colourless powder, mp 138–139 °C (hexane). ^{1}H NMR (C_6D_6) δ: 1.35 (s, 18H, Me), 1.71–1.79 and 1.83–1.91 (m, 4H, CH_2P), 2.74–2.81 (m, 4H, CH_2Ar), 3.27 (dq, 1H, $^1J_{PH}$ 195.3 Hz, $^3J_{HH}$ 7 Hz), 7.15–7.17 and 7.36–7.38 (m, 8H, Ar). ^{13}C NMR (C_6D_6) δ: 22.31 (d, CH_2P, $^1J_{PC}$ 11.9 Hz), 31.08 (Me), 33.90 (*C*Me), 34.03 (d, *C*H_2Ar, $^1J_{PC}$ 10.7 Hz), 125.07 ($C_{o\text{-Ar}}$), 127.80 ($C_{m\text{-Ar}}$), 139.35 (d, $C_{i\text{-Ar}}$, $^3J_{PC}$ 8.0 Hz), 148.32 ($C_{p\text{-Ar}}$). ^{31}P NMR ($CDCl_3$) δ: –68.67 (d, $^1J_{PH}$ 195.9 Hz). Found (%): C, 81.47; H, 10.03; P, 8.81. Calc. for $C_{24}H_{35}P$ (%): C, 81.31; H, 9.95; P, 8.74.

§ *Preparation of tris[4-(*tert*-butyl)phenethyl]phosphine* **3**. A solution of styrene **1** (5.5 g, 34.3 mmol) in DMSO (6.5 ml) was added dropwise for 1 h 40 min to a suspension of KOH (20 g, 357.1 mmol), DMSO (60 ml) and water (1.5 ml), blown through argon and saturated with phosphine, at 70 °C under stirring and continuous bubbling of the phosphine. The phosphine feeding was stopped, the mixture was blown through argon, and a solution of styrene **1** (2.8 g, 17.5 mmol) was added. The reaction mixture was heated (120 °C) and stirred for 1 h, then cooled, diluted with water, and extracted with toluene. The toluene extract was washed with water, dried over K_2CO_3, the toluene was removed, the residue was washed with hexane (10 ml) and dried in a vacuum to afford 6.1 g (69%) of phosphine **3**, colourless powder, mp 114–116 °C (hexane). ^{1}H NMR (C_6D_6) δ: 1.37 (s, 27H, Me), 1.75–1.79 (m, 6H, CH_2P), 2.08–2.86 (m, 6H, CH_2Ar), 7.20–7.26 and 7.39–7.40 (m, 12H, Ar). ^{13}C NMR (C_6D_6) δ: 29.55 (d, CH_2P, $^1J_{PC}$ 14.5 Hz), 31.40 (Me), 32.14 (d, *C*H_2Ar, $^2J_{PC}$ 14.5 Hz), 34.25 (*C*Me), 127.64 ($C_{o\text{-Ar}}$), 127.87 ($C_{m\text{-Ar}}$), 140.24 (d, $C_{i\text{-Ar}}$, $^3J_{PC}$ 9.5 Hz), 148.63 ($C_{p\text{-Ar}}$). ^{31}P NMR ($CDCl_3$) δ: –26.57. Found (%): C, 83.96; H, 9.83; P, 5.81. Calc. for $C_{36}H_{51}P$ (%): C, 84.00; H, 9.99; P, 6.02.

¶ For characteristics of compounds **4a**,**b** and **5a**–**c**, see Online Supplementary Materials.