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ScienceDirect
Mendeleev Commun., 2010, **20**, 275–276
Mendeleev Communications

Reaction of phosphine with allylbenzene in the KOH–DMSO system: regioselective synthesis of (1-phenylprop-2-yl)phosphine and bis(1-phenylprop-2-yl)phosphine

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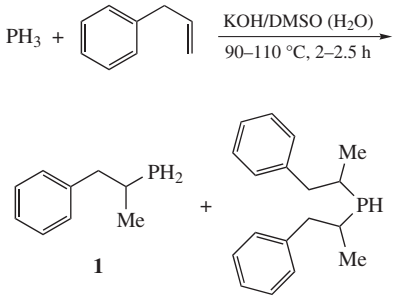
DOI: 10.1016/j.mencom.2010.09.012

Phosphine reacts with allylbenzene in the KOH–DMSO system (90–110 °C, 2–2.5 h, atmospheric pressure) to afford Markovnikov adducts, (1-phenylprop-2-yl)phosphine and/or bis(1-phenylprop-2-yl)phosphine in 53–80% yields.

Reactions of phosphine, PH_3, with allylic compounds are scarcely documented. Radical addition of phosphine (UV-irradiation or AIBN, 80 °C, high pressure) to allyl alcohol or allylamine gave a mixture of the corresponding primary, secondary and tertiary phosphines of anti-Markovnikov pattern.[1] The literature lacks the data on the addition of phosphine to allylic compounds under basic conditions, though vinyl(het)arenes do add phosphine under superbasic conditions.[2]

Here, we report on the base-catalyzed addition of phosphine to allylbenzene.

In fact, phosphine and allylbenzene under the action of the superbasic catalytic system KOH–DMSO in the presence of small amounts of water at 90–110 °C (2–2.5 h, atmospheric pressure) afford Markovnikov products, namely (1-phenylprop-2-yl)phosphine **1** and bis(1-phenylprop-2-yl)phosphine **2** (Scheme 1). Phosphine was generated in a separate reactor by the addition of aqueous KOH to the suspension of red phosphorus in toluene.[3]



Scheme 1

The conditions for the target preparation of either phosphine **1** or **2** have been elaborated. Primary phosphine **1** has been synthesized in 53% yield by slow addition of allylbenzene to a suspension of KOH–DMSO at 90 °C under continuous passing a vigorous flow of phosphine through the suspension (the yield of secondary phosphine **2** being 30%).† To attain the addition of phosphine to two molecules of allylbenzene, the reaction was carried out at higher temperature (90–110 °C), an extra equivalent of allylbenzene being fed after the flow phosphine was ceased. Under these conditions, phosphine **2** was obtained selectively in 80% yield, whereas neither primary **1** nor tertiary phosphines were formed (^{31}P NMR data).‡ The synthesized phosphines **1** and **2** are colourless oils, stable at ambient temperature under inert atmosphere and well soluble in organic solvents.

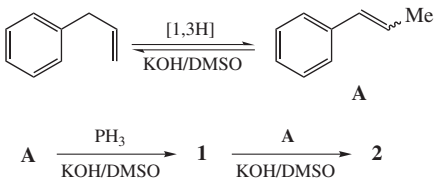
In the absence of KOH no reaction occurs. This fact confirms base-catalyzed mechanism of the process, which can be outlined by Scheme 2. In the first stage, due to [1,3H] isomerization of allylbenzene under the action of the superbase, 1-phenylprop-1-ene **A** is generated. The latter reacts with PH_3

† The ^{1}H, ^{13}C and ^{31}P NMR spectra were measured on a Bruker DPX 400 (400.13, 100.61 and 161.98 MHz, respectively) spectrometer. IR spectra were recorded on a Bruker IFS-25 spectrometer in films. Phosphine–hydrogen mixture was prepared from red phosphorus, KOH and H_2O according to the published procedure.[3]

Preparation of (1-phenylprop-2-yl)phosphine **1**. To a suspension of $KOH·0.5H_2O$ (20.0 g, 0.31 mol), DMSO (50 ml) and water (3 ml), blown with argon and saturated with phosphine, a solution of allylbenzene (6.0 g, 0.05 mol) in DMSO (10 ml) was added dropwise for 1.5 h at 90 °C under stirring and continuous passing of phosphine at a rate of 15 ml min^{-1}. The flow of phosphine was maintained at 90 °C for additional 0.5 h, then the mixture was blown with argon, cooled, diluted with water (100 ml) and extracted with diethyl ether (2×50 ml). The extract was washed with water (3×30 ml), dried over K_2CO_3, diethyl ether was evaporated, and the residue was fractionized *in vacuo* to give primary phosphine **1** (4.1 g, 53%), secondary phosphine **2** (2.1 g, 30%) and (*E*)-1-phenylprop-1-ene (1.0 g, 17%).

For **1**: colourless oil, bp 60–63 °C (1 Torr). ^{1}H NMR ($CDCl_3$) δ: 1.12 (dd, 3H, Me, $^3J_{HH}$ 7.0 Hz, $^3J_{PH}$ 13.1 Hz), 2.21–2.23 (m, 1H, CH, $^3J_{HH}$ 10.4 Hz, $^3J_{HH}$ 8.0 Hz), 2.67 (dm, 2H, PH, $^1J_{PH}$ 194 Hz, $^3J_{HH}$ 10.5 Hz, $^3J_{HH}$ 5.6 Hz), 2.64 and 2.74 (ddd, 2H, CH_2, $^2J_{HH}$ 13.6 Hz, $^3J_{HH}$ 10.4 Hz, $^3J_{HH}$ 8.0 Hz, $^3J_{PH_a}$ 8.1 Hz, $^3J_{PH_b}$ 7.2 Hz), 7.19–7.34 (m, 5H, Ph). ^{13}C NMR ($CDCl_3$) δ: 22.54 (d, Me, $^2J_{PC}$ 9.2 Hz), 24.55 (d, CH, $^1J_{PC}$ 6.0 Hz), 45.87 (d, CH_2, $^2J_{PC}$ 7.9 Hz), 126.38 (*p*-C_{Ph}), 128.46 (*m*-C_{Ph}), 129.15 (*o*-C_{Ph}), 140.81 (d, *i*-C_{Ph}, $^3J_{PC}$ 5.9 Hz). ^{31}P NMR ($CDCl_3$) δ: –112.35 (t, $^1J_{PH}$ 194 Hz). IR (KBr, ν/cm^{-1}): 3083, 3061, 3026, 2961, 2915, 2865, 2851, 2290, 1599, 1597, 1496, 1452, 1305, 1278, 1069, 1029, 963, 910, 736, 694. Found (%): C, 71.15; H, 8.50; P, 20.54. Calc. for $C_9H_{13}P$ (%): C, 71.04; H, 8.61; P, 20.35.

For **2**: colourless oil, bp 169–170 °C (1 Torr). IR (KBr, ν/cm^{-1}): 3080, 3060, 3024, 2968, 2917, 2865, 2850, 2294, 1601, 1598, 1491, 1455, 1304, 1276, 1040, 968, 914, 736, 695. Found (%): C, 79.83; H, 8.44; P, 11.21. Calc. for $C_{18}H_{23}P$ (%): C, 79.97; H, 8.58; P, 11.46. Major diastereomer: ^{1}H NMR ($CDCl_3$) δ: 1.03 (dd, 6H, Me, $^3J_{HH}$ 7.0 Hz, $^3J_{PH}$ 13.2 Hz), 2.07 (m, 2H, CH), 2.51 and 2.85 (ddd, 4H, CH_2, $^2J_{HH}$ 10.0 Hz, $^3J_{PH}$ 9.9 Hz, $^3J_{PH}$ 8.0 Hz, $^3J_{HH}$ 10.0 Hz, $^3J_{HH}$ 5.9 Hz), 2.78–2.87 (m, 2H, CH_2), 3.03 (dm, 1H, PH), 7.10–7.26 (m, 10H, Ph). ^{13}C NMR ($CDCl_3$) δ: 19.30 (d, Me, $^2J_{PC}$ 15.8 Hz), 27.29 (d, CH, $^1J_{PC}$ 10.6 Hz), 42.76 (d, CH_2, $^2J_{PC}$ 13.9 Hz), 126.04 (*p*-C_{Ph}), 128.22 and 129.01 (*o*-C_{Ph}, *m*-C_{Ph}), 140.68 (d, *i*-C_{Ph}, $^3J_{PC}$ 8.1 Hz). ^{31}P NMR ($CDCl_3$) δ: –22.76 (d, $^1J_{PH}$ 180.4 Hz).



Scheme 2

according to a nucleophilic addition mode to give primary phosphine **1** which further interacts with 1-phenylprop-1-ene **A** to produce secondary phosphine **2**.

The intermediate (*E*)-1-phenylprop-1-ene was in fact isolated from the reaction mixture,[†,‡] which can be the evidence of the above mechanism.

In conclusion, the reaction of phosphine with allylbenzene in the superbasic system can serve (when applied to other alkenylarenes) a simple, convenient and atom-economic route to new primary and secondary phosphines. The phosphines obtained are prospective ligands for metal complex catalysts,[4] promising precursors for valuable tertiary phosphines and corresponding phosphine chalcogenides,[5] as well as intermediates and coordinating solvents for the preparation of conductive nanomaterials.[6]

This work was supported by the Russian Foundation for Basic Research (grant no. 08-03-00251).

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Received: 11th May 2010; Com. 10/3524

Minor diastereomer: ^{1}H NMR ($CDCl_3$) δ: 1.06 (dd, 6H, Me, $^3J_{HH}$ 7.0 Hz, $^3J_{PH}$ 13.2 Hz), 2.07, 2.47 and 2.81 (ddd, three-spin system ABM, 3H, CH and CH_2, $^2J_{AB}$ 10.0 Hz, $^3J_{PH_A}$ 8.0 Hz, $^3J_{PH_B}$ 9.8 Hz, $^3J_{H_AH_M}$ 5.9 Hz, $^3J_{H_BH_M}$ 10.0 Hz), 3.03 (dm, 1H, PH), 7.10–7.26 (m, 10H, Ph). ^{13}C NMR ($CDCl_3$) δ: 19.17 (d, Me, $^2J_{PC}$ 16.5 Hz), 27.28 (d, CH, $^1J_{PC}$ 10.6 Hz), 42.62 (d, CH_2, $^2J_{PC}$ 13.2 Hz), 126.04 (*p*-C_{Ph}), 128.22 and 129.01 (*o*-C_{Ph}, *m*-C_{Ph}), 140.60 (d, *i*-C_{Ph}, $^3J_{PC}$ 7.3 Hz). ^{31}P NMR ($CDCl_3$) δ: –28.26 and –17.41 (d, $^1J_{PH}$, 207.3 and 199.2 Hz). The presence of the three signals in the ^{31}P NMR spectrum can be due to the presence of asymmetric centres in the molecule.

For (E)-*1-phenylprop-1-ene*: bp 35–40 °C (1 Torr). ^{1}H NMR ($CDCl_3$) δ: 2.03 (d, 3H, Me, $^3J_{HH}$ 6.1 Hz), 6.37 (dd, 1H, =C*H*Me, $^3J_{HH}$ 15.4 Hz, $^3J_{HH}$ 6.1 Hz), 6.58 (d, 1H, =C*H*Ph, $^3J_{HH}$ 15.4 Hz), 7.28–7.43 (m, 5H, Ph). Found (%): C, 91.40; H, 8.41. Calc. for C_9H_{10} (%): C, 91.47; H, 8.53.

‡ *Preparation of bis(1-phenylprop-2-yl)phosphine* **2**. To a suspension of $KOH \cdot 0.5H_2O$ (20.0 g, 0.31 mol), DMSO (50 ml) and water (3 ml), blown with argon and saturated with phosphine, a solution of allylbenzene (7.8 g, 0.066 mol) in DMSO (10 ml) was added dropwise for 1.5 h at 90 °C under stirring and continuous passing of the phosphine at a rate of 15 ml min^{-1}. The phosphine feeding was stopped, the mixture was blown with argon, and more solution of allylbenzene (3.9 g, 0.033 mol) in DMSO (5 ml) was added. The reaction mixture was heated to 110 °C and stirred for 1 h, then cooled, diluted with water (100 ml), and extracted with diethyl ether (2×50 ml). The extract was washed with water (3×30 ml), dried over K_2CO_3, diethyl ether was evaporated, and the residue was fractionized *in vacuo* to give phosphine **2** (10.7 g, 80%) and (*E*)-1-phenylprop-1-ene (1.5 g, 13%).