Letters to the Editor

Synthesis of primary phosphines from phosphine and arylethylenes

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Phosphine is known to add to styrene in hexane in the presence of radical initiators under elevated (28—30 atm) pressure at 70 °C giving (2-phenylethyl)phosphine, bis(2-phenylethyl)phosphine, and tris(2-phenylethyl)phosphine in 36, 29, and 6 % yields respectively.[1]

We have found that (2-phenylethyl)phosphine (**1**) and (2-methyl-2-phenylethyl)phosphine (**2**) can be obtained under normal pressure from styrene or α-methylstyrene and phosphine generated, along with hydrogen, from red phosphorus and saturated aqueous solution of alkali metal hydroxide. Phosphorylation takes place by the action of a superstrong base when phosphine—hydrogen mixture is vigorously passed through a suspension of KOH/DMSO heated up to 50—55 °C and simultaneously 1-phenylalkene is slowly added to the reaction vessel. The yield of primary phosphines (**1**, **2**) is 20—30 % (not optimized).

$$Ph(R)C{=}CH_2 + PH_3(H_2) \xrightarrow{KOH/DMSO} \underset{\textbf{1,2}}{Ph(R)CHCH_2PH_2}$$

R = H (**1**), Me (**2**)

In the absence of KOH no reaction occurs, which is evidence of its nucleophilic character.

(2-Phenylethyl)phosphine (1). To a suspension of 10 g of KOH, 40 mL of DMSO, and 6.45 mL of water saturated with phosphine-hydrogen mixture (obtained in accordance with a known procedure[2]), a solution of 2.96 g of styrene in 10 mL of DMSO was added dropwise over 4 h at 55—57 °C with continuous bubbling of phosphine-hydrogen mixture at a rate of 20—25 mL min^{-1}. The reaction mixture was stirred for 2 h at 50—55 °C with a flow of phosphine, then cooled, flushed with nitrogen, diluted with water, and extracted with ether. Ethereal extracts were washed with water and dried over K_2CO_3. Ether was evaporated, and the residue was fractionated *in vacuo* to give 1.05 g (20 %) of phosphine **1**, b.p. 46—48 °C (1 Torr), n_D^{20} 1.5532 (see Ref. 1: b.p. 75 °C (8 Torr), n_D^{20} 1.5494; see Ref. 3: b.p. 73 °C (3 Torr), n_D^{20} 1.5565). ^{31}P NMR ($CDCl_3$, δ): −139.7 (J_{H-P-H} = 198 Hz). IR, ν/cm^{-1}: 2280 (P—H). Found (%): C, 69.05; H, 7.88; P, 21.98. $C_8H_{11}P$. Calculated (%): C, 69.55; H, 8.03; P, 22.42.

(2-Methyl-2-phenylethyl)phosphine (2) was prepared as described above from α-methylstyrene and phosphine in 30 % yield, b.p. 65—67 °C (2 Torr), n_D^{20} 1.5482. ^{31}P NMR ($CDCl_3$, δ): −148.6 (J_{H-P-H} = 198 Hz). IR, ν/cm^{-1}: 2280 (P—H). Found (%): C, 71.45; H, 8.28; P, 19.95. $C_9H_{13}P$. Calculated (%): C, 71.04; H, 8.61; P, 20.35.

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