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Nucleophilic Addition of Phosphine to Aryl- and Hetarylethenes A Convenient Synthesis of Bis(2-arylalkyl)- and Bis(2-hetaralkyl)phosphines

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Abstract

A number of secondary phosphines $[RCH(R')CH_2]_2PH$ (R = aryl or hetaryl, R' = H or Me) have been obtained in good yields by introducing phosphine at normal pressure into a mixture of the alkenes $R(R')C{=}CH_2$, potassium hydroxide and dimethylsulfoxide.

Addition of phosphine to alkenes is usually carried out under high pressure in the presence of a radical initiator[1]. The addition does not proceed selectively: from styrene, for example, a mixture of the primary, secondary and tertiary phosphines has been obtained with the ratio of 36 : 29 : 6. We previously reported[2] on the preparation of triorganylphosphine oxides in good yields from red phosphorus and electrophiles (organyl halides, aryl- and hetarylalkenes, including styrene) in strongly basic systems such as combinations of alkali metal hydroxide and dipolar aprotic solvents or under phase-transfer conditions[2]. The present communication deals with the selective formation of secondary phosphines by introducing phosphine into a mixture of aryl- or hetarylethenes, potassium hydroxide and dimethylsulfoxide. In the absence of KOH no reaction occurred.

$$\underset{\mathbf{1}}{2\,\mathrm{R(R')C{=}CH_2}} + \mathrm{PH_3} \xrightarrow[60^{\circ}\mathrm{C}]{\mathrm{KOH/DMSO}} \underset{\mathbf{2}}{\mathrm{[R(R')CH{-}CH_2]_2PH}}$$

The addition is presumed to occur through the phosphide anion, formed in small concentrations. Styrene, 4-fluorostyrene and 2-vinylthiophene reacted smoothly, but 2-vinylfuran and α-methylstyrene seemed to react less readily, while 1-methyl-2-vinylpyrrole was recovered almost completely. The decrease of the reactivity may be caused by electron release from the methyl group (inductive) or furyl and 1-methylpyrryl group (mesomeric) making the double bond less electrophilic.

Experimental procedure

A 2-l round-bottomed, three-necked flask was fitted with a gas inlet, combined with a pressure-equalized dropping funnel, a gas-tight mechanical stirrer and a combination of outlet and thermometer. In the flask were placed 32 g of red phosphorus and 90 ml of dioxane, in the dropping funnel 180 g of a 50% (by weight) aqueous solution of potassium hydroxide. The flask was connected, *via* a washing bottle (filled with paraffin oil), with a 1-l, three-necked reaction flask containing 22 g of potassium hydroxide, 90 ml of dimethylsulfoxide and 15 ml of water. The second flask was equipped with an efficient mechanical stirrer, a combination of a gas inlet tube and a dropping funnel containing a mixture of 0.20 mol of the alkene and 40 ml of dimethylsulfoxide, and a combination of a gas outlet and a thermometer. It was connected with another washing bottle containing paraffin oil. All connections were made gas-tight. After the apparatus had been flushed with nitrogen, the contents of the first-mentioned flask were heated at 65 - 75°C and those of the reaction flask at 60 - 65°C. The addition of the potassium hydroxide solution was started and the flow of nitrogen stopped. The rate of this addition was adjusted such that phosphine was evolved at a rate of 40 - 50 bubbles per minute. Ten minutes after the evolution of phosphine had begun, dropwise addition of the alkene was started. This addition was completed after 2.5 h. During and 30 min after this period the temperatures of the flask for generating PH_3 and of the reaction flask were maintained at the levels mentioned. Finally, a rapid flow (2 - 3 l/ min) of N_2 was passed through the apparatus during 50 min in order to remove phosphine. After cooling to room temperature (introduction of N_2 being continued at a much lower rate), the reaction mixture was diluted with 150 ml of ice water and five extractions with ether (75 ml portions) were carried out. After washing three times with water, the organic solution was dried over K_2CO_3 and concentrated *in vacuo*. Distillation of the remaining liquid through 10-cm Vigreux column at low pressure gave the following secondary phosphines **2**:

$(PhCH_2CH_2)_2PH$, b.p. 153°C/ 0.3 mm Hg, n^{20}_D 1.596, (lit.[1] gives b.p. 158°C/ 0.5 mm Hg, n^{20}_D 1.595), yield 79% .

NMR[3]:

^1H ($CDCl_3$): 7.24 - 7.02 (m), 10H; 3.15 (broadened singlet), 1H; 2.80 - 2.55 (m), 4H; 1.90 - 1.70 (m), 4H;

^{31}P ($CDCl_3$): –71 (P), $^1J_{PH}$ 183;

$[Ph(Me)CHCH_2]_2PH$, b.p. 156°C/ 0.2 mm Hg, yield 63%.

NMR[3]:

^{31}P ($CDCl_3$) – 83.3, $^1J_{PH}$ 185;

$(4\text{-}F\text{-}C_6H_4CH_2CH_2)_2PH$, b.p. 169°C/ 0.3 mm Hg, n^{20}_D 1.554, yield 73%;

NMR[3]:

^1H ($CDCl_3$): 7.24 - 7.14 (m), 4H; 7.09 - 6.97 (m), 4H; 3.25 (broadened singlet), 1H; 2.88 - 2.78 (m), 4H; 1.96 - 1.67 (dt), 4H; $^3J_{HP}$ 1.3, $^3J_{HH}$ 8;

^{13}C ($CDCl_3$): 161.1 (d), $^1J_{CF}$ 244, 137.7, 129.3 (d), $^3J_{CF}$ 7.8, 115.1 (d), $^2J_{CF}$ 32, 33.45 (d), $^1J_{CP}$ 11, 22.1 (d), $^2J_{CP}$ 11;

^{31}P ($CDCl_3$): –70.6 (P), $^1J_{PH}$ 199.

$(2\text{-Thienyl-}CH_2CH_2)_2PH$, b.p. 164°C/ 0.3 mm Hg, n^{20}_D 1.609, yield 77%;

NMR[3]:

^1H ($CDCl_3$): 7.24 - 7.20 (m), 2H; 7.04 - 7.02 (m), 2H; 6.94 - 6.92 (m), 2H; 3.37 (s), 1H; 3.16 - 3.08 (m), 4H; 2.08 - 2.02 (m), 4H; 144.8 (d);

^{13}C ($CDCl_3$): $^3J_{CP}$ 8,4, 126.4, 123.9, 123.0, 28.35 (d), $^1J_{CP}$ 12, 22.25 (d), $^2J_{CP}$ 12;

^{31}P ($CDCl_3$): –71.0 (P), $^1J_{PH}$ 198.

$(2\text{-Furyl-}CH_2CH_2)_2PH$, b.p. 123°C/ 1.5 mm Hg, n^{20}_D 1.539, yield 60%.

NMR[3]:

^1H ($CDCl_3$): 7.34 (dd), 2H; $^2J_{HH}$ 1.9, $^3J_{HH}$ 0.8; 6.31 (dd), 2H, $^2J_{HH}$ 1.7, $^2J_{HH}$ 3.1; 6.06 (m), 2H; 3.52 (quintet), 1H; 2.90 - 2.80 (m), 4H; 2.03 - 1.81 (m), 4H; .

^{13}C ($CDCl_3$): 155.4, 140.7, 109.9, 104.8, 26.50 (d), $^1J_{CP}$ 11.8, 18.40 (d), $^2J_{CP}$ 11.0;

^{31}P ($CDCl_3$): –70.1 (P), $^1J_{PH}$ 201.

All compounds showed a strong infrared absorption at 2260 - 2265 cm^{-1} (ν P–H). The high resolution mass spectral data of the phosphines **2** were in agreement with the calculated.

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3. All spectra were recorded on a Bruker AC 300 machine, all δ in ppm and all couplingconstants in Hz.

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