One-step synthesis of unsymmetrical tertiary phosphine oxides from red phosphorus and organyl halides

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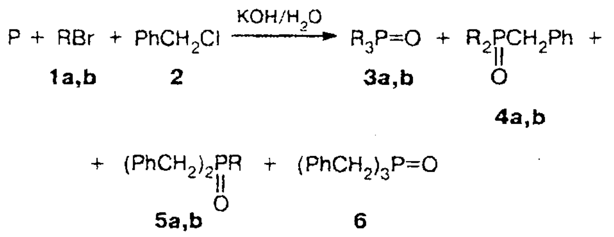
Organyl halides are known[1] to react with red phosphorus in the presence of a strong base (generated in the KOH—DMSO system or under conditions of phase-transfer catalysis) to give the corresponding triorganylphosphine oxides.

In the present work, we showed for the first time the real possibility of one-step synthesis of not easily available unsymmetrical tertiary phosphine oxides, which are promising ligands for catalyst design. A mixture of alkyl bromide (**1**) and benzyl chloride (**2**) was phosphorylated with red phosphorus. The reaction occurs at 65—75 °C in a suspension containing red phosphorus, a concentrated aqueous solution of KOH, dioxane, and benzyl(triethyl)ammonium chloride as a phase-transfer catalyst to give both symmetrical and unsymmetrical tertiary phosphine oxides, namely, trialkyl-, dialkyl(benzyl)-, alkyl(dibenzyl)-, and tribenzylphosphine oxides (**3**—**6**), in a total yield of up to 45%.



$$P + RBr + PhCH_2Cl \xrightarrow{KOH/H_2O} R_3P{=}O + R_2P(O)CH_2Ph + (PhCH_2)_2P(O)R + (PhCH_2)_3P{=}O$$

1a,b **2** **3a,b** **4a,b** **5a,b** **6**

R = Et (**a**); Pr^n (**b**)

Because of the large differences in boiling points and solubility, individual phosphine oxides **4a,b** and **5a,b** are easily isolated from the reaction mixture in 12—17% yield. The yield primarily depends on the ratio of the starting organyl halides. Now, we are searching for preparative conditions of this reaction. Attempts to involve other electrophiles in one-step synthesis of unsymmetrical phosphine oxides are also being continued.

^{1}H and ^{31}P NMR spectra were recorded on a Jeol FX-90 Q spectrometer (90 MHz) in $CDCl_3$ with HMDS as the internal standard (^{1}H) and 85% H_3PO_4 as the external standard (^{31}P).

Synthesis of tertiary phosphine oxides (general procedure). A 60% aqueous solution of potassium hydroxide (67 g) was added with stirring to a mixture of red phosphorus (130 mmol), alkyl bromide (150 mmol), benzyl chloride (50 mmol), and benzyl(triethyl)ammonium chloride (0.1 g) in dioxane (40 mL). The reaction mixture was heated at 65—75 °C for 4 h and cooled. The organic layer was dried with potassium carbonate. The unreacted benzyl chloride, trialkylphosphine oxide **3**, and dialkyl(benzyl)phosphine oxide **4** were isolated by fractionation *in vacuo*. Crystalline products **5** and **6** were separated from the still bottoms. The latter were diluted with ether (15 mL), tribenzylphosphine oxide **6** was filtered off, and the filtrate was concentrated to give phosphine oxide **5**.

Benzyl(diethyl)phosphine oxide (4a), yield 15%, b.p. 166—170 °C (1 Torr) (Ref. 2: 148—149 °C (0.5 Torr)). Found (%): C, 67.37; H, 8.74; P, 15.60. $C_{11}H_{17}OP$. Calculated (%): C, 67.33; H, 8.73; P, 15.78. ^{1}H NMR ($CDCl_3$), δ: 1.02 (m, 6 H, CH_3); 1.58 (m, 4 H, CH_2); 3.06 (d, 2 H, CH_2Ph, ^2J = 14.3 Hz); 7.24 (m, 5 H, Ph). ^{31}P NMR ($CDCl_3$), δ: 48.3.

Dibenzyl(ethyl)phosphine oxide (5a), yield 17%, m.p. 64—66 °C (from hexane). Found (%): C, 73.92; H, 7.54; P, 10.54. $C_{16}H_{19}OP$. Calculated (%): C, 74.40; H, 7.41; P, 11.99. ^{1}H NMR ($CDCl_3$), δ: 0.96 (m, 3 H, CH_3); 1.52 (m, 2 H, CH_2); 3.05 (d, 4 H, CH_2Ph, ^2J = 14.4 Hz); 7.25 (m, 10 H, Ph). ^{31}P NMR ($CDCl_3$), δ: 44.3.

Benzyl(dipropyl)phosphine oxide (4b), yield 12%, b.p. 167—171 °C (1.5 Torr). Found (%): C, 69.63; H, 9.27; P, 12.73. $C_{13}H_{21}OP$. Calculated (%): C, 69.64; H, 9.37; P, 13.84. ^{1}H NMR ($CDCl_3$), δ: 0.98 (m, 6 H, CH_3); 1.58 (m, 8 H, CH_2CH_2); 3.06 (d, 2 H, CH_2Ph, ^2J = 14.4 Hz); 7.25 (m, 5 H, Ph). ^{31}P NMR ($CDCl_3$), δ: 45.2.

Dibenzyl(propyl)phosphine oxide (5b), yield 16%, m.p. 90—92 °C (from hexane). Found (%): C, 75.97; H, 7.98; P, 11.02. $C_{17}H_{21}OP$. Calculated (%): C, 75.00; H, 7.72; P, 11.40. ^{1}H NMR ($CDCl_3$), δ: 0.92 (m, 3 H, CH_3); 1.52 (m, 4 H, CH_2CH_2); 3.05 (d, 4 H, CH_2Ph, ^2J = 14.1 Hz); 7.26 (m, 10 H, Ph). ^{31}P NMR ($CDCl_3$), δ: 42.8.

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