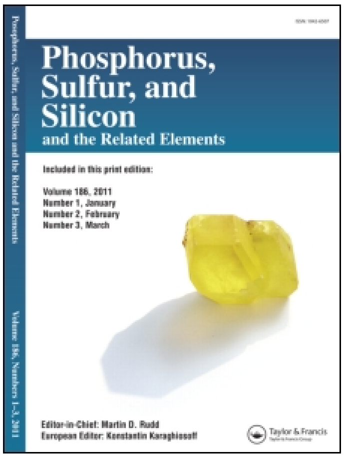

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A CONVENIENT SYNTHESIS OF TERTIARY PHOSPHINES FROM RED PHOSPHORUS AND ARYL- OR HETEROARYLETHENES

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A CONVENIENT SYNTHESIS OF TERTIARY PHOSPHINES FROM RED PHOSPHORUS AND ARYL- OR HETEROARYLETHENES

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Tertiary phosphines $(RCH_2CH_2)_3P$ (R = aryl, heteroaryl) have been obtained in good yields by nucleophilic addition of potassium phosphide, generated from red phosphorus, potassium and *t*-butanol in liquid ammonia, to aryl- and heteroarylethenes

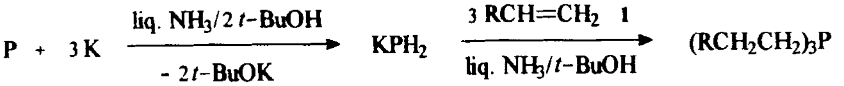
Keywords: red phosphorus, potassium phosphide, weakly electrophilic alkenes, tris(arylethyl)- and tris(heteroarylethyl)phosphines.

INTRODUCTION

Until recently only few data were known about nucleophilic addition of phosphorus-centered anions, generated from elemental phosphorus[1,2] or phosphine[3,4] in the presence of alkali hydroxide, to alkenes. In these reactions, strongly electrophilic olefines, for example, acrylonitrile, acrylamide[1–3], vinyldiorganylphosphine oxides and -sulfides, as well as dialkylvinylphosphonates[4] were usually used.

We previously reported on the formation of secondary phosphines $(RCH_2CH_2)_2PH$ from aryl- or heteroarylethenes, $RCH=CH_2$, **1** and phosphine, generated from red phosphorus and potassium hydroxides[5,6]. This addition occurred in the super base system of type KOH - polar aprotic solvents such as DMSO and HMPT. In the same system red phosphorus reacted with styrene to give tris(2-phenylethyl)phosphine oxide[6,7].

The present communication deals with a convenient selective synthesis of tertiary phosphines **2** by nucleophilic addition of potassium phosphide to aryl-and heteroarylethenes **1**. Potassium phosphide is prepared *in situ* from red phosphorus and potassium in liquid ammonia using *t*-BuOH as proton donor which drastically assists the fission of P-P bond in the phosphorus molecule[8,9].



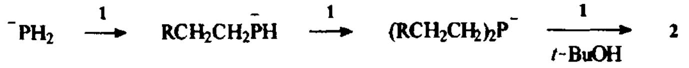
$$P + 3K \xrightarrow[-\ 2t\text{-BuOK}]{\text{liq. } NH_3/2t\text{-BuOH}} KPH_2 \xrightarrow[\text{liq. } NH_3/t\text{-BuOH}]{3\ RCH{=}CH_2\ \mathbf{1}} (RCH_2CH_2)_3P$$

2

R = Ph, 4-F-C_6H_4, 2-furyl, 2-thienyl

RESULTS AND DISCUSSION

The formation of the tertiary phosphines **2** is presumed to proceed through a series of nucleophilic additions of the intermediary phosphides to the double bond.



$$^{-}PH_2 \xrightarrow{\mathbf{1}} RCH_2CH_2\overset{-}{P}H \xrightarrow{\mathbf{1}} (RCH_2CH_2)_2P^{-} \xrightarrow[t\text{-BuOH}]{\mathbf{1}} \mathbf{2}$$

Primary and secondary phosphines are not formed in this reaction even when alkene **1** is used in an amount less than necessary for tertiary phosphine formation (for example, at the molar ratio P : alkene = 1 : 1.5).

It is important that *t*-BuOH be added in two portions: for the generation of KPH_2 and after the introduction of alkene **1** for quenching the carbanion, formed in the last stage of the process. As an example, using styrene, the simultaneous addition of the second portion of *t*-BuOH and alkene was shown to decrease the yield of tris(2-phenylethyl)phosphine (from 82 to 55%). In this case, the protonation of potassium phosphide with *t*-BuOH is supposed to compete.

Styrene, 4-fluorostyrene and 2-vinylthiophene react smoothly, but with 2-vinylfurane the reaction proceeds sluggishly, while 1-methyl–2-vinylpyrrole does not give any product. The low reactivity of the latter olefines may be explained by the (mesomeric) electron donation from the hetero atom, making the double bond less electrophilic.

EXPERIMENTAL

^1H and ^{31}P spectra were recorded on a Bruker AC 300 spectrometer (δ, ppm, $CDCl_3$). The given yields in every case are based on red phosphorus used. All operations were carried out under nitrogen.

Tris (2-arylalkyl) - and tris (2-heteroarylalkyl)phosphines (general procedure). To 1.5 l of anhydrous liquid ammonia, a slurry of red phosphorus (0.2 mole, 6.2 g) in 20 ml of dry THF was introduced, followed by addition of potassium (0.9 mole, 35.1 g), freshly cut into pieces of 0.2–0.4 g, over 10 min. A mixture of *t*-BuOH (0.7 mole, 51.8 g) and 40 ml of diethyl ether or THF was then added dropwise over **1** h with very efficient stirring. The mixture was stirred until the blue colour disappeared and a yellowish suspension formed. To the suspension, alkene 1 (0.8 mole) was added in 5–7 min followed by dropwise addition[10] of a mixture of *t*-BuOH (0.2 mole, 14.8 g) and 10 ml of diethyl ether during 2 h. After an additional **1** h the ammonia was evaporated at ~40°C. To the residue, diethyl ether or pentane (200 ml) and a solution of 100 g of ammonium chloride in 500 ml of water were successively added. After vigorous stirring the layers were separated, followed by three extractions with diethyl ether or pentane. The organic solution was dried over K_2CO_3, the solvent and excess alkene **1** were removed in *vacuo*. Distillation of the remaining liquid at low pressure gave the following tertiary phosphines **2.**

Tris(2-phenylethyl)phosphine, yield 82%, b.p.$_{0.3}$ 220°C, m.p. 30–32°C (lit.[11] gives b.p.$_{0.35}$ 218–224°C). NMR (^1H; ^{31}P): 7.51–7.36 (m), 15H; 2.99–2.91 (m), 6 H; 2.00–1.94 (m), 6 H; -26.8 (P). (Found: C, 82.91; H, 7.87; P, 8.56. Calc. for $C_{24}H_{27}P$: C, 83.20; H, 7.85; P, 8.94%).

Tris[2-(4-F-phenyl)ethyl]phosphine, yield 52%, b.p.$_{0.3}$ 237°C, m.p . 44–46°C. NMR (^1H; ^{31}P): 7.25–7.14 (m), 6 H; 7.01-6.96 (m), 6 H; 2.75–2.72 (m), 6 H; 1.77–1.72 (m), 6 H; -27.8 (P). (Found: C, 71.63; H, 6.24; P, 7.69; F, 13.93. Calc. for $C_{24}H_{24}F_3P$: C, 71.99; H, 6.04; P, 7.74; F, 14.23%).

Tris(2-thienylethyl)phosphine, yield 57%, b.p.$_{0.3}$ 230°C. NMR (^1H; ^{31}P): 7.16–7.14 (m), 3 H; 6.96–6.93 (m), 3 H; 6.85–6.83 (m), 3 H; 3.05–2.96 (m), 6 H; 1.90–1.84 (m), 6 H; -27.1 (P). (Found: C, 59.63; H, 5.53; P, 8.59; S, 26.87. Calc. for $C_{18}H_{21}PS_3$: C, 59.31; H, 5.81; P, 8.50; S, 26.39%).

Tris(2-furylethyl)phosphine, yield 20% (not optimized), b.p.$_{0.3}$ 180°C. NMR (^1H; ^{31}P): 7.4–7.2 (m), 3 H; 6.3–6.1 (m), 3 H; 6.0–5.9 (m), 3 H; 3.1–2.7 (m), 6 H; 2.3–1.9 (m), 6 H; -27. 8 (P). (Found: C, 67.98; H, 6.75; P, 9.45. Calc. for $C_{18}H_{21}O_3P$: C, 68.34; H, 6.69; P, 9.79%).

Acknowledgements

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[10] If to start the addition of t-butanol 2 h after the introduction of alkene **1** is completed, the process of polymerization occurs to give an undistillable mixture.

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