Reactions of alkali metal acetylides with red phosphorus

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The two-step cleavage of red phosphorus with an alkali metal and an alkali metal acetylide (an alkyl halide was added at each step) gives β-substituted acetylenic phosphines.

Acetylenic phosphines are usually synthesised by the reaction of alk-1-ynyllithium with dialkylphosphinous chlorides.[1] Recently,[2] we found the C_{sp}–P bond formation by direct cleavage of the yellow phosphorus molecule (P_4) with but-1-ynyllithium. Here we report that less reactive red phosphorus[†] also reacts with an alkali metal acetylide[‡] (but-1-ynylsodium) in liquid ammonia (Scheme 1) to give, upon alkylation of the reaction mixture, acetylenic phosphines **1** and **2** in low yields (5%).[§]

$$\mathrm{P}_n \xrightarrow{\substack{\text{i, EtC}\equiv\text{CNa, NH}_3\text{ (liquid)}\\ \text{ii, EtBr}}} \underset{\mathbf{1}}{\mathrm{EtC{\equiv}CPEt_2}} + \underset{\mathbf{2}}{\mathrm{(EtC{\equiv}C)_2PEt}}$$

Scheme 1

To improve the yields of acetylenic phosphines (up to 10–12%), a two-step cleavage of the red phosphorus macromolecule in liquid ammonia was used (Scheme 2). One equivalent of potassium metal and an excess of sodium acetylide were used at the first and second steps, respectively. An alkyl halide was added to the reaction mixture at each step.

According to published data,[3] polyphosphide anions **A** are formed at the first step; these ions give corresponding polyalkylphosphines **3** after alkylation. The treatment of the latter with alkali metal acetylides followed by the alkylation of intermediate alkyl(organoethynyl)phosphide anions **B** yields dialkyl(organoethynyl)phosphines **1** and **4**.[¶]

$$\mathrm{P}_n \xrightarrow[\text{NH}_3\text{ (liquid)}]{n\text{K}} \underset{\mathbf{A}}{[\mathrm{P}_n^-]} \xrightarrow{n\text{EtBr}} \underset{\mathbf{3}}{[(\mathrm{PEt})_n]} \xrightarrow{\text{an excess of RC}\equiv\text{CNa}}$$

$$\underset{\mathbf{B}}{n[\mathrm{RC{\equiv}C\bar{P}Et}]} \xrightarrow{\text{an excess of EtBr}} \underset{\substack{\mathbf{1}\ \mathrm{R = Et}\\ \mathbf{4}\ \mathrm{R = Ph}}}{n\mathrm{RC{\equiv}CPEt_2}}$$

Scheme 2

A search for optimum conditions of the synthesis of acetylenic phosphines by direct reactions of red phosphorus with alkali metal acetylides is in progress.

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[†] Red phosphorus was successively washed with an aqueous sodium carbonate solution, acetone and diethyl ether and dried in a vacuum.

[‡] Alkali metal acetylides were prepared from alkali metal amides and corresponding acetylenes in liquid ammonia.[4]

[§] *Reaction of red phosphorus with but-1-ynylsodium and ethyl bromide*: 0.4 mol of but-1-ynylsodium was added to a suspension of 0.1 mol of red phosphorus in 1 dm^3 of liquid ammonia, and the mixture was stirred for 0.5 h. Next, 0.5 mol of ethyl bromide was added dropwise for 1 h, and the reaction mixture was stirred for 3 h until the evaporation of liquid ammonia. Diethyl ether (200 ml) and water (250 ml) were successively added to the residue. After vigorous stirring, the layers were separated followed by triple extraction with diethyl ether. The organic solution was dried with K_2CO_3; the solvent and the by-product (hex-3-yne) were removed *in vacuo*. Distillation of the remaining liquid at a low pressure gave 0.79 g of a product with bp 40–70 °C (0.3 Torr). This product contained (according to GLC) 29% phosphine **1** (yield 2%) and 71% phosphine **2** (yield 3%). All operations were carried out under a nitrogen atmosphere. Spectroscopic data for the mixture are identical to those for the sample obtained previously.[2]

[¶] *General method for the synthesis of* **1** *and* **4**: 0.2 mol of potassium metal was added to a suspension of 0.2 mol of red phosphorus in 1 dm^3 of liquid ammonia, and the mixture was stirred until a blue colour disappeared, and a yellow-brown suspension was formed. Thereafter, 0.2 mol of ethyl bromide was added for 5 min. A suspension of 0.3 mol of an alkali metal acetylide in liquid ammonia was introduced into the reaction mixture. The reaction mixture was stirred for 0.5 h; next, 0.3 mol of ethyl bromide was added dropwise for 1 h. After 0.5 h, the ammonia was evaporated at ~40 °C. Diethyl ether (200 ml) and water (250 ml) were successively added to the residue. After vigorous stirring, the layers were separated followed by triple extraction with diethyl ether. The organic solution was dried with K_2CO_3; the solvent and the by-product (an alkylated acetylide) were removed *in vacuo*. Distillation of the remaining liquid at a low pressure gave phosphines **1** and **4**. All operations were carried out under a nitrogen atmosphere. The residues contained small amounts of di(but-1-ynyl)ethylphosphine **2** and ethyl[bis(phenylethynyl)]phosphine (GLC, GC–MS and ^{31}P NMR data), respectively, among other high-boiling compounds.

But-1-ynyl(diethyl)phosphine **1**: yield 10%, bp 40–45 °C (0.3 Torr). Spectroscopic data are identical to those for the sample obtained previously.[2]

Diethyl(phenylethynyl)phosphine **4**: yield 12%, bp 100–105 °C (0.3 Torr) [lit.,[5] 105–107 °C (0.7 Torr)]. ^{1}H NMR ($CDCl_3$) δ: 1.05–1.35 (m, 6H, Me), 1.6–1.8 (m, 4H, CH_2P), 7.2–7.6 (m, 5H, Ph). ^{13}C NMR ($CDCl_3$) δ: 9.93 (Me, $^2J_{CP}$ 10.65 Hz), 19.29 (CH_2, $^1J_{CP}$ 6.90 Hz), 88.23 ($\equiv$CP, $^2J_{CP}$ 24.0 Hz), 104.52 (PhC$\equiv$), 123.35 (C_{arom}), 128.28 (CH_{arom}), 128.33 (CH_{arom}), 131.66 (CH_{arom}). ^{31}P NMR ($CDCl_3$) δ: –38.5. MS, *m*/*z*: 190 [M^+]. IR (ν/cm^{-1}): 2173 (C$\equiv$C).