Addition of secondary phosphines to phenylcyanoacetylene as a route to functional phosphines

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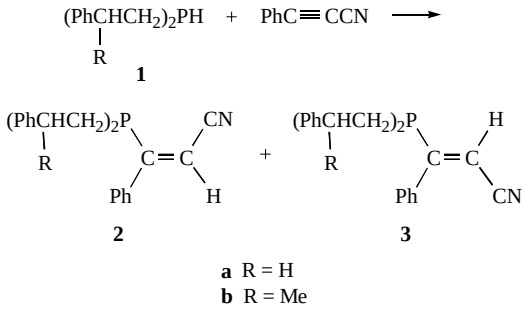
Bis(2-phenylethyl)phosphine **1a** and bis(2-phenylpropyl)phosphine **1b** react chemo- and regioselectively with phenylcyanoacetylene to give [bis(2-phenylalkyl)](1-phenyl-2-cyanoethenyl)phosphines **2** and **3** in quantitative total yields.

Amphiphilic functional phosphines with polar hydrophilic groups and hydrophobic branched chains are promising ligands for the design of metal complex catalysts that combine the properties of phase-transfer and micellar catalysts. The synthesis of these phosphines is a topical problem. Here we report an approach to the synthesis of a new family of ternary arylalkylphosphines bearing an acrylonitrile substituent. The nucleophilic addition of bis(2-phenylethyl)phosphine **1a** and bis(2-phenylpropyl)-phosphine **1b**, which can be easily prepared from elemental phosphorus and arylalkenes,[1] to phenylcyanoacetylene is used as an example.

It is well known that cyanoacetylenes (primarily phenylcyanoacetylene) easily add N-, O- and S-nucleophiles [ammonia,[2] piperidine,[2] N-(*tert*-butyl)hydroxylamine,[3] azoles,[4] imidazolethiones[5] and mercaptoquinolines[6]] to form, in most cases, *Z*-isomers of 3-substituted acrylonitriles. The reaction of secondary phosphines with cyanoacetylene proceeds in the same direction.[7] However, there are no data on the interaction of phenylcyanoacetylene with PH species, while this reaction makes it possible not only to solve the above problem and to synthesise new functional organophosphorus compounds, but also to obtain additional information on the reactivity of disubstituted acetylenes.

The aim of this work was to study the reaction of activated disubstituted acetylenes with secondary phosphines in order to determine its mechanism and chemo-, regio- and stereoselectivity.



Scheme 1 *Reagents and conditions*: molar ratio **1**:PhC≡CCN = 1:1, dioxane, room temperature, 1.5 h (for **1a**), 5 h (for **1b**).

Scheme 1 demonstrates that phosphines **1a** and **1b** add readily to phenylcyanoacetylene giving new [bis(2-phenylalkyl)]-(1-phenyl-2-cyanoethenyl)phosphines **2** and **3** in almost quantitative total yields.† The process is chemo- and regioselective: neither 2-substituted acrylonitriles nor products of further addition of starting phosphine **1** to the double bond of compounds **2** and **3** (even with an excess of **1**) were formed.

The reaction of bis(2-phenylethyl)phosphine **1a** with phenylcyanoacetylene proceeds stereoselectively to afford **2a**; corresponding *E*-isomer **3a** was formed in negligible amounts (~5%). This fact is in agreement with the *trans*-mode of nucleophile addition (in particular, P-nucleophiles[7,8]) to activated acetylenes.[9]

In contrast to phosphine **1a**, more branched bis(2-phenylpropyl)phosphine **1b** reacts with phenylcyanoacetylene to form not only the *Z*-isomer of [bis(2-phenylpropyl)](1-phenyl-2-cyanoethenyl)phosphine **2b**, but also a considerable amount of the *E*-isomer of **3b** (the ratio **2b**:**3b** = 3:2). It is unlikely that phosphine **3b** resulted from post-isomerization of phosphine **2b**, which was formed initially, because the configurational transformation of *Z*-isomer **2b** into *E*-isomer **3b** has been found to occur on heating at 180–200 °C for 5 h. Therefore, the successful competition between the *trans*- and *cis*-addition to a triple bond occurs in the case of phosphine **1b** because of steric hindrances.

Note that the EPR spectrum of the reaction mixture of bis(2-phenylethyl)phosphine **1a** and phenylcyanoacetylene in dioxane exhibits a high-resolution signal as a doublet of multiplets with $g = 2.0029$ and a doublet hyperfine structure constant of ~3 mT. This signal can be attributed[10] to the interaction of an unpaired electron with the phosphorus nucleus; this fact indicates that the reaction can proceed *via* a stage of one-electron transfer. This presumption was also confirmed by UV spectra of the reaction mixture. These spectra exhibited a charge-transfer absorption band at 412 nm, which varied with time.[11]

At the same time, the addition of small amounts of hydroquinone (up to 3 wt%) to the reaction mixture had almost no effect on the product yields and the reaction time. This fact suggests that the reaction is a nucleophilic addition rather than a chain-radical process. It is likely that the reaction proceeds

† *General experimental techniques*. ^{31}P and ^{1}H NMR spectra were measured on a Jeol-90Q spectrometer. IR spectra were recorded on a Specord 75-IR spectrometer. EPR spectra were studied on an SE/X-2547 EPR spectrometer equipped with an NMR magnetometer and a microwave frequency meter (Radiopan, Poland) at room temperature. UV spectra were recorded on a Specord UV-Vis spectrometer.

For **2a** (oil): ^{1}H NMR ($CDCl_3$) δ: 1.96 (m, 4H, CH_2P), 2.65 (m, 4H, CH_2Ph), 5.81 (d, 1H, HC=C, $^{3}J_{PH}$ 16.2 Hz), 7.07–7.37 (m, 15H, Ph). ^{31}P NMR ($CDCl_3$) δ: –13.2.

For **3a**: ^{31}P NMR ($CDCl_3$) δ: –9.9.

For **2b**: ^{1}H NMR ($CDCl_3$) δ: 1.23 (m, 6H, Me), 1.70 (m, 4H, CH_2P), 2.66 (m, 2H, C*H*Ph), 5.74 (d, 1H, HC=C, $^{3}J_{PH}$ 17.9 Hz), 7.19–7.35 (m, 15H, Ph). ^{31}P NMR ($CDCl_3$) δ: –21.4, –22.4, –23.3.

For **3b** (oil): ^{1}H NMR ($CDCl_3$) δ: 1.20 (m, 6H, Me), 1.72 (m, 4H, CH_2P), 2.70 (m, 2H, C*H*Ph), 5.34 (d, 1H, HC=C, $^{3}J_{PH}$ was too small to be determined), 7.20–7.35 (m, 15H, Ph). ^{31}P NMR ($CDCl_3$) δ: –16.7, –16.8, –17.1. Three signals in the ^{31}P NMR spectra of **2b** and **3b** can be explained by the presence of two asymmetrical centres in the molecules of these compounds).

Satisfactory elemental analyses were obtained for phosphines **2** and **3**.

For **4** (it was identified in the mixture with **2a** by ^{1}H and ^{31}P NMR spectroscopy): ^{1}H NMR ($CDCl_3$) δ: 2.42 (m, 4H, CH_2P), 2.90 (m, 4H, CH_2Ph), 6.02 (d, 1H, HC=C, $^{3}J_{PH}$ 29.2 Hz), 7.19–7.37 (m, 15H, Ph). ^{31}P NMR ($CDCl_3$) δ: 38.8.

For **5**: yield 71%, mp 70–74 °C ($CHCl_3$–Et_2O). ^{1}H NMR ([$^{2}H_6$]acetone) δ: 2.70 (d, 3H, Me, $^{2}J_{PH}$ 13.6 Hz), 3.00–3.50 (m, 8H, CH_2P, CH_2Ph), 6.93–7.61 (m, 16H, HC=C, Ph). ^{31}P NMR ([$^{2}H_6$]acetone) δ: 34.53. Found (%): C, 61.88; H, 5.80; I, 23.47; N, 2.73; P, 5.06. Calc. for $C_{26}H_{27}INP$ (%): C, 61.07; H, 5.32; I, 24.83; N, 2.74; P, 6.06.

In the IR spectra of compounds **1**–**5**, an absorption band at 2210 cm^{-1} ($\nu_{C\equiv N}$) was present, and no absorption corresponding to C≡C and C≡N bonds of the initial phenylcyanoacetylene (2270 cm^{-1} with a shoulder) was observed.

via an intermediate ion-radical pair which dissociates to only a small extent.

The structure and configuration of phosphines **2** and **3** were confirmed by ^{1}H and ^{31}P NMR spectroscopy (from the ^{31}P–^{1}H coupling of an ethenyl group[12]) and also by chemical transformations. Thus, phosphine **2a** was oxidised in air to [bis(2-phenylethyl)](*Z*-1-phenyl-2-cyanoethenyl)phosphine oxide **4**. In contrast to the majority of ternary phosphines, the oxidation of **2a** proceeds slowly; this is probably due to a decrease in the electron density at the phosphorus atom as a result of the conjugation of its lone electron pair with the carbon-carbon double bond and next with the nitrile group. Upon the treatment of phosphine **2a** with methyl iodide in dioxane at room temperature, methyl[bis(2-phenylethyl)](*Z*-1-phenyl-2-cyanoethenyl)phosphonium iodide **5** was prepared.

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