(Cyanomethyl)phosphines from Trimethylsilylphosphines

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(Cyanomethyl)phosphines, R<sub>n</sub>-P(CH<sub>3</sub>CN), are known for n = 1. They were prepared from phosphinites and chloroacetonitrile followed by reduction of the product R<sub>n</sub>P(O)CH<sub>3</sub>CN, a method which is not feasible for preparation of (cyanomethyl)phosphines with n = 2 or 3.

We describe here a more general method for preparation of (cyanomethyl)phosphines, viz. reaction of trimethylsilylphosphines with chloroacetonitrile (eqn. 1). Trimethylsilylphosphines

\[ \text{Ph}_{3-n}P(SiMe}_3)_n + n\text{CHCICN} \rightarrow \text{Ph}_{3-n}P(CH_3CN)_n + n\text{Me}_3SiCl \]  

(1)

have been used mostly for preparation of acylphosphines, \(^2\), although one reaction with methyl iodide \(^3\) and a few reactions with reactive chloro compounds, e.g. diethyl dichloromaleate, \(^5\) are known. Less reactive alkyl chlorides do not react, e.g. Ph<sub>3</sub>SiMe<sub>3</sub> is reported not to react with CICH<sub>2</sub>CH<sub>2</sub>Cl. \(^6\)

We have found that CICH<sub>2</sub>CN reacted in a moderately exothermic reaction with Ph<sub>n</sub>P(SiMe<sub>3</sub>), n = 1, 2, or 3, and Me<sub>3</sub>SiCl could be isolated in 80–90% yield. In the cases n = 1 and 2, Ph<sub>2</sub>PCH<sub>2</sub>CN and PhP(CH<sub>3</sub>CN), respectively, were isolated in good yields by distillation, but no P(CH<sub>3</sub>CN)<sub>3</sub> could be obtained in this way. The reaction in the case of n = 3 yields predominantly a dark intractable material which is apparently polymeric. It contained, however, some P(CH<sub>3</sub>CN)<sub>3</sub> (NMR) which could be isolated in low yield by sublimation.

In contrast to Ph<sub>2</sub>PCH<sub>2</sub>CN, which is oxidized slowly in air, \(^1\) PhP(CH<sub>3</sub>CN)<sub>3</sub> and P(CH<sub>3</sub>CN)<sub>3</sub> are stable towards air in the solid state. They are rather easily oxidized in solution or when melted. Their nucleophilic reactivities are very low, as expected. \(^1\) Thus P(CH<sub>3</sub>CN)<sub>3</sub> is unchanged after 24 h reflux with an excess of ETL in acetone.

The reaction of trimethylsilylphosphines with chloroacetonitrile thus seems to be a convenient method of obtaining cyanomethylphosphines with one or two cyanomethyl groups, but less so with three cyanomethyl groups. We are presently examining other synthetic pathways to cyanomethylphosphines in general and P(CH<sub>3</sub>CN)<sub>3</sub> in particular.

Experimental. Analyses were carried out by the Microanalysis Department of this laboratory. NMR spectra were obtained on a Bruker HX-90 E Spectrometer. Chemical shifts (ppm) are relative to internal TMS for ¹H data (δ<sub>H</sub>) and external 85% H<sub>3</sub>P<sub>4</sub>O for ³¹P data (δ<sub>P</sub>), and are given as positive for low-field shifts. All stated ¹H – ³¹P couplings have been verified by decoupling experiments. ¹H spectra were recorded on a Perkin Elmer 337 Grating Infrared Spectrometer, MS spectra on an AEI-902 Mass Spectrometer at 70 eV, inlet temp. 180 °C.

All reactions with phosphines were performed under nitrogen. The trimethylsilylphosphines were prepared by published methods and their purity checked by °H and ³¹P NMR. Ph<sub>3</sub>SiMe<sub>3</sub> gave δ<sub>H</sub> = 67.3 (neat). Ph<sub>2</sub>P(SiMe<sub>3</sub>)<sub>2</sub>, b.p. 65–66 °C/0.2 mmHg, δ<sub>P</sub> = 136.0 (CDCl<sub>3</sub>) (lit. b.p. 76 °C/0.05 mmHg, 67 °C/0.01 mmHg \(^7\) could not be corroborated, δ<sub>P</sub> = 137 (neat)\(^8\)). Ph<sub>3</sub>P(SiMe<sub>3</sub>)<sub>3</sub>, 17% yield, b.p. 64–66 °C/1.2 mmHg, δ<sub>P</sub> = 252.0 (neat), 249.9 (CDCl<sub>3</sub>) (lit. 62% yield and b.p. 50–52 °C/0.1 mmHg \(^8\) could not be obtained, b.p. 105 °C/16 mmHg; δ<sub>P</sub> = 251.2 (neat)\(^9\)).

 Dichlorophenylphosphinocyanidene (Ph<sub>2</sub>PCH<sub>2</sub>CN). Ph,P(SiMe<sub>3</sub>) (12.9 g, 0.05 mol) and CICH<sub>2</sub>CN (3.8 g, 0.05 mol) were mixed and stirred at 25 °C in a flask equipped with a Claissen head with condenser. After the exothermic reaction had subsided the mixture was heated in an oil bath (temp. ca. 110 °C), whereupon Me<sub>3</sub>SiCl (4.4 g, 80%) distilled. The red-brown residue gave upon distillation in vacuo (same apparatus) Ph<sub>2</sub>PCH<sub>2</sub>CN (8.0 g, 71%), b.p. 138–140 °C/0.1 mmHg, δ<sub>P</sub> = 17.8 (CDCl<sub>3</sub>) (lit.\(^1\) 146–147 °C/0.35 mmHg, δ<sub>P</sub> = 17.8 (CDCl<sub>3</sub>)). No impurities were observable from its °H NMR spectrum.

Phenylphosphinodicyanidene (PhP(CH<sub>3</sub>CN)). Ph,P(SiMe<sub>3</sub>) (5.1 g, 0.02 mol) and CICH<sub>2</sub>CN (3.0 g, 0.04 mol) gave when treated as above Me<sub>3</sub>SiCl (3.9 g, 90%) and PhP(CH<sub>3</sub>CN) (1.9 g, 50%), b.p. 148–150 °C/0.25 mmHg, m.p. 59–62 °C. Anal. C<sub>11</sub>H<sub>9</sub>N<sub>2</sub>P: C, H, N, NMR (ca. 2 M in CDCl<sub>3</sub>): δ<sub>P</sub> = 31.0 (ABX system); δ<sub>HH</sub> (A) 2.866, 2.802, J<sub>PHH</sub> 5.4 Hz, J<sub>PHH</sub> 16.7 Hz. Ph: δ<sub>H</sub> 7.4–7.7 (m). IR (KBr): \(^\infty\) 2246, 2234 cm<sup>–1</sup>. Ph,P(CH<sub>3</sub>CN) is very soluble in CHCl<sub>3</sub> and insoluble in H<sub>2</sub>O.

Phenylphosphinotricyanidene (P(CH<sub>3</sub>CN))<sub>2</sub>. Ph,P(SiMe<sub>3</sub>) (5.0 g, 0.02 mol) and CICH<sub>2</sub>CN (4.5 g, 0.08 mol) gave when treated as above Me<sub>3</sub>SiCl (5.2 g, 80%) and a dark red residue. °H NMR (CDCl<sub>3</sub>) on the residue showed as the most prominent signal a doublet, δ<sub>H</sub> 2.89, J 5.3 Hz, δ<sub>P</sub> = 33.5 (determined by ³¹P decoupling) assigned to P(CH<sub>3</sub>CN)₂. The amount of P(CH<sub>3</sub>CN)₂ was estimated as ca. 30% of the theoretical yield by comparison of the P(CH<sub>3</sub>CN)₂ signal with that from a known amount of added CH<sub>3</sub>Cl<sub>2</sub>. Attempted vacuum distillation through a Claissen head (0.2–0.5 mmHg, bath up to 220 °C) gave no distillate, and the residue turned black. However, a small amount (ca. 0.5 ml) of a liquid consisting mostly of CH<sub>3</sub>CN (°H NMR) had collected in the dry-ice trap. Sublimation of the residue.
(0.1 mmHg, 180 °C) gave a small amount (0.3 g, 10 %) of slightly impure (yellow) P(CH$_2$CN)$_3$, which on sublimation or recrystallization from water (with a small amount of hydroquinone) gave the pure compounds as colourless needles, m.p. 112–113 °C. Anal. C$_4$H$_8$N$_4$P: C, H, N. NMR: $\delta_P = -33.4$, $\delta_H = 2.88$, $^3J_{PH} = 5.3$ Hz (CD$_2$CN), $\delta_P = -32.9$, $\delta_H = 3.12$, $^3J_{PH} = 4.3$ Hz [(CD$_3$)$_2$SO]. IR (KBr): $\nu_{CN}$ 2245 cm$^{-1}$. MS: m/e 151 (M$^+$, 41 %), 111 (M$^+$ – CH$_2$CN, 100 %), 71 (M$^+$ – 2CH$_2$CN, 36 %), “metastable” 81.6 (151→111). P(CH$_2$CN)$_3$ is soluble in DMSO, CH$_2$CN, and (CH$_3$)$_2$CO, slightly soluble in CH$_3$OH and H$_2$O, and nearly insoluble in CHCl$_3$.

Phenylphosphonouclidiacetonitrile (PhP(O)·(CH$_2$CN)$_3$)$_1$. PhP(CH$_2$CN)$_3$ (1.88 g) in CH$_2$Cl$_2$ (35 ml) was oxidized by bubbling NO$_2$ through the stirred solution until a yellow colour remained. The solution was evaporated to dryness and the residue recrystallized from H$_2$O. Yield 1.43 g (79 %), m.p. 135.5–136.5 °C. Anal. C$_6$H$_8$N$_4$OP: C, H, N. NMR [(CD$_3$)$_2$SO]: $\delta_P = 26.4$, $\delta_H = 3.99$, $^3J_{PH} = 14.2$ Hz. IR (KBr): $\nu_{CN}$ 2259, 2250 cm$^{-1}$, $\nu_{PO}$ 1200 cm$^{-1}$. PhP(O)(CH$_2$CN)$_3$ is very soluble in DMSO, (CH$_3$)$_2$CO and CH$_2$CN, and slightly soluble in CHCl$_3$ and H$_2$O.

Phosphoryltriacetonitrile (P(O)(CH$_2$CN)$_3$)$_1$. To P(CH$_2$CN)$_3$ (0.15 g) in hot water (3 ml) was added dropwise 35 % H$_2$O$_2$ (0.5 ml). The oxide precipitated during the reaction. After cooling to 0 °C the compound was collected by centrifugation, washed with water and dried in vacuo. Yield 0.15 g (90 %), m.p. ca. 260 °C (dec.). Anal. C$_6$H$_8$N$_4$OP: C, H, N. NMR [(CD$_3$)$_2$SO]: $\delta_P = 27.9$, $\delta_H = 3.81$, $^3J_{PH} = 14.8$ Hz. IR (KBr): $\nu_{CN}$ 2256 cm$^{-1}$, $\nu_{PO}$ 1229, 1225, 1204, 1197 cm$^{-1}$. P(O)(CH$_2$CN)$_3$ is very soluble in DMSO, slightly soluble in H$_2$O and CH$_2$CN, and insoluble in CHCl$_3$.


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