

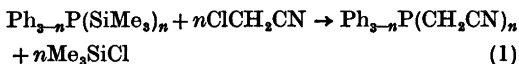
(Cyanomethyl)phosphines from Trimethylsilylphosphines

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(Cyanomethyl)phosphines, $R_{3-n}P(CH_2CN)_n$, are known for $n=1$.¹ They were prepared from phosphinites and chloroacetonitrile followed by reduction of the product $R_2P(O)CH_2CN$, 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



have been used mostly for preparation of acylphosphines,^{2,3} although one reaction with methyl iodide⁴ 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_2PSiMe_3 is reported not to react with $ClCH_2CH_2Cl$.⁵

We have found that $ClCH_2CN$ reacted in a moderately exothermic reaction with $Ph_{3-n}P(SiMe_3)_n$, $n=1, 2$, or 3, and Me_3SiCl could be isolated in 80–90% yield. In the cases $n=1$ and 2, Ph_2PCH_2CN and $PhP(CH_2CN)_2$, respectively, were isolated in good yields by distillation, but no $P(CH_2CN)_3$ 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 $P(CH_2CN)_3$ (NMR) which could be isolated in low yield by sublimation.

In contrast to Ph_2PCH_2CN , which is oxidized slowly in air,¹ $PhP(CH_2CN)_2$ and $P(CH_2CN)_3$ 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 $P(CH_2CN)_3$ is unchanged after 24 h reflux with an excess of EtI 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 $P(CH_2CN)_3$ 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_H) and external 85% H_3PO_4 for ^{31}P data (δ_P), and are given as positive for low-field shifts. All stated $^1H-^{31}P$ couplings have been verified by decoupling experiments. IR 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 1H and ^{31}P NMR: Ph_2PSiMe_3 ,⁶ $\delta_P -57.3$ (neat). $PhP(SiMe_3)_2$,⁷ b.p. 65–66 °C/0.2 mmHg, $\delta_P -136.0$ ($CDCl_3$) (lit. b.p. 76 °C/0.05 mmHg,⁷ and 67 °C/0.01 mmHg⁸ could not be corroborated, $\delta_P -137$ (neat)⁹). $P(SiMe_3)_3$,⁹ 17% yield, b.p. 64–65 °C/1.2 mmHg, $\delta_P -252.0$ (neat), –249.9 ($CDCl_3$) (lit. 62% yield and b.p. 50–52 °C/0.1 mmHg⁹ could not be obtained, b.p. 105 °C/16 mmHg,¹⁰ $\delta_P -251.2$ (neat)¹¹).

Diphenylphosphinoacetonitrile (Ph_2PCH_2CN). Ph_2PSiMe_3 (12.9 g, 0.05 mol) and $ClCH_2CN$ (3.8 g, 0.05 mol) were mixed and stirred at 25 °C in a flask equipped with a Claisen head with condenser. After the exothermic reaction had subsided the mixture was heated in an oil bath (temp. *ca.* 110 °C), whereupon Me_3SiCl (4.4 g, 80%) distilled. The red-brown residue gave upon distillation *in vacuo* (same apparatus) Ph_2PCH_2CN (8.0 g, 71%), b.p. 138–140 °C/0.1 mmHg, $\delta_P -17.8$ ($CDCl_3$) [lit.¹ 146–147 °C/0.35 mmHg, $\delta_P -17.8$ ($CDCl_3$)]. No impurities were observable from its 1H NMR spectrum.

Phenylphosphinediylacetonitrile ($PhP(CH_2CN)_2$). $PhP(SiMe_3)_2$ (5.1 g, 0.02 mol) and $ClCH_2CN$ (3.0 g, 0.04 mol) gave when treated as above Me_3SiCl (3.9 g, 90%) and $PhP(CH_2CN)_2$ (1.9 g, 50%), b.p. 148–150 °C/0.25 mmHg, m.p. 59–62 °C. Anal. $C_{10}H_9N_2P$: C, H, N. NMR (*ca.* 2 M in $CDCl_3$): $\delta_P -31.0$. CH_2CN (ABX system): $\delta_{H(A)} 2.866$, $^2J_{PH(A)} 5.9$ Hz, $\delta_{H(B)} 2.820$, $^2J_{PH(B)} 5.4$ Hz, $^2J_{H(A)H(B)} 16.7$ Hz. Ph: $\delta_H 7.4-7.7$ (m). IR (KBr): $\nu_{CN} 2246, 2234$ cm^{-1} . $PhP(CH_2CN)_2$ is very soluble in $CHCl_3$ and insoluble in H_2O .

Phosphinetriyltriacetonitrile ($P(CH_2CN)_3$). $P(SiMe_3)_3$ (5.0 g, 0.02 mol) and $ClCH_2CN$ (4.5 g, 0.06 mol) gave when treated as above Me_3SiCl (5.2 g, 80%) and a dark red residue. 1H NMR (CD_3CN) on the residue showed as the most prominent signal a doublet, $\delta_H 2.89$, $J 5.3$ Hz, $\delta_P -33.5$ (determined by ^{31}P decoupling) assigned to $P(CH_2CN)_3$. The amount of $P(CH_2CN)_3$ was estimated as *ca.* 30% of the theoretical yield by comparison of the $P(CH_2CN)_3$ signal with that from a known amount of added CH_2Cl_2 . Attempted vacuum distillation through a Claisen 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_3CN (1H 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) $P(CH_2CN)_3$, which on resublimation or recrystallization from water (with a small amount of hydroquinone) gave the pure compounds as colourless needles, m.p. 112–113 °C. Anal. $C_6H_6N_3P$: C, H, N. NMR: δ_P –33.4, δ_H 2.88, $^3J_{PH}$ 5.3 Hz (CD_3CN), δ_P –32.9, δ_H 3.12, $^3J_{PH}$ 4.3 Hz [$(CD_3)_2SO$]. IR (KBr): ν_{CN} 2245 cm^{-1} . MS: m/e 151 (M^+ , 41 %), 111 ($M^+ - CH_2CN$, 100 %), 71 ($M^+ - 2CH_2CN$, 36 %), “metastable” 81.6 (151 → 111). $P(CH_2CN)_3$ is soluble in DMSO, CH_3CN , and $(CH_3)_2CO$, slightly soluble in CH_3OH and H_2O , and nearly insoluble in $CHCl_3$.

Phenylphosphonyldiacetonitrile ($PhP(O)-(CH_2CN)_2$). $PhP(CH_2CN)_2$ (1.88 g) in CH_2Cl_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_2O . Yield 1.43 g (70 %), m.p. 135.5–136.5 °C. Anal. $C_{10}H_8N_2OP$: C, H, N. NMR[$(CD_3)_2SO$]: δ_P 26.4, CH_2CN : δ_H 3.99, $^3J_{PH}$ 14.2 Hz. IR (KBr): ν_{CN} 2259, 2250 cm^{-1} , ν_{PO} 1200 cm^{-1} . $PhP(O)(CH_2CN)_2$ is very soluble in DMSO, $(CH_3)_2CO$ and CH_3CN , and slightly soluble in $CHCl_3$ and H_2O .

Phosphoryltriacetonitrile ($P(O)(CH_2CN)_3$). To $P(CH_2CN)_3$ (0.15 g) in hot water (3 ml) was added dropwise 35 % H_2O_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. $C_6H_6N_3OP$: C, H, N. NMR[$(CD_3)_2SO$]: δ_P 27.9, δ_H 3.81, $^3J_{PH}$ 14.8 Hz. IR (KBr): ν_{CN} 2256 cm^{-1} , ν_{PO} 1229, 1225, 1204, 1197 cm^{-1} . $P(O)(CH_2CN)_3$ is very soluble in DMSO, slightly soluble in H_2O and CH_3CN , and insoluble in $CHCl_3$.

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