A Convenient Synthesis of (Cyanomethyl)phosphines

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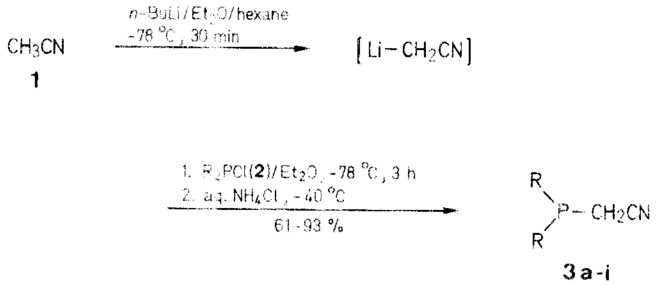
Dialkyl- and diaryl(cyanomethyl)phosphines were conveniently prepared in 61–93% yields by the reaction of the corresponding diorganochlorophosphine with the lithium derivative of acetonitrile.

(Cyanomethyl)phosphines as examples of tertiary phosphines with functional substituents have recently attracted considerable interest. This is due largely to the interesting structural and chemical properties of their complexes with transition metals.[1–5] Dialkyl- and diaryl(cyanomethyl)phosphines have hitherto been prepared by the Arbuzov reaction of ethyl phosphinites with chloroacetonitrile to give the corresponding (cyanomethyl)phosphine oxides followed by reduction with diphenylsilane at 150–240 °C.[6,7] This method has been successfuly applied only to the synthesis of dimethyl-, diethyl-, and diphenyl(cyanomethyl)phosphines. In the cases of synthesis of (cyanomethyl)phosphines containing secondary or tertiary alkyl substituents, the first step has been deviated from the normal Arbuzov reaction to give phosphinic chlorides as major product.[6,8] This deviation is ascribed to competitive attack by phosphinites on the chlorine atom of chloroacetonitrile. Diphenyl(cyanomethyl)phosphine has been prepared also by the reaction of diphenyl(trimethylsilyl)phosphine with chloroacetonitrile[9] or by desulfuration of diphenyl(cyanomethyl)phosphine sulfide.[1] Dichloro(cyanomethyl)phosphine has been prepared in 23% yield by treating tributylstannylacetonitrile with phosphorus trichloride.[10] These methods are tedious and cumbersome, or use difficultly obtainable starting materials.

We now report here a convenient and general method for the synthesis of (cyanomethyl)phosphines, which consists of the reaction of dialkyl- and diarylchlorophosphines with an excess of the lithium derivative of acetonitrile in anhydrous ether at −78 °C.[11]



The yields of (cyanomethyl)phosphines containing secondary or tertiary alkyl substituents are above 90%. In the cases of primary alkyl substituents the expected product **3** was isolated in *ca.* 60% yield, together with a small amount of diphosphino-substituted acetonitrile which was readily removed by distillation (Tables 1 and 2).

Table 1. (Cyanomethyl)phosphines **3** Prepared

Product	R	Yield[a] (%)	b.p. (°C)/mbar[b]	Molecular Formula[c] or Lit. b.p. (°C)/mbar
3a	C_2H_5	61	85–86/13	90–92/1.7[6]
3b	n-C_3H_7	62	69–71/3	$C_8H_{16}NP$ (157.2)
3c	i-C_3H_7	90	64.5–65/3	92–92.5/7[6]
3d	n-C_4H_9	63	83–85/3	$C_{10}H_{20}NP$ (185.2)
3e	i-C_4H_9	63	73–75/1	$C_{10}H_{20}NP$ (185.2)
3f	s-C_4H_9	91	89–90/3	$C_{10}H_{20}NP$ (185.2)
3g	t-C_4H_9	93	74–75/1	118–119/8[6]
3h	c-C_6H_{11}	92	152–153/3	$C_{14}H_{24}NP$ (237.3)
3i	C_6H_5	77	165–166/2	146–147/0.5[6]

[a] Isolated yield based on **2**.
[b] Uncorrected.
[c] Satisfactory microanalyses obtained: C ±0.34, H ±0.25, N ±0.15, P ±0.31.

Table 2. Spectral Data of (Cyanomethyl)phosphines **3**

Compound	IR (film)[a] ν_{CN}(cm^{-1})	^{31}P-NMR[b] ($CDCl_3$/$H_3PO_{4(ext)}$) δ	^{1}H-NMR ($CDCl_3$/TMS)[b] δ, J(Hz)
3a	2220	−24.53	0.96–1.32 (m, 6H); 1.52–1.76 (m, 4H); 2.40 (d, 2H, J = 4.8)
3b	2230	−34.09	0.94–1.11 (m, 6H); 1.40–1.65 (m, 8H); 2.39 (d, 2H, J = 5.4)
3c	2240	0.83	1.04–1.30 (m, 12H), 1.79–2.04 (m, 2H); 2.35 (d, 2H, J = 5.4)
3d	2230	−37.65	0.85–1.00 (m, 6H); 1.28–1.65 (m, 12H); 2.39 (d, 2H, J = 6.3)
3e	2230	−41.07	0.90–1.22 (m, 12H); 1.25–2.05 (m, 6H); 2.36 (d, 2H, J = 6.3)
3f	2240	−5.80; −5.72;	0.92–1.30 (m, 10H); 1.30–1.95 (m, 8H); 2.30–2.44 (m, 2H)
3g	2250	−4.41[c] 27.01	1.06 (d, 18H, J = 10.8); 2.35 (d, 2H, J = 2.0)
3h	2230	−7.72	1.00–1.50 (m, 10H); 1.50–2.10 (m, 12H); 2.34 (d, 2H, J = 4.5)
3i	2280	−22.63	2.85 (d, 2H, J = 4.5); 7.40 (m, 10H)

[a] Recorded on an IR-440 Infrared spectrophotometer.
[b] Obtained on a FX-90 Q spectrometer at 90 M Hz.
[c] Multiplicity is observed due to chirality of the molecule.

(Cyanomethyl)phosphines 3; General Procedure:
A 2 molar hexane solution of BuLi (21 mL, 42 mmol) is added dropwise to a stirred solution of acetonitrile (1.7 g, 42 mmol) in dry ether (30 mL) at −78 °C under N_2. After 30 min, a solution of the diorganochlorophosphine[12,13] (20 mmol) in dry ether (15 mL) is added. After stirring for 3 h at −78 °C, the mixture is warmed to −40 °C and a 10% aqueous solution of NH_4Cl (15 mL) is added dropwise. The organic phase is separated, washed with water (3 × 10 mL), dried ($MgSO_4$) and the solvent is removed. Distillation of the residue affords pure **3** (Tables 1 and 2).

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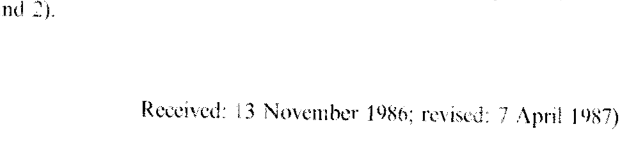

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