

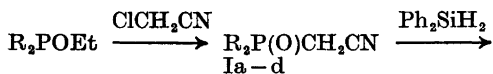
Reduction of Phosphinoacetonitriles to Phosphinoacetonitriles

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Four phosphinoacetonitriles, R_2PCH_2CN , have been prepared from the corresponding phosphine oxides by reduction with diphenylsilane. Their reactivities have been investigated. The results show that a cyanomethyl substituent lowers both the nucleophilic reactivity and the rate of oxidation of a tertiary phosphine.

Cyano groups are strong electron withdrawing substituents which generally lower the nucleophilic reactivity of nearby nucleophilic centers. Thus $P(CH_2CH_2CN)_3$ is a much weaker nucleophile than Et_3P and even Ph_3P .¹ A cyanomethyl substituent is expected to lower the nucleophilic reactivity more than a 2-cyanoethyl substituent, but not so strongly as a directly bonded cyano group. For example, the phosphorus atom in $P(CN)_3$ ² has lost nearly all nucleophilic properties and becomes electrophilic. Cyanomethylphosphines, $R_nP(CH_2CN)_{3-n}$, are virtually unknown in the literature. Two compounds, $P(CH_2CN)_3$ ³ and Ph_2PCH_2CN ,⁴ have been mentioned in patents, but neither physical data nor preparative directions have been given. As a part of a study of the preparation and properties of cyanomethylphosphines we now describe some phosphinoacetonitriles, II, prepared by the following sequence:



R_2PCH_2CN
IIa-d

R = a: Et; b: Prⁱ; c: Bu^t; d: Ph.

The first step is the well-known Arbuzov reaction which has been shown to give high

yields of Ia⁵ and Id.⁶ When applied to Prⁱ-POEt the expected compound, Ib, was isolated in 80 % yield, together with a small amount of Prⁱ₂P(O)Cl. However, Bu^t₂POEt gives equal amounts of Bu^t₂P(OEt)CHCN and Bu^t₂P(O)Cl. Phosphine oxide Ic is obtained only by subsequent addition of HCl to this mixture. This deviation from the normal Arbuzov reaction is ascribed to competitive attack by R₂POEt on the chlorine atom of ClCH₂CN when R is sterically demanding. The reaction will be described in detail in a forthcoming report.⁷

The last step is the reduction of the phosphinoacetonitriles I to the phosphinoacetonitriles II. Whereas lithium aluminium hydride could not be used in presence of cyano groups, diphenylsilane was found to reduce I to II in high yields at 150–240 °C.

Silanes have been used previously for the reduction of various phosphoryl compounds to primary, secondary, or tertiary phosphines.^{8,9} We attempted similar reductions of Ph(EtO)-P(O)CH₂CN (to PhPHCH₂CN) and (EtO)₂-P(O)CH₂CN (to PH₂CH₂CN) with diphenylsilane. However, after 4 h at 160–190 °C only CH₃CN (ca. 40 and 60 %, resp.) could be isolated by distillation.

The phosphines II were characterized by ³¹P NMR, ¹H NMR and IR spectroscopy (Table 1). The phosphorus chemical shifts are displaced high-field relative to the phosphine oxides I, and show the expected¹⁰ variation with the substituents R. The coupling constants ²J_{PH} of II are smaller than those of I, as generally found for ²J_{PH} of methylphosphines relative to methylphosphine oxides. The small

Table 1. ^{31}P NMR, ^1H NMR, and IR data^a for phosphinoylacetonitriles and phosphinoacetonitriles.

No.	Compound	δ_{P}	δ_{H}^b	$^2J_{\text{PH}}^b$	ν_{CN}
Ia	$\text{Et}_3\text{P}(\text{O})\text{CH}_2\text{CN}$	47.3	2.96	14.2	2252
Ib	$\text{Pr}^i_3\text{P}(\text{O})\text{CH}_2\text{CN}$	53.7	2.84	13.5	2249
Ic	$\text{Bu}^t_3\text{P}(\text{O})\text{CH}_2\text{CN}$	58.2	2.82	12.6	2248
Id	$\text{Ph}_3\text{P}(\text{O})\text{CH}_2\text{CN}$	25.0	3.39	15.1	2253
IIa	$\text{Et}_2\text{PCH}_2\text{CN}$	-24.4	2.42	5.1	2234
IIb	$\text{Pr}^i_2\text{PCH}_2\text{CN}$	0.7	2.36	4.5	2238
IIc	$\text{Bu}^t_2\text{PCH}_2\text{CN}$	27.0	2.36	2.5	2243
IId	$\text{Ph}_2\text{PCH}_2\text{CN}$	-17.8	2.89	4.4	2242

^a NMR: Ca. 10 % solutions in CDCl_3 at ca. 30 °C, chemical shifts in ppm relative to internal TMS (δ_{H}) or external 85 % H_3PO_4 (δ_{P}), coupling constants (J) in Hz. Chemical shifts are positive for low-field shifts. IR: Ca. 10 % solutions in CHCl_3 at ca. 25 °C, ν in cm^{-1} . ^b For the CH_2CN group.

values of $^2J_{\text{PH}}$ found for $\text{R}_2\text{P}(\text{O})\text{CH}_2\text{X}$ compounds where X is an electronegative substituent¹¹ are not observed in the case of I. The presence of nitrile groups are evident from the sharp band found in the IR spectra in the 2235–2255 cm^{-1} region.¹² IIa was further characterized by reaction with ethyl bromide to give $\text{Et}_3\text{P}^+\text{CH}_2\text{CN Br}^-$, which was identical with the compound obtained from Et_3P and BrCH_2CN .

The nucleophilic reactivity of compounds II are low, as expected. Although IIa dissolves in CS_2 to give a red solution, no adduct could be isolated. Compounds IIb and IIc gave only faintly red solutions. Alkyl halides react slowly with IIa–d to give quaternary salts. Kinetic measurements on the reaction of IId with EtI in acetone at 35 °C, using the conductivity method of Henderson and Buckler,¹ showed, that IId reacts 8 times slower than Ph_3P and 22 times slower than Ph_2EtP . From the equation given by Henderson and Buckler¹ a Taft σ^* value of +1.7 for the CH_2CN group is calculated. This is in agreement with the σ^* value of +1.71 given by Stevenson and Williamson.¹³

The phosphines II are oxidized by exposure to air, although slowly. Thus only 30 % of IId was oxidized to Id when a few drops of IId was exposed to air on a watchglass for 72 h. The relative rates of oxidation of II in an oxygen atmosphere, initiated by azobis-

isobutyronitrile (AIBN), were estimated by competition experiments. IId was mixed with approximately equal amounts of IIa, IIb, IIc, or Ph_3P and the mixtures were oxidized at ca. 100 °C with a deficit of oxygen in the presence of AIBN. The ratios I/II were determined by NMR. Only small amounts of oxidation products other than I were observed. Assuming the same rate expressions (first order in R_2P) for these oxidation reactions, relative rate constants were calculated:

Compound	k_{rel}
$\text{Et}_2\text{PCH}_2\text{CN}$	6.2
$\text{Pr}^i_2\text{PCH}_2\text{CN}$	2
$\text{Bu}^t_2\text{PCH}_2\text{CN}$	1.1
$\text{Ph}_2\text{PCH}_2\text{CN}$	1.0
Ph_3P	1.7

Although data for comparison are scarce in the literature,^{14,15} these results indicate that (i) a cyanomethyl group reduces the rate of oxidation of a phosphine ($\text{Ph}_2\text{PCH}_2\text{CN} < \text{Ph}_3\text{P}$ and, presumably, $\text{Ph}_2\text{P} < \text{Ph}_2\text{EtP}$), (ii) there seems to be a steric effect on the rate ($\text{Et}_2\text{PCH}_2\text{CN} > \text{Pr}^i_2\text{PCH}_2\text{CN} > \text{Bu}^t_2\text{PCH}_2\text{CN}$).

EXPERIMENTAL

Analyses were carried out by the Micro-analysis Department of this laboratory. IR spectra were obtained on a Perkin Elmer 337 Grating Infrared Spectrometer. NMR spectra were recorded on a Bruker HX-90 E Spectrometer. All NMR spectra were run in CDCl_3 at ca. 30 °C with internal deuterium lock on CDCl_3 . Chemical shifts (ppm) are relative to internal TMS for ^1H spectra (δ_{H}) and external 85 % H_3PO_4 for ^{31}P spectra (δ_{P}), and are given as positive for lowfield shifts. The δ_{P} values are in most cases obtained from ^1H spectra by ^{31}P selective decoupling, and all assignments of coupling to phosphorus have been verified by ^{31}P decouplings.

Phosphines and phosphinites were handled in a nitrogen atmosphere. The following compounds were prepared according to the literature: Pr^i_2POEt ,¹⁶ $\text{Et}_2\text{P}(\text{O})\text{CH}_2\text{CN}$,⁵ $\text{Bu}^t_2\text{P}(\text{O})\text{CH}_2\text{CN}$,⁷ $\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{CN}$,⁶ $\text{Ph}(\text{EtO})\text{P}(\text{O})\text{CH}_2\text{CN}$,¹⁷ and $(\text{EtO})_2\text{P}(\text{O})\text{CH}_2\text{CN}$.¹⁸

P,P-Diosopropylphosphinoylacetonitrile (Ib). Pr^i_2POEt (16.2 g, 0.10 mol) was added in ca. 2 ml portions to slightly heated (ca. 50 °C) ClCH_2CN (8.3 g, 0.11 mol) with stirring. The reaction was strongly exothermic and a reflux condenser was necessary. The reaction mixture was distilled *in vacuo* through a Claisen head. A forerun, b.p. 61–63 °C/0.5 mmHg (0.5 g)

consisted mainly of $\text{Pr}_2\text{P}(\text{O})\text{Cl}$ (lit.¹⁹ b.p. $50^\circ\text{C}/0.2$ mmHg. NMR: CH_3 : δ_{H} 1.15–1.50, multiplet, CH : δ_{H} 2.36, $^2J_{\text{PH}}$ ca. 7 Hz, $^3J_{\text{HH}}$ ca. 7 Hz, in good agreement with literature.²⁰ δ_{P} 86.8). $\text{Pr}_2\text{P}(\text{O})\text{CH}_2\text{CN}$ distilled at 121.5 – $122.5^\circ\text{C}/0.30$ mmHg (13.8 g, 80 %). The product crystallized upon standing, m.p. 58 – 61°C . It is strongly hygroscopic and satisfactory elemental analysis could not be obtained. However, ^1H NMR showed no impurities other than water. NMR data: δ_{P} 53.7. CH_2CN : δ_{H} 2.84, $^2J_{\text{PH}}$ 13.5 Hz. CH_3 : Nonequivalent CH_3 groups, $\delta_{\text{H(A)}}$ 1.33, $^3J_{\text{PH(A)}}$ 16.0 Hz, $\delta_{\text{H(B)}}$ 1.32, $^3J_{\text{PH(B)}}$ 16.6 Hz, Δ_{AB} 0.9 Hz, $^3J_{\text{HH}}$ 7.2 Hz. CH : δ_{H} 2.26, $^2J_{\text{PH}}$ 8.8 Hz (the assignment was assisted by data in CDCl_3 – C_6D_6 mixtures where Δ_{AB} was larger).

P,P-Diethylphosphinoacetonitrile (IIa). A mixture of $\text{Et}_2\text{P}(\text{O})\text{CH}_2\text{CN}$ (14.5 g, 0.10 mol) and Ph_2SiH_2 (18.4 g, 0.10 mol) was heated with stirring to 150°C for 5 h. The reaction mixture was distilled *in vacuo* through a 15 cm Vigreux column to give $\text{Et}_2\text{PCH}_2\text{CN}$, b.p. 90 – $92^\circ\text{C}/13$ mmHg (11.0 g, 85 %). No impurities were observable from its ^1H NMR spectrum. NMR data: δ_{P} –24.4. CH_2CN : δ_{H} 2.42, $^2J_{\text{PH}}$ 5.1 Hz. CH_3 : δ_{H} ca. 1.11, $^3J_{\text{PH}}$ ca. 16 Hz, $^3J_{\text{HH}}$ ca. 7 Hz. CH_2CH_3 : δ_{H} ca. 1.6, $^2J_{\text{PH}} < 2\text{Hz}$ (second order spectrum).

P,P-Diisopropylphosphinoacetonitrile (IIb). A mixture of $\text{Pr}_2\text{P}(\text{O})\text{CH}_2\text{CN}$ (17.3 g, 0.10 mol) and Ph_2SiH_2 (20.2 g, 0.11 mol) was heated with stirring to 200°C for 3 h. Distillation *in vacuo* through a 15 cm Vigreux column gave $\text{Pr}_2\text{PCH}_2\text{CN}$, b.p. 92 – $92.5^\circ\text{C}/5.0$ mmHg (11.8 g, 75 %). No impurities were observable from its ^1H NMR spectrum. NMR data: δ_{P} 0.7. CH_2CN : δ_{H} 2.36, $^2J_{\text{PH}}$ 4.5 Hz. CH_3 : Nonequivalent CH_3 groups, $\delta_{\text{H(A)}}$ 1.17, $^3J_{\text{PH(A)}}$ 15.2 Hz, $\delta_{\text{H(B)}}$ 1.14, $^3J_{\text{PH(B)}}$ 11.7 Hz, $^3J_{\text{HH}}$ 7.0 Hz, Δ_{AB} 3.0 Hz. CH : δ_{H} 1.96, $^2J_{\text{PH}}$ 2.2 Hz.

P,P-Di-*t*-butylphosphinoacetonitrile (IIc). A mixture of $\text{Bu}_t^2\text{P}(\text{O})\text{CH}_2\text{CN}$ (4.02 g, 0.02 mol) and Ph_2SiH_2 (3.7 g, 0.02 mol) was heated with stirring to 240°C for 15 h. Distillation *in vacuo* through a 10 cm Vigreux column gave $\text{Bu}_t^2\text{PCH}_2\text{CN}$, b.p. 118 – $119^\circ\text{C}/5.8$ mmHg, m.p. 6 – 8°C (2.8 g, 75 %). No impurities were observable from its ^1H NMR spectrum. NMR data: δ_{P} 27.0. CH_2CN : δ_{H} 2.36, $^2J_{\text{PH}}$ 2.5 Hz. CH_3 : δ_{H} 1.23, $^3J_{\text{PH}}$ 11.7 Hz.

P,P-Diphenylphosphinoacetonitrile (IIId). A mixture of $\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{CN}$ (24.1 g, 0.10 mol) and Ph_2SiH_2 (18.4 g, 0.10 mol) was heated with stirring to 190°C for 6 h. Distillation *in vacuo* through a Claisen head gave $\text{Ph}_2\text{PCH}_2\text{CN}$, b.p. 146 – $147^\circ\text{C}/0.35$ mmHg (18.0 g, 80 %). No impurities were observable from its ^1H NMR spectrum. NMR data: δ_{P} –17.8. CH_2CN : δ_{H} 2.89, $^2J_{\text{PH}}$ 4.4 Hz. Ph : δ_{H} 7.4 (m).

(Cyanomethyl)triethylphosphonium bromide.

A mixture of $\text{Et}_2\text{PCH}_2\text{CN}$ (0.26 g, 2×10^{-3} mol) and EtBr (0.6 g, 6×10^{-3} mol) in acetone (2 ml) was heated in an ampule to 100°C

for 24 h. The residue after evaporation was recrystallized from 2-propanol to give $\text{Et}_2\text{P}^+\text{CH}_2\text{CN Br}^-$ (0.38 g, 80 %), m.p. 228 – 230°C . (Found: C 40.18; H 7.18; N 5.68; Br 33.25. Calc. for $\text{C}_8\text{H}_{17}\text{BrNP}$: C 40.35; H 7.20; N 5.88; Br 33.56). IR (KBr): ν_{CN} 2252 cm^{-1} . NMR ($(\text{CD}_3)_2\text{SO}$): δ_{P} 41.1. CH_2CN : δ_{H} 4.51. $^2J_{\text{PH}}$ 15.3 Hz. CH_3 : δ_{H} 1.35, $^3J_{\text{PH}}$ 19.7 Hz, $^3J_{\text{HH}}$ 7.6 Hz. CH_2CH_3 : δ_{H} 2.54, $^2J_{\text{PH}}$ 13.5 Hz.

The compound prepared from Et_2P and BrCH_2CN had identical m.p., and NMR spectra.

Kinetic measurements. The conductivities were measured with a Radiometer type CDM 2 Conductivity Meter and a cell with platinized platinum electrodes. Acetone and EtI were purified through a column of Al_2O_3 (Woelm W 200 basic) and had conductivities of 0.3 – $2\ \mu\text{S}$. Solutions of $\text{Ph}_2\text{PCH}_2\text{CN}$ (0.106 M) and EtI (0.192 M) in acetone were prepared, and 25 ml of each mixed in the conductivity cell at $35 \pm 0.1^\circ\text{C}$. The conductivity was measured until less than 0.4 % of $\text{Ph}_2\text{PCH}_2\text{CN}$ had reacted. The concentration of $\text{Ph}_2\text{EtP}^+\text{CH}_2\text{CN I}^-$ was calculated from the conductivity values by comparison with the conductivities of standard solutions of the phosphonium salt. Similar experiments were made with Ph_3P . The rate constants were calculated from eqn. (4) of Henderson and Buckler.¹ Found for $\text{Ph}_2\text{PCH}_2\text{CN}$: $k = 7.2 \pm 0.2 \times 10^{-6}\ \text{l mol}^{-1}\ \text{s}^{-1}$; for Ph_3P : $k = 5.8 \pm 0.2 \times 10^{-5}\ \text{l mol}^{-1}\ \text{s}^{-1}$. The value for Ph_3P was higher than that (3.78×10^{-5}) given by Henderson and Buckler¹ probably because of residual water in our solvents.

(Cyanomethyl)diphenylethylphosphonium iodide. A mixture of $\text{Ph}_2\text{PCH}_2\text{CN}$ (0.45 g, 2×10^{-3} mol) and EtI (1 ml, 12×10^{-3} mol) in acetone (5 ml) was refluxed for 4 h. After cooling, $\text{Ph}_2\text{EtP}^+\text{CH}_2\text{CN I}^-$ was filtered off and recrystallized from abs. ethanol. Yield 70 %, m.p. 179 – 179.5°C . (Found: C 50.40; H 4.61; N 3.65; I 33.52. Calc. for $\text{C}_{16}\text{H}_{17}\text{INP}$: C 50.41; H 4.50; N 3.67; I 33.29).

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