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The Synthesis and Spectroscopic Properties of Some Cyanophosphines

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The preparation and characterization of several cyanophosphine compounds have been previously reported.[1-5] These reports have usually presented preparations involving rather extensive reaction times and have given little spectral data. In this work a rapid and easy method of preparation is presented for the routine synthesis of compounds of the type $R_xP(CN)_{3-x}$ (where $x = 0$, 1, or 2 and R = C_6H_5, CH_3O, C_2H_5O, $(CH_3)_2N$, or CH_3). Also, the infrared, proton nmr, phosphorus nmr, and mass spectral data of these compounds are presented and discussed.

Experimental Section

Instrumentation.—The phosphorus nmr spectra were obtained on a Varian Associates Model DA-60 spectrometer at 24.29 MHz and are referenced to 85% orthophosphoric acid as an external standard. Proton nmr spectra were taken on a Varian Associates Model A-57/60-D instrument with tetramethylsilane as an internal standard. The infrared spectra were obtained on a Perkin-Elmer Model 225 grating spectrophotometer with sodium chloride optics and *n*-hexane as a solvent in all cases except for $P(CN)_3$ and $CH_3P(CN)_2$ where $CHCl_3$ was used. Mass spectra were recorded on a Hitachi Perkin-Elmer Model RMU-6 instrument using the liquid inlet system with an ion source temperature of 200° and an ionizing voltage of 70 eV for all samples except $P(CN)_3$, where the solid inlet was used at a temperature of 50° and an ionizing voltage of 70 eV.

Materials.—$C_6H_5PCl_2$, $(C_6H_5)_2PCl$, $(C_2H_5O)_3P$, and $(CH_3O)_3P$ were purchased from Aldrich Chemical Co., Milwaukee, Wis., and CH_3PCl_2 was obtained as a gift from the Department of the Army, Edgewood Arsenal, Edgewood, Md. $C_2H_5OPCl_2$,[6] $(C_2H_5O)_2PCl$,[6] $(CH_3)_2PCl$,[7] $(CH_3)_2NPCl_2$,[2] and $[(CH_3)_2N]_2PCl$[2] were prepared according to previously described methods.

The compounds $(CH_3O)_2PCl$ and CH_3OPCl_2 were prepared by mixing appropriate molar ratios of $(CH_3O)_3P$ and PCl_3 in a manner described as follows. When a 2:1 molar ratio of $(CH_3O)_3P$ to PCl_3, for example, is stirred under N_2 at room temperature for several minutes, an exothermic reaction ensues forming $(CH_3O)_2PCl$. This product is identified in the ^1H nmr spectrum by a doublet resonance which is expectedly downfield (due to decreased shielding) from the similar doublet for $(CH_3O)_3P$; stirring for 24 hr at room temperature ensures complete reaction which is characterized by the disappearance of the $(CH_3O)_3P$ doublet in the ^1H nmr spectrum. When the opposite molar ratio is mixed at room temperature, $(CH_3O)_2PCl$ is again formed; however, if the reaction mixture is warmed slightly (70°) for 3 hr, CH_3OPCl_2 is formed. This reaction is also followed by ^1H nmr spectroscopy, CH_3OPCl_2 exhibiting a doublet resonance downfield from the resonance of $(CH_3O)_2PCl$. Although some decomposition is evidenced by formation of an unidentified orange solid and CH_3Cl (singlet in the ^1H nmr at 2.95 ppm), the reactions are essentially quantitative. *Caution! It was not found possible to purify these chlorophosphites by distillation (either at reduced pressures or atmospheric pressure) because decomposition was rapidly accelerated by the application of heat, and invariably an explosion resulted.* These compounds then, whose purity was checked by ^1H nmr, were used without purification and with good results.

Preparation of Cyanophosphine Compounds.—The compounds $P(CN)_3$,[1] $(CH_3)_2NP(CN)_2$,[2] $[(CH_3)_2N]_2PCN$,[2] $(C_2H_5O)_2PCN$,[3] $C_2H_5OP(CN)_2$,[3] and $C_6H_5P(CN)_2$[4] have been prepared previously by refluxing the appropriate phosphorus halide with AgCN for 12–24 hr in solvents such as $CHCl_3$, CCl_4, and $(C_2H_5)_2O$. This method of preparation has been slightly modified for the above compounds and the compounds of this work to use acetonitrile as the reaction solvent. This allows for the compounds to be formed quickly by simply stirring at room temperature in a nitrogen atmosphere for about 2 hr. $CH_3P(CN)_2$[5] has previously been prepared using acetonitrile as the solvent; however, reflux temperatures were employed for 5 hr.

Two methods were used for isolation of the products from the reaction mixtures. (A) After about 2 hr of stirring, the reaction mixture was filtered under nitrogen to remove the AgCl (and any unreacted AgCN) and washed well with acetonitrile, and the acetonitrile was removed on a water aspirator. The remaining liquid was vacuum distilled (vacuum sublimed for solids) (see Table I) to give the colorless liquid or white solid product.

TABLE I

EXPERIMENTAL AND NMR AND INFRARED SPECTRAL DATA

Compound	Method of isolation	Bp, °C (mm)[b]	$\delta(^1H)$, ppm	J_{PH}, Hz	$\delta(^{31}P)$, ppm	$\nu(CN)$,[a] cm^{-1}
$(C_6H_5)_3P$		>360 (760)			+6.0[b]	. . .
$(C_6H_5)_2PCN$	A	110 (0.1)	7.20	9.0[d]	+36.4	2173 s
$C_6H_5P(CN)_2$	A	68–70 (0.1)	7.60[c]	10.0[d]	+75.6	2184 s 2092 m
$(CH_3O)_3P$		111 (760)	3.43	10.5	−141[b]	. . .
$(CH_3O)_2PCN$	B	58 (10)	3.75	10.3	−122.4	2186 s
$CH_3OP(CN)_2$	B	65 (6)	3.88	9.0	−24.4	2179 s 2030 w
$(C_2H_5O)_3P$		158 (760)	3.85[e] 1.19[f]	7.5[g]	−139.0[b]	. . .
$(C_2H_5O)_2PCN$	A	51 (5)	4.08[e] 1.30[f]	7.5[g]	−117.0	2180 s
$C_2H_5OP(CN)_2$	B	51 (5)	4.20[e] 1.40[f]	7.0[g]	−17.6	2178 s 2133 w
$[(CH_3)_2N]_3P$		29 (1)	2.44[h]	8.9[h]	−123.0[b]	. . .
$[(CH_3)_2N]_2PCN$	B	48 (1)	2.75	10.0	−66.1	2168 s
$(CH_3)_2NP(CN)_2$	B	65–69 (8)	2.90	14.0	+5.7	2179 s 2060 w
$(CH_3)_3P$		40–42 (760)	0.90	2.7	+62.0[b]	. . .
$(CH_3)_2PCN$	B	40–45 (10)	1.47	4.5	+62.6	2172 s
$CH_3P(CN)_2$	A	50–60 (0.1)[i]	1.90	7.5	+81.4[j]	2191 s 2095 m
$P(CN)_3$	A	50–60 (0.1)[i]	. . .	. . .	+138.3[j]	2186 s 2096 m

[a] Abbreviations: s, strong; m, medium; w, weak. [b] See ref 8. [c] Most intense peak. [d] Approximate coupling to ortho protons. [e] Methylene protons. [f] Methyl protons. [g] Coupling to methylene protons. [h] R. B. King, *Inorg. Chem.*, **2**, 936 (1963). [i] Sublimed. [j] CH_3CN solution.

(B) The reaction mixture was vacuum distilled, after about 2 hr of stirring, collecting first the acetonitrile and second the cyanophosphine product and leaving the silver salts in the reaction vessel. This method of isolation was particularly effective for those phosphorus compounds which formed insoluble complexes with the silver salts in the reaction mixture and which would have been lost in filtration, but it could also be used as a general method for isolation of the somewhat lower boiling liquid products.

It should be noted that $(CH_3O)_2PCN$ was also prepared by method A. However, after approximately half of the material had been distilled, the distillation pot exploded rather violently, perhaps due to some unreacted $(CH_3O)_2PCl$; therefore method B is recommended.

Results and Discussion

In contrast to the previously reported preparative methods for cyanophosphines, the preparations in acetonitrile proceeded rapidly at room temperature and in good yields. All of the compounds are hygroscopic and

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TABLE II

MASS SPECTRAL DATA
(RELATIVE INTENSITY OF IDENTIFYING PEAKS IN PERCENTAGES)

Compound	Ion							
	R_2PCN	R_2P	RP	RPCN	PCN	$RP(CN)_2$	$P(CN)_2$	$P(CN)_3$
$(C_6H_5)_2PCN$	96	2.8	100	4.3	7.1			
$C_6H_5P(CN)_2$			12.5	15.3	9.7	50.0	2.4	
$(CH_3O)_2PCN$	15.9	100	9.5	7.9	9.5			
$CH_3OP(CN)_2$			21.9	100	35.8	38.7	8.8	
$(C_2H_5O)_2PCN$	15.3	18.1	16.2	20.0	8.6			
$C_2H_5OP(CN)_2$			3.5	8.8	49.2	5.3	26.4	
$[(CH_3)_2N]_2PCN$	25.6	14.0	10.5	53.5	3.5			
$(CH_3)_2NP(CN)_2$			6.2	100	21.2	27.5	3.0	
$(CH_3)_2PCN$	100	6.6	9.8	67.2	24.6			
$CH_3P(CN)_2$			91.8	47.1	83.5	67.1	11.8	
$P(CN)_3$					100		8.3	25

usually become yellow to red after any exposure to air. This apparent decomposition, however, did not seem to affect further reactions of these compounds in any appreciable way. (Reactions of these cyanophosphine ligands with metal carbonyls will be published later.)

Nmr.—The proton nmr chemical shifts, listed in Table I, are observed to shift steadily downfield as organic groups are replaced by cyanide groups on the phosphorus atom. In addition, the cyanide compounds are invariably slightly downfield (less shielding) from the corresponding chloride compounds and are, therefore, easily identified in the reaction mixtures.

The ^{31}P nmr chemical shifts are shown in Table I. The resonances shift upfield as organic groups are replaced by cyanide groups on the phosphorus atom. This trend in the chemical shifts is opposite to the downfield shift exhibited by the corresponding chloride compounds; for example, the ^{31}P chemical shifts for $(CH_3O)_2PCl$, CH_3OPCl_2, and PCl_3 are -169, -180, and -220 ppm, respectively.[8] Therefore, cyanide magnetically shields the phosphorus atom while chloride deshields phosphorus. This effect, along with the trends in the ^1H chemical shifts may be attributed at least partly to the diamagnetic anisotropic shielding of the cyanide triple bond. It has been shown by X-ray diffraction of solid $P(CN)_3$[9] that the $P—C\equiv N$ linkage is very nearly linear (172° angle). Therefore, if the same linkage is linear in the organic substituted compounds, the phosphorus atom should lie in the positive region of shielding, while the protons of the organic groups may lie in the negative region of shielding and experience a downfield shift. In addition, it is noteworthy to point out that the small C–P–C bond angle of 94° found in $P(CN)_3$[9] indicates that the lone pair on phosphorus has a large percentage of s character. This would also account for the effective shielding of the phosphorus nucleus and give rise to the upfield shifts.

The phosphorus–hydrogen coupling constants, also listed in Table I, vary with the organic group on phosphorus. J_{PH} is observed to increase in absolute value as CH_3, $N(CH_3)_2$, or C_6H_5 is replaced by cyanide on the phosphorus atom. However, as cyanide groups replace either OCH_3 or OC_2H_5, J_{PH} decreases in absolute magnitude.

Mass Spectra.—The mass spectra were obtained to confirm the identity of the products and perhaps to give some information on the phosphorus–cyanide bond strengths. Some of these data are presented in Table II. For $P(CN)_3$, it was found that the peak at m/e 57 which is represented as PCN^+ was the most intense peak, followed by CN^+ (86% relative intensity) and then $P(CN)_3^+$ (25%). This demonstrates the ease with which two of the cyanides are cleaved from the phosphorus and indicates that, under these conditions, $P(CN)_2^+$ (8.3% intensity) is somewhat unstable with respect to PCN^+. This trend is, in general, paralleled in the other compounds especially in the dicyano species where mass spectral peaks for PCN^+ and $P(R)(CN)^+$ are always stronger than that for $P(CN)_2^+$. In the compound $C_6H_5P(CN)_2$, $P(C_6H_4)(CN)^+$ is the most intense peak and is formed by the splitting of a neutral HCN molecule off of the parent compound, as evidenced by the metastable peaks observed at m/e 110.6 (calculated at m/e 110.56): m^* 110.6, $C_6H_5P(CN)_2^+ \rightarrow C_6H_4PCN^+ + HCN$. As expected, the phenyl derivatives exhibit strong parent peaks with the ion peak at m/e 211 for $(C_6H_5)_2PCN^+$ showing a 96% relative intensity and the ion peak m/e 160 for $C_6H_5P(CN)_2^+$ exhibiting a relative intensity of 50%.

The phosphites showed strong peaks for those species with the phosphorus–oxygen bond intact. For example, in the spectrum of $(CH_3O)_2PCN$, the most intense peak is at m/e 93 corresponding to $P(OCH_3)_2^+$ with $P(OCH_3)(OH)^+$ being next strongest at 56% relative intensity. Although in the spectra of the compounds $[(CH_3)_2N]_2PCN$ and $(CH_3)_2NP(CN)_2$ some ions are observed in which the P–N bond has been cleaved, as evidenced by the presence of immonium ions, there was a high abundance of ions with the P–N bond intact. This can be contrasted to the dimethylaminodihalophosphines which show a high abundance of fragments which contain only phosphorus and the halogen.[10] In the spectrum of $(CH_3)_2NP(CN)_2$, the ion peak at m/e 101, represented as the fragment $P(CN)[N(CH_3)_2]^+$ (relative intensity 100%), is much stronger than the mass spectral peak at m/e 57 for the PCN^+ ion (20%) and very much stronger than the peak at m/e 83 for $P(CN)_2^+$ (4%).

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