The Preparation and Characterisation of some Organocyanophosphide(I) Salts

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Summary Salts containing the novel organocyanophosphide(I) ions $RP(CN)^-$ (R = Me, Et, or Ph) have been prepared, and characterised by ^{31}P n.m.r. and i.r. spectroscopy, and elemental analysis.

SALTS containing the dicyanophosphide(I) ion, $P(CN)_2^-$, have previously been prepared and studied.[1,2] Their preparation has involved the reaction of $P(CN)_3$ with (a) a dialkylphosphite in the presence of base, (b) the sodium salt of a dialkylphosphite, or (c) the cyanide ion[3,4] *via* the decomposition of $P(CN)_4^-$. No other derivatives of this kind have been described. We report the first preparation of organocyanophosphide(I) ions, $RP(CN)^-$ (R = Me, Et, or Ph), made by an analogous procedure to (c).

TABLE 1. δ ^{31}P[a] for $RP(CN)^-$ ions in CH_2Cl_2.

R	Me	Et	Ph
δ (^{31}P)	62·9	70·9	61·3

[a] In p.p.m. relative to external 85% H_3PO_4 with the downfield direction taken as positive.

Addition of a small amount of Et_4NCN to a solution of $MeP(CN)_2$ or $EtP(CN)_2$ in dichloromethane caused the appearance of two new peaks in the ^{31}P n.m.r. spectrum, one upfield and one downfield from the starting material. On the addition of more cyanide the upfield signal disappeared and only a single resonance at lower field was apparent (Table 1). The upfield signal is ascribed to the adduct $RP(CN)_3^-$, and the residual signal to the organocyanophosphide(I) ion, formed by elimination of cyanogen [equation (1)].

$$RP(CN)_2 + CN^- \rightarrow RP(CN)_3^- \rightarrow RP(CN)^- + (CN)_2 \quad (1)$$
$$(R = Me \text{ or } Et)$$

In the case of $PhP(CN)_2$, addition of a small amount of Et_4NCN produced a lower field signal only, apart from a peak due to unchanged starting material. Further addition of cyanide yielded a single resonance at the same shift position (Table 1). In this instance the intermediate $PhP(CN)_3^-$ appears to be too unstable to be detected by n.m.r. spectroscopy under the experimental conditions.

The ions were isolated as their tetraethylammonium salts by removing the solvent *in vacuo* from 1:1 molar ratios of the appropriate reactants. The methylcyanophosphide salt was in the form of a viscous orange liquid which solidified in an inert atmosphere box, and the other compounds appeared as dark brown, viscous liquids. Satisfactory elemental analyses were obtained for the methyl and phenyl compounds, but the ethyl derivative could not be freed completely from dichloromethane, as confirmed by the i.r. spectrum of the product. Indeed one preparation analysed approximately as a 1:1 mixture of $Et_4N^+EtP(CN)^-$ and CH_2Cl_2. All three compounds gave a similar pattern in the C≡N stretching region of the i.r. spectrum with a strong, broad band present, which differed considerably in appearance from the spectrum of the original organophosphorus(III) dicyanide (Table 2). The isolated compounds all gave single ^{31}P n.m.r. peaks, in excellent agreement with the shift values given in Table 1.

TABLE 2. C≡N stretching frequencies/cm^{-1} in the i.r. spectra of $RP(CN)^-$ and $RP(CN)_2$.

R	Me	Et	Ph
$RP(CN)^-$	2160 (m), 2120—2080 (s, br)	2160—2070 (s, br)	2160—2080 (s, br)
$RP(CN)_2$	2188 (s), 1976 (m)	2180 (s), 2086 (m)	2246 (w), 2180 (s)

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