# Pentaco-ordinate Phosphorus Compounds by Nucleophilic Addition to Activated Alkenes

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*Summary* The reactions between a variety of tricoordinate phosphorus compounds and acrylonitrile or ethyl acrylate provide a novel route to pentaco-ordinate phosphorus compounds.

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Although a large number of pentaco-ordinate phosphorus compounds have appeared in the literature over the last decade,[1,2] many of them are monocyclic or bicyclic (spirophosphorane) structures since incorporation of 4- or 5-membered rings apparently confers extra stability on the phosphoranes. Thus, general preparative routes to acyclic phosphoranes,[3] especially those containing both P–C and P–O bonds, are somewhat rare.[4,5]

During a study of the nucleophilic addition of tricoordinate phosphorus compounds to activated olefins (the first step in the homogeneous catalysis of the dimerisation of such olefins)[6,7] it was noticed that in the presence of alcohols, pentaco-ordinate phosphorus compounds could be obtained in high yields from phosphinites and phosphonites (equation 1). A selection of the results obtained so far is

$$R^1_nP(OR^2)_{3-n} + CH_2{=}CHX \xrightarrow{R^3OH} R^1_nP(OR^2)_{3-n}(OR^3)CH_2CH_2X \qquad (1)$$

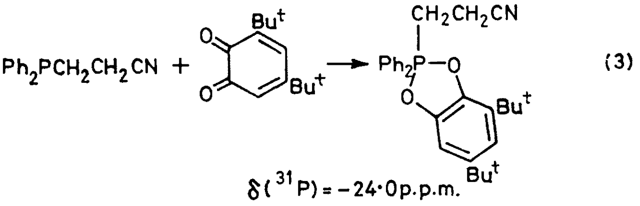
$$n = 1 \text{ or } 2 \qquad X = CN \text{ or } CO_2Et$$

reported in the Table and the method is being extended to include sulphur- and nitrogen-containing phosphoranes.

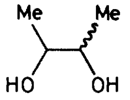
The phosphoranes were identified by $^1H$ and $^{31}P$ n.m.r. spectra and, in the cases of Nos. 4 and 8, independent syntheses using established procedures[4,8] (equations 2 and 3) confirmed the proposed structures.

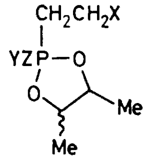
$$Ph_2PCH_2CH_2CN + Et_2O_2 \rightarrow Ph_2P(OEt)_2CH_2CH_2CN \quad (2)$$

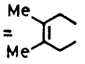
$$\delta\ (^{31}P) = -52{\cdot}3 \text{ p.p.m.}$$

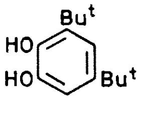


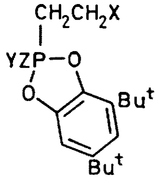
In the absence of moisture all the phosphoranes were fairly stable although, for the acyclic compounds, a slow decomposition to oxides (for the phosphoranes obtained from phosphinites) and to phosphinates (for those obtained from phosphonites) was observed over several days at room temperature.


(1)

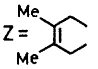

(2) Y = Z = Ph

(3) Y,Z =



(4)


(5) Y = Z = Ph

(6) Y = Ph, Z = OEt

(7) Y,Z =


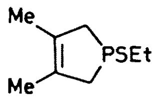
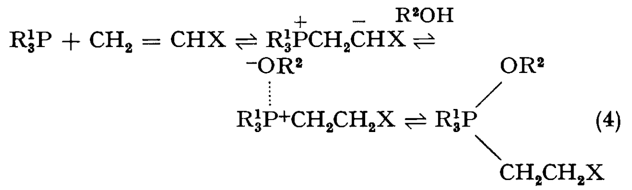

(8)

TABLE. The reactions of phosphinites and phosphonites with $CH_2{=}CHX$ in benzene and in the presence of alcohols, diols, or catechols

| No. | $R^1_nP(OR^2)_{3-n}$ | $R^3OH$ | X | Product | $\delta(^{31}P)^{a,b}$ | % Yield | Comments |
|---|---|---|---|---|---|---|---|
| 1 | $Ph_2POMe$ | MeOH | $CO_2Et$ | $Ph_2P(OMe)_2CH_2CH_2X$ | −48·2 | 55 | 99% reaction, 100 min |
| 2 | $Ph_2POEt$ | EtOH | $CO_2Et$ | $Ph_2P(OEt)_2CH_2CH_2X$ | −50·6 | 75 | 99% reaction, 100 min |
| 3 | $(p\text{-}Pr^iOC_6H_4)_2POPr^i$ | $Pr^iOH$ | $CO_2Et$ | $Ar_2P(OPr^i)_2CH_2CH_2X$ | −51·5 | 21 | Remainder, oxide |
| 4 | $Ph_2POEt$ | EtOH | CN | $Ph_2P(OEt)_2CH_2CH_2X$ | −52·4 | 80 | *ca.* 20 min |
| 5 | $Ph_2POEt$ | $Bu^tOH$ | CN | $Ph_2P(OEt)(OBu^t)CH_2CH_2X$ | −52·8 | 30 | — |
| 6 | $PhP(OEt)_2$ | EtOH | $CO_2Et$ | $PhP(OEt)_3CH_2CH_2X$ | −36·5 | 80 | 150 min |
| 7 | $Ph_2POEt$ | (1) | CN | (2) | −39·9<br>−39·3 | 58<br>22 | *meso* + (±) |
| 8 | $Ph_2POEt$ | (4) | CN | (5) | −24·3 | 76 | *ca.* 2 h |
| 9 | $PhP(OEt)_2$ | (4) | CN | (6) | −16·6<br>−16·0 | 55<br>7 | Two diastereomers<br>no pseudorotation? |
| 10 | (8) | (4) | $CO_2Et$ | (7) | +4·0 | 80 | |
| 11 | (8) | (1) | $CO_2Et$ | (3) | −12·7<br>−13·3 | 61<br>9 | *meso* + (±) |

[a] Negative shifts upfield from $H_3PO_4$ in p.p.m. [b] For comparison purposes, $Ph_3P(OEt)_2$ has $\delta(^{31}P)$ −54·0 and $Ph_2P(OEt)_3$ has $\delta(^{31}P)$ −44·1 p.p.m.

It seems reasonable to assume that the reaction proceeds through protonation of an intermediate betaine by the alcohol and collapse of the resultant ion-pair to phosphorane (equation 4) and it is interesting to note that inclusion of two or three phosphorus–carbon bonds promotes formation of the acyclic phosphoranes at the expense of the phosphoryl structures. In contrast a very recent report[9] reveals that the reaction of phosphites with activated olefins in the presence of t-butyl alcohol yields a phosphonate.†



$$R^1_3P + CH_2 = CHX \rightleftharpoons \overset{+}{R^1_3P}CH_2\overset{-}{C}HX \overset{R^2OH}{\rightleftharpoons} {}^-OR^2 \cdots R^1_3P^+CH_2CH_2X \rightleftharpoons R^1_3P\begin{smallmatrix}OR^2\\ CH_2CH_2X\end{smallmatrix} \quad (4)$$

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† With $(EtO)_3P$ and $CH_2{:}CHCO_2Et$ in benzene-EtOH we observed 4% $(EtO)_4PCH_2CH_2CO_2Et$ (δ − 47·6) after 1 day but only $(EtO)_2P(O)CH_2CH_2CO_2Et$ (δ + 29·4) after 13 days.

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