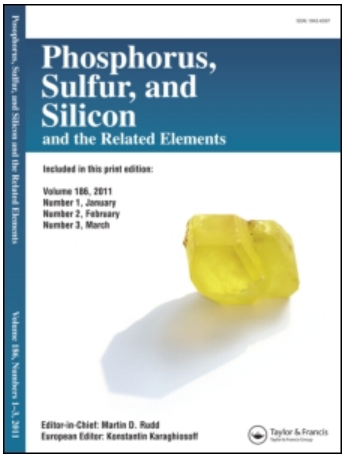


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

PENTACO-ORDINATE PHOSPHORUS COMPOUNDS BY NUCLEOPHILIC ADDITION TO ACTIVATED ALKENES AND ALKYNES IN THE PRESENCE OF ALCOHOLS AND PHENOLS

Paul D. Beer[a]; Robert C. Edwards[a]; C. Dennis Hall[a]; J. R. Jennings[b]; R. J. Cozens[b]
[a] Department of Chemistry, King's College, Strand London [b] Corporate Laboratory, The Heath, Imperial Chemical Industries, P.L.C., Runcorn, Cheshire

To cite this Article Beer, Paul D. , Edwards, Robert C. , Hall, C. Dennis , Jennings, J. R. and Cozens, R. J.(1983) 'PENTACO-ORDINATE PHOSPHORUS COMPOUNDS BY NUCLEOPHILIC ADDITION TO ACTIVATED ALKENES AND ALKYNES IN THE PRESENCE OF ALCOHOLS AND PHENOLS', Phosphorus, Sulfur, and Silicon and the Related Elements, 17: 3, 283 — 295
To link to this Article: DOI: 10.1080/03086648308077549
URL: http://dx.doi.org/10.1080/03086648308077549

Phosphorus and Sulfur, 1983, Vol. 17, pp. 283–295
0308-664X/83/1703-0283/$18.50/0

PENTACO-ORDINATE PHOSPHORUS COMPOUNDS BY NUCLEOPHILIC ADDITION TO ACTIVATED ALKENES AND ALKYNES IN THE PRESENCE OF ALCOHOLS AND PHENOLS

PAUL D. BEER, ROBERT C. EDWARDS and C. DENNIS HALL*

Department of Chemistry, King's College, Strand, London WC2R 2LS

J. R. JENNINGS[1] and R. J. COZENS[2]

Imperial Chemical Industries, P.L.C., Corporate Laboratory, The Heath, Runcorn, Cheshire

(*Received May 5, 1983; in final form July 25, 1983*)

The reactions of a variety of trico-ordinate phosphorus compounds, $Ar_nP(OR)_{3-n}$ (n = 1 or 2), and cyclic analogues, with acrylonitrile, ethyl acrylate or ethyl phenylpropiolate and alcohols or phenols in low polarity media gives rise to a wide range of pentaco-ordinate phosphorus compounds. Attempts to extend this synthetic route to phosphoranes containing P—N or P—S bonds met with no success.

INTRODUCTION

Pentaco-ordinate phosphorus compounds may be prepared by a range of synthetic methods[3] the most important of which are the insertion of trico-ordinate phosphorus compounds into weak sigma bonds (e.g. peroxides[4] and sulphenate esters[5]) and the addition of trico-ordinate phosphorus to α-dicarbonyl compounds.[6] The majority of phosphoranes now known are monocyclic or bicyclic (spirophosphorane) structures since incorporation of four- or five-membered rings apparently confers extra stability on the phosphoranes.[7] Thus, although the sulphenate route offers a method of wide utility, general synthetic routes to acyclic phosphoranes are still somewhat rare.

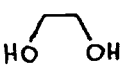
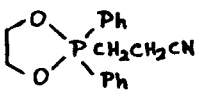
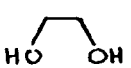
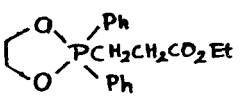
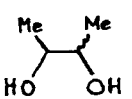
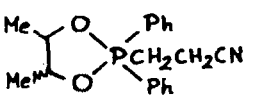
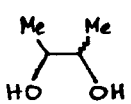
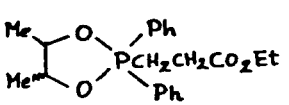
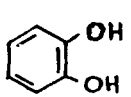
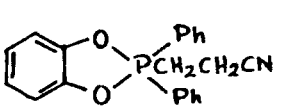
During a study of the reactions of trico-ordinate phosphorus compounds with activated alkenes it was noticed that in the presence of alcohols, pentaco-ordinate phosphorus compounds (**5**) could be obtained from phosphinites and phosphonites[8] (Scheme 1). An investigation of the scope and utility of this reaction is the subject of this paper.

RESULTS AND DISCUSSION

The initial study was limited to the synthesis of oxygen-containing phosphoranes using a variety of alcohols, diols and catechols. The reactions were carried out in non-polar media (benzene or toluene) with the reactants in equimolar quantities and the results are recorded in Table I.

TABLE I

The reactions of phosphinites and phosphonites with CH_2=CHX in benzene or dioxan and in the presence of alcohols, diols, catechols, aminoalcohols, diamines and thiols

$R_nP(OR)_{3-n}$	ROH	X	Product	δ ^{31}P	% Yield[a]	Comments[b]
Ph_2POMe	MeOH	CO_2Et	$Ph_2P(OMe)_2CH_2CH_2CO_2Et$	−48.2	55	100% reaction, 100 min
Ph_2POEt	EtOH	CO_2Et	$Ph_2P(OEt)_2CH_2CH_2CO_2Et$	−50.6	75	100% reaction, 100 min
$(p\text{-}Pr^iOC_6H_4)_2POPr^i$	Pr^iOH	CO_2Et	$Ar_2P(OPr^i)_2CH_2CH_2CO_2Et$	−51.5	21	After 120 min; remainder oxide
Ph_2POEt	EtOH	CN	$Ph_2P(OEt)_2CH_2CH_2CN$	−52.4	80	After 20 min
Ph_2POEt	Bu^tOH	CN	$Ph_2P(OEt)(OBu^t)CH_2CH_2CN$	−52.8	30	After 60 min; remainder oxide
$PhP(OEt)_2$	EtOH	CO_2Et	$PhP(OEt)_3CH_2CH_2CO_2Et$	−36.5	80	150 min
Ph_2POEt		CN		−35.1	60	100% reaction, 3 h
Ph_2POEt		CO_2Et		−33.0	50	100% reaction, 3 h
Ph_2POEt		CN		−39.9 −39.3	58 22	$\frac{\text{meso}}{(\pm)}$, 2 h
Ph_2POEt		CO_2Et		−38.1 −37.3	65 15	$\frac{\text{meso}}{(\pm)}$, 2 h
Ph_2POEt		CN		−21.0	30	Remainder oxide; 2 h

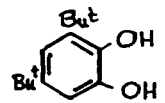
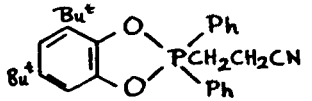
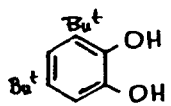
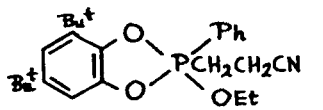
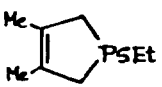
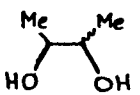
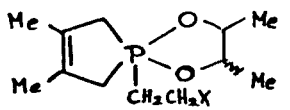
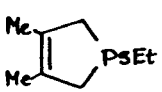
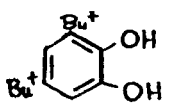
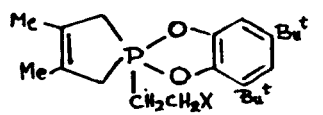
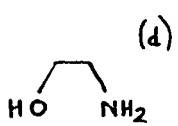
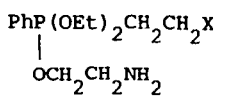
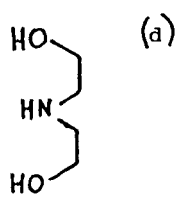
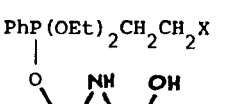
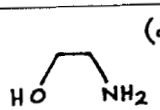
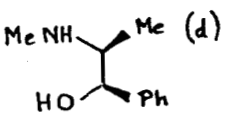
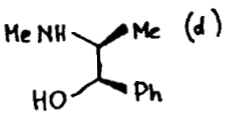
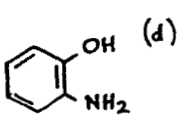
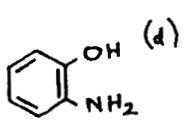
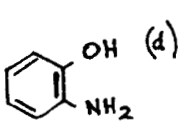
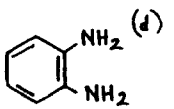
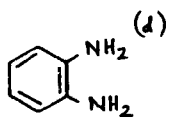
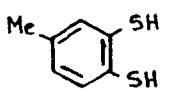
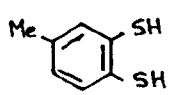
Ph_2POEt		CN		−24.3	76	2 h
$PhP(OEt)_2$		CN		−16.6 −16.0	55 7	67% reaction, 2.5 h
		CO_2Et		−12.7 −13.3	61 9	$\frac{\text{meso}}{(\pm)}$, 24 h
		CO_2Et		+4.0	80	24 h
$PhP(OEt)_2$		CN		−40.9	20[c]	100% reaction, 3 h
$PhP(OEt)_2$		CO_2Et CN		−37.6 −40.6	26[c] 27[c]	100% reaction, 24 h 100% reaction, 24 h

TABLE I (continued)

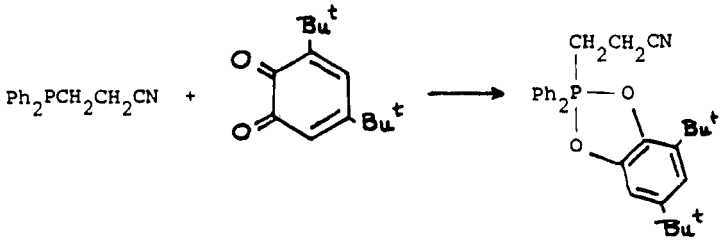
$R_nP(OR)_{3-n}$	ROH	X	Product	δ ^{31}P	% Yield[a]	Comments[b]
Ph_2POEt	 (d)	CO_2Et	Acyclic?	−51.2	8[c]	60% reaction, 5 h 90% oxide δ ^{31}P 27.9
Ph_2POEt	 (d)	CN	No Phosphorane	—	—	90% oxide δ ^{31}P 27.1
$PhP(OEt)_2$	 (d)	CN	No Phosphorane	—	—	90% oxide δ ^{31}P 37.9
$PhP(OEt)_2$	 (d)	CN	Acyclic?	−33.2	26[c]	100% reaction, 48 h
$PhP(OEt)_2$	 (d)	CO_2Et	Acyclic?	−30.3	18[c]	100% reaction, 48 h
Ph_2POEt	 (d)	CO_2Et	Acyclic?	−53.5	5[c]	100% reaction, 48 h 90% oxide δ ^{31}P 27.8

$PhP(OEt)_2$		CO_2Et	$PhP(OEt)_3CH_2CH_2X$?	−37.0	18[c]	100% reaction, 40 h
Ph_2POEt		CO_2Et	No Phosphorane	—	—	95% oxide δ ^{31}P, 27.8
Ph_2POEt	EtSH	CN	No Phosphorane[c]	—	—	100% reaction, 23 h
$PhP(OEt)_2$	EtSH	CN	No Phosphorane[c]	—	—	100% reaction, 23 h
Ph_2POEt		CN	No Phosphorane[c]	—	—	80% reaction, 23 h
$PhP(OEt)_2$		CN	No Phosphorane[c]	—	—	60% reaction, 23 h

[a]Yields based on integrations of ^{31}P nmr spectra.
[b]Reaction times based on disappearance of olefinic protons.
[c]In these cases a complicated mixture of tetraco-ordinated phosphorus species was observed in the ^{31}P nmr (δ + 21–δ + 50).
[d]Reactions carried out in dioxan.

Each reaction was monitored by observing the gradual disappearance of the olefinic protons from the ^1H nmr spectrum and hence an estimate of the time required for phosphorane formation was obtained before the ^{31}P nmr spectra were recorded. In two cases independent syntheses by established procedures (Eqs. (A) and (B)) confirmed the proposed structures.

$$Ph_2PCH_2CH_2CN + Et_2O_2 \longrightarrow Ph_2P(OEt)_2CH_2CH_2CN \qquad (A)$$



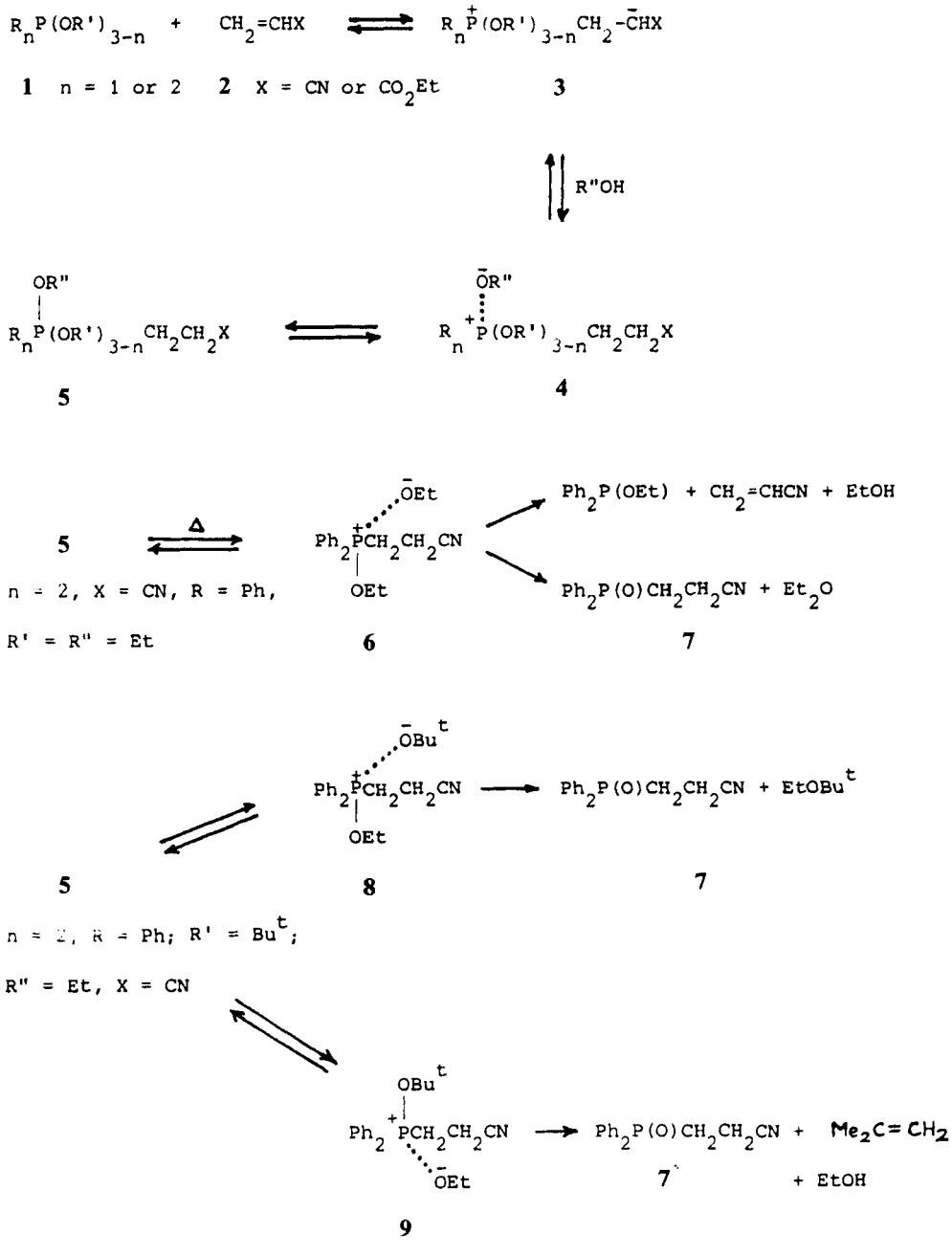
(B)

Table I reveals a gradual trend of δ ^{31}P values from acyclic (δ $^{31}P \approx -50$) through monocyclic (δ ^{31}P, -20) to bicyclic (δ ^{31}P, $+4.0$) phosphoranes in which the phosphorus is most deshielded. These δ ^{31}P values are in accord with literature values for phosphoranes of similar structures[7,9] and hence it is clear that dihydric alcohols and catechols can displace alkoxy or thioalkyl groups from phosphorus to form cyclic phosphoranes. A similar phenomenon has been reported by Denney in the exchange of alkoxy groups of acyclic phosphoranes with diols and ethanolamines.[10]

Isolation and complete characterisation of the phosphoranes was not achieved since repeated attempts to separate the acyclic pentaco-ordinates by distillation or recrystallization resulted in breakdown of the pentaco-ordinate structure to starting materials and/or some β-cyanoethyldiphenylphosphine oxide. This result implies dissociation of the phosphorane **5**, (R = Ph, R′, R″ = Et, n = 2, X = CN) at least to an ion-pair **6**, followed by a β-elimination or dealkylation (Scheme 1). A similar reaction is observed during the synthesis of **5** from 2-cyanoethyldiphenylphosphine and diethyl peroxide (see Experimental). In the absence of water and air all the phosphoranes were fairly stable although with the acyclic systems, a slow decomposition to oxide was observed over several days at room temperature.

By analogy with similar systems[11] it seems reasonable to assume that the mechanism of the reaction involves nucleophilic attack by phosphorus on the α-carbon of **2** followed by protonation of the intermediate betaine **3** and collapse of the resultant ion pair **4** to phosphorane **5**—Scheme 1.

A contrasting report revealed that the reaction of phosphites with nitroethene **10** in the presence of t-butanol gave phosphonates **11** with no evidence for phosphorane products.[12] It may be significant that with t-butanol as the proton source, lower yields of phosphorane were obtained (Table I) and in fact there is reason to believe that steric crowding promotes instability in pentaco-ordinate structures[13] and therefore that phosphoranes containing t-butoxy groups would decompose by dealkylation via **8** or β-elimination via **9** (Scheme 1). Further evidence for this is provided in



1 n = 1 or 2 **2** X = CN or CO_2Et **3**

5 **4**

5 **6** **7**

n = 2, X = CN, R = Ph, R' = R" = Et

5 **8** **7**

n = 2, R = Ph; R' = Bu^t; R" = Et, X = CN

9

SCHEME 1

the catalytic dimerisation of acrylonitrile[14] where the use of *t*-butanol led to short catalyst lifetimes due to the rapid formation of phosphine oxide.

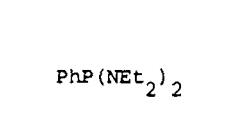
$$(RO)_3P + CH_2{=}CHNO_2 \xrightarrow{Bu^tOH} (RO)_2P(O)CH_2CH_2NO_2$$

10 **11**

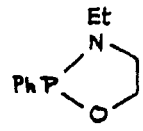
An attempt was made to extend the method to the synthesis of nitrogen and sulphur containing phosphoranes by the use of proton sources such as ethanolamine, diethanolamine, *o*-aminophenol, *L*-ephedrine, *o*-phenylenediamine, ethanethiol and 3,4-toluene-dithiol. Somewhat surprisingly no cyclic phosphoranes were observed but with some aminoalcohols low yields of what appeared to be acyclic phosphoranes were obtained (Table I). With the thiols and diamine, complete reaction was achieved within 24 h but the products were mainly phosphine oxide (**7**, from phosphinites) and phosphinates (from phosphonites) derived by dealkylation of the intermediate alkoxy–phosphonium salts.

The results suggest either that the P—N and P—S bonds in the incipient pentaco-ordinate structures are less stable than the analogous P—O bonds, or that with amines, aminoalcohols or thiols, dealkylation is more facile than collapse of the protonated betaine to a pentaco-ordinate structure. There are in fact very few examples of phosphoranes containing P—S links but numerous examples of phosphoranes containing P—N bonds.[7] Hence the ease of dealkylation is the more likely explanation especially since the insolubility of aminoalcohols and *o*-phenylenediamine in non-polar media necessitated the use of dioxan as solvent which may have promoted ionisation of the incipient P(V) and hence the dealkylation.

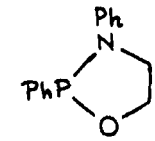
Thus an attempt was made to prepare phosphoranes containing P—N and P—S links by reacting trico-ordinates (**12–17**) containing these links with acrylonitrile. All the nitrogen containing molecules (**12–15**) *polymerised* the acrylonitrile and the dithiophosphonites **16** and **17** showed no detectable reaction by ^{31}P nmr after 24 h at room temperature.



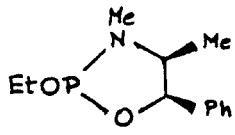
12



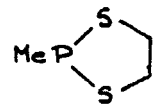
13



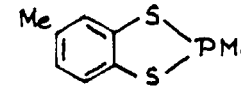
14



15



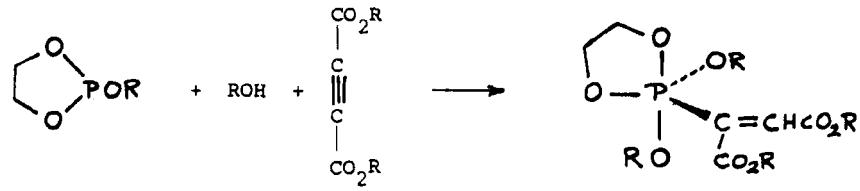
16



17

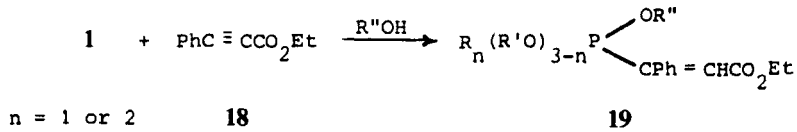
The interaction of trico-ordinate phosphorus compounds with alkynes generally does not lead to phosphoranes[11] but an exception was reported by Burgada[15] who

obtained monocyclic phosphoranes from cyclic phosphites and alkynes (Eq. (C))



(C)

However, the reaction of phosphinites and phosphonites with methyl propiolate in benzene in the presence of ethanol failed to produce phosphoranes. In each case the methyl propiolate polymerised to give a dark brown solution leaving the tricoordinated phosphorus virtually intact. Greater success was achieved with ethyl phenylpropiolate **18** as substrate and Table II summarises the results as analysed by ^{31}P nmr. It seems that the presence of the phenyl group on the α-carbon of the alkyne sterically hinders the approach of the intermediate betaine to a second molecule of **18** thus inhibiting polymerisation and promoting the formation of the phosphorane **19**.



As with the alkenes, attempts to isolate the phosphoranes resulted in decomposition to reactants and hence the ^1H nmr data is derived from the spectra of mixtures in which the phosphoranes were present in high yield.

Thus the synthetic method appears to be limited to compounds containing P—C and P—O bonds and it seems likely that a combination of the correct proton donating ability plus the weak nucleophilicity of the alkoxide ion relative to RS^- or RNH_2 allows alcohols to be used more successfully in the synthetic procedure.

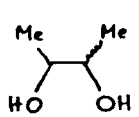
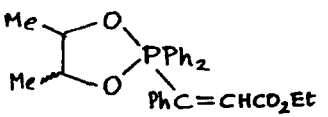
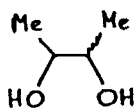
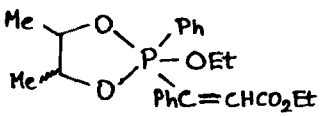
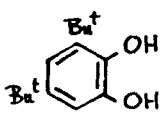
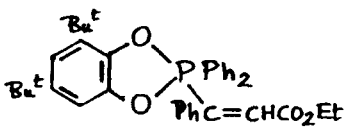
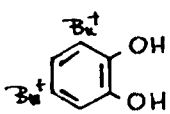
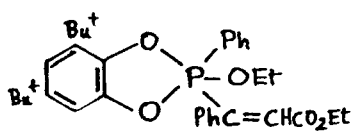
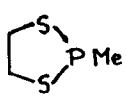
EXPERIMENTAL

The following compounds were available commercially from the sources indicated and were used without further purification. From BDH: ethyl acrylate; ethane-1,2-diol; butane-2,3-diol [66% meso, 34%(±)]; ethanolamine; diethanolamine; ethane-1,2-thiol; ethanethiol; 2-aminophenol; *o*-phenylenediamine; 3,5-di-*t*-butylcatechol; methyl propiolate; from Fluka: 3,4-toluene-dithiol; from Aldrich: *L*-ephedrine and ethyl-3-phenylpropiolate. Methyl diphenylphosphinite, ethyl diphenylphosphinite and diethyl phenylphosphonite were obtained from Maybridge Chemical Co., and were redistilled before use to give pure material containing only one ^{31}P nmr signal in each case at δ 116.4, 109.4, and 153.5 ppm (in C_6D_6) respectively. Acrylonitrile was a freshly distilled sample obtained from ICI (Corporate Laboratory) and stored over Gade 4A molecular sieves. Isopropyl di-*p*-isopropoxyphenylphosphinite and 2-cyanoethyldiphenylphosphine were also gifts from ICI. Diethyl peroxide, 1,3,4-trimethyl-Δ^3-phospholene and 1-ethanethio-3,4-dimethyl-Δ^3-phospholene were all prepared as described previously.[16]

Preparation of bis(diethylamino)phenylphosphine $PhP(NEt_2)_2$ **12**. Phenylphosphonous dichloride (17.9 g, 0.1 mol) in dry ($LiAlH_4$) benzene (80 ml) was added dropwise over a period of 1.5 h into a stirred solution of diethylamine (114.6 g, 0.2 mol) and triethylamine (20.2 g, 0.2 mol) in dry ($LiAlH_4$) benzene (30 ml) at 0–5°C. The resulting mixture was stirred for another hour and subsequently heated to reflux for 45 min. Triethylamine hydrochloride was removed by filtration and the solvent removed *in vacuo*. The

TABLE II

The reactions of trico-ordinate phosphorus compounds with ethyl phenylpropiolate $PhC{\equiv}CCO_2Et$ in toluene and in the presence of alcohols, diols and catechols

$R_nP(OR)_{3-n}$	ROH	Product	$\delta^{31}P$ of P (V)	Yield[a]	Comments
Ph_2POEt	EtOH	$Ph_2(EtO)_2PCPh{=}CHCO_2Et$	−53.9	63	100% reaction, 24 h
$PhP(OEt)_2$	EtOH	$Ph(EtO)_3PCPh{=}CHCO_2Et$	−45.1	70	100% reaction, 24 h
Ph_2POEt			−36.7 −38.1	50 22	$\frac{\text{meso}}{(\pm)}$, 24 h
$PhP(OEt)_2$			−32.4 −30.4	41 9	$\frac{\text{meso}}{(\pm)}$, 24 h
Ph_2POEt			−23.5	43	—
$PhP(OEt)_2$			−21.7	68	—
	EtOH	No Phosphorane		—	After 20 h. 10% reactant P (III) left, 90% tetracoordinate-P, δ + 76 to + 38 ppm

[a]Yields based on integration of ^{31}P nmr spectra.

residue was distilled to give a colourless oil (20.1 g, 80%), b.p. 105–110°C at 0.04 mmHg, lit.,[17] 123–125°C at 0.2 mmHg; δ ^{31}P (C_6D_6) 97.2; δ ^{1}H (C_6D_6) 1.05 (12 H, t, $^3J_{HH}$ 6 Hz), 3.05 (8 H, dq, $^3J_{PH}$ 4 Hz, $^3J_{HH}$ 6 Hz), and 7.1–7.7 (5 H, m).

Preparation of 1,3,2-oxazaphospholidines **13** *and* **14**. A mixture of *bis*(diethylamino)phenylphosphine **12** (2.52 g, 0.01 mol) and *N*-ethylaminoethanol (0.9 g, 0.01 mol) was heated for 3 h at 150–170°C and the resulting residue was distilled to give (1.4 g, 70%) of **13**, b.p. 60°C at 0.05 mmHg, *lit.*[18] b.p. 79–81°C at 1 mmHg; δ ^{31}P (C_6D_6): 140.1; δ ^{1}H (C_6D_6) 1.05 (3 H, t, ^3J = 6 Hz), 2.3–3.1 (4 H, m), 3.5–3.9 (2 H, m) and 7.05–7.6 (5 H, m).

Likewise a sample of **12** (2.52 g, 0.01 mol) when heated under reflux in xylene with *N*-phenylaminoethanol (1.37 g, 0.01 mol) for 2.5 h gave (1.8 g, 80%) of **14**, b.p. 135°C at 0.05 mmHg and m.p. 75°C, lit.[18] b.p. 130–132°C at 0.03 mmHg and m.p. 75–76°C; δ ^{31}P nmr (C_6D_6) 127.7; δ ^{1}H nmr (C_6D_6) 2.7–3.15 (2 H, m), 3.45–4.15 (2 H, m) and 6.7–7.55 (10 H, m).

Preparation of 2-chloro-3,4-dimethyl-5-phenyl-1,3,2-oxazaphospholidine **20**. A solution of phosphorus trichloride (2.75 g, 0.02 mol) in dry ($LiAlH_4$) benzene (25 ml) was added dropwise to a stirred solution of *L*-ephedrine (3.3 g, 0.02 mol) and *N*-methyl morpholine (4.04 g, 0.04 mol) at 0–5°C. When the addition was complete the resulting mixture was allowed to warm to ambient and stirred for 1 h. *N*-methyl morpholine hydrochloride was removed by filtration and the solvent removed *in vacuo*. Distillation of the residue gave a colourless liquid, (1.88 g, 41%), b.p. 120–125°C at 0.05 mm, lit.,[19] 130°C at 0.2 mm; δ ^{31}P (C_6D_6) 174.2; δ ^{1}H (C_6D_6) 0.74 (3 H, d C—CH_3, ^3J_H 7 Hz), 2.72 (3 H, d, N—CH_3, ^3J_P 16 Hz), 3.35–3.85 (1 H, m, N—C—H), 5.85 (1 H, dd, O—C—H, ^3J_H 7 Hz, ^3J_P 1 Hz) and 7.15–7.45 (5 H, m).

Preparation of 2-ethoxy-3,4-dimethyl-5-phenyl-1,3,2-oxazaphospholidine **15**. A solution of ethanol (0.046 g, 1×10^{-3} mol) and triethylamine (0.11 g, 1×10^{-3} mol) in dry ($LiAlH_4$) benzene (10 ml) was added dropwise to a stirred solution of **20** (0.23 g, 1×10^{-3} mol) at 5°C. The resulting mixture was stirred for 1 h and the triethylamine hydrochloride filtered off. Removal of the solvent *in vacuo* and distillation of the residue gave a colourless oil, (0.16 g, 67%), b.p. 130–135°C at 0.05 mm, δ ^{31}P (C_6D_6) 138.7, δ ^{1}H (C_6D_6) 0.5 (3 H, d, C—CH_3, ^3J_H 7 Hz), 1.11 (3 H, t, OCH_2CH_3, ^3J_H 7 Hz), 2.48 (3 H, NCH_3, ^3J_P 12 Hz), 3.05–4.0 (3 H, m, NCH, P—OCH_2), 5.61 (1 H, dd, P—O—CH, ^3J_H 7 Hz, ^3J_P 1 Hz) and 7.0–7.35 (5 H, m).

Preparation of 2-methyl-1,3,2-dithiaphospholane **16**. Methylphosphonous dichloride (5.85 g, 0.05 mol) in dry ($LiAlH_4$) benzene was added dropwise to a cold solution of ethanedithiol (4.7 g, 0.05 mol) and triethylamine (10.1 g, 0.1 mol) at 0–5°C. The mixture was stirred for 1 h and allowed to warm to ambient. Triethylamine hydrochloride was removed by filtration and solvent removed *in vacuo*. The residue was distilled to give a colourless liquid, (4.7 g, 88%), b.p. 70°C at 0.9 mmHg, lit.,[20] 90°C at 5 mmHg; δ ^{31}P (C_6D_6) 41.4; δ ^{1}H (C_6D_6) 1.04 (3 H, d, $^2J_{PH}$ 11 Hz) and 2.7 (4 H, s).

Preparation of 2,7-dimethyl[4,5]-benzo-1,3,2-dithiophospholane **17**. The same experimental procedure was adopted to prepare **17** in 65% yield, b.p. 80–85°C at 0.05 mmHg, lit.,[20] 110–114°C at 2 mmHg, δ ^{31}P (C_6D_6) 55.4; δ ^{1}H (C_6D_6) 1.2 (3 H, d, $^2J_{PH}$ 11 Hz) 1.92 (3 H, s) and 7.05–7.3 (3 H, m).

The reaction of trico-ordinated phosphorus compounds with acrylonitrile and ethyl acrylate. In a typical reaction the trico-ordinated phosphorus compound (10^{-3} mol) was added to a solution of the alkene (10^{-3} mol) together with an alcohol or catechol (10^{-3} mol) in dry ($LiAlH_4$) benzene (3 ml). The reactions were followed in the ^{1}H nmr by observing the disappearance of the olefinic protons. The following ^{1}H nmr data on the phosphoranes were deduced from reaction mixtures which contained a high proportion of the phosphorane product.

$Ph_2P(OEt)_2CH_2CH_2CO_2Et$: δ, 0.8 (6 H, t, ^3J = 7, 2 × $POCH_2CH_3$), 1.2 (3 H, t, ^3J = 7, $CO_2CH_2CH_3$), 2.5–3.05 (4 H, m, PCH_2CH_2), 3.4–4.3 (6 H, m, 2 × $POCH_2CH_3$ and $CO_2CH_2CH_3$), 7.1–8.1 (10 H, m, aromatic protons).

$Ph_2P(OEt)_2CH_2CH_2CN$: δ, 0.8 (6 H, t, ^3J = 7, 2 × $POCH_2CH_3$), 2.3–2.85 (4 H, m, PCH_2CH_2), 3.3–3.9 (4 H, m, 2 × $POCH_2CH_3$) and 7.0–8.0 (10 H, m, aromatic protons).

$PhP(OEt)_3CH_2CH_2CO_2Et$: δ, 1.0 (9 H, t, 3 × $POCH_2CH_3$), 1.03 (3 H, t, $COCH_2CH_3$), 2.2–3.0 (4 H, m, PCH_2CH_2), 3.25–3.85 (6 H, m, 3 × $POCH_2CH_3$), 4.0 (2 H, q, $CO_2CH_2CH_3$) and 7.1–7.7 (5 H, m, aromatic).

$Ph_2(CNCH_2CH_2)POCHMe \cdot CHMeO$: δ, 0.94–1.2 (9 H, m, 2 × C—CH_3 and CH_3CH_2OH displaced from P), 1.7–2.2 (4 H, m, PCH_2CH_2), 3.2–3.84 (5 H, m, 2 × POCH and CH_3—CH_2OH displaced from P) and 7.1–7.6 (10 H, m, aromatic).

$Ph_2(EtO_2CCH_2CH_2)POCHMe \cdot CHMeO$: δ, 0.97–1.21 (11 H, m, 2 × CCH_3, $CO_2CH_2CH_3$ and CH_3CH_2OH displaced from P), 2.4–2.51 (4 H, m, PCH_2CH_2), 3.2–4.04 (7 H, m, 2 × POCH, $CO_2CH_2CH_3$ and CH_3CH_2OH displaced from P) and 7.0–7.6 (10 H, m, aromatic).

$Ph_2(CNCH_2CH_2)POC_6H_2Bu^t_2O$: δ, 1.05 (3 H, t, CH_3CH_2OH displaced from P), 1.25 (9 H, s, $(CH_3)_3C$), 1.34 (9 H, s, $(CH_3)_3C$) 1.9–2.2 (4 H, m, PCH_2CH_2), 3.5 (2 H, q, CH_3CH_2OH displaced from P) and 6.9–7.7 (12 H, m, aromatic).

$CH_2MeC{=}CMeCH_2PO(CHMe)_2O$: δ, 1.0 (6 H, m, $CO_2CH_2CH_3$ and CH_3CH_2SH displaced from P), 1.05 (6 H, d, 2 × CH_3—CH), 1.5 (6 H, s, $CH_3C{=}CCH_3$), 2.1–2.85 (10 H, m, 2 × PCH_2, PCH_2CH_2 and CH_3CH_2SH displaced from P) and 3.3–4.15 (4 H, m, 2 × POCH and $CO_2CH_2CH_3$).

$CH_2MeC{=}CMeCH_2POC_6H_2Bu^t_2O$
$CH_2CH_2CO_2Et$
δ, 0.9 (3 H, t, CH_3CH_2SH displaced from P), 1.02 (3 H, t, $CO_2CH_2CH_3$), 1.25 and 1.30 (18 H, both s, 2 × $(CH_3)_3C$), 1.45 (6 H, s, $CH_3C{=}CCH_3$), 2.0–2.95 (10 H, m, 2 × PCH_2, PCH_2CH_2 and CH_3CH_2SH displaced from P), 3.85 (2 H, q, $CO_2CH_2CH_3$) and 6.9–7.3 (2 H, m).

The reaction of trico-ordinated phosphorus compounds with ethyl phenylpropiolate. The same experimental procedure was employed and the reactions were followed in the ^1H nmr by observing the appearance of the olefinic proton of the products. The following ^1H nmr data on the phosphoranes were deduced from reaction mixtures which contained a high proportion of the phosphorane product.

$Ph_2P(OEt)_2CPh{=}CHCO_2Et$: δ, 0.74 (6 H, t, 2 × $POCH_2CH_3$), 0.93 (3 H, t, $CO_2CH_2CH_3$), 3.3–4.2 (6 H, m, 2 × $POCH_2CH_3$ and $CO_2CH_2CH_3$), 6.6 (1 H, d, ^3J_P = 25, PC=CH) and 6.85–7.92 (15 H, m, aromatic).

$PhP(OEt)_3CPh{=}CHCO_2Et$: δ, 0.8 (9 H, t, 3 × $POCH_2CH_3$), 1.0 (3 H, t, $CO_2CH_2CH_3$), 3.2–4.2 (8 H, m, 3 × $POCH_2CH_3$ and $CO_2CH_2CH_3$), 6.29 (1 H, d, ^3J_P = 25, PC=CH) and 6.8–7.95 (10 H, m, aromatic).

$Ph_2(EtO_2CCH{=}CPh)POCHMe \cdot CHMeO$: δ, 0.7–1.3 (12 H, m, 2 × CH_3C, $CO_2CH_2CH_3$ and CH_3CH_2OH displaced from P), 3.25–4.2 (7 H, m, 2 × POCH, $CO_2CH_2CH_3$ and CH_3CH_2OH displaced from P), 6.15 (1 H, d, ^3J_P = 19, PC=CH) and 6.75–8.0 (15 H, m, aromatic).

$Ph(EtO)(EtO_2CCH{=}CPh)POC_6H_2BU^t_2O$: δ, 0.7–1.6 (27 H, m, $POCH_2CH_3$, 2 × $(CH_3)_3C$, $CO_2CH_2CH_3$ and CH_3CH_2OH displaced from P), 3.3–4.1 (7 H, m, $POCH_2CH_3$, $CO_2CH_2CH_3$ and CH_3CH_2OH displaced from P), 6.2 (1 H, d, ^3J_P = 28, PC=CH) and 6.85–7.95 (12 H, m, aromatic).

The reaction of 2-cyanoethyldiphenylphosphine with 3,5-di-t-butyl-o-quinone. 2-Cyanoethyldiphenylphosphine (0.19 g, 10^{-3} mol) in benzene (1 ml) was added to a solution of 3,5-di-*t*-butyl-*o*-quinone (0.22 g, 10^{-3} mol) in benzene (2 ml). After 130 min the following ^{31}P and ^1H nmr spectra were recorded: δ ^{31}P (C_6D_6) −24.0; δ ^1H (C_6D_6) 1.25 (9 H, s), 1.32 (9 H, s), 1.85–2.1 (4 H, m) and 6.8–7.7 (12 H, m).

The reaction of 2-cyanoethyldiphenylphosphine with diethyl peroxide. 2-Cyanoethyldiphenylphosphine (0.196 g, 10^{-3} mol) was mixed with diethylperoxide (0.18 g, 2 × 10^{-3} mol) in perdeuterobenzene (2 ml) and allowed to stand at room temperature in a sealed nmr tube. After three days the mixture contained **3**, (R = Ph, R' = Et, *n* = 2, X = CN) at δ −52.3 (26%), 2-cyanoethyldiphenylphosphine (δ −16.2, 39%), 2-cyanoethyldiphenylphosphine oxide (δ 28.7, 13%), ethyl diphenylphosphinite (δ 110.8, 8%) and diphenyltriethoxyphosphorane (δ −43.6, 14%). The identity of the latter was confirmed by independent synthesis from ethyl diphenylphosphinite and diethyl peroxide and the remaining components of the mixture (except **3**) were identified by addition of authentic samples of each compound and recording ^{31}P nmr data after each addition.

ACKNOWLEDGMENTS

We thank the SERC for financial support.

REFERENCES

1. Present address: ICI, Agricultural Div., Billingham, Cleveland.
2. Present address: ICI, Petrochemicals and Plastics Div., Welwyn Garden City, Hertfordshire.
3. J. Emsley and C. D. Hall, "The Chemistry of Phosphorus," Harper and Row, (1976), Chapter 6.
4. (a) D. B. Denney, D. Z. Denney, B. C. Chang and K. L. Marsi, *J. Am. Chem. Soc.*, **91**, 5243 (1969); (b) D. B. Denney and D. H. Jones, *J. Am. Chem. Soc.*, **91**, 5821 (1969).
5. D. B. Denney, D. Z. Denney, P. J. Hammond and Y.-P. Wang, *J. Am. Chem. Soc.*, **103**, 1785 (1981).
6. F. Ramirez, *Acc. Chem. Res.*, **1**, 168 (1968).
7. R. R. Holmes, "Pentacoordinated Phosphorus Structure and Spectroscopy," A.C.S. Monograph, Washington D.C. (1980), Vol. I.
8. P. D. Beer, R. C. Edwards, C. D. Hall, J. R. Jennings and R. J. Cozens, *J. Chem. Soc., Chem. Commun.*, 351 (1980).
9. P. J. Smith and A. P. Tupciauskas, *Ann. Rep. NMR Spectroscopy*, **8**, 291 (1978).
10. B. C. Chang, W. Conrad, D. B. Denney, D. Z. Denney, R. Edelman, R. L. Powell and D. W. White, *J. Am. Chem. Soc.*, **93**, 4004 (1971).
11. M. A. Shaw and R. S. Ward, "Topics in Phosphorus Chemistry," New York (1972), Vol VII, p. 11.
12. D. Ranganathan, C. B. Rao and S. Ranganathan, *J. Chem. Soc., Chem. Commun.*, 975 (1979).
13. P. J. Hammond, J. R. Lloyd and C. D. Hall, *Phosphorus and Sulphur*, **10**, 41 (1981).
14. R. J. Cozens, J. R. Jennings, P. J. Hogan and L. S. M. Kelly, U.S. Patent, 4,238,422 (1981).
15. R. Burgada, J. Leroux and Y. O. El Khoshnieh, *Tetrahedron Lett.*, 925 (1980).
16. P. J. Hammond, G. Scott and C. D. Hall, *J. Chem. Soc., Perkin Trans. 2*, 205 (1982).
17. O. Mitsunobu, T. Ohashi, M. Kikuchi and T. Mukaiyama, *Bull. Chem. Soc. Japan*, **39**, 214 (1966).
18. O. Mitsunobu, T. Ohashi, M. Kikuchi and T. Mukaiyama, *Bull. Chem. Soc. Japan*, **40**, 2964 (1967).
19. C. R. Hall and T. D. Inch, *Tetrahedron Lett.*, **40**, 3645 (1976).
20. M. Wieber, J. Otto and M. Schmidt, *Angew. Chem. Int. Ed. Engl.*, **3**, 586 (1964).