# The Kinetics and Mechanism of the Reactions of Acyclic Trico-ordinate Phosphorus Compunds with Diethyl Peroxide

John R. Lloyd, Nicholas Lowther, and C. Dennis Hall *
Department of Chemistry, King's College, University of London, Strand, London WC2R 2LS

The kinetics of the reactions of acyclic phosphinites, phosphonites, and phosphines with diethyl peroxide in benzene or acetonitrile as solvent are reported together with the activation parameters for phosphinites and phosphonites and Hammett ρ values for all three types of trico-ordinate phosphorus. The data reveal a bimolecular, non-polar transition state for each reaction with ρ values which are virtually independent of the nature of the trico-ordinate phosphorus species.
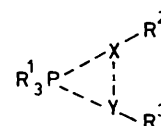
The reactions of trico-ordinate phosphorus compounds with weak σ bonds as in peroxides [1,2] and sulphenate esters [3,4] are now well established routes to pentaco-ordinate phosphorus. Both substrates exhibited anomalous rate sequences [2,5,6] which were not consistent with nucleophilic attack by phosphorus and were explained as a biphilic insertion into the σ bond through a non-polar transition state. Kinetic studies [7,8] using diethyl peroxide and cyclic P^{III} compounds confirmed this hypothesis as revealed by a second-order reaction and activation parameters consistent with a bimolecular transition state coupled with a low sensitivity of reaction rate to solvent polarity and Hammett ρ values in the region of −0.3. Strikingly similar kinetic results were obtained by Baumstark using triarylphosphines and dioxetane as substrate [9] and the resultant picture is of a very low nucleophilic component from phosphorus in a transition state (Figure 1) leading directly to the pentaco-ordinated structure. The work described below extends the kinetic studies of the reaction with diethyl peroxide to a range of acyclic phosphorus compounds, $Ar_nP(OR)_{3-n}$ [equation (1)] where $n = 0$—3, in an attempt to refine the mechanistic picture.

$$Ar_nP(OR)_{3-n} + Et_2O_2 \longrightarrow Ar_nP(OR)_{3-n}(OEt)_2 \quad (1)$$
$$(1)$$
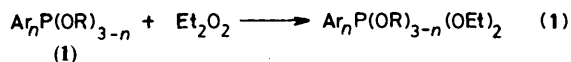
Results and Discussion

The reactions of isopropyl diphenylphosphinite (1; $n = 2$) and di-isopropyl phenylphosphonite (1; $n = 1$) with diethyl peroxide in benzene as solvent were monitored by ^{31}P n.m.r. The phosphinite reaction initially produced low concentrations of species with ^{31}P n.m.r. signals at δ_P +28.5 [$Ph_2P(O)OEt$] and +27.1 p.p.m. [$Ph_2P(O)OPr^i$] and then after 52 min a signal at δ_P −43.9 p.p.m., assigned to $Ph_2P(OPr^i)(OEt)_2$, followed by a signal developing at δ_P −44.5 p.p.m., assigned to $Ph_2P(OEt)_3$ from the disproportionation of the initial phosphorane. A typical set of results is shown in Table 1 and after three weeks at room temperature the mixture contains 64.7% as phosphoranes, 32.1% as oxides, and 3.1% as unchanged phosphinite based on the total digitized integration versus an internal standard (Ph_3PO). The results suggest that the initial phosphorane (3) may disproportionate to (4) and (5) and thence possibly to (6), all of which may ultimately dealkylate to a mixture of oxides (7) and (8) (Scheme 1). Only two phosphoranes, [probably (3) and (4)] are, however, observable as separate signals.

The assignment of chemical shifts, although to some extent tentative, is in agreement with the value for $Ph_2P(O)OPr^i$ (this work) and with literature values for $Ph_2P(O)OEt^1$ and $Ph_2P(OEt)_3$.[1] The rationalization is also in accord with the fact that phosphoranes containing large alkoxy groups (e.g. Pr^iO and Bu^tO) are relatively unstable due to steric crowding within the pentaco-ordinate structure.[10] A similar sequence of events occurs with di-isopropyl phenylphosphonite (Table 2) in which

X,Y = O; R^2, R^3 = Et

X = O, Y = S; R^2 = alkyl, R^3 = aryl

Figure 1. Representation of transition state for reactions of trico-ordinate phosphorus compounds with dialkyl peroxides and sulphenate esters.
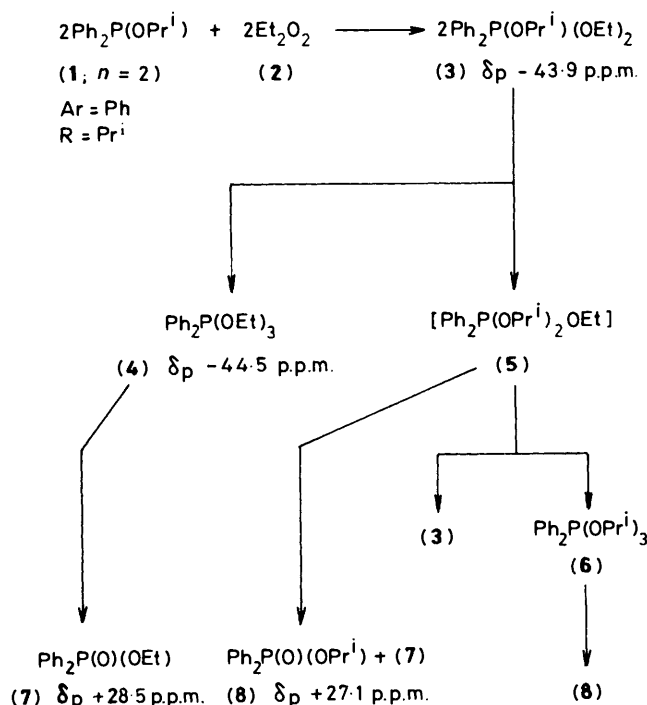
Scheme 1. Reaction of $Ph_2P(OPr^i)$ with Et_2O_2 in benzene

the initial phosphorane at δ −58.9 p.p.m., assigned to PhP-$(OPr^i)_2(OEt)_2$, slowly dealkylates to give three oxides but, as its concentration increases, also disproportionates to give two more detectable tetra-alkoxyphosphoranes whose precise structure remains unknown. The theoretical possibilities are outlined in Scheme 2 but since (12) which is expected to have the highest positive chemical shift has a known δ_P of 16.9 p.p.m.,[11] it seems

Table 1. The reaction of isopropyl diphenylphosphinite (1; $n = 2$) with (2) in benzene at 35 °C

Time (min)	δ_P (p.p.m.)				
	104.9 %[a]	28.5 %	27.1 %	-43.9 %	-44.5 %
18	90.7	1.3	8.0		
52	83.7	3.1	10.9	2.3	
79	80.3	3.2	10.0	4.3	2.2
108	75.7	4.2	9.8	6.4	3.9
139	71.6	4.5	10.0	7.2	6.7
171	68.9	3.9	9.6	8.3	9.3
199	65.1	4.0	10.4	10.0	10.5
234	60.5	4.1	10.9	12.0	12.5
269	58.7	3.7	10.6	11.4	15.6
306	55.7	3.8	10.6	12.7	17.2
343	52.7	4.3	12.3	13.0	17.7
380	47.6	5.2	11.3	16.5	19.4
413	45.8	4.4	12.0	16.1	21.7
454	43.6	4.9	11.7	17.5	22.3
30 000	3.1	8.1	24.0	32.7	32.0
Assignments[b]	Ph_2POPr^i	$Ph_2P(O)OEt$	$Ph_2P(O)OPr^i$	$Ph_2P(OPr^i)(OEt)_2$	$Ph_2P(OEt)_3$

[a] Percentage of total digitized integration. [b] See text.

Table 2. The reaction of $PhP(OPr^i)_2$ (1; $n = 1$) with (2) in benzene at 35 °C

Time (min)	δ_P (p.p.m.)						
	151.1 %[a]	21.5 %	16.5 %	15.5 %	-58.4 %	-58.9 %	-59.8 %
0	100						
65	98.8			1.2			
135	96.9			1.6		1.5	
200	94.3			2.5		3.2	
245	92.6			2.3		5.1	
290	89.3			2.7		7.9	
335	87.7			2.9		9.4	
1 290	55.6	6.6	1.6	6.0		30.2	
1 510	52.7	6.6	1.7	6.6		32.3	
1 690	47.9	8.0	2.1	7.8	3.7	30.6	
2 760	34.3	8.9	5.8	8.2	8.4	34.4	
2 955	30.7	8.3	3.6	8.9	11.9	36.5	
3 135	28.3	9.4	6.9	9.2	19.8	27.8	1.1
4 200	24.4	9.0	4.5	10.3	19.3	30.9	1.5
Assignments[b]	$PhP(OPr^i)_2$	$PhP(O)H(OPr^i)$	$PhP(O)(OEt)_2$	$PhP(O)(OPr^i)(OEt)$ and/or $PhP(O)(OPr^i)_2$	$PhP(OPr^i)(OEt)_3$	$PhP(OPr^i)_2(OEt)_2$	$PhP(OEt)_4$

[a] Percentage of total digitized integration. [b] Tentative, see text.

likely that the signal at δ_P 21.5 p.p.m. is due to $PhP(O)H(OPr^i)$ (lit.,[12] δ_P 20.8) formed perhaps as a consequence of the attack of (1) on (9). The complexity of the system prevents quantitative evaluation of the relative amounts of all the components in the reaction mixture but the general hypothesis receives support from a study of the reaction between di-isopropyl p-dimethyl-aminophenylphosphonite (1; $n = 1$, Ar $= p\text{-}Me_2NC_6H_4$) and (2). By using a reduced sweep width (1 kHz versus 10 kHz) and a modified pulse offset, five phosphorane signals were observed at δ_P -57.2, -57.4, -57.8, -58.3, and -59.2 p.p.m. as expected by phosphorane disproportionation (Scheme 3). It is therefore possible that the two signals from phosphoranes derived from $Ph_2P(OPr^i)$ actually represent three phosphoranes and by analogy the three high-field signals derived from $PhP(OPr^i)_2$ represent five phosphoranes. Modifying the pulse offset once more to concentrate on the oxide region and using the same sweep width (1 kHz) gave the three oxide signals at δ_P $+20.4$, $+19.4$, and $+18.4$ p.p.m. anticipated from this reaction. With triphenylphosphine, a signal was observed at δ_P -50.9 p.p.m.

Table 3. Rates of reaction of (1; $n = 1$ or 2) with (2) in benzene at 22.0—55.5 °C

Ph_2POPr^i		$PhP(OPr^i)_2$	
$T/°C$	$10^6 k_2/$ l mol^{-1} s^{-1}	$T/°C$	$10^6 k_2/$ l mol^{-1} s^{-1}
22.0	22.5	22.5	4.0
22.0	23.0	22.5	3.7
33.3	62.9	33.3	14.4
33.3	61.8	33.3	15.6
43.5	130	43.5	22.7
43.5	130	43.5	25.2
55.5	345	55.5	80.9
55.5	341	55.5	80.3

due to $Ph_3P(OEt)_2$, together with triphenylphosphine oxide at $+30.1$.[1,3]

The rates of the reactions of (1; $n = 0$—3) with an equimolar concentration of diethyl peroxide in benzene were determined

by monitoring the disappearance of (1) using ^{31}P n.m.r. and the second-order rate constants for Ph_2POPr^i and $PhP(OPr^i)_2$ over a range of temperature are recorded in Table 3. The resultant activation parameters appear in Table 4 and are consistent with a bimolecular transition state involving association of trico-ordinate phosphorus with (2). In all cases the rate of disappearance of (1) was, within experimental error, equal to the rate of appearance of total products and the rates measured with or without an internal standard (Ph_3PO) were identical. A single reaction with triphenylphosphine gave k_2 (308 K) 3.1×10^{-6} 1 mol^{-1} s^{-1} and a reaction between tri-iso-propyl phosphite and (2) gave no detectable products after three days. Thus at 308 K the rate sequence for reaction with (2) is $Ph_2P(OPr^i) > PhP(OPr^i)_2 > Ph_3P > (Pr^iO)_3P$ (rate ratio at 306 K, 20:5:1: $\ll$1) which affords quantitative confirmation of earlier studies on the peroxide reaction.[2,5] In addition, the rate for Ph_2POPr^i in CH_3CN for which 10^6k_2 (298 K) $= 32$, when compared with 10^6k_2(298 K) $= 30$ in benzene, denotes a nonpolar transition state.

The rate of reaction with various substituents, X, in the phenyl rings of (1; $n = 1$ or 2) is recorded in Table 5 together

with the Hammett ρ values derived from these data by a corre-lation with the σ constants of X. The 'fair' to 'poor' correlation coefficients are a reflection of the imprecision of the kinetic method over a small rate range and graphical representations
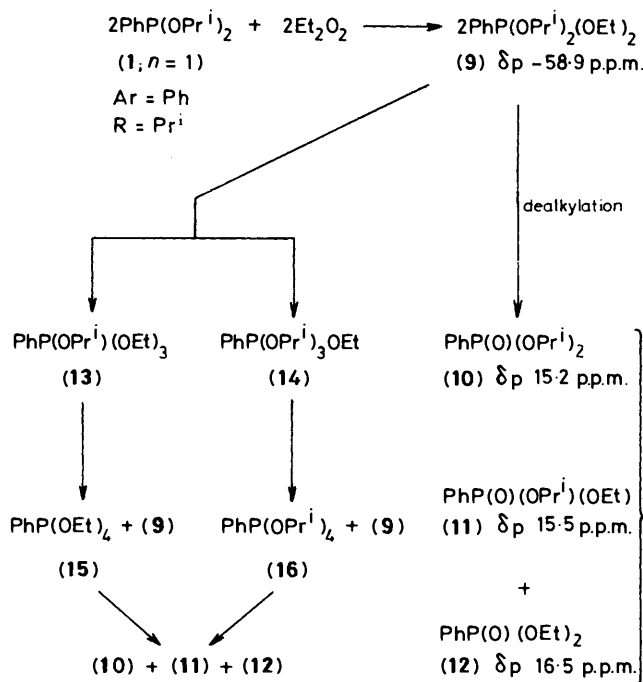
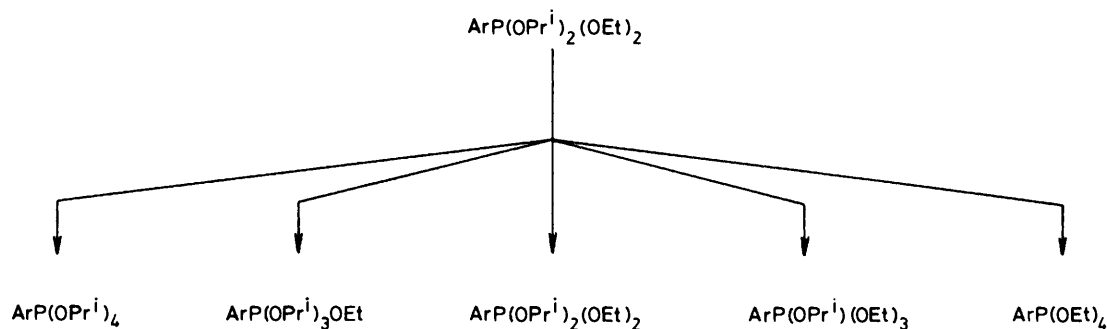**Scheme 2.** Reaction of Ph_2POPr^i with Et_2O_2 in benzene at 31 °C

Table 4. Rate coefficients at 25 °C and activation parameters for the reaction of (1; $n = 1$ or 2) with (2) in benzene

Parameter	$Ph_2P(OPr^i)$	$PhP(OPr^i)_2$
10^6k_2 (25 °C)/l mol^{-1} s^{-1}	30	5.4
E_A/kcal mol^{-1}	15.4	16.9
$\Delta G^{\ddagger}$/kcal mol^{-1}	19.5	20.5
$\Delta H^{\ddagger}$/kcal mol^{-1}	14.8	16.3
$\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}	$-16(\pm2)$	$-14(\pm2)$

Table 5. Rate coefficients and Hammett ρ values for the reaction of Ar_2POPr^i and $ArP(OPr^i)_2$ with (2) in benzene at 35 °C

Ar_2POPr^i			$ArP(OPr^i)_2$		
Ar	10^6k_2/l mol^{-1} s^{-1}	$\Sigma\sigma^a$	Ar	10^6k_2/l mol^{-1} s^{-1}	$\Sigma\sigma^a$
$2 \times p$-$Pr^iOC_6H_4$	143	-0.90	p-$Me_2NC_6H_4$	35	-0.83
C_6H_5, p-$Et_2NC_6H_4$	116	-0.61	p-$MeOC_6H_4$	28	-0.27
C_6H_5, p-$MeOC_6H_4$	93	-0.27	p-$Pr^iOC_6H_4$	17	-0.45
C_6H_5, p-$Pr^iOC_6H_4$	87	-0.45	p-MeC_6H_4	15	-0.17
$2 \times m$-MeC_6H_4	68	-0.14	C_6H_5	16	0
$2 \times C_6H_5$	63	0	p-$CF_3C_6H_4$	11	$+0.54$
$2 \times p$-ClC_6H_4	63	$+0.46$			
$2 \times p$-BrC_6H_4	43	$+0.46$			
$2 \times p$-$CF_3C_6H_4$	45	$+1.08$			

ρ -0.27 ± 0.05 (r 0.930) ρ -0.34 ± 0.11 (r 0.850)

^{a} Values from (i) D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, 1958, **23**, 420 and (ii) C. D. Ritchie and W. F. Sayer, *Prog. Phys. Org. Chem.*, 1964, **2**, 334.
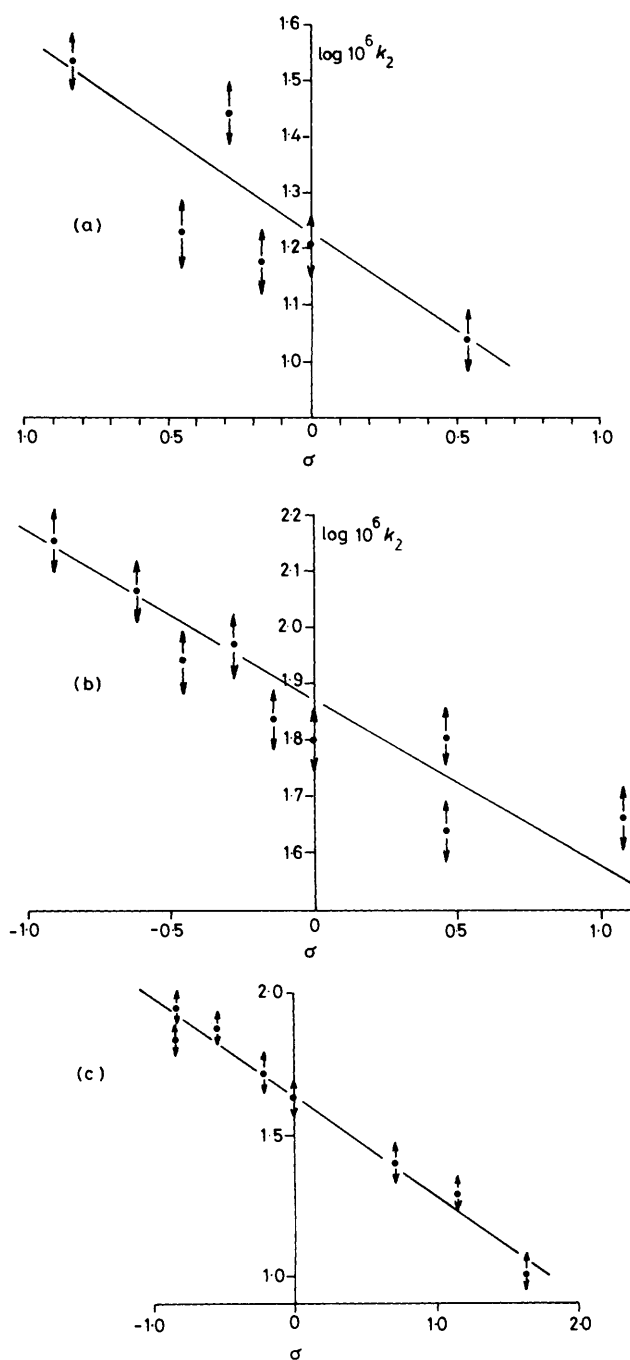

Scheme 3. Ar $= p$-$Me_2NC_6H_4$

Figure 2. Hammett plots of log k_2 versus σ for the reactions of diethyl peroxide with (a) $ArP(OPr^i)_2$, (b) $Ar_2P(OPr^i)$, and (c) Ar_3P in benzene at 35 °C

Table 6. Relative rates and Hammett ρ values for the reaction of Ar_3P with (2) in benzene at 306 K

Competition (P_A/P_B)	Product ratio $P_A(OEt)_2/P_B(OEt)_2$	$\Delta\sigma$
$(m\text{-MeC}_6H_4)_3P/(C_6H_5)_3P$	1.2	-0.21
$(p\text{-MeOC}_6H_4)_2PC_6H_5/(m\text{-MeC}_6H_4)_3P$	1.5	-0.33
$(C_6H_5)_3P/(p\text{-ClC}_6H_4)_3P$	1.3	-0.69
$(p\text{-ClC}_6H_4)_3P/(m\text{-ClC}_6H_4)_3P$	1.6	-0.44
$(m\text{-ClC}_6H_4)_3P/(p\text{-CF}_3C_6H_4)_3P$	2.1	-0.55
$p\text{-Me}_2NC_6H_4P(C_6H_5)_2/(p\text{-MeOC}_6H_4)_3P$	1.03	-0.29

Average ρ -0.35 ± 0.03 (r 0.981)

phosphorus reactant. We have observed a similar phenomenon with a variety of substrates and the results of these experiments will be the subject of subsequent papers.*

Experimental

Routine ^1H n.m.r. data were recorded on a Perkin-Elmer R12B spectrometer operating at 60 MHz with tetramethylsilane as internal standard. The ^{31}P n.m.r. data were recorded on a Brüker HFX 90 instrument operating at 36.43 MHz and all chemical shifts are reported in p.p.m. (downfield, positive) relative to external 85% H_3PO_4. All solvents were rigorously dried and deoxygenated before use and diethyl peroxide was prepared as described previously.[7] The triarylphosphines were all obtained commercially (Alfa, Lancaster Synthesis, Maybridge, or Strem) and were purified before use either by chromatography on alumina (CH_2Cl_2 eluant) and/or recrystallized from ethanol. The phosphorus chemical shifts (in benzene) and m.p.s are compiled in Supplementary Publication No. SUP 56122 (4 pp.).†

Preparation of Bis-substituted Isopropyl Diarylphosphinites. **(1; n = 2).**—These compounds were prepared by the reactions of Grignard reagents with isopropyl phosphorodichloridite and a typical procedure is described below.

Preparation of isopropyl phosphorodichloridite. Propan-2-ol (120 g, 2 mol) was added dropwise with vigorous stirring to phosphorus trichloride (329 g, 2.3 mol) at -5 °C during 2 h and the reaction mixture was stirred at ambient temperature overnight. Isopropyl phosphorodichloridite (96 g, 30%) was distilled as a liquid, b.p. 129—131 °C at 760 mmHg (lit.,[13] 40 °C at 20 mmHg), $\delta_P(C_6D_6)$ 173.9 p.p.m; δ_H (CDCl$_3$) 4.56—5.52 (m, 1 H) and 1.40 (d, 6 H, J 6 Hz).

Preparation of isopropyl bis-(p-trifluoromethyl)phenyl-phosphinite. A solution of p-trifluoromethylphenylmagnesium bromide (0.069 mol) in dry (LiAlH$_4$) tetrahydrofuran (100 ml) was added dropwise to a stirred solution of the above dichloridite (5.45 g, 0.034 mol) in tetrahydrofuran (50 ml) during 2 h at -40 °C. The mixture was stirred at room temperature overnight and pyridine (10 g, 0.13 mol) was then added dropwise with stirring. After filtration under nitrogen the solvent was removed *in vacuo* and the residue was triturated with n-pentane

including error bars give convincing linear relationships (Figure 2). Table 6 records a series of *relative rates* observed with (1; $n = 3$) and the corresponding ρ value derived from a plot against σ (Figure 2c). In each case the ρ values are low and negative indicating a low sensitivity to substituent effects but a slight nucleophilic component to the transition state. This is entirely consistent with previous data on the peroxide reaction [7,8,9b] and emphasises, yet again, that only a low degree of positive charge develops on phosphorus in reaching the transition in line with the observed solvent effect. It should also be noted that, despite a rate range of 20, the observed ρ value is entirely independent of the nature of the trico-ordinate

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* We are indebted to a referee for pointing out that since σ values are derived from equilibria in aqueous solution, they may not offer a suitable model for reactions in aprotic media. However, σ gives the best correlation for this and a series of reactions with other substrates (to be reported) and has been shown to be the appropriate parameter in numerous earlier studies of the reactions of trico-ordinate phosphorus compounds in aprotic media (*e.g.* P. D. Bartlett and G. Meguerian, *J. Am. Chem. Soc.*, 1956, **78**, 3710; B. B. Jarvis and B. A. Marien, *J. Org. Chem.*, 1976, **41**, 2182).

† For details of Supplementary Publications see Instructions for Authors in *J. Chem. Soc., Perkin Trans.* 2, 1985, Issue 1.

(2 × 75 ml). The washings were combined, filtered, and after removal of the solvent the residue was distilled (Kugelrohr) to give the phosphinite (4.9 g, 35%), b.p. 135 °C at 0.01 mmHg.

The same procedure was employed for the synthesis of all the disubstituted phosphinites. The mono-substituted arylphenyl-phosphinites were prepared by the reaction of the appropriate Grignard reagent with isopropyl phenylphosphorochloridite, PhP(OPr^i)Cl, and were kindly supplied by I.C.I. Corporate Laboratory, The Heath, Runcorn, Cheshire. A full compilation of yields, b.p. data, and ^{31}P n.m.r. shifts are recorded in SUP 56122. Molecular masses of all the novel phosphinites were verified by mass spectrometry.

In each case the ^{1}H n.m.r. spectra were entirely consistent with the proposed structures and showed the appropriate number of aromatic protons together with the expected resonance signals for each aromatic substituent. In the case of the disubstituted (and parent) phosphinites the isopropoxy signals appeared as a 14 line signal at δ 3.65—4.40 (1 H, ^3J_P 9.3 Hz) and a doublet at 1.15 (6 H, ^3J_H 6.3 Hz). It is interesting to note that the fully coupled ^{19}F n.m.r. spectrum of (p-FC$_6$H$_4$)$_2$POPr^i showed the theoretical 18 line pattern with ^5J_P 4.9, ^4J_H 5.6, and ^3J_H 9.2 Hz.

With the three unsymmetrically substituted phosphinites, the isopropoxy group again gave a 14 line pattern at δ ca. 4, but the methyl signals appeared as a doublet of doublets (Δδ 0.05 p.p.m.) due to the non-equivalence of the methyl groups.

Preparation of Di-isopropyl Arylphosphonites (**1**; n = 1).— These compounds were prepared by the reaction of the appropriate Grignard reagents with the di-isopropyl phosphorochloridite and a typical procedure is described below.

Preparation of di-isopropyl phosphorochloridite. Pyridine (79.1 g, 1 mol) was added dropwise to a stirred solution of phosphorus trichloride (137.3 g, 1 mol) in dry (LiAlH$_4$) benzene (750 ml) whilst maintaining the temperature of the mixture at 0 °C. On completion of the addition a solution of propan-2-ol (60.1 g, 1 mol) in *NN*-dimethylaniline (121.2 g, 1 mol) was added dropwise during 20 min with the mixture maintained between 0 and −5 °C. A further quantity of propan-2-ol (60.1 g, 1 mol) was then added dropwise with stirring during 30 min and after filtration and removal of the solvent *in vacuo* the residue was distilled to give the chloridite (73.8 g, 40%), b.p. 66—67 °C at 14 mmHg (lit.,^{14} 62—64 °C at 12 mmHg), δ$_P$(C$_6$D$_6$) +165.8 p.p.m.; δ$_H$(C$_6$D$_6$) 4.08—4.83 (m, 2 H) and 1.17 (d, 12 H, ^3J_H 6 Hz).

*Preparation of di-isopropyl-*p-(NN-*dimethylamino*)*phenyl-phosphonite.* A solution of p-(NN-dimethylamino)phenyl-magnesium bromide (0.025 mol) in dry (LiAlH$_4$) tetrahydrofuran (50 ml) was added dropwise with stirring to a solution of the above chloridite (4.61 g, 0.025 mol) in tetrahydrofuran (50 ml) during 2 h at −30 to −40 °C. The solution was stirred and allowed to reach room temperature overnight. Pyridine (6 g, 0.076 mol) was then added slowly, with stirring, and the mixture was allowed to stand for 2 h. After filtration under nitrogen, the solvent was removed *in vacuo* and the residue was triturated with n-pentane (2 × 50 ml). The combined washings were filtered and after removal of the solvent the residue was distilled through a short Vigreux column to give the phosphonite (4.7 g, 68%) as an oil, b.p. 106—108 °C at 0.1 mmHg.

The same procedure was employed for a series of phos-phonites and the yields, b.p. data, and ^{31}P chemical shifts are recorded in SUP 56122. The molecular masses for each of these compounds were verified by mass spectrometry. In each case the ^{1}H n.m.r. spectra were entirely consistent with the required structures and again the isopropoxy groups showed a 14 line

pattern centred at δ ca. 4.2 (2 H) and a doublet of doublets (Δδ 0.05 p.p.m.) for the non-equivalent methyl groups of each isopropoxy unit centred at δ ca. 1.2.

Kinetic Procedures.—(a) *Phosphinites and phosphonites.* In a typical kinetic run, isopropyl di-*m*-tolylphosphinite (0.544 g, 2.0 mmol) and triphenylphosphine oxide (0.124 g, 0.43 mmol) were dissolved in [^{2}H$_6$]benzene (1.6 ml) in a 10 mm n.m.r. tube and then thermostatted at 30 °C. A sample of pure diethyl peroxide (223 μl, 0.18 g, 2.0 mmol) was then injected and the reaction was monitored by ^{31}P n.m.r. taking the digitized integration of phosphinite against the integration of the internal standard (Ph$_3$PO) as a measure of the remaining concentration of phosphinite. A plot of [phosphinite]$^{-1}$ *versus* time then gave a straight line (r > 0.99) the slope of which gave the second-order rate constant for each reaction.

(b) *Phosphines* (*competitive kinetics*). In a typical experiment a mixture of triphenylphosphine (0.25 g, 0.95 mmol) and tri-*m*-tolylphosphine (0.287 g, 0.95 mmol) in [^{2}H$_6$]benzene (2 ml) was thermostatted at 306 K and a sample of diethyl peroxide (106 μl, 0.95 mmol) was added. After 4 h at 306 K (< 10% reaction) the mixture was analysed by ^{31}P n.m.r. for the product ratios [Ph$_3$P(OEt)$_2$ and (*m*-CH$_3$C$_6$H$_4$)$_3$P(OEt)$_2$ plus their corres-ponding oxides] and this ratio was taken as a reflection of the relative rate for each phosphine. Repeating this procedure for six pairs of phosphines allowed a plot of log [product ratios] *versus* σ to be constructed from which a value of ρ was calculated.

References

1 D. B. Denney, D. Z. Denney, B. C. Chang, and K. L. Marsi, *J. Am. Chem. Soc.*, 1969, **91**, 5243.
2 D. B. Denney and D. H. Jones, *J. Am. Chem. Soc.*, 1969, **91**, 5821.
3 L. L. Chang, D. B. Denney, D. Z. Denney, and R. J. Kazior, *J. Am. Chem. Soc.*, 1977, **99**, 2293.
4 D. A. Bowman, D. B. Denney, and D. Z. Denney, *Phosphorus Sulfur*, 1978, **4**, 229.
5 D. B. Denney, D. Z. Denney, C. D. Hall, and K. L. Marsi, *J. Am. Chem. Soc.*, 1972, **94**, 245.
6 D. B. Denney, D. Z. Denney, and D. M. Gavrilovic, *Phosphorus Sulfur*, 1981, **11**, 1.
7 G. Scott, P. J. Hammond, C. D. Hall, and J. D. Bramblett, *J. Chem. Soc., Perkin Trans. 2*, 1977, 882.
8 P. J. Hammond, G. Scott, and C. D. Hall, *J. Chem. Soc., Perkin Trans. 2*, 1982, 205.
9 (a) P. D. Bartlett, A. L. Baumstark, M. E. Landis, and C. L. Lerman, *J. Am. Chem. Soc.*, 1974, **96**, 5267; (b) A. L. Baumstark, C. J. McLoskey, T. E. Williams, and D. R. Chrisope, *J. Org. Chem.*, 1980, **45**, 3593.
10 (a) P. J. Hammond, J. R. Lloyd, and C. D. Hall, *Phosphorus Sulphur*, 1981, **10**, 47; (b) P. D. Beer, R. C. Edwards, C. D. Hall, J. R. Jennings, and R. J. Cozens, *ibid.*, 1983, **17**, 283.
11 K. Moedritzer, L. Maier, and L. C. D. Groenweghe, *J. Chem. Eng. Data*, 1962, **7**, 307.
12 V. Mark, C. H. Dungan, M. M. Crutchfield, and J. R. Van Wazer, *Top. Phosphorus Chem.*, 1967, **5**, 318.
13 G. Schrader, Ger. P. 1, 175, 659/1964 (*Chem. Abstr.*, 1964, **62**, 1566q).
14 J. Michalski, T. Modro, and A. Zwierak, *J. Chem. Soc.*, 1961, 4904.