Kinetics and Mechanism of the Reaction of Δ^3-Phospholens with Diethyl Peroxide

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A kinetic study of the reaction of Δ^3-phospholens with diethyl peroxide in a variety of solvents (cyclohexane, tetrahydrofuran, and acetonitrile) is reported. The kinetic order, solvent effect, activation parameters, and lack of inhibitory effect by galvinoxyl lead to the proposal of a rate-determining biphilic attack of the phospholen on the peroxide followed by a fast fragmentation of the intermediate phosphorane to *trans,trans*-hexa-2,4-diene and a diethyl alkyl (or aryl) phosphonite.

WE have described the reaction of a mixture of the diastereoisomeric 1,2,5-trimethyl-Δ^3-phospholens (1a and b) with diethyl peroxide (2) in cyclopentane, cyclohexane, and chloroform, which gave diethyl methylphosphonite (4; R = Me) and exclusively *trans,trans*-hexa-2,4-diene (5).[1,2] The diene was assumed to arise

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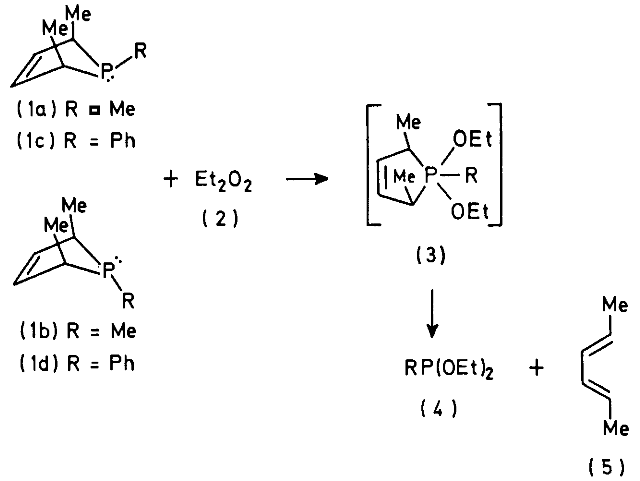
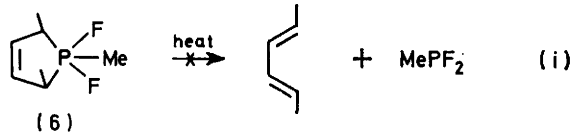
[1] D. B. Denney, D. Z. Denney, C. D. Hall, and K. L. Marsi, *J. Amer. Chem. Soc.*, 1972, **94**, 245.

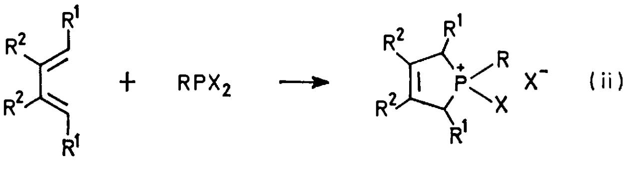
[2] C. D. Hall, J. D. Bramblett, and F. S. Lin, *J. Amer. Chem. Soc.*, 1972, **94**, 9264.

from a stereospecific fragmentation of an undetected pentaco-ordinate phosphorus intermediate (3; R = Me). Pentacovalent phosphorus compounds are now commonplace[3,4] and the reaction of trico-ordinate phosphorus compounds with diethyl peroxide is a well established route to such compounds.[1,5,6] Furthermore, certain phosphoranes [*e.g.* (6)] containing the Δ^3-phospholen ring are stable and do not undergo the reverse cycloaddition reaction to any detectable extent[7] [equation (i)].



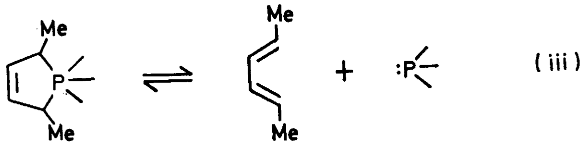


This is perhaps not surprising in view of the fact that condensation of phosphonous dihalides with dienes is the principal synthetic route to Δ^3-phospholens[8,9] [equation (ii)], a reaction which is known to be a stereospecific, disrotatory process.[10]

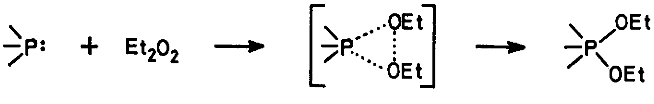


R^1 = Me or H   R = alkyl or aryl
R^2 = Me or H   X = Cl or Br

Thus there appears to be an equilibrium between pentaco-ordinate species containing a phospholen ring and the corresponding trico-ordinate species and diene [equation (iii)]. The equilibrium position seems to depend upon a number of factors, including the nature of the exocyclic *P*-substituents, the position of ring substituents, and possibly the disposition of the phospholen ring (apical-equatorial or diequatorial) in the phosphorane. This problem will be the subject of a subsequent paper, but we note here that in the case of reactions denoted by equation (ii) with X = Cl or Br, the equilibrium may be forced to the right by *precipitation* of the phospholenium salt during the reaction.



For some time evidence has been accumulating to suggest that the reaction of P^{III} compounds with diethyl peroxide occurs through a concerted, biphilic transition state (7), produced by insertion of phosphorus into the peroxide bond.[1,5,6] The fragmentation reaction (ii) offered an excellent opportunity to study this reaction quantitatively, by monitoring either the appearance of diene (by u.v.) or the disappearance of phospholen and appearance of phosphorus products (by ^{31}P n.m.r.). The work was undertaken with a view to providing evidence for or against the concerted mechanism.



(7)

EXPERIMENTAL

Diethyl peroxide was prepared as described elsewhere.[11] After one redistillation of the crude product, a second redistillation in the presence of *ca.* 2% of triethyl phosphite (to remove hydroperoxide and water) gave diethyl peroxide of >99% purity, which was stored in a refrigerator over molecular sieves.

The phospholens were derived from the reduction of the corresponding phospholen oxides with phenylsilane[12] or reduction of the phospholenium salts with magnesium in tetrahydrofuran (THF).[13] A mixture of the diastereoisomeric 1,2,5-trimethylphospholen oxides was obtained by hydrolysis of 1-chloro-1,2,5-trimethylphospholenium chloride derived from the stereospecific cycloaddition reaction between *trans,trans*-hexa-2,4-diene and methylphosphonous dichloride.[10,14] Likewise the diastereoisomeric mixture of

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[3] 'Organic Phosphorus Compounds,' ed. G. M. Kosolopoff and L. Maier, vol. 3, Wiley–Interscience, New York, 1972.

[4] J. Emsley and C. D. Hall, 'The Chemistry of Phosphorus,' Harper–Row, New York, 1976.

[5] D. B. Denney, D. Z. Denney, B. C. Chang, and K. L. Marsi, *J. Amer. Chem. Soc.*, 1969, **91**, 5243.

[6] D. B. Denney and D. H. Jones, *J. Amer. Chem. Soc.*, 1969, **91**, 5821.

[7] N. J. De Ath, D. Z. Denney, D. B. Denney, and C. D. Hall, *Phosphorus*, 1974, **3**, 205.

[8] L. D. Quin in '1,4-Cycloaddition Reactions,' ed. J. Hamer, Academic Press, New York, 1967.

[9] K. D. Berlin and D. M. Hellwege, *Topics Phosphorus Chem.*, 1969, **6**, 1.

[10] A. Bond M. Green, and S. C. Pearson, *J. Chem. Soc.* (*B*), 1968, 929.

[11] B. C. Chang, W. E. Conrad, D. B. Denney, D. Z. Denney, R. Edelman, R. C. Powell, and D. W. White, *J. Amer. Chem. Soc.*, 1971, **93**, 4004.

[12] K. L. Marsi, F. B. Burns, and R. T. Clark, *J. Org. Chem.*, 1972, **37**, 238.

[13] L. D. Quin and T. P. Barkett, *J. Amer. Chem. Soc.*, 1970, **92**, 4304.

[14] W. B. McCormack, U.S.P. 2,664,736/1955.

2,5-dimethyl-1-phenylphospholen oxides was obtained by hydrolysis of 1-bromo-2,5-dimethyl-1-phenylphospholenium bromide produced by the stereospecific cycloaddition of *trans,trans*-hexa-2,4-diene to phenylphosphonous dibromide. Use of phenylphosphonous dichloride gives rise to a substantial degree of isomerisation of the Δ^3-phospholenium salt to the Δ^2-salt. Isomer ratios for the phospholens and phospholen oxides were assessed by ^1H, ^{31}P, and ^{13}C n.m.r.

Diethyl methylphosphonite was prepared from the reaction of methylphosphonous dichloride with ethyl alcohol in ether in the presence of triethylamine.[15] Bis-(2,2,2-trichloroethyl) methylphosphonite (b.p. 107° at 0.2 mmHg) was prepared by a similar route from methylphosphonous dichloride and 2,2,2-trichloroethanol.

^1H, ^{31}P, and ^{13}C N.m.r. data for starting materials are collected in Tables 1—3 together with ^{31}P n.m.r. data for the reaction products $MeP(OEt)_2$, $MeP(OEt)_4$, $PhP(OEt)_2$, and $PhP(OEt)_4$.

Cyclohexane and cyclopentane were purified by drying over sodium (× 2) and distillation. Tetrahydrofuran was washed with saturated iron(II) sulphate solution, distilled, dried over sodium, and redistilled from lithium aluminium hydride. Acetonitrile was spectroscopic grade (B.D.H.), stored over molecular sieves (4A).

RESULTS

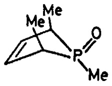
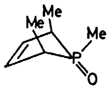
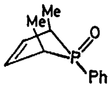
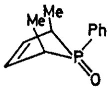
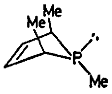
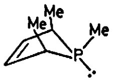
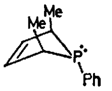
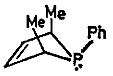
Kinetic Procedures.—(1) *U.v. spectroscopy*. Reactions were monitored by following the appearance of diene at λ 227 nm (using 0.01 mm pathlength silica cells in the thermostatted cell housing of a Unicam SP 1700 spectrophotometer). Data were collected in digital (paper tape) form by means of a Digico analogue-digital converter connected to a paper-tape punch. The data were then processed by a least-squares linear regression program by use of the University of London CDC 6600 computer to obtain first-order rate constants (k_{obs}). Reaction mixtures always contained a minimum of 15M excess of diethyl peroxide over phospholen, and values of k_{obs} are the averages of two or more runs.

(2) ^{31}P *N.m.r.* Samples were prepared by injecting the appropriate amount of phospholen into thermostatted solutions of diethyl peroxide in the chosen solvent (under nitrogen) in 9 mm n.m.r. tubes. Again, the peroxide was always in sufficient excess to give first-order kinetics. The disappearance of phospholen and the appearance of the products $MeP(OEt)_2$ and $MeP(OEt)_4$ were then monitored by peak height and peak area from the Fourier transform spectra obtained with a Bruker HFX 90 spectrometer operating at 36.43 MHz. The accumulation of Fourier transform data required *ca.* 5 min for each point, during which time the progress of each reaction was invariably small (<2%). The amount of phospholen remaining (P_t) at time t was recorded as a percentage of all the products observed in the spectrum, and a plot of $\log_e (P_t)$ *vs.* t gave a straight line, the gradient of which gave k_{obs}. Agreement between calculations based on peak height and on peak area was generally good (±5%), but since better linearity in the first-order plots was obtained with the integration figures, these were used to derive the quoted values of k_{obs}.

Rate data. Although u.v. spectroscopy was the most convenient and precise way of following the fragmentation reaction, the only way it could be used was to monitor the appearance of diene. The starting 1,2,5-trimethylphospholen was a diastereoisomeric mixture of *cis*- and *trans*-isomers and, as expected, the rates of reaction of the diastereoisomers with diethyl peroxide were slightly different. Since ^{31}P n.m.r. was able to distinguish the two diastereoisomers it became the method of choice for establishing the kinetic order of the reaction by monitoring the disappearance of phospholen. Table 4 shows the results obtained with acetonitrile as solvent. Plots of k_{obs} *vs.* $[Et_2O_2]$ gave straight lines which, within experimental error, passed through the origin; their slopes gave values of k_2.

TABLE 1

^{31}P N.m.r. data (solvent CD_3CN unless otherwise indicated)

(a) Phospholens and oxides		(b) Phosphonites and phosphonates	
Compound	δ *	Compound	δ *
	−61.5	$MeP(OEt)_2$	−176.5
	−78.5	$MeP(O)(OEt)_2$	−29.0
	−54.2	$MeP(OEt)_4$	+45.0
		$PhP(OEt)_2$	−155.9
	−73.2	$PhP(O)(OEt)_2$	−16.9
	+7.1	$PhP(OEt)_4$	+56.9
		$MeP(O{\cdot}CH_2{\cdot}CCl_3)_2$	−197.8 †
	+6.0	$MeP(O)(O{\cdot}CH_2{\cdot}CCl_3)_2$	−32.0 †
	−11.4	$MeP(O)(OEt)(O{\cdot}CH_2{\cdot}CCl_3)$	−30.7
	−15.2		

* P.p.m. from 85% H_3PO_4. † In C_6D_6.

Table 5 shows a similar set of rate data obtained by u.v. spectroscopy for 2,5-dimethyl-1-phenyl-Δ^3-phospholen [(1c) >95%; (1d) <5%]. Both sets of data reveal first-order behaviour in phospholen and in diethyl peroxide.

The results obtained by u.v. spectroscopy with 1,2,5-trimethyl-Δ^3-phospholen [(1a) : (1b) 9 : 1] in a variety of solvents and with a variety of diethyl peroxide concentrations are shown in Table 6. Plots of k_{obs} *vs.* $[Et_2O_2]$ all gave straight lines which *do not* pass through the

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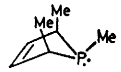
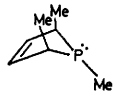
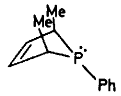
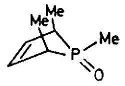
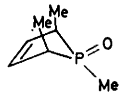
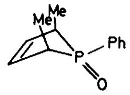
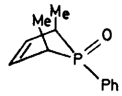
[15] F. W. Hoffmann and J. R. Moore, *J. Amer. Chem. Soc.*, 1958, **80**, 1150.

origin. The slopes of these lines are, for MeCN, 2.05×10^{-5}; for THF, 2.08×10^{-5}; and for cyclohexane, 2.07×10^{-5} l mol^{-1} s^{-1}. With lines passing through the origin, these slopes would represent k_2; lines drawn through points below 2.5M in diethyl peroxide and including the origin give $k_2 = 3.51 \times 10^{-5}$ for MeCN (*cf.* Table 4) and 3.51×10^{-5} l mol^{-1} s^{-1} for cyclohexane. Various factors may contribute to the artificially low rates at high [Et_2O_2] (see Discussion section) but the important point is that the rate of reaction shows no significant variation over a solvent polarity range from cyclohexane to acetonitrile.

TABLE 2

^{13}C N.m.r. data

Phospholens and oxides	δ *					J_{PC}/Hz			
Compound	PMe	C-2, -5	C-3, -4	C*Me*	PPh	P, Me	P, C-2, -5	P, C-3, -4	P, C*Me*
	0.54	38.24	134.54	13.86		24.4	12.2	4.9	0
	12.76	43.37	134.13	21.00		18.6	9.8	3.7	28.1
		40.19	131.9 (m)	14.67	131.9 (m)		12.3		0
		43.89	131.9 (m)	21.97	131.9 (m)		11.0		30.5
	6.12	36.14	132.17	12.75		59.8	65.9	14.7	3.7
	15.24	37.48	132.71	14.53		62.3	65.9	14.7	3.7
		38.03	128.22	12.24	132.65 (m)		65.9	9.8	4.9
		37.79	129.80	14.19	132.65 (m)		67.1	9.8	3.7

* P.p.m. to low field of Me_4Si.

The rates of reaction of a 9 : 1 mixture of *cis*- and *trans*-isomers (1a and b) at a variety of temperatures in cyclohexane and acetonitrile and of (1c and d) at a variety of temperatures in acetonitrile are shown in Table 7. The derived activation parameters are given in Table 8. Finally, Table 9 records the rate of reaction of (1a) with diethyl peroxide in acetonitrile at 30 °C monitored by ^{31}P n.m.r. and conducted in the presence of galvinoxyl, added either at the beginning or half-way through a kinetic run. In all the kinetic runs, including those where galvinoxyl was introduced, the only diene detected in the final product by g.l.c. was the *trans,trans*-isomer. Furthermore reactions carried out on a preparative scale in the presence of 2,2'-azoisobutyronitrile at 55 °C also produced only the *trans,trans*-diene.

DISCUSSION

The ^{31}P n.m.r. spectra revealed no trace of the proposed pentaco-ordinate intermediate (3) (*i.e.* the intermediate is present, if at all, to the extent of <1%);* this is confirmed by the Figure, which demonstrates that the rate of disappearance of phospholen equals the rate of appearance of the products $RP(OEt)_2$ and $RP(OEt)_4$. Subsequent, quantitative rate measurements by ^{31}P n.m.r. (for the disappearance of phospholen) and by u.v. spectroscopy (for the appearance of diene) confirmed this finding.

The data in Tables 4—6 indicate first-order behaviour in phospholen and in diethyl peroxide. This leads to the kinetic scheme of equation (iv). The fragmentation of the pentaco-ordinate intermediate has already been

$$\Delta^3\text{-phospholen} + Et_2O_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [P^V] \xrightarrow{k_2} RP(OEt)_2 + \text{diene} \quad \text{(iv)}$$

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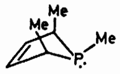
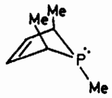
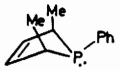
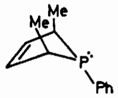
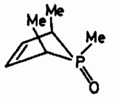
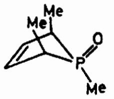
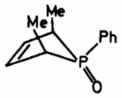
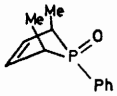
* Recent experiments with 1-ethoxy-3,4-dimethyl-Δ^3-phospholen and diethyl peroxide have shown that the pentaco-ordinate species 1,1,1-triethoxy-3,4-dimethyl-Δ^3-phospholen is formed faster than the fragmentation reaction occurs, thus supporting the proposal of a pentaco-ordinate intermediate.

TABLE 3

^{1}H n.m.r. data

(a) Phospholens and oxides

Compound	δ					J_{PH}/Hz				J_{HH}/Hz	
	PCH_3	PPh	CCH_3	=CH–	–CH–	PCH_3	$PCCH_3$	PCCH	PCH	–$CHCH_3$	CH–CH=
	0.75		1.12	5.55	2.85	3	10	6		8	1
	0.97		1.19	5.65	2.35 (m)	3	17	6		8	1
		7.42 (m)	1.03	5.78	2.66—3.51 (m)		11	6	22	7	2
		7.42 (m)	1.34	5.74	2.66—3.51 (m)		18	8	22	7	2
	1.28		1.23	5.64	2.24—3.10 (m)	12	14	26		7.5	1
	1.48		1.17	5.79	2.24—3.10 (m)	12.5	16	23.5		7.5	1
		7.72 (m)	1.07	5.86	3.10—3.55 (m)		17	25.5		7.5	1
		7.72 (m)	1.35	5.97	3.10—3.55 (m)		15	27		7.5	1

(b) Phosphonites

Compound	δ			J_{PH}/Hz		
	PCH_3	OCH_2	$O{\cdot}CCH_3$	PCH_3	$POCH_2$	$POCCH_3$
$MeP(O{\cdot}CH_2{\cdot}CCl_3)_2$	1.22	4.16		8.6	7.5	
$MeP(O{\cdot}CH_2{\cdot}CH_3)_2$	1.12	3.81	1.19	8.0	31.0	15.0 *

* K. E. Daugherty, W. A. Eychaner, and J. I. Stevens, *Appl. Spectroscopy*, 1968, **22**, 95.

shown to be concerted and disrotatory,[2] as required by a six-electron cheletropic process, and hence is analogous to the stereospecific fragmentation of the *cis*- and *trans*-isomers of 2,5-dimethyl-2,5-dihydrothiophen 1,1-dioxide.[16] Both diene and diethyl alkyl- (or aryl-) phosphonite are produced at a concentration of 10^{-4}M, which makes the fragmentation step virtually irreversible.* Hence in the kinetic scheme (iv), either $k_{-1} \gg k_2$, *i.e.* step 2 is rate-limiting, or $k_2 \gg k_{-1}$, when step 1 becomes rate-limiting.

TABLE 4

Values of k_{obs} and k_2 for the reaction of *cis*- (1a) and *trans*- (1b) 1,2,5-trimethyl-Δ^3-phospholen with Et_2O_2 in MeCN at 30 °C

$[Et_2O_2]$ / N	$10^4k_{obs}(cis)$ / s^{-1}	$10^5k_2(cis)$ / l mol^{-1}s^{-1}	$10^4k_{obs}(trans)$ / l mol^{-1}s^{-1}	$10^5k_2(trans)$ / s^{-1}
6.48	2.5 ± 0.2		1.2 ± 0.1	
5.55	2.4 ± 0.2	3.5 ± 0.3	0.95 ± 0.1	1.7 ± 0.2
4.95	1.5 ± 0.2			
4.00	1.3 ± 0.2		0.6 ± 0.1	

The first case is extremely unlikely since, in the light of bond strength data alone, cleavage of the peroxide link requires 147 kJ mol^{-1} whereas formation of two P–O bonds probably affords *ca.* 630 kJ mol^{-1}.[17] Reversibility of the first step is rendered even less likely by the finding (by ^{31}P n.m.r.) that a mixture of bis-(2,2,2-trichloroethyl) methylphosphonite and diethyl peroxide in CD_3CN

TABLE 5

Values of k_{obs} (s^{-1}) for the reaction of 2,5-dimethyl-1-phenyl-Δ^3-phospholen (1c and d) * with Et_2O_2 in MeCN at 31.4 °C

$[Et_2O_2]$/M	4.35	3.90	2.95	1.63
10^5k_{obs}/s^{-1}	4.38 ± 0.05	4.24 ± 0.05	3.07 ± 0.05	1.57 ± 0.05

$k_2 = 1.05 \pm 0.05 \times 10^{-5}$ l mol^{-1} s^{-1}

* (1c) : (1d) ≥ 95 : 5.

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* We have recently shown that phospholenium salts, for example when dissolved in MeCN at *ca.* 10^{-2}M, give hexa-2,4-diene and (presumably) $MePCl_2$ by a reversal of the McCormack condensation.

[16] W. L. Mock, *J. Amer. Chem. Soc.*, 1966, **88**, 2857.

[17] J. R. Van Wazer, 'Phosphorus and its Compounds,' Vol. 1, Interscience, New York, 1958.

gave no diethyl methylphosphonite after 24 h at ambient temperature. The phosphorane $\mathrm{MeP(OEt)_2(O{\cdot}CH_2{\cdot}CCl_3)_2}$ was not detected, but its existence was assumed in view of the observation of its phosphonate products $\mathrm{MeP(O)\,(OEt)_2}$ (δ −29.0 p.p.m.), $\mathrm{MeP(O)\,(OEt)\,(O{\cdot}CH_2{\cdot}CCl_3)}$ (δ −30.7 p.p.m.), and $\mathrm{MeP(O)(O{\cdot}CH_2{\cdot}CCl_3)_2}$ (δ −32.0 p.p.m.).

TABLE 6

Values of k_{obs} for the reaction of a mixture of (1a) (90%) and (1b) (10%) with Et_2O_2 in MeCN, THF, and cyclohexane at 31.4 °C §

Solvent MeCN

$[Et_2O_2]/M$	8.13	6.50	3.90	1.63
$10^4k_{obs}/s^{-1}$	1.91	1.52	1.10	0.58

$k_{obs} = 2.05 \times 10^{-5}[Et_2O_2] + 2.4 \times 10^{-5}$.

Solvent C_6H_{12}

$[Et_2O_2]/M$	8.26	6.61	5.78	4.96	3.96	2.47	1.65
$10^4k_{obs}/s^{-1}$	1.97	1.59	1.43	1.32	1.08	0.90	0.54

$k_{obs} = 2.07 \times 10^{-5}[Et_2O_2] + 2.6 \times 10^{-5}$.

Solvent THF

$[Et_2O_2]/M$	6.07	4.50	3.04
$10^4k_{obs}/s^{-1}$	1.35	1.01	0.72

$k_{obs} = 2.08 \times 10^{-5}[Et_2O_2] + 0.8 \times 10^{-5}$.

§ Determined by appearance of diene at λ 227 nm.

TABLE 7

Effect of temperature on the values of k_{obs} for the reaction of Δ^3-phospholens with Et_2O_2 in cyclohexane and acetonitrile

(i) Phospholen: mixture of (1a) (90%) and (1b) (10%)

(a) Solvent: C_6H_{12}; $[Et_2O_2]$ 4.42M

Temp. (°C)	28.6	32.2	36.2	40.0
$10^4k_{obs}/s^{-1}$	0.94	1.04	1.39	1.72

(b) Solvent: MeCN; $[Et_2O_2]$ 2.56M

Temp. (°C)	26.0	31.4	39.7
$10^4k_{obs}/s^{-1}$	0.52	0.81	1.59

(ii) Phospholen: mixture of (1c) (>95%) and (1d) (<5%)
Solvent: MeCN; $[Et_2O_2]$ 2.94M

Temp. (°C)	26.0	31.4	39.7
$10^4k_{obs}/s^{-1}$	0.19	0.31	0.71

Application of the steady-state approximation to equation (iv) gives the differential rate expression represented by equation (v). Since the first step is rate-limiting, one must ask whether the operative mechanism is (*a*) nucleophilic attack of trico-ordinate phosphorus on peroxide [equation (vi)] (*b*) a radical reaction (vii), or (*c*) a concerted mechanism *via* a biphilic transition state represented by (7).

TABLE 8

Activation parameters for the reactions of Δ^3-phospholens with Et_2O_2 in cyclohexane and acetonitrile

Phospholen	Solvent	E_a / kJ mol⁻¹	$\Delta G^\ddagger$ at 30 °C / kJ mol⁻¹	$\Delta S^\ddagger$ at 30 °C / J mol⁻¹ K⁻¹
(1a) (90%) + (1b) (10%)	C_6H_{12}	46 ± 4	100.2 *	−187 *
(1a) (90%) + (1b) (10%)	MeCN	63 ± 1	100.2 *	−130 *
(1c) (>95%) + (1d) (<5%)	MeCN	74 ± 2	103.3 §	−104 §

* Values based on k_2 for (1a) in Table 4. § Values based on k_2 for mixture at 30 °C = 0.95×10^{-5} l mol⁻¹ s⁻¹.

$$-\mathrm{d[phospholen]}/\mathrm{d}t = \mathrm{d[diene]}/\mathrm{d}t = k_1k_2\,[\mathrm{phospholen}][Et_2O_2]/(k_2 + k_{-1}) = k_1\,[\mathrm{phospholen}][Et_2O_2] \text{ for } k_2 \gg k_{-1} \quad \text{(v)}$$

$$\geqslant\mathrm{P}\!: + \mathrm{EtO{\cdot}OEt} \xrightarrow[\text{rate-limiting}]{\text{slow}} \geqslant\overset{+}{\mathrm{P}}\mathrm{OEt}\ \bar{\mathrm{O}}\mathrm{Et} \longrightarrow \geqslant\mathrm{P(OEt)_2} \quad \text{(vi)}$$

$$\geqslant\mathrm{P}\!: + \mathrm{EtO{\cdot}OEt} \xrightarrow[\text{rate-limiting}]{\text{slow}} \geqslant\dot{\mathrm{P}}\mathrm{OEt}\ {\cdot}\mathrm{OEt} \longrightarrow \geqslant\mathrm{P(OEt)_2} \quad \text{(vii)}$$

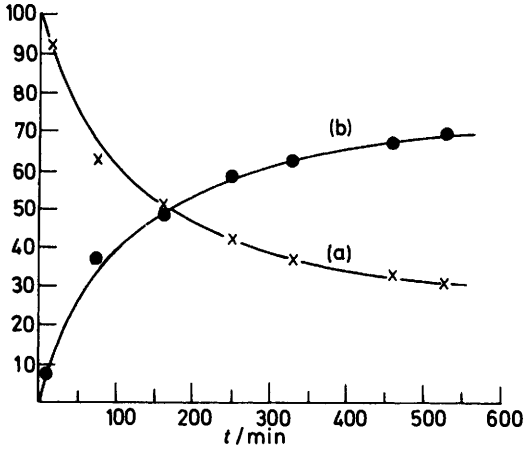
It has already been established that within a series of phosphines, the rates of reaction with Et_2O_2 vary in the order phosphetans > phospholans > phosphorinans ≈ analogous acyclic phosphines, and this is the reverse of nucleophilic reactivity of the same series of phosphines towards alkyl halides.[1] A similar reversal of relative reactivity has been observed for phosphites in reactions with diethyl peroxide and ethyl iodide.[6] The relative reactivities towards diethyl peroxide appear to parallel the stabilities of the pentaco-ordinate products, and this is probably associated with the relief of strain in progressing from P^{III} to P^V with phosphines containing small (four- and five-membered) rings. The solvent effects in the peroxide reactions [1] were also small and this is confirmed, quantitatively, by the fragmentation reactions reported here. The second-order rate constants were, within experimental error, identical for cyclohexane, THF, and acetonitrile (Table 6). This effectively eliminates the mechanism involving nucleophilic attack by the phosphine on peroxide.

TABLE 9

Reaction of (1a) with diethyl peroxide in MeCN at 30 °C in the presence of galvinoxyl

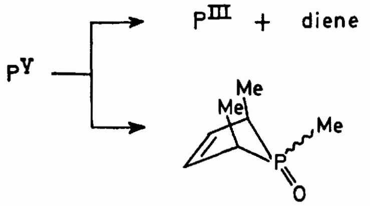
$[Et_2O_2]/M$	$10^5k_{obs}/s^{-1}$	10^5k_2/l mol⁻¹ s⁻¹
3.0 [a]	7.5	2.5
4.95 [b]	14.2	2.9
4.95 [c]	14.4	2.9

[a] Galvinoxyl added at start of reaction. [b] No galvinoxyl initially. [c] Galvinoxyl added after *ca.* two half-lives (150 min).



Relative peak areas in the ^{31}P n.m.r. spectrum for the reaction of (1a and b) with Et_2O_2 in cyclopentane; (a) mole % (1a) + (1b); (b) mole % $\mathrm{MeP(OEt)_2}$ + $\mathrm{MeP(OEt)_4}$

Incidentally, although plots of k_{obs} *vs.* $[Et_2O_2]$ produce good straight lines they also reveal an apparent intercept on the ordinate. This intercept, however, is an experimental artefact associated with the use of u.v. spectroscopy to follow the appearance of diene. In the first place, with a mixture of diastereoisomers the ratio of *cis*- and *trans*-isomers may be altered by an initial, very fast reaction of phosphine with a small quantity of oxidant (probably hydroperoxide) in the diethyl peroxide to give phosphine oxide. The *cis*-phosphine reacts with the oxidant preferentially, and hence, as the diethyl peroxide concentration rises, the ratio of *cis*- to *trans*-phosphine remaining to react with diethyl peroxide decreases. The net result is an overall rate decrease (*trans* rate < *cis* rate). Secondly, at high peroxide concentration, a small amount of phosphine oxide is produced *during the reaction* with diethyl peroxide. Apparently, at high $[Et_2O_2]$ the intermediate P^V tends to give more oxide and undergo less fragmentation [equation (viii)]. This may well be associated with a more significant concentration of $MeP(OEt)_4$* at higher concentrations of Et_2O_2. In any event, if the % loss to oxide increases as a particular reaction progresses, the result will be a lower infinity value for diene absorption and, in consequence, a lower value of k_{obs}.



(viii)

The results of reactions in the presence of galvinoxyl (Table 9) suggest that radical intermediates are not involved in the reaction, since galvinoxyl would be expected to intercept at least a proportion of the radical intermediates and hence alter the rate. It is well known [18-20] that di-t-butyl peroxide reacts with tricoordinate phosphorus compounds by a radical mechanism, and that the alkoxyl radicals are rapidly deoxygenated by tertiary phosphines to give high yields of the corresponding phosphine oxides or phosphates, although in some cases α-scission of intermediate radicals is also observed.[21] Apart from a small quantity (generally <10%) of phosphine oxide formed immediately on mixing (see above) the reactions between the phospholens and diethyl peroxide produced very little oxide.

Diethyl disulphide in cyclopentane (or other aprotic media) does not react with Δ^3-phospholens at ambient temperature. However, when experiments were carried out at 50 °C in the presence of 2,2′-azoisobutyronitrile, reaction occurred to give a variety of phosphorus-containing products [including $(EtS)_2P(S)Me$ detected by ^{31}P n.m.r., δ −69.4 p.p.m.], and fragmentation produced a mixture of *trans,trans*-, *cis,trans*-, and *cis,cis*-dienes in the ratios 1.98 : 1.0 : 0.06, *i.e.* close to the values for thermodynamic equilibration (1.96 : 1.0 : 0.15).[22] *trans,trans*-Hexa-2,4-diene is stable under the same reaction conditions, *i.e.* does not undergo isomerisation in cyclopentane at 50 °C in the presence of diethyl disulphide and azoisobutyronitrile. Whatever the mechanism of this complex reaction, it seems likely that an intermediate phosphoranyl radical is involved which undergoes fragmentation, *via* a radical process (initially α-scission), to a mixture of dienes. Reactions of Δ^3-phospholens with diethyl peroxide in the presence of azoisobutyronitrile at 55—60 °C produced only the *trans,-trans*-diene. It therefore seems most unlikely that radical intermediates are involved in the peroxide reaction; if they are, such radicals must never escape the solvent cage but instead collapse rapidly to the P^V intermediate which instantly undergoes fragmentation in a stereospecific process.†

One is left with the proposal of a biphilic, insertion mechanism. The activation parameters (Table 8) are consistent with such a proposal although they can be interpreted equally well by tight ion-pair or caged-radical mechanisms. The entropies of activation are all highly negative, indicating a high degree of orientation in the transition state. A comparison of activation parameters for (1a and b) in cyclohexane and in acetonitrile indicates that a higher degree of orientation in the former solvent ($-\Delta S^\ddagger$ for cyclohexane > $-\Delta S^\ddagger$ for MeCN) is compensated by a lower activation enthalpy, indicating a higher degree of bond formation in the cyclohexane system. Likewise, in MeCN, the lower degree of orientation in the transition state for (1c and d) is offset by a higher activation enthalpy, which indicates a lower degree of bond formation in the transition state in the 1-phenyl case than in the 1-methyl case (1a and b). This is due, presumably, to the bulk of the phenyl group preventing access of the peroxide to phosphorus.

In conclusion, the concerted, biphilic mechanism seems to offer the best explanation of the results. Whether in such a mechanism, a distinction can be made between apical-equatorial or diequatorial attack of the peroxide remains to be seen.

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* $MeP(OEt)_4$ may dissociate to $Me\overset{+}{P}(OEt)_3$ $\overset{-}{O}Et$, and the ethoxide ion could catalyse the formation of oxide from P^V.

† For a caged radical mechanism it would be reasonable to expect a CIDNP effect on the pentaco-ordinate product (see, for example, C. Brown, R. F. Hudson, A. Maron, and K. A. F. Record, *J.C.S. Chem. Comm.*, 1976, **663**). In a variety of reactions where the pentaco-ordinate product is stable, however (see refs. 1, 5, and 6), no such effect was observed.

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