The Reaction of 1-Substituted 3,4-Dimethyl-Δ^3-phospholens with Diethyl Peroxide: a Correlation Between Rate and ^{31}P Nuclear Magnetic Resonance Shift

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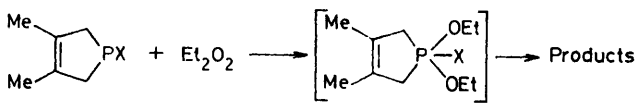
The reactions of a variety of 1-X-3,4-dimethyl-Δ^3-phospholens (where X = Br, Me, Ph, NMe_2, SEt, H, and OR) with diethyl peroxide are described. The rates of reaction show a broad correlation with the ^{31}P n.m.r. chemical shifts of the starting phospholens, with low field shifts corresponding to the highest reactivity. The results are discussed in terms of the biphilic mechanism for the reaction of trico-ordinate phosphorus compounds with weak σ-bonds.

THE reactions of trico-ordinate compounds with weak σ-bonds as in peroxides [1,2] and sulphenate esters,[3,4] are now well established routes to pentaco-ordinate phosphorus compounds. A number of relative-rate studies revealed a sequence of reactivity for cyclic phosphines [5] and cyclic phosphites [2] towards diethyl peroxide which was the reverse of that observed for the reaction of the same P^{III} compounds with ethyl iodide. These data prompted the proposal that trico-ordinate phosphorus reacted with diethyl peroxide by a biphilic mechanism involving insertion into the peroxide link. It was suggested that the rates were determined by the relative stabilities of the transition states leading to pentaco-ordinate intermediates and/or the relief of ring strain when phosphetans or phospholans adopted an apical–equatorial disposition of the ring in the pentaco-ordinated products. The concept of a biphilic mechanism was then reinforced by rate data involving kinetic order, solvent effects, and activation parameters derived from studies of the reactions of 1-substituted 2,5-dimethyl-Δ^3-phospholens with diethyl peroxide [6] and the reactions of phosphines with dioxetans.[7] Throughout this work it was noticed that acyclic trico-ordinated phosphorus compounds also presented an unusual reactivity sequence towards diethyl peroxide [2] and sulphenate esters [8] in that rates of reaction decreased in the order $Ar_2POR > ArP(OR)_2 > Ar_3P > P(OR)_3$ whereas the 'normal' sequence of reactivity as nucleophilic reagents (*e.g.* towards EtI) was $Ar_3P > Ar_2POR > ArP(OR)_2 > P(OR)_3$. This, perhaps, may also be interpreted in terms of the stability of the transition state leading to pentaco-ordinated products but it opposes the idea of nucleophilic attack on the σ-bonds being the only mechanistic feature of the reaction. Attempts to detect radical intermediates or caged radical pairs in these reactions were unsuccessful and the biphilic insertion mechanism remained as the best possible explanation of the results. Assuming this to be true the question then arises as to whether one can establish the mode of entry of the peroxide into the developing trigonal biypramid as either diequatorial (A) or apical–equatorial (B).

Theory predicts [9] that for a four-electron process (A) should be the 'allowed' pathway with (B) forbidden but for a six-electron process the reverse should hold. The problems associated with this analysis however are (i) that it is difficult to estimate the difference in energy between 'allowed' and 'forbidden' processes and (ii) for the peroxide reaction, one does not know whether the reaction is a four-electron [lone pair(P) + two σ electrons] or a six-electron [lone pair(P) + two σ electrons + lone pair(O)] process.

(A) (B)

It was decided that an attempt should be made to obtain further experimental data from a study of the reactions of a range of substituted Δ^3-phospholens (1a—m) with diethyl peroxide (2) in order to establish the influence of the group X on the rate of reaction to the initial pentaco-ordinate structure. The 1-X-3,4-dimethyl-Δ^3-phospholens (1a—m) were chosen rather than



(1) (2)

a; X = Br
b; X = CH_3
c; X = C_6H_5
d; X = $N(CH_3)_2$
e; X = SCH_2CH_3
f; X = H
g; X = $O[CH_2]_4CH_3$
h; X = OCH_2CH_3
i; X = p-$CH_3OC_6H_4$
j; X = p-$CH_3C_6H_4$
k; X = p-$CF_3C_6H_4$
l; X = p-ClC_6H_4
m; X = p-$(CH_3)_2NC_6H_4$
n; X = I

the 1-X-2,5-dimethyl-Δ^3-phospholens because a wide range of the former were available from the 1-bromophospholen (1a), the analogue of which has not been prepared in the 2,5-dimethyl series. Also, compounds of type (1) were obtainable as single isomers rather than as mixtures of *cis*- and *trans*-diastereoisomers which are encountered with the 2,5-dimethylphospholens.

RESULTS AND DISCUSSION

A series of 1-substituted 3,4-dimethyl-Δ^3-phospholens (1a—m) was prepared and the ^{31}P n.m.r. absorption of each compound was recorded. Each phospholen, with the exception of the bromophospholen (1a), was then allowed to react at ambient temperature in CD_3CN with a 7 mol. (or greater) excess of diethyl peroxide. The reaction of the bromophospholen proved too vigorous under these standard conditions and an alternative method was employed. The course of each reaction was monitored by ^{31}P n.m.r.

The reaction of trivalent phosphorus compounds with diethyl peroxide to give pentaco-ordinated species is well established and several stable P^V compounds have been prepared by this method.[1,2,5] In certain instances however the initial phosphoranes are unstable and decompose rapidly. This occurs for example in the reactions of 1-alkyl/aryl-2,5-dimethyl-Δ^3-phospholens with diethyl peroxide when, although a P^V species is not observed, the nature of the final products necessitates the involvement of such an intermediate.[6]

The reactions of (1a—m) with diethyl peroxide exhibited similar characteristics and in most of the reactions various proportions of intermediates and final products were observed which implied the involvement of an intermediate phosphorane. In only one instance was *the initial* pentaco-ordinated species sufficiently stable to allow its observation by ^{31}P n.m.r. Thus when (1h) was treated with diethyl peroxide a ^{31}P n.m.r. absorption was observed at δ −13 p.p.m. which corresponded to a ring-containing triethoxyphosphorane.[10] This was expected to be a relatively stable phosphorane due to the inductive effect of the three ethoxy-groups. The progress of a typical reaction as monitored by ^{31}P n.m.r. is shown in Table 1.

In many of these reactions phosphorane fragmentation residues comprise only a small percentage of the final reaction mixture. They do not therefore represent a unique decomposition pathway for the initially formed pentaco-ordinated species. In these cases the major products of the reactions are isomeric phospholen oxides found in varying proportions according to the influence of the 1-substituent on the course of the reaction. The

TABLE 1

Product composition (%) from the reaction of (1b) with (2) as monitored by ^{31}P n.m.r. (solvent CD_3CN)

	δ_P (p.p.m.) 176	54	50	49	38	29	−24	−27	−45	−49
	Assignment									
t/min	$MeP(OEt)_2$	(3b)	(4b)	(4b)	*a*	$MeP(O)(OEt)_2$	*b*	*b*	$MeP(OEt)_4$	(1b)
0	—	—	—	—	—	—	—	—	—	100
30	6	3	3	3	—	—	17	9	—	58
60	14	4	9	6	3	5	15	9	5	30
85	14	6	20	10	5	2	8	7	10	17
115	10	7	18	13	13	6	6	2	15	10
145	8	8	22	17	19	2	3	—	16	4
193	4	9	22	18	23	2	2	—	19	1
∞	—	40	19	16	5	19	—	—	1	—

[a] Identity uncertain but apparently the precursor to Δ^3-phospholen oxide at δ 54. [b] Probably isomeric cyclic phosphoranes.

TABLE 2

Product composition (%) from the reactions of (1a—h) with (2) in CD_3CN

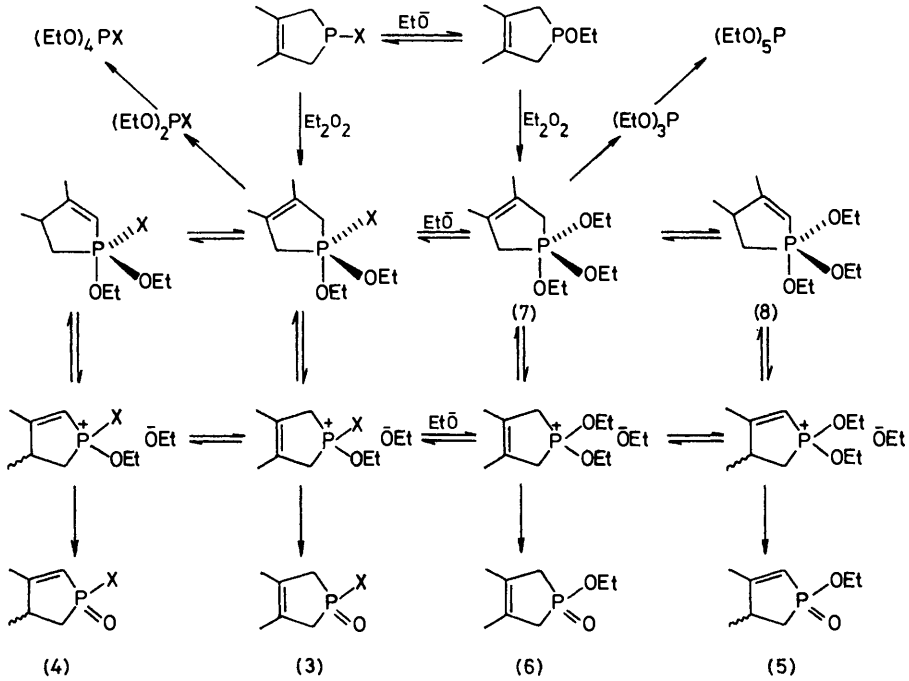
	Products $XP(OEt)_2$	$XP(OEt)_4$	(4)	(3)	(5)	(6)	(7)	(8)	
Substrate	*a*	*a*	*a*	*a*	(66.3) [l] (68.0) [l]	(65.0) [h]	(−13.4) [l]	(−17.8) [l]	Footnote
(1a)	—	—	—	—	—	100	—	—	
(1b)	—	—	35	40	—	—	—	—	*b*
	—	—	(49.8), (50.5) [l]	(53.8) [h]	—	—	—	—	
(1c)	52	34	3	7	—	—	—	—	*c*
	(155.9) [i]	(−56.9)	(39.3) [l]	(45.9) [h]	—	—	—	—	
(1d)	17	—	—	17	23	27	—	11	*d*
	(138.1) [k]	—	—	(58.6) [h]	—	—	—	—	
(1e)	—	—	—	—	19	44	—	—	*e*
(1f)	32	—	—	25	—	—	15	28	*f*
	(138.1) [k]	—	—	(36.6) [h]	—	—	—	—	
(1g)	5	—	—	—	—	62	17	16	*g*
	(138.1) [k]	—	—	—	—	—	—	—	
(1h)	42	1	—	—	2	24	7	24	
	(138.1) [k]	(−69.5) [j]	—	—	—	—	—	—	

[a] Where X is variable the ^{31}P n.m.r. shift is given in parentheses below. [b] Also 19% $MeP(O)(OEt)_2$, δ_P 29.0. [c] Ratios after 3.5 h. [d] $XP(OEt)_2 = (EtO)_3P$. [e] Also 18% of a sulphide, δ_P 106.1; possibly 1-ethoxy-3,4-dimethyl-Δ^3-phospholen sulphide. [f] $XP(OEt)_3 = (EtO)_3P$; ratios after 20 h. [g] Ratios after 63 min. [h] See Experimental section. [i] Ref. 1. [j] Ref. 3. [k] Ref. 10*b*. [l] Most reasonable, although not definite, assignment.

percentages of the major products in a series of these reactions are recorded in Table 2 and are accounted for by the mechanistic pathways outlined in Scheme 1.

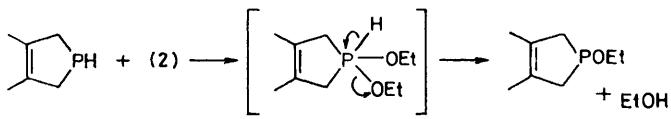
The presence in many reactions of both ring-retained oxide products and fragmentation products is indicative of competing pathways for decomposition of the intermediate phosphorane. It has been shown elsewhere that the rate of the fragmentation reaction is significantly enhanced by steric compression in the P^V structure.[11] Therefore, whereas phosphoranes containing a 2,5-dimethyl-substituted phospholen ring usually decompose preferentially by fragmentation, those containing the less sterically crowded, 3,4-dimethyl-substituted ring may do so by alternative, more energetically favourable mechanisms. There is, however, no simple rationalisation of the product ratios obtained with the various phospholens. It is perhaps significant that large groups [*e.g.* (1c)] lead to a high proportion of fragmentation products (86%) and that groups which stabilise the phosphorane [*e.g.* (1h)] also lead to considerable fragmentation (43%) whereas groups which would ionise more easily [*e.g.* (1e)] lead to ring-retained products by dealkylation. There is a suggestion that steric factors also play a part in the dealkylation process since with a larger alkoxy-group [*e.g.* (1g)] over 90% dealkylation was observed. The extreme case of dealkylation was observed for (1a) where a 100% yield of the cyclic phosphinate (3h) was obtained. This reaction however is believed to proceed by a slightly different mechanism. The reaction of (1f; X = H) was so slow that after 20 h, 33% of the starting material remained. The product ratios are therefore quoted on the basis of the phospholen reacted and show, at first sight surprisingly, a 32% yield of fragmentation product. This, however, is triethyl phosphite formed by decomposition of the initial phosphorane to the ethoxyphospholen (1h) which then reacts with diethyl peroxide and fragments in the usual way.

The reactions of (1) with (2) were conducted following



SCHEME 1

a previously described kinetic procedure[6] and were monitored by ^{31}P n.m.r. In all but one instance a 7—15 mol. excess of peroxide was used to ensure that the rate of disappearance of the phospholen followed first-order kinetics. The reaction of the bromophospholen



(1f) (1h)

(1a) was extremely fast and could only be monitored using an equimolar amount of peroxide at either 234 or 243 K. From all the data obtained, second-order rate constants were calculated for the reactions of (1a—m) with (2) and these are collected together with the ^{31}P n.m.r. shifts of the initial phospholen in Table 3.

It is obvious from Table 3 that there is a general trend towards faster reaction rates among those phospholens with chemical shift values at lower field. The rate of reaction of the bromophospholen (1a) is clearly anomalous, being 10^3 fold greater than that found with

any other substituent. No satisfactory rationalisation for this can be found within the context of the biphilic insertion mechanism The reaction may therefore proceed *via* rate-determining nucleophilic displacement of

TABLE 3

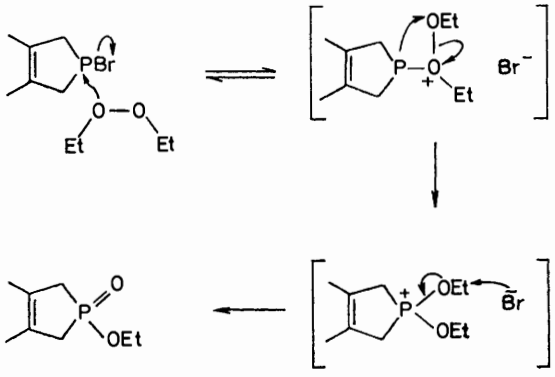
^{31}P N.m.r. shifts and rates of reaction with (2) of phospholens (1a—m)

Phospholen	δ_P (p.p.m.)	$10^5 k_2$ (CD_3CN)/ l mol^{-1} s^{-1}
(1g)	127.1	50.1
(1h)	127.4	40.4
(1a)	104.9	4 710 [a]
(1d)	52.6	9.9
(1e)	22.4 [b]	25.3
(1k)	−29.9	2.5
(1c)	−31.7	6.3
(1l)	−32.4	3.9
(1j)	−33.7	7.0
(1i)	−34.5	8.0
(1m)	−35.7	9.7
(1b)	−49.2	3.8
(1f)	−82.6	2.0

[a] Calculated from low-temperature observations. [b] Solvent C_6D_6 whereas $CDCl_3$ in all other cases.

bromide by the peroxide (an α-nucleophile) and subsequent rearrangements to products (Scheme 2).

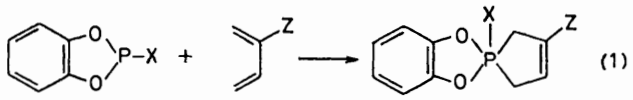
Among the other phospholens the relationship between ^{31}P n.m.r. chemical shifts and reaction rates can best be rationalised in terms of the relative electronegativities of the 1-substituents. Increased electronegativity of ligands on phosphorus is known to cause deshielding of the central atom and a consequent migration of the ^{31}P n.m.r. chemical shift to lower field.[10] The same substituent property may also explain the relative rates of



SCHEME 2

reaction of the various phospholens. Since it is known that pentaco-ordinated compounds are stabilised by electronegative ligands [12] it seems reasonable to suggest that faster reaction rates are a reflection of increased stabilisation of an initially formed P^V intermediate. It is evident that other steric and electronic factors are also involved since the relative reaction rates of (1e and d) would be reversed if the rates were dependent on electronegativities alone.

Razumova has shown that there is an electrophilic component at phosphorus in the condensation of trico-ordinate phosphorus compounds with dienes [equation (1)]. The relative rate order observed in these reactions was Z = Me > H > Cl.[13] Furthermore, variation of the substituents X on phosphorus revealed a rate decrease in the order X = Ph > Br > CH_3 > NCS > Cl > SR > F > OR > NR_2.[14] Since there is no obvious correlation with a single empirical parameter (*e.g.* apicophilicity) it seems likely yet again that a combination of electronic and steric factors is influencing the ground states and/or the transition states in these reactions.



With the arylphospholens (1i—m), however, the only factor which needs to be considered is the electronic effect of the *para*-substituent on the reaction rate. Table 3 shows that electron-donating substituents enhance the rate and although the effect is small (ρ −0.5 ± 0.2) its validity is strongly reinforced by the observations that the reactions of triarylphosphines, diaryl phosphinites, and aryl phosphinites with diethyl peroxide [15] and the reaction of triarylphosphines with dioxetan [16] all show similar, negative ρ values. Thus there is also a detectable *nucleophilic* component at phosphorus to the reaction between Δ^3-phospholens and diethyl peroxide. However, the low ρ value signifies very little charge development in the transition state which in turn explains the lack of sensitivity to solvent effects.[6] It is not possible, however, to use these results to distinguish between apical–equatorial and diequatorial attack by peroxide without assuming that the electronic effects apply predominantly to the transition state rather than the ground state. In view of the small energy changes involved ($\delta\Delta G^{\ddagger}$ *ca.* 1.5 kJ mol^{-1} across the range of phenyl substituents) it is not possible to justify this assumption and hence the problem remains unsolved.

Thus the major contribution of this work is the finding of a relationship between the ^{31}P n.m.r. chemical shift of a phospholen and its rate of reaction with diethyl peroxide which suggests a common factor between these parameters. This is probably the electronegativity of the 1-substituent which may dictate the rate of reaction by stabilisation of a pentaco-ordinate intermediate. Further evidence has also been provided for the biphilic nature of the reaction between trico-ordinated phosphorus compounds and diethyl peroxide in that the system reveals both the electrophilic and nucleophilic character of the trico-ordinated phosphorus component.

EXPERIMENTAL

All operations involving phospholens were carried out under a nitrogen atmosphere and using rigorously dried solvents. Except where otherwise stated, distillations were conducted using a Kugelrohr apparatus, and in consequence, b.p.s reflect the temperature of the oven rather than true values.

^{31}P and some ^{1}H n.m.r. spectra were recorded on a Bruker HFX-90 spectrometer operating at 36.43 and 90 MHz,

respectively. Routine ^1H n.m.r. spectra were recorded on a Perkin-Elmer R12B spectrometer operating at 60 MHz. All ^{31}P chemical shifts are reported in p.p.m. relative to external 85% H_3PO_4 with downfield shifts given a positive sign. All ^1H n.m.r. chemical shifts are reported relative to internal tetramethylsilane. The kinetic procedure was as reported elsewhere.[6]

Preparation of Diethyl Peroxide (2).—Diethyl peroxide was prepared as described previously.[6]

Preparation of 1-*Bromo*-3,4-*dimethyl*-Δ^3-*phospholen* (1a).—The bromophospholen (1a) was prepared by reduction of a McCormack cycloadduct using triphenylphosphine, as reported by Quin,[17] b.p. 103 °C at 26 mmHg (lit.,[17] 99—102 °C at 27 mmHg), δ_P (C_6D_6) 104.9, δ_H (C_6D_6) 1.37 (6 H, s) and 2.60 (4 H, m).

Preparation of 1,3,4-*Trimethyl*-Δ^3-*phospholen* (1b).—1,3,4-Trimethyl-Δ^3-phospholen oxide (3b) was prepared by the method of Quin,[18] b.p. 105 °C at 0.05 mmHg (lit.,[18] sublimed at 100 °C and 5 mmHg), δ_P ($CDCl_3$) 57.1, δ_H (CCl_4) 1.48 (3 H, d, $^2J_{PH}$ 12.2 Hz), 1.68 (6 H, s), and 2.25 (4 H, m).

To the phospholen oxide (3b) (9.1 g, 63 mmol) was added phenylsilane (2.27 g, 21 mmol) and the mixture was heated at 100 °C for 1 h under nitrogen. Distillation gave (1b) (6.37 g, 79%), b.p. 100 °C at 50 mmHg (lit.,[18] 160—161 °C at 760 mmHg), δ_P ($CDCl_3$) −49.2, δ_H (C_6D_6) 0.89 (3 H, d, $^2J_{PH}$ 5 Hz), 1.63 (6 H, s), and 2.45 (4 H, m).

Preparation of 3,4-*Dimethyl*-1-*phenyl*-Δ^3-*phospholen* (1c).—Preparation of (1c) followed the procedure described for (1b). Phenylphosphonous dibromide (10.0 g, 37 mmol) was allowed to react with 2,3-dimethylbuta-1,3-diene (3.0 g, 37 mmol). Hydrolytic work-up gave (3c) (6.7 g, 88%) as an oil which solidified upon standing, b.p. 160 °C at 0.18 mmHg (lit.,[19] 173 °C at 0.3 mmHg), δ_P ($CDCl_3$) 49.8, δ_H (CCl_4) 1.80 (6 H, s), 2.64 (4 H, m), and 7.56 (5 H, m).

Reduction of (3c) (2.43 g, 12 mmol) using phenylsilane (0.42 g, 4 mmol) gave (1c) (1.31 g, 59%), b.p. 110 °C at 0.3 mmHg (lit.,[19] 74—75 °C at 0.15 mmHg), δ_P ($CDCl_3$) −31.7.

Preparation of 1-(NN-*Dimethylamino*)-3,4-*dimethyl*-Δ^3-*phospholen* (1d).—The dimethylamino-substituted phospholen was prepared by nucleophilic displacement of halogen from (1a) using dimethylamine. Dimethylamine (6.0 g, 133 mmol) was condensed into a dry flask then dissolved in dry diethyl ether (100 ml). The solution was stirred at −70 °C and (1a) (2.17 g, 11 mmol) was added dropwise over 20 min. When addition was complete the mixture was allowed to warm to room temperature and the excess of dimethylamine was evaporated off. After filtration, the solvents were removed and the residue was distilled to give (1d) (0.83 g, 47%), b.p. 105 °C at 22 mmHg, δ_P ($CDCl_3$) 52.6, δ_H (C_6D_6) 1.52 (6 H, s), 2.38 (6 H, d, $^3J_{PH}$ 10 Hz), and 2.32 (4 H, m).

Addition of a small amount of hydrogen peroxide to a sample of (1d) gave a ^{31}P n.m.r. signal at δ 58.6. This was assigned to the corresponding phospholen oxide.

Preparation of 1-*Ethylthio*-3,4-*dimethyl*-Δ^3-*phospholen* (1e).—Triethylamine (1.95 g, 19 mmol) was added dropwise to a solution of ethanethiol (1.20 g, 19 mmol) in dry benzene (40 ml). The resultant solution was cooled to 0 °C under nitrogen and (1a) (2.64 g, 19 mmol) was added dropwise over 30 min. Dry diethyl ether (50 ml) was added and solids then removed by filtration. The solvent was removed at reduced pressure (*ca.* 100 mmHg) and distillation of the residue gave (1e) (1.77 g, 54%), b.p. 125 °C at 45 mmHg, δ_P (C_6D_6) 22.4, δ_H ($CDCl_3$) 1.28 (3 H, t, $^3J_{HH}$ 7.5 Hz), 1.67 (6 H, s), 2.56 (2 H, dq, $^3J_{PH}$ 8.0, $^3J_{HH}$ 7.5 Hz), and 2.84 (4 H, m).

Preparation of 3,4-*Dimethyl*-Δ^3-*phospholen* (1f).—A suspension of lithium aluminium hydride (0.49 g, 13 mmol) in diethyl ether (50 ml) was added dropwise to a stirred suspension of 1,1-dibromo-3,4-dimethyl-Δ^3-phospholenium bromide (4.60 g, 13 mmol) in dry diethyl ether (20 ml) at −78 °C. When the addition was complete the mixture was allowed to warm to room temperature overnight. Methanol (0.5 ml) was added and the mixture stirred for 1 h and then 5% sodium hydroxide solution (5 ml) was added and stirring continued for a further 1 h. The mixture was dried (Na_2SO_4) and filtered. The solvents were removed and the residue was distilled to give (1f) (0.79 g, 47%), b.p. 113 °C at 90 mmHg, δ_P ($CDCl_3$) −82.6 ($^1J_{PH}$ 190 Hz), δ_H 1.60 (6 H, s), 2.37 (4 H, m), and 1.14 and 3.60 (1 H, two m, $^1J_{PH}$ *ca.* 200 Hz).

Some reaction mixtures showed a second, small ^{31}P n.m.r. signal at δ 36.6. This resonance was assigned to the phospholen oxide (3f). Undecoupled spectra revealed a strong coupling, $^1J_{PH}$ 466 Hz, typical of a phosphorus atom bonded directly to a proton.

Preparation of 1-*Ethoxy*-3,4-*dimethyl*-Δ^3-*phospholen* (1h).—A solution of sodium (0.30 g, 13 mmol) in ethanol (6 ml) was added dropwise to a solution of (1a) (1.90 g, 9.8 mmol) in dry methylene dichloride (10 ml) at −78 °C. The mixture was then stirred for 1 h, the solvents removed, and the residue distilled to yield (1h) (1.03 g, 67%), b.p. 105 °C at 5 mmHg, δ_P ($CDCl_3$) 127.4, δ_H (C_6D_6) 0.82 (3 H, t, $^3J_{HH}$ 7.5 Hz), 1.41 (6 H, s), 2.28 (4 H, m), and 3.36 (2 H, dq, $^3J_{PH}$ 7.5, $^3J_{HH}$ 7.5 Hz).

Preparation of 3,4-*Dimethyl*-1-(*n-pentyloxy*)-Δ^3-*phospholen* (1g).—A solution of (1a) (1.0 g, 5.2 mmol) in methylene dichloride (5 ml) was added dropwise to a vigorously stirred suspension of lithium n-pentoxide (0.55 g, 5.8 mmol) in methylene dichloride (5 ml). When the addition was complete the mixture was stirred at ambient temperature overnight. The solvent was removed and the residue was distilled to yield (1g) (0.6 g, 59%), b.p. 80 °C at 0.1 mmHg, δ_P (C_6D_6) 127.1.

Preparation of 1-*Bromo*-3,4-*dimethyl*-Δ^3-*phospholen Oxide* (3a).—To a suspension of 1,1-dibromo-3,4-dimethyl-Δ^3-phospholenium bromide (10.6 g, 30 mmol) in dry methylene dichloride at 0 °C was added dropwise a solution of methanol (0.91 g, 28.5 mmol) and triethylamine (2.90 g, 28.5 mmol) in methylene dichloride (20 ml). The mixture was stirred overnight and then diluted to 100 ml with diethyl ether. After standing for 1 h the precipitate was removed, the filtrate was concentrated, and the residue distilled to give (3a) (4.47 g, 71%), b.p. 160 °C at 0.08 mmHg, δ_P ($CDCl_3$) 68.4, δ_H ($CDCl_3$) 1.77 (6 H, s) and 3.07 (2 H, m).

General Method of Preparation of 1-(p-*Methoxy*-, 1-p-*Methyl*-, *and* 1-p-*Trifluoromethyl*)-*phenyl*-3,4-*dimethyl*-Δ^3-*phospholen Oxides* (3i—k).—Each of these *para*-substituted phenylphospholen oxides (3i—k) was prepared by reaction of the appropriate Grignard reagent with the bromo-oxide (3a). In a typical reaction the appropriate *para*-substituted bromobenzene (21.6 mmol) was dissolved in tetrahydrofuran (20 ml) and a few drops of this solution were added to dry magnesium turnings (22.6 mg-atom). The reaction was initiated with a few drops of 1,2-dibromoethane and then the remaining solution was added dropwise. When the addition was complete the mixture was stirred for 1 h then decanted and added dropwise to an ice-cold solution of (3a) (19.2 mmol) in diethyl ether (20 ml). The mixture was allowed to warm to room temperature, stirred overnight, and then quenched by slow addition to a saturated solution

of ammonium chloride (50 ml). The organic layer was separated and the aqueous phase washed with methylene dichloride (4 × 10 ml). After removal of solvents the crude product of each reaction was a viscous oil. The *p*-methoxy- (3i) and *p*-trifluoromethyl- (3k) substituted products were then isolated as crystalline solids from diethyl ether–light petroleum (b.p. 60—80 °C). The *p*-tolyl compound (3j) was distilled at 120 °C and 0.2 mmHg. Yields in all cases were *ca.* 50% and ^{31}P and ^{1}H n.m.r. data were in accord with the assigned structures, δ_P ($CDCl_3$) (3i) 49.3, (3j) 49.5, (3k) 49.3.

Preparation of 1-p-*Chlorophenyl*-3,4-*dimethyl*-Δ^3-*phospholen Oxide* (3l).—*p*-Chlorophenylphosphonous dibromide was prepared by an exchange route and then condensed with the appropriate diene. *p*-Chlorophenylphosphonous dichloride (9.90 g, 46.4 mmol) and phosphorus tribromide (25.0 g, 92.4 mmol) were stirred together at room temperature for 12 h and then at 160 °C for 1 h. Fractional distillation of the mixture gave *p*-chlorophenylphosphonous dibromide (12.6 g, 90%), b.p. 100 °C at 0.15 mmHg. 2,3-Dimethylbuta-1,3-diene (1.5 g, 18.3 mmol) was added to *p*-chlorophenylphosphonous dibromide (5.5 g, 18.2 mmol) and the mixture was stored under nitrogen for two days. Hydrolytic work-up of the adduct as described in the preparation of (1b) gave (3l) (2.61 g, 64%), b.p. 155 °C at 0.1 mmHg, δ_P ($CDCl_3$) 49.0, δ_H ($CDCl_3$) 1.79 (6 H, s), 2.79 (4 H, m), and 7.61 (4 H, m).

General Method of Preparation of 1-p-*Methoxy-*, 1-p-*Methyl-*, 1-p-*Trifluoromethyl-, and* 1-p-*Chloro-phenyl*-3,4-*dimethyl*-Δ^3-*phospholens* (1i—l).—Each phospholen was prepared by reduction of the corresponding phospholen oxide (3i—l) using phenylsilane. In a typical reaction the phospholen oxide (6.8 mmol) was mixed with phenylsilane (2.4 mmol) and stirred under nitrogen at 80 °C for 2 h, then at 110 °C for a further 1 h. Each product phospholen was distilled directly from the corresponding reaction mixture in high yield (>70%): (1i), b.p. 119 °C at 0.1 mmHg, δ_P ($CDCl_3$) −34.5; (1j), b.p. 125 °C at 0.2 mmHg, δ_P ($CDCl_3$) −33.7; (1k), b.p. 115 °C at 0.2 mmHg, δ_P −29.9; (1l), b.p. 125 °C at 0.4 mmHg, δ_P ($CDCl_3$) −32.4.

Preparation of 1-p-NN-*Dimethylaminophenyl*-3,4-*dimethyl*-Δ^3-*phospholen* (1m).—The phospholen (1m) was prepared by reaction of *p*-*NN*-dimethylaminophenyl-lithium with the bromophospholen (1a).

Lithium (0.39 g, 56 mg-atom) was crushed and placed in a three-necked flask under dry diethyl ether (10 ml). A solution of *p*-bromo-*NN*-dimethylaniline (5.65 g, 28 mmol) in dry diethyl ether (20 ml) was added and the mixture was heated under reflux for 24 h to dissolve the lithium. The precipitate of lithium bromide was removed by filtration and (1a) (5.46 g, 28 mmol) was added dropwise to the resultant brown solution at −10 °C. When the addition was complete diethyl ether (25 ml) was added and the mixture was heated under reflux for 1 h. Benzene (20 ml) was then added at ambient temperature and after stirring for 2 h a 40% solution of ammonium chloride (20 ml) was added. The benzene layer was separated, dried, and the solvent removed *in vacuo*. The residue was redissolved in dry methylene dichloride and precipitated from diethyl ether. After filtration, distillation gave a mixture (2.08 g, 31.7%) of two compounds. Integration of the ^{1}H n.m.r. spectrum showed the distillate to be a mixture of *p*-$BrC_6H_4NMe_2$ (22.5%) and (1m) (77.5%), δ_P ($CDCl_3$) −35.7, δ_H ($CDCl_3$) 1.72 (6 H, s), 2.75 (4 H, m), 2.92 (6 H, s), and 7.04 (4 H, m).

Preparation of 1-*Ethoxy*-3,4-*dimethyl*-Δ^3-*phospholen Oxide* (3h).—A solution of sodium ethoxide (0.65 g, 9.6 mmol) in ethanol–diethyl ether (1 : 1; 8 ml) was added to a stirred, ice-cooled solution of (3a) (2.0 g, 9.6 mmol) in diethyl ether (30 ml) and the mixture was stirred at room temperature overnight. After removal of solids, the filtrate was concentrated and (3h) (1.10 g, 66%) was distilled as a liquid which crystallised on standing, b.p. 100 °C at 4 mmHg, δ_P ($CDCl_3$) 68.4, δ_H ($CDCl_3$) 1.35 (3 H, t, $^3J_{HH}$ 7.5 Hz), 1.73 (6 H, s), 2.44 (4 H, m), and 4.11 (2 H, dq, $^3J_{HH}$ 7.5, $^3J_{PH}$ 7.5 Hz).

Preparation of 1-*Iodo*-3,4-*dimethyl*-Δ^3-*phospholen* (1n).—A solution of iodine monochloride (4.8 g, 29.6 mmol) in methylene dichloride (20 ml) was added dropwise to an ice-cooled solution of (1f) (3.0 g, 26.3 mmol) and triethylamine (3.1 g, 30.6 mmol) in dry benzene (15 ml). The mixture was stirred overnight at room temperature. After diethyl ether (50 ml) was added the supernatant liquid was decanted and the solvents removed. Distillation of the residue yielded the iodophospholen (1n) (3.0 g, 48%), b.p. 100 °C at 33 mmHg, δ_P (C_6D_6) 109.2, δ_H ($CDCl_3$) 1.75 (6 H, s) and 2.82 (4 H, m).

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