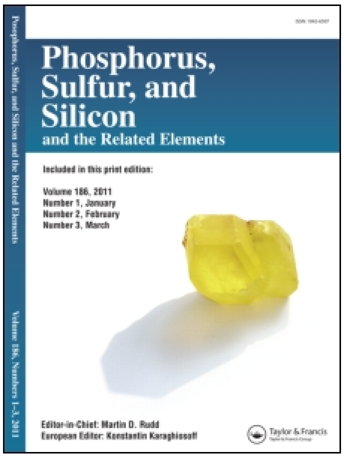

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THE REACTIONS OF Δ^3-PHOSPHOLENES WITH SULPHENATE ESTERS AND SULPHENAMIDES

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THE REACTIONS OF Δ^3-PHOSPHOLENES WITH SULPHENATE ESTERS AND SULPHENAMIDES

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The reactions of 1-methyl and 1-phenyl-Δ^3-phospholenes with sulphenate esters give rise to a range of products involving rearrangement of the endocyclic double bond, dealkylation to phospholene oxides and fragmentation of the ring. When reacted with N,N-diethyl methylsulphenamide, the same phospholenes give ylids by loss of a proton from position-2 or 5 of an intermediate phospholenium amide.

The reactions of trico-ordinate phosphorus compounds with weak σ bonds now constitutes a major synthetic route to pentaco-ordinate phosphorus compounds.[1,2] Thus peroxides,[3–5] cyclic disulphides[6] and more recently sulphenate esters[7] have provided a range of acyclic, monocyclic and bicyclic phosphoranes. In parallel with this work we have been engaged on a study of the reactions of Δ^3-phospholenes with peroxides and disulphides because the resultant phosphoranes often fragment to diene and tri-coordinate phosphorus. It therefore seemed pertinent to examine the reactions of Δ^3-phospholenes (**1ab** and **2ab**) with sulphenate esters (**3**) and sulphenamide Et_2NSMe (**22**) with a view to establishing the nature of the products and hence the course of the reactions.

RESULTS AND DISCUSSION

i) Sulphenate Esters

The reactions between *cis/trans*-1,2,5-trimethyl-Δ^3-phospholene (**1a** + **1b**) or *cis/trans*-1-phenyl-2,5-dimethyl-Δ^3-phospholene (**2a** + **2b**) and either ethyl benzenesulphenate (**3a**) or *n*-pentyl methylsulphenate (**3b**) were carried out in deuteriochloroform or deuteriotoluene solvents and were monitored by ^1H and ^{31}P nmr. The conditions and the results of the experiments are recorded in Tables I, II and III. In each case a mixture of diastereomeric phospholenes (**1a** + **1b** and **2a** + **2b**) was used and in each case the reactions were rapid, even at $-60°$, and a large number of products (≥ 10) was observed by ^{31}P nmr. The tables show a material balance of $\geq 70\%$ because only the more important ($\geq 2\%$) products were recorded and in some instances a considerable number of minor products remained unidentified. The assignment of product structure was achieved by comparison with the ^{31}P nmr spectra of known compounds and by augmentation of the ^{31}P nmr absorbances of some components of the product mixture by the addition of known compounds. In addition, *t,t*-hexa-2,4-diene (**5**) was identified by glc on a 4m ODP† column operating at 60°C.

Scheme 1 depicts some of the possible products from the reaction of Δ^3-phospholenes with sulphenate esters. These products all arise from the initial reaction to an unstable phosphorane (**4**) which may then fragment (path A), ionise (paths B and C) or react with more sulphenate ester to form another, unstable dialkoxyphosphorane (path D). This gives rise to nine possible phosphorus products which might be detectable from one diastereomeric Δ^3-phospholene (e.g. the *cis*-isomer, as depicted in the Scheme). The use of the second diastereomer offers another three possible products where the ring structure is retained. Since diastereomeric mixtures of phospholenes were used, one might anticipate at least twelve products. In addition, the sulphenate esters are known to add to double bonds[10] and therefore another twenty-four compounds are conceivable from the mixtures of phospholene oxides (Scheme 2) and likewise from the phospolene sulphides.

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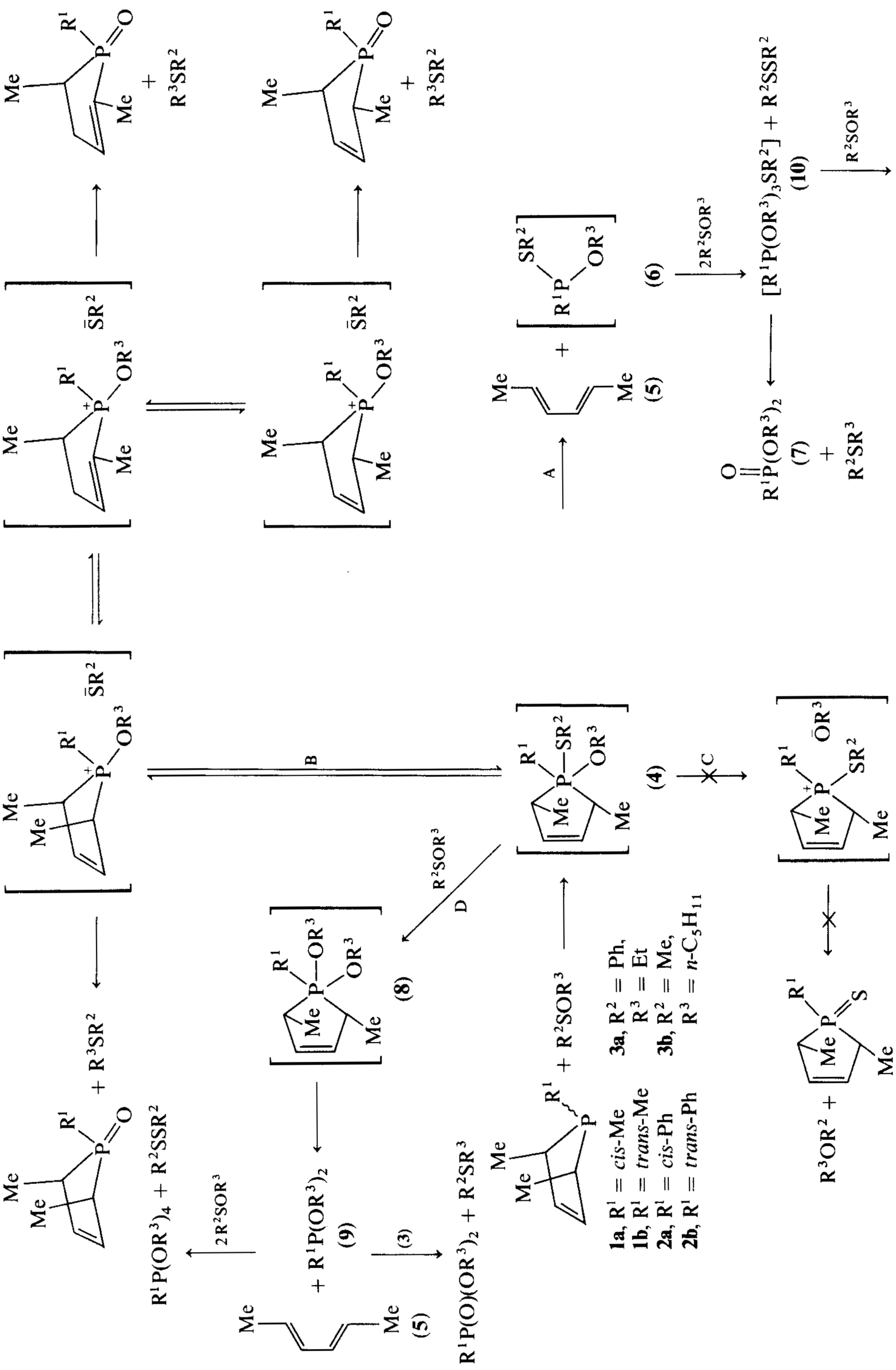
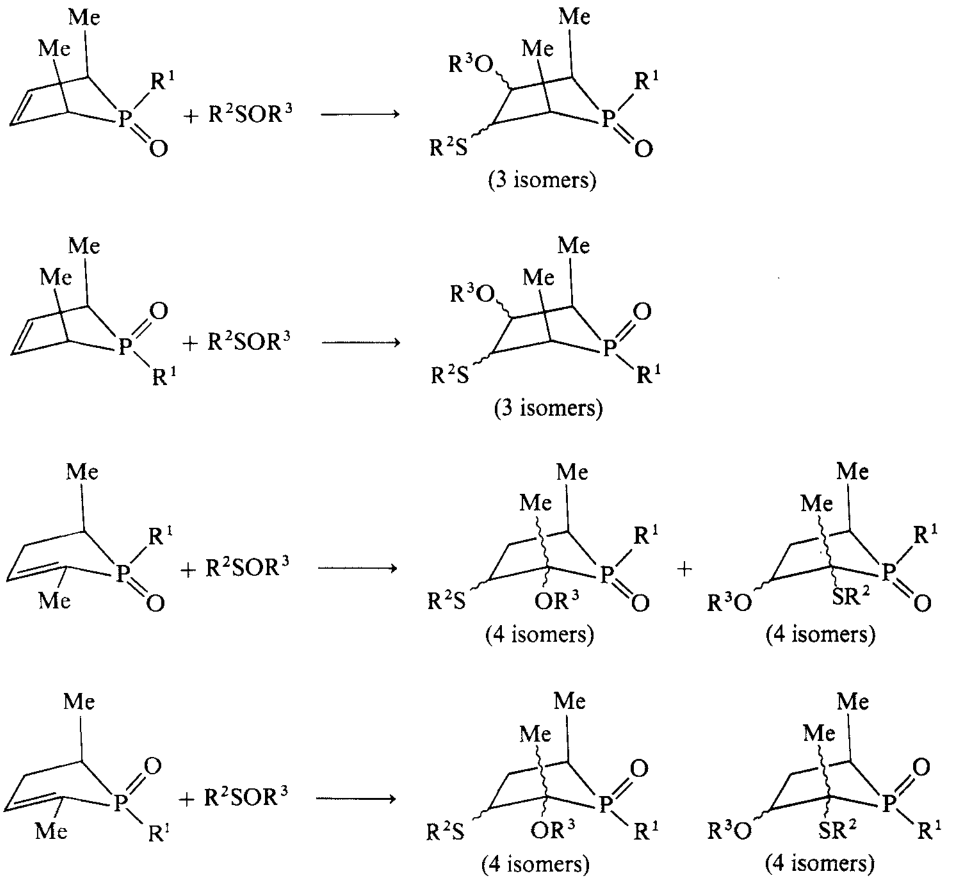
† (Oxydipropionitrile).



$1a$, R^1 = *cis*-Me
$1b$, R^1 = *trans*-Me
$2a$, R^1 = *cis*-Ph
$2b$, R^1 = *trans*-Ph

$3a$, R^2 = Ph, R^3 = Et
$3b$, R^2 = Me, R^3 = n-C_5H_{11}

SCHEME 1



SCHEME 2

In fact, one can immediately eliminate any significant contribution from path C (and therefore the formation of all thiophosphoryl compounds) because none of the known Δ^3-phospholene sulphides were detected by ^{31}P nmr as major components of the product mixture.

Fragmentation of the ring occurs as evidenced by the formation of phosphonate products and the detection of (**5**) by glc. Since, under controlled conditions,† the fragmentation is stereospecific, it seems unlikely that radical intermediates are involved in these reactions[8,9] but it is not possible to decide whether path A or path D represents the fragmentation route.

Except on one occasion at -60°C (see Table I) no tri-co-ordinate intermediates (e.g. **6** or **9**) were detected during these reactions which emphasises the reactivity of such compounds towards sulphenate esters,[7] but the reaction of (**2ab**) with (**3a**) at -60°C in deuteriotoluene gave *two* penta-co-ordinate compounds at -24.5 and -59 ppm upfield from H_3PO_4. One of these (*ca.* -59 ppm) is probably due to $PhP(OEt)_4$[4] (route A or D) but a substantial proportion of the reaction mixture must have retained the ring structure since, on warming, a mixture of Δ^2- and Δ^3-phospholene oxides was observed. Since phosphoranes of type (**8**) have never been detected due to rapid fragmentation,[8,9] it is possible that the peak at -24.5 is due to (**4**) but it may also be due to acyclic thiophosphoranes such as (**10**). The major pathway in all the reactions is B which involves ionisation of the thioalkyl group followed by dealkylation to Δ^3-phospholene oxide or thioalkyl anion-catalysed proton transfer followed by dealkylation to Δ^2-phospholene oxides. This is consistent with

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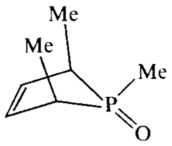
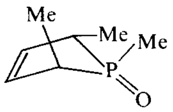
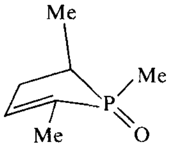
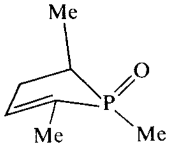
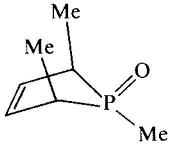
† Uncontrolled, highly exothermic reactions between (**1ab**) or (**2ab**) and (**3a**) gave a mixture of *t*, *t*,-, *t*,*c* and *c*,*c*-dienes in the ratio 5:1:0.3 suggesting a radical reaction.[8,9]

TABLE I

The product compositions (%) from the reaction of 1,2,5-trimethyl-Δ^3-phospholene (**1ab**)[a] with ethylbenzene sulphenate (**3a**) in deuteriotoluene

Molar ratio **1ab**:**3a**	Temp °C	δ ^{31}P (ppm from H_3PO_4)									
		79	69	66.5	63.5	62.5	45.5	28.5	11.5	−6	−7.1
		product composition(%)									
1:1	−60[b]	6	1	4	7	3	2	17	0	27	22
1:1	Amb[c]	7	4	8	10	6	3	16	12	3	22
1:1	Amb	20	4	15	14	29	2	7	0	0	0
1:2	Amb	11	1	9	9	22	6	15	0	0	0
Assignment							?	$MeP(O)OEt)_2$	?	**(1a)**	**(1b)**

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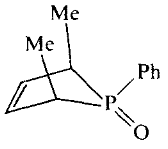
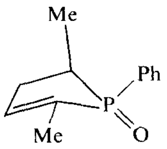
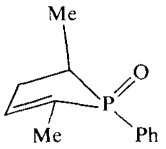
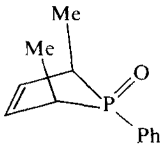
[a] Isomer ratio **1a**(*cis*): **1b**(*trans*) = 4:1

[b] Minor products (< 1 %) observed at 147.4 (?), 115.6 (?) and −45 [$MeP(OEt)_4$].

[c] After reaction at −60°, mixture allowed to warm to ambient temperature to give this series of products.

TABLE II

The product compositions (%) from the reaction of 1-phenyl-2,5-dimethyl-Δ^3-phospholene (**2ab**)[a] with (**3a**) in 1:1 molar ratio

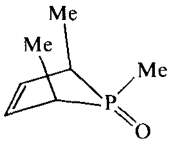
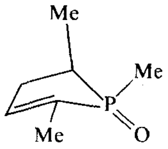
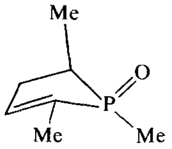
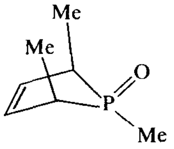
Solvent	Temp °C	δ ^{31}P (ppm from H_3PO_4)									
		74	64	58.5	56	43	27.5	18.5	15.2/ 11.4	−24.5	−59
$CDCl_3$	Amb	5	5	9	5	6	15	15	0	0	0
C_7D_8	−60	0	0	0	0	0	0	0	76	9	11
C_7D_8	Amb[b]	6	5	10	4	6	2	13	37	0	0
Assignment						?	?	PhP(O) (OEt)$_2$	**2a/b**	PhP(SEt) (OEt)$_3$	PhP (OEt)$_4$

[a] Isomer ratio: **2a** (*cis*): **2b** (*trans*) ~9:1.

[b] After reaction at −60°, mixture allowed to warm to ambient temperature to give this series of products.

TABLE III

The product compositions (%) from the reactions of (**1ab**)[a] with pentyl methanesulphenate (**3b**)

Solvent	Molar ratio **1a**: **3b**	Temp °C	δ ^{31}P (ppm, H_3PO_4) 79	67	66/64.5/64	63.5	62.5	45.5	29.5	% diene (by glc)
$CDCl_3$	1:1	Amb	—	9	44	17	—	4	9	—
$CDCl_3$	1:2	Amb	—	13	22	14	—	9	21	—
$CDCl_3$	1:3	Amb	—	17	—	21	—	9	20	—
$CDCl_3$	1:1	−60°	4	7	36	12	5	—	6	10
$CDCl_3$	>1:1[b]	Amb	14	3	5	4	3	—	14	10
C_7D_8	1:2	−60	5	10	6	15	7	—	35	14
C_7D_8	1:2	−60	6	22	26	13	—	—	20	—
C_7D_8	1:2	−60	3	12	19	14	—	—	29	—
	Assignments				?			?	MeP(O) $(OC_5H_{11})_2$	

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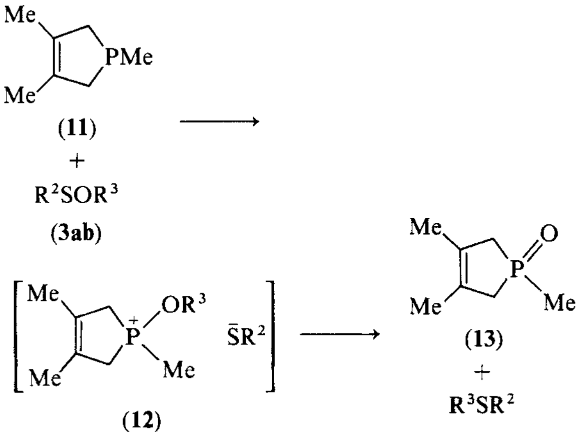
[a] Isomer ratio, (**1a**: **1b**) = 4:1.
[b] Unreacted phosphine = 54%.

what is known about the reactions of phosphines with sulphenate esters[11] and the desulphurisation of sulphoxides by trimethylphosphite.[12,13] In addition, the reaction of 1,3,4-trimethyl-Δ^3-phospholene (**11**) with (**3a**) and (**3b**) in toluene at $-60°C$ gave the corresponding phospholene oxide (**13**, δ $^{31}P = 57.1$) as the sole product, presumably *via* (**12**).†



In a similar manner, ethyl diphenylphosphinite reacted with (**3a**) and (**3b**) in toluene to give diphenylphosphinate (δ $^{31}P = +27.9$) in quantitative yield.

In summary, although the reactions of sulphenate esters with phospholenes are of some mechanistic interest, the large number of products renders the reactions of little value from a synthetic point of view.

ii) Sulphenamides

The reactions between (**2ab**) and N,N-diethyl methanesulphenamide (**22**) were carried out either neat or in benzene or toluene solution and were monitored by ^1H and ^{31}P nmr.

After 48h at ambient temperature a neat, 1:1 mole mixture of (**2ab**) and (**22**) gave a ^{31}P nmr spectrum containing only two peaks at $\delta = +25.7$ (17%) and +26.6 (83%). The ^1H nmr revealed the presence of diethylamine [δ 0.98 (3H, *t*, $^3J = 7$ Hz), δ 2.44 (2H, *q*, $^3J = 7$ Hz and δ 0.5 (1H, *s*, NH)] and the phosphorus products retained the phospholene ring structure as evidenced by the ^1H nmr and by the fact that treatment with excess HCl gas gave a mixture of five phospholene sulphides (**15**–**19**), Scheme 3).

The identities of (**15**), (**16**), (**17**) and (**19**) were confirmed by independent synthesis and (**18**) was deduced as the fifth product from the condensation of $PhPBr_2$ with (**5**) at 40°C (a somewhat higher temperature than normal) followed by hydrolysis to oxide, reduction with phenyl silane[9] to a mixture of *three* phospholenes and reaction of the mixture with sulphur to form a mixture of (**15**), (**19**) and (**18**). The ^1H nmr of this mixture showed no evidence for Δ^2-isomers (see Experimental).

The reaction of *trans*-1-phenyl-Δ^3-phospholene (**2b**) with (**22**) gave, after several weeks at ambient temperature a ^{31}P nmr spectrum with only one peak at 26.3 ppm. The ^1H nmr again revealed diethylamine and after removal of the solvent and amine under vacuum at 25°, the ^1H nmr of the residue showed, $\delta(C_6D_6) \sim 7.7$ (2H, m) 7.15 (3H, broad s) 7.05 (1 H, broad s) 6.5 (1H, broad *q*) 5.7 (1H, broad m), 2.02 (3H, d, $^3J_{PH} = 14$) 1.85 (3H, broad s) and 1.58 (3H, b koad d, $^3J = 7$). In $CDCl_3$ the same compound showed $\delta = ca.$ 7.4 (5H, m) 6.85 (1H, broad s) *ca.* 6.65 (1H, broad q) 5.8 (1H, broad m) 2.3 (3H, d, J = 14) 1.85 (3H, broad s) and 1.85 (3H, d, J = 7). Treatment with HCl gave a mixture of sulphides almost identical to that obtained from the earlier experiment with a mixture of phospholenes.

The evidence suggests that (**2b**) reacts with (**22**) to give an ylid (**14b**) derived by removal of a proton from the ring by the diethylamino anion (Scheme 4).

The SMe protons resonate at $\delta \sim 2.0$ with $^3J_{PH} = 14$ Hz consistent with the spectra of thiolophosphonates (e.g. (EtO)MeP(O)SMe)[14] and the ring methyl groups are apparently unsplit by phosphorus presumably due to flattening of the ring. The olefinic and tertiary hydrogens are more difficult to assign but presumably the multiplet *ca.* 5.7 is the tertiary ring hydrogen (possibly shifted downfield by the quaternary phosphorus) and the quartet is probably the hydrogen at C-4 since this seems most likely to couple with phosphorus and the tertiary hydrogen at C-5. The appearance of H-3 as a singlet (*ca.* 6.9) is something of a puzzle but is probably associated with the change in ring geometry.

What is certain is that the tertiary hydrogen is not exchanging on the nmr time scale across the ring from C-5 to C-2 since this would render the

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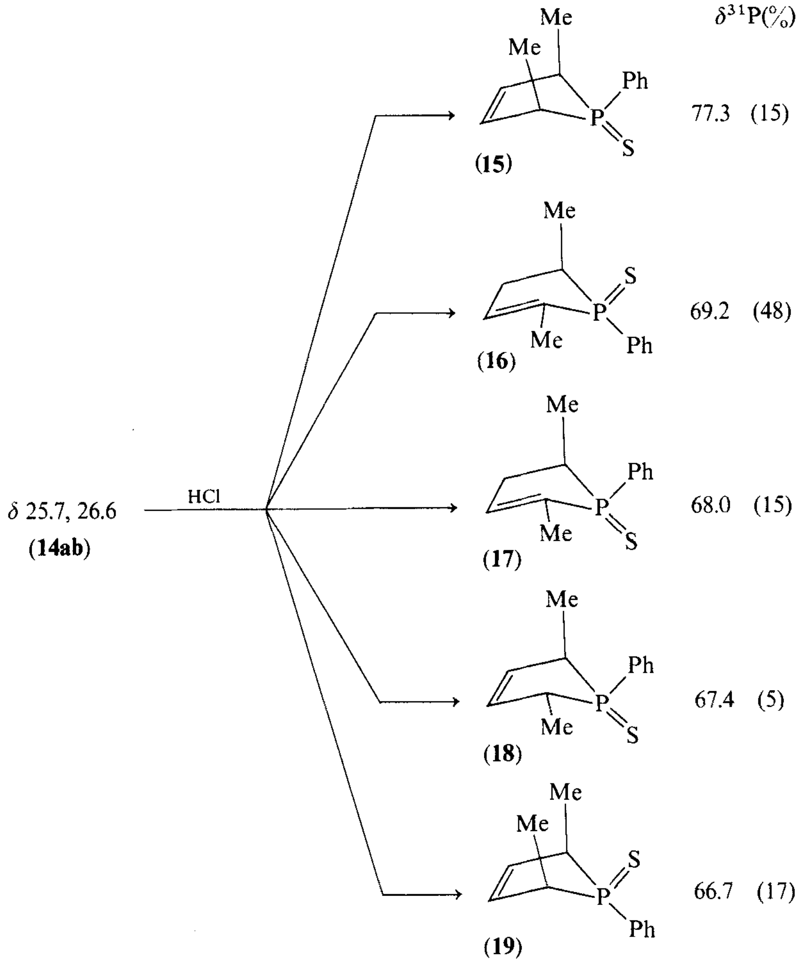
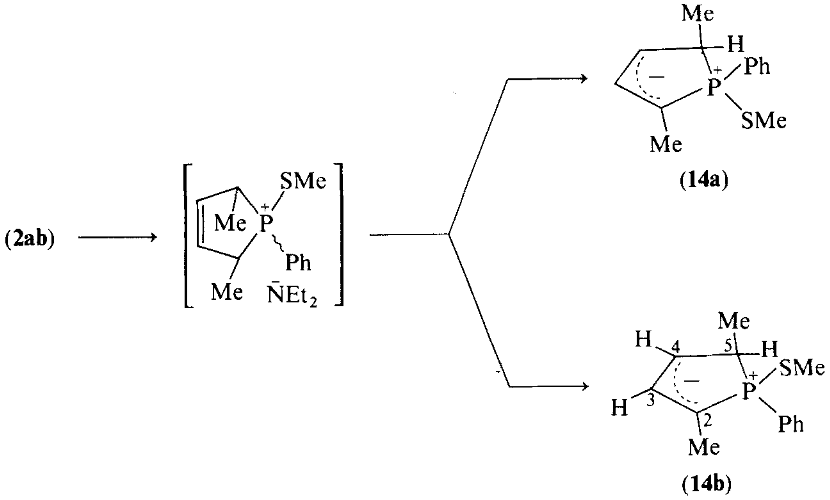
† The fragmentation reaction is known to be far less facile with methyl groups in the 3,4 rather than the 2,5 positions (P. J. Hammond and G. Scott, unpublished results).

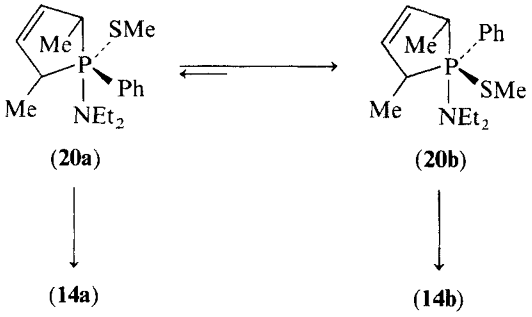


SCHEME 3



SCHEME 4

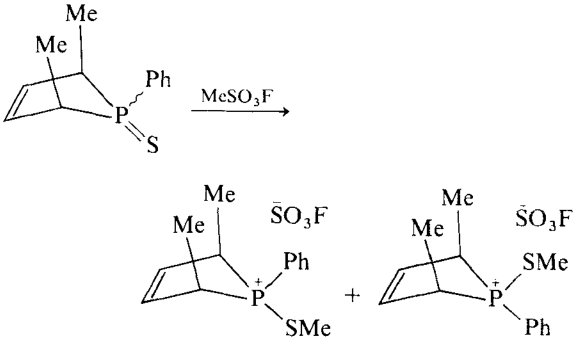
ring hydrogens equivalent and the ring methyl groups equivalent. Thus it is seems highly unlikely that the diastereomeric ylids (**14a**) and (**14b**) would interconvert rapidly by H-exchange. Nevertheless, the mixture of phospholenes which is predominantly (90%) *cis* (i.e. **2a**) gives predominantly (83%) the *trans*-ylid (**14b**). The results imply that a pentacoordinate intermediate (**20ab**) is formed, possibly by insertion into the S—N bond, *prior to ionisation and deprotonation.* The *cis* form of the pentacoordinate (**20a**) may then partially isomerise by pseudorotation, to the *trans* form (**20b**) hence giving rise to a mixture of ylids.



(**20a**) (**20b**)

(**14a**) (**14b**)

Attempts to prepare the ylids by independent routes met with little success. The *cis*- (or *trans*-)-Δ^3-phospholene sulphides (**15** and **19**) were readily alkylated with Magic Methyl to give the salts (**21ab**) in quantitative yield [^{1}H, $\delta = 2.7$, $^3J_{PH} = 14$, $\overset{+}{\mathrm{P}}$S*Me* for (**21a**) and δ 2.35, $^3J_{PH} = 14$ for (**21b**)] but treatment of the salts with either



(**21a**) (**21b**)

lithium diethylamide, *n*-butyllithium or phenyllithium in each case gave a mixture of products which included varying amounts of the starting sulphides and their analogous phospholenes (presumably by nucleophilic attack on sulphur) but only minor quantities (<10%) of the ylids at δ ^{31}P, 26.5 and 25.4. The explanation may be that ylid formation occurs by dissociation of an intermediate PV (**20a** or **20b**) to an *ion-pair* followed by removal of the ring proton by the diethylamide anion *within the ion-pair.*

The reaction of (**1ab**) with (**22**) gives a mixture of 1-methyl-Δ^2 and Δ^3-phospholene sulphides and the intermediate ylids were detected at δ 8.2 and 7.4 after several weeks at ambient temperature in benzene (Table IV). The ^{1}H nmr again showed diethylamine and an S-CH$_3$ doublet at $\delta = 2.0$

TABLE IV

Major peaks observed in the ^{31}P nmr spectrum of the reaction of (lab) with (22) at ambient temperature in benzene

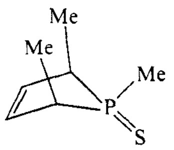
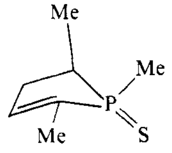
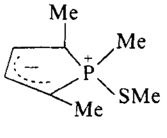
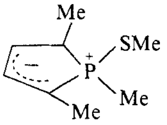
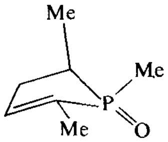
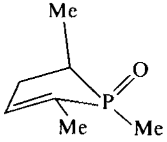
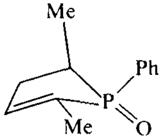
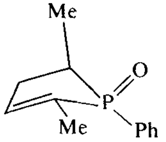
Compound	δ ^{31}P (ppm, H_3PO_4)	% 3 weeks	% 5 weeks
	73.4	18	17
	60.7	18	18
?	63.3	2	3
?	62.4	2	2
?	57.6	8	11
?	56.6	5	10
?	33.4	2	4
?	23.6	6	16
	8.2	27	6
	7.4	11	9
?	−8.3	—	5

TABLE V

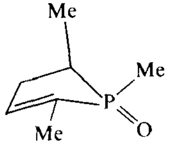
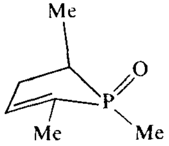
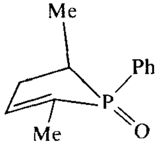
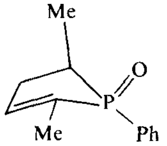
^1H and ^{31}P nmr data of Δ^2-phospholene oxides in $CDCl_3$

	δ ^{31}P	δ ^1H/ppm						J_{PH}/Hz				J_{HH}/Hz	
	(ppm)	PCH_3	PPh[a]	H-3	H-4, -5	H-6	H-7	PCH_3	P, H-3	P, H-6	P, H-7	H-3, H-6	H-5, H-7
	66.3	1.44	—	6.32	2.08-3.20	1.95	1.28	12.3	38.2	10.7	16.4	1.3	7.1
	62.3	1.55	—	6.32	2.08-3.20	1.94	1.27	12.6	38.2	10.7	14.6	10	7.0
	63.8	—	7.61	6.66	2.08-3.24	1.89	0.92	—	38.2	10.9	17.0	2.3	7.0
	57.8	—	7.61	6.66	2.08-3.24	1.85	1.32	—	38.2	11.2	15.4	1.8	7.2

[a] Centre of multiplet.
[b] Not analyzed but *ca.* 1 Hz.

TABLE VI

^{13}C n.m.r. data of Δ^2-phospholene oxides in $CDCl_3$

	δ^{13} C/ppm							J_{PC}/Hz						
	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-1	C-2	C-3	C-4	C-5	C-6	C-7
	10.82	135.36	141.38	35.92	33.13	12.78	13.49	62.36	88.90	29.19	14.60	71.65	10.60	0
	14.95	134.54	141.67	36.80	29.93	12.59	13.51	66.34	86.25	31.84	11.94	72.98	10.70	2.0
	128.68[a]	134.15	144.98	36.38	33.75	12.96	13.72	—	88.25	30.52	14.60	72.98	10.61	0
	128.68[a]	133.97	144.98	37.44	31.34	12.72	13.64	—	88.25	30.52	11.94	72.98	10.42	4.0

[a] Multiplet, not resolved.

($^3J_{PH} = 13$ Hz) but since the ylids were never observed free of substantial proportions of sulphides, the reaction was not pursued further.

No reaction was observed between 1,3,4-trimethyl-Δ^3-phospholene (**11**) and (**22**) even after five weeks but ethyldiphenylphosphinite reacted overnight to give a 30% yield of a single product, δ $^{31}P = 27.8$ which in all probability is N,N-diethyldiphenylphosphinamidate, $Ph_2P(O)NEt_2$, through dealkylation by the methane thiol anion. It is interesting to note that in this case it is the less basic but more nucleophilic thiyl group which affects the dealkylation. Furthermore, the reaction with the phosphinite compared with the lack of reaction with (**11**) suggests yet again,[3–7] an insertion into a weak σ (S—N) bond to form a PV intermediate rather than nucleophilic attack by tricoordinate phosphorus as the slow- rate-limiting step.

EXPERIMENTAL

N.m.r. spectra were recorded on a Bruker HFX 90 (^{31}P or ^1H) or a Perkin Elmer R.12 (^1H) using H_3PO_4 or TMS as references. For the phosphorus spectra, signals downfield of H_3PO_4 are quoted as *positive* in line with the current convention. G.l.c. data were acquired using a Perkin Elmer F11 instrument equipped with F.I.D. and using a 4 m ODP† on Chromosorb column operating at 60° to give an effective separation of *cis*, *cis*-, *cis*, *trans*- and *trans*,*trans*-hexa-2,4-dienes.

The Δ^3-phospholenes were prepared as described previously[9,14] and where necessary were separated by distillation using a Nester-Faust spinning band column followed by isomerisation in chloroform.[14] The Δ^2-phospholenes were prepared as follows.

1,2,5-Trimethyl-Δ^2-phospholene

A sample of 1-chloro-1,2,5-trimethyl-Δ3-phospholenium chloride (0.53 g, 2.7×10^{-3} mole) was dissolved in ethanol-free chloroform (15 ml) and the solution was heated under reflux in a nitrogen atmosphere for 24 h to isomerise the salt to the Δ^2-isomer. After hydrolysis with aqueous sodium carbonate, the oxide products were extracted into chloroform (2 × 20 ml), dried and after removal of the solvent, distilled to give a diastereomeric mixture of *cis*- and *trans*-Δ^2-phospholene oxides, b.p. 81–83°/0.12 mm; δ $^{31}P = 66.3$ (*cis*, 72%) and 62.3 (*trans*, 28%). The ^1H and ^{13}C nmr are collected in Tables V and VI.

The mixture of *cis*- and *trans*-Δ^2-oxides (0.24 g, 1.7×10^{-3} mole) was added to phenyl silane (0.06 g, 5.6×10^{-4} mole) and the mixture was heated to 100° under N_2 for 1 h. A Kugelrohr distillation gave 0.17 g (81%) of a mixture of *cis*-Δ^2-phospholene (0.12 g, 71% δ $^{31}P = -7.0$) and *trans*-Δ^2-phospholene (0.05 g, 29% δ $^{31}P = +5.8$) the mixture boiling at 72–4°/60 mm. The ^1H nmr of the mixture (in C_6D_6) showed for the *cis*-isomer δ 0.84 (3H, d, P—CH_3 $^2J_{PH} = 2.5$) and δ 1.01 (3H, q, —CH—CH_3, $^3J_{PH} = 9.5$, $^3J_{HH} = 6.5$) and for the *trans*-isomer, δ 0.96 (3H, d, PCH_3, $^2J_{PH} = 2.5$) and δ 1.26 (3H, q, —CHCH_3, $^3J_{PH} = 16.5$, $^3J_{HH} = 6.5$). There was also a broad multiplet between δ 1.68 and 3.08 (6H) and a broad doublet δ 5.47–5.93 ($J_P \simeq 12$) corresponding to the olefinic ring hydrogen of both isomers. No ^{13}C data are available.

1-*Phenyl-2,5-dimethyl-Δ^2-phospholene*

A mixture of *cis*- and *trans*-1-phenyl-2,5-dimethyl-Δ^2-phospholene oxides was prepared by isomerisation of 1-bromo-1-phenyl-2,5-dimethyl-Δ^3-phospholenium bromide in chloroform followed by hydrolysis, extraction and distillation to give 49% yield of the mixture of diastereomers, b.p. 153–5°/0.12 mm. δ $^{31}P = 63.8$ (*cis*, 83%) and 57.8 (*trans*, 17%). The ^1H and ^{13}C nmr data appear in Tables V and VI.

A phenylsilane reduction of the mixture of oxides (see above) gave 78% of a mixture of phospholenes, b.p. 149°/25 mm (lit. b.p. 85–94°/1 mm),[15] δ ^{31}P, 10.2 (*cis*-isomer, 77%) and δ 22.8 (*trans*-isomer, 22%). The ^1H nmr (C_6D_6) showed for the *cis*-isomer, δ 0.77 (3H, q, CHCH_3, $^3J_{PH} = 11.0$, $^3J_{HH} = 6.5$) and δ 6.01 (1H, broad d, ring olefinic hydrogen, $^3J_{PH} \simeq 6$) and for the *trans*-isomer, δ 1.22 (3H, q, CHCH_3, $^3J_{PH} = 18.5$, $^3J_{HH} = 6.5$) and δ 5.82 (1H, broad d, $^3J_{PH} \simeq 6$). Multiplets were also observed at δ 1.68–3.01 and δ 7.0–7.75 (aromatic H).

Sulphides were prepared from the corresponding phospholenes with retention of configuration at phosphorus by reaction with elemental sulphur.

Ethyl benzenesulphenate was prepared by the reaction of benzenesulphenyl chloride with sodium ethoxide[16] and *n*-pentyl methanesulphenate was prepared from methylsulphenyl chloride and lithium *n*-pentyloxide by a modification of the method due to Moore and O'Connor.[17] Methanesulphenyl chloride (16.5 g, 0.2 mole) was dropped into a solution of lithium pentyloxide (18.8 g) in dry, 1,2-dimethoxyethane (100 ml) at −70°. After warming to 20°, chloroform (100 ml) was added and the mixture was washed with cold water (2 × 100 ml). After drying over $MgSO_4$, fractional distillation of the organic layer gave 10.3 g of a mixture, b.p. 53.4°/15 mm containing pentyl methanesulphenate (59% equivalent to 23% yield) and pentanol (41%). Fractional distillation using a spinning band column increased the proportion of ester in one fraction to 89% but some pentanol was always present in the the reactions with phospholenes.

The N,N-diethylmethanesulphenamide(**22**) was prepared from methanesulphenyl chloride and diethylamine[18] and distillation through a spinning band column gave a >99% pure sample in 16% yield, b.p. 59°/58 mm; ^1H nmr ($CDCl_3$) 1.18 (6H, t, $^3J = 7$), 2.11 (3H, s, SCH_3) and 2.83 (4H, q).

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† Oxypropionitrile.

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