Dialkylphosphinic-N,N-Dichloroamides and Related Azides

by

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A Thesis

presented for the degree of

Doctor of Philosophy

in the Faculty of Science

of the

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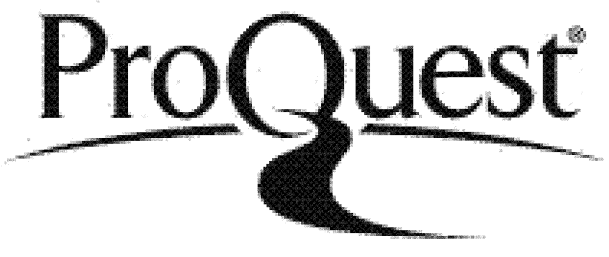

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STATEMENT

The experimental work described in this thesis has been carried out by the author in the laboratories of the Department of Chemistry of The University of Leicester between October 1972 and July 1975.

No part of this work has been presented, or is concurrently being presented for any other degree.

Signed

M. A. STEPHEN

OCTOBER 1978

ACKNOWLEDGEMENTS

I would like to thank my supervisor, Dr. M. J. P. Harger for his guidance and encouragement throughout all stages of this work and Mrs. S. Davies for help in running 100 MHz ^{1}H nmr spectra and variable temperature spectra.

Finally, I would like to thank my wife for her support and constant encouragement, and the Science Research Council for a maintenance grant.

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SUMMARY

Azido, N-chloroamino, and N,N-dichloroamino derivatives of dialkylphosphinic acids have been synthesised.

The azides upon photolysis in alcohols (except isopropanol) or t-butylamine give products derived from alkyl migration from phosphorus to nitrogen with incorporation of a molecule of solvent. Diisopropyl and di-t-butylphosphinic azides also give amides and products derived from insertion of a formal nitrene into the O-H bond of the alcohol. Diethylphosphinic azide undergoes predominantly nucleophilic substitution by the methanol solvent. Anhydrides formed in the photolysis of di-t-butylphosphinic azide in cyclohexane and benzene arise from the presence of adventitious moisture and accompany nitrene products. The formation of these products is discussed in terms of independent routes involving either a metaphosphonimidate intermediate (only trapped in protic solvents) or a singlet nitrene that decays to a triplet nitrene.

An equilibrium has been shown to exist between amides, N-chloroamides, and N,N-dichloroamides. The chloroamides add to phenylethylenes to yield anti-Markovnikov products after reduction, these cyclise with base to aziridines. The formation of cis and trans adducts in the reaction of t-1-(N-chloro-N-methylamino)-2,2,r-3,4,4-pentamethylphosphetan-1-oxide with styrene is discussed in terms of a pseudorotation mechanism. The initial N-chloro adduct has been isolated in the reaction of (N,N-dichloro)di-t-butylphosphinic amide with styrene.

Attempts to form ring expanded products in the reaction of t-1-(N-chloroamino)- and t-1-(N,N-dichloroamino)-2,2,r-3,4,4-pentamethylphosphetan-1-oxides (141) and (140) respectively yielded only the parent amide. The formation of an anionic species in these reactions was shown by trapping with methyl iodide.

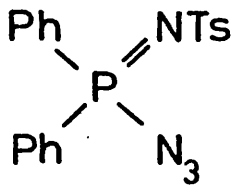
The N-chloroamides with anthracene give 9-chloro and 9,10-dichloroanthracenes. The o:m:p ratio of chloroanisoles formed in the reaction of the chloroamides (140) and (141) is used to elucidate the nature of the mechanism of the chlorination reactions.

Triphenylarsine has been tried as a trap for nitrenes generated from N,N-dichloroamides and azides, without success.

1 PHOSPHINIC AZIDES

1.1 Synthesis and Reactions of Quinquevalent Phosphorus Azides

The P(V) azides (1)[1], (2)[2,3,4], (3)[3,5,6,7], (4)[8], (5)[9,10] and (6)[11,12] have been prepared from the corresponding chlorides and sodium azide in a variety of solvents. A procedure developed originally for the synthesis of sulphonyl azides[13], namely the reaction of the hydrazide with nitrous acid, has been used in the synthesis of (3, R = Ar)[7], although only in low yield. Using lithium azide in acetonitrile Paciorek[14] has synthesised (2, R = Ph) from its chloride, and hydrazoic acid has been employed in the synthesis of (2), (3)[3] and (5)[10] from the corresponding chlorides.



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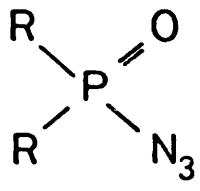

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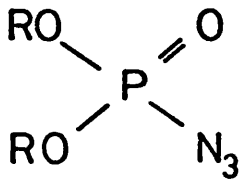

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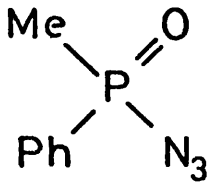

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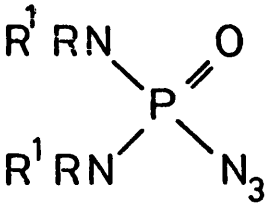

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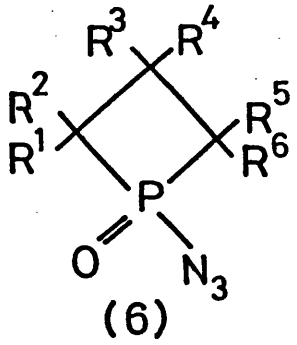
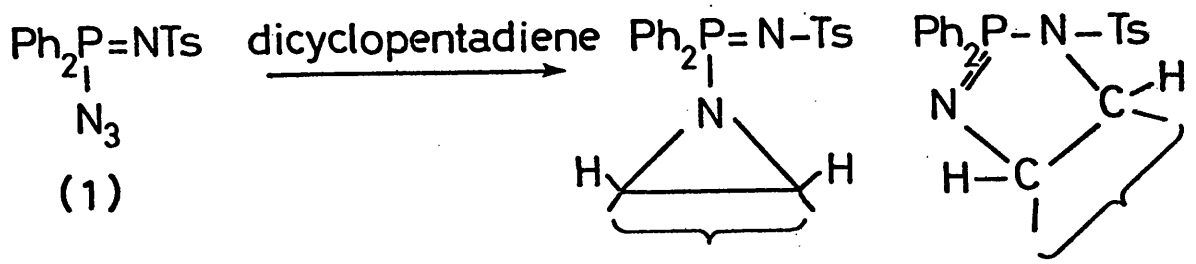


(6)

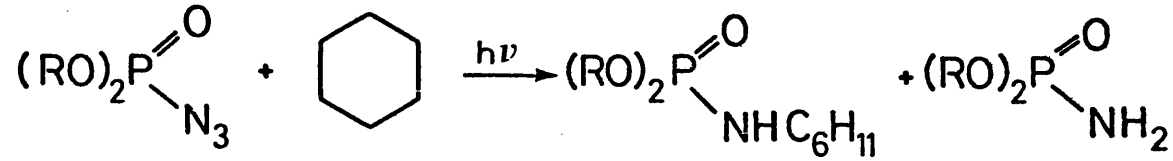
The decomposition reactions of phosphinic azides have received very little attention. Evidence for phenyl migration has been found by Reichle[15] in the vacuum pyrolysis of diphenylphosphinic azide (2, R = Ph) and the aryl azides (2, R = Ph) are reported to decompose thermolytically by a nitrene mechanism.[16] The copper catalysed decomposition of the

phosphazene azide (1) in the presence of dicyclopentadiene gives a product derived from addition of a nitrene to a double bond with no phenyl migration. The authors could not decide between the two possible structures shown.[1]



Vetter[9] has reported that the azide (5, R= R^1 = Me) remains unchanged even after irradiation with UV light for 24 hours in boiling benzene and similar behaviour was observed by Cremlyn[10] with the azide (5, R = H, R^1 = Benzyl).

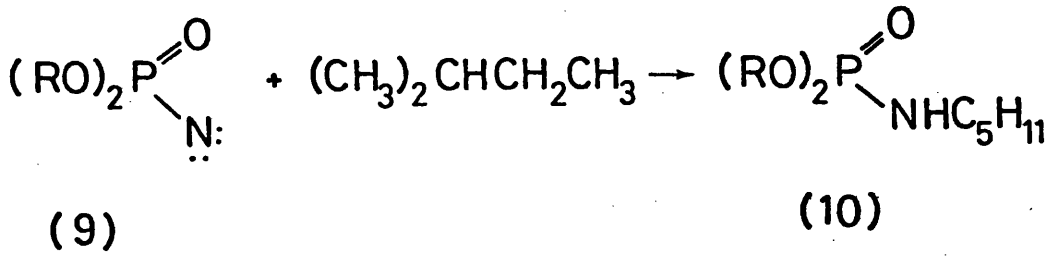
Photolytic decomposition of the phosphoryl azides (3, R = Et or Ph) in cyclohexane leads to the products (7) derived from insertion of a formal nitrene into the C-H bonds of cyclohexane. In addition with (3, R = Et) a 12% yield of the parent amide (8) is obtained.[29]



(3) (7) (8)

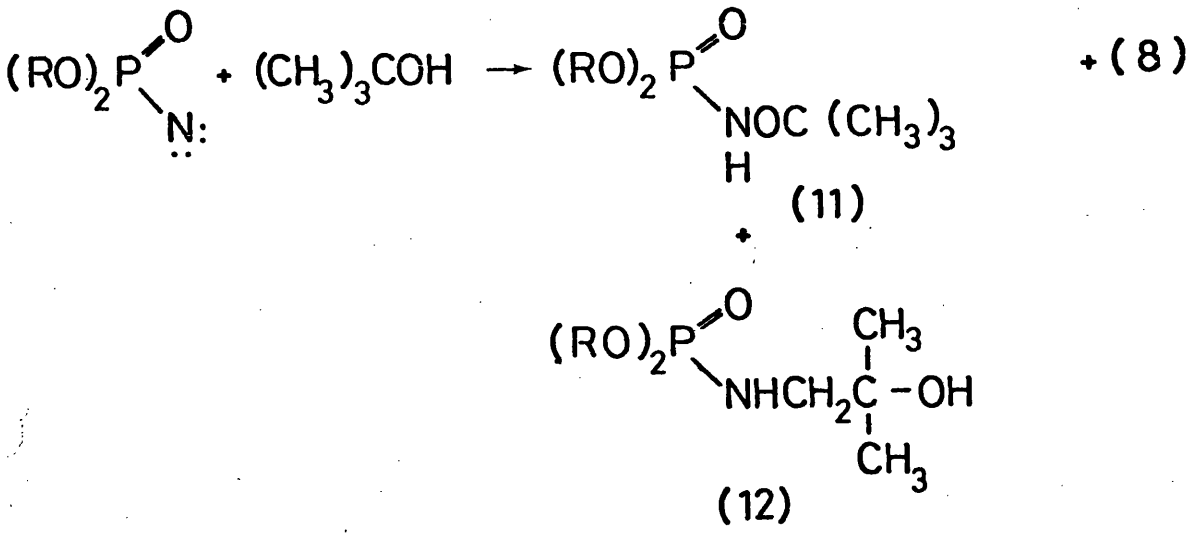
The phosphoryl nitrenes (9, R = Et or Ph) seem to be highly reactive and unselective since insertion into the primary, secondary, and tertiary C-H bonds of 2-methylbutane occurs equally well to yield the

isomeric products (10).[29]



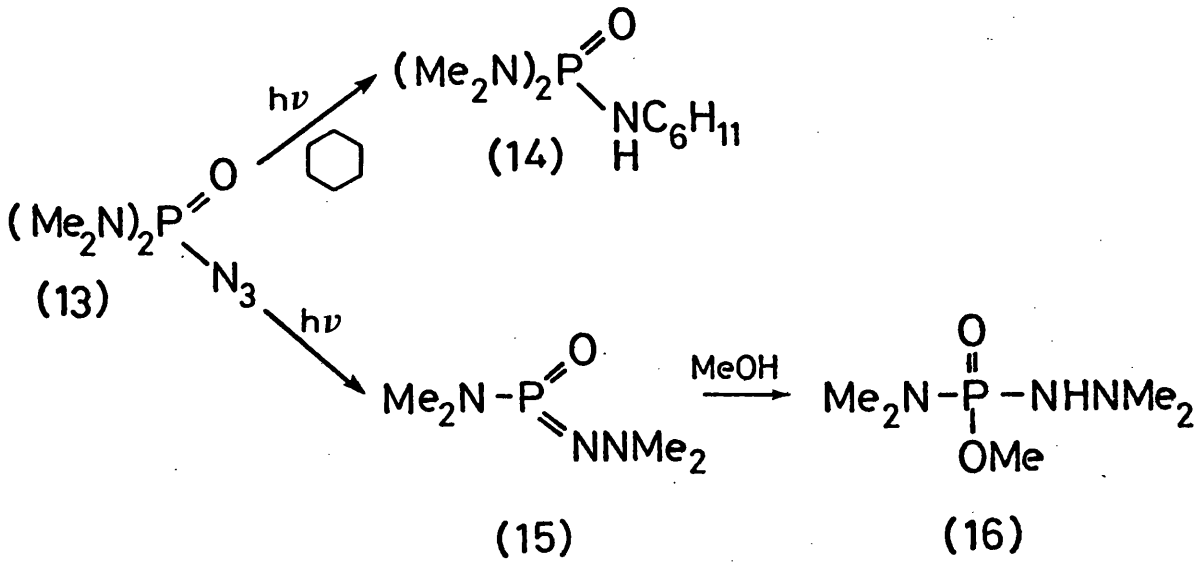
(9) (10)

As further evidence for non-selectivity, photolysis of a phosphoryl azide in t-butanol gives not only the amide (8) and the product (11) arising from insertion into the O-H bond but also the product (12) formed by insertion of the nitrene (9) into the C-H bonds of the methyl groups.[29]



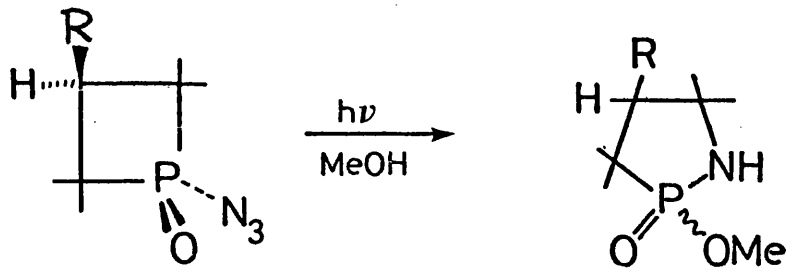
(11) (12)

The phosphorodiamidic azide (13) gives a low yield of the C-H insertion product (14) upon photolysis in cyclohexane, whereas in methanol rearrangement occurs by migration of a dimethylamino group onto nitrogen to yield (16), presumably via an intermediate metaphosphorimidate species (15). In the absence of trapping agents, such as methanol, high molecular weight polymers of (15) are obtained.[29]



The first reported photochemical decomposition of a phosphinic azide was by Harger,[12] who studied the rearrangement of the methyl substituted azido phosphetan-1-oxide system (6) in methanol.

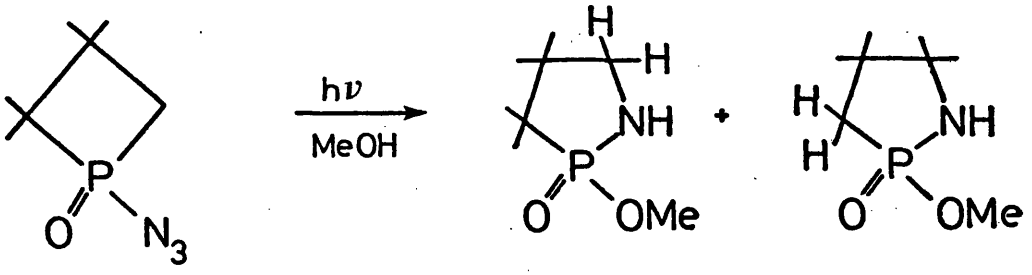
The symmetrically substituted azides (17, R = H or Me) ring expand by migration of a C-P ring bond onto the exocyclic nitrogen to yield the 1,2-azaphospholidines (18), whereas the unsymmetrical azide (19)



(17) (18)

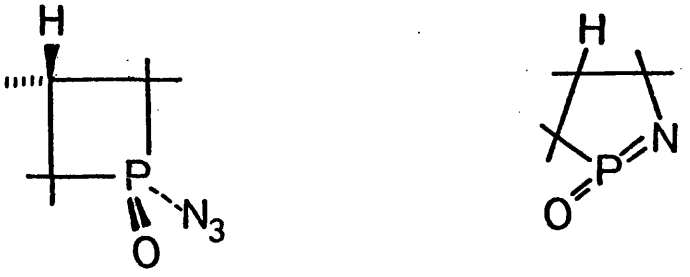
ring expands by migration of either of the C-P ring bonds to yield the isomeric products (20) and (21). In all three cases (17, R = H or Me) and (19) products resulting from rupture of the phosphorus-tertiary carbon bond are also formed (see p. 20).

A more detailed study of the photolysis of the trans-pentamethyl-



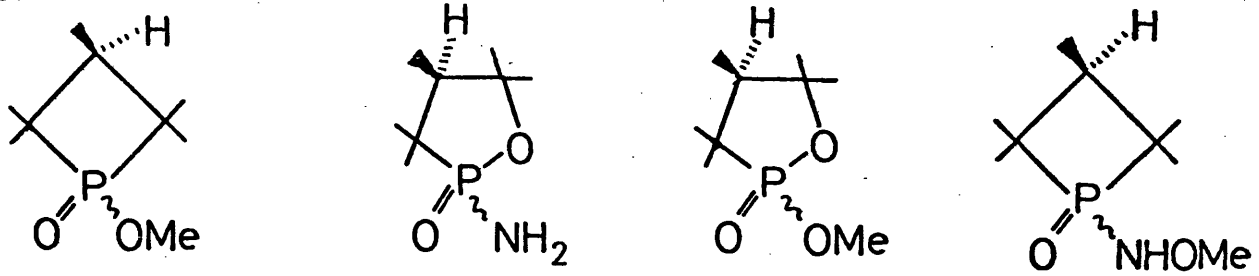
(19) (20) (21)

phosphetan-1-oxide (17, R= Me) and its cis isomer (22) by Wiseman and Westheimer[11] made use of high pressure liquid chromatography (HPLC). They found that the ratio of the cis and trans isomers of 2-methoxy-1,2-azaphospholidine-2-oxide (18, R= Me) produced was independent of the stereochemistry of the starting azide, indicating a common intermediate (23) in the two reactions.



(22) (23)

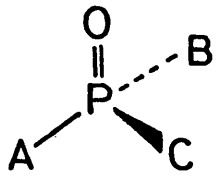
Along with the products isolated by Harger they also detected the cis and trans esters (24), formed by nucleophilic attack by methanol on the corresponding azide, the cis and trans phostonate amides (25), the cis and trans methyl phostonates (26) and one isomer of the product (27) formed by insertion of a formal nitrene into the O-H bond of the solvent.



(24) (25) (26) (27)

1.2 Structure of the Azide Group

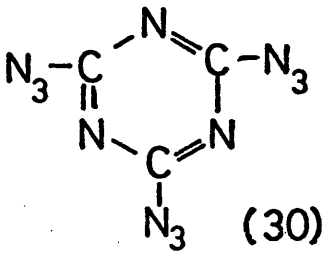
Throughout the following work four-coordinate phosphorus compounds containing the phosphoryl moiety will be considered. The geometry around the phosphorus atom is known to be tetrahedral[17] (28).



(28)

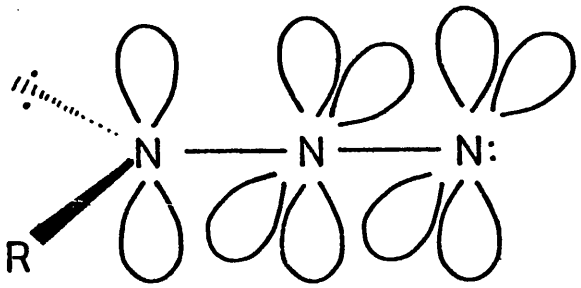
CH_3N_3

(29)



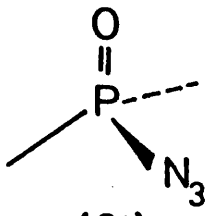
(30)

The structure of the azide group has been shown to be linear[18] by electron diffraction studies on methyl azide[19] (29) and X-ray analysis on cyanuryl azide[20] (30). The α-nitrogen can be considered to be sp^2 hybridised whereas the other two are sp hybridised. Overlap of the hybrid orbitals gives rise to the σ bonding, with π bonding arising from overlap of the 2p orbitals on the nitrogen atoms.



Cyclic as well as acyclic structures can be formulated when the azide moiety is bonded directly to a phosphoryl (31 and 32) sulphonyl (33 and 34) or carbonyl group (35 and 36). However, it is only for the thio analogues of (35) that the equilibrium favours the cyclic structure;[21] no infrared stretching vibrations are seen in the region 2140-

2160 cm^{-1}, considered diagnostic of the azide group.



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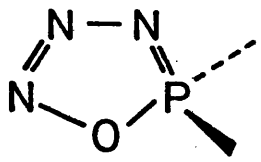

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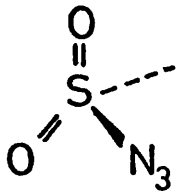

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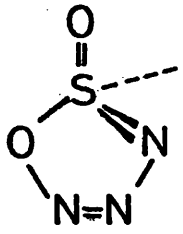

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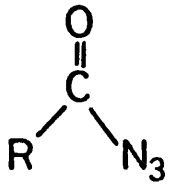

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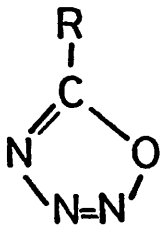


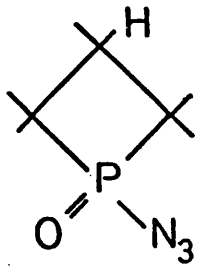
(36)

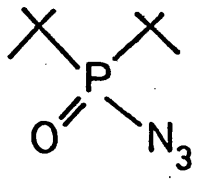
The dialkylphosphinic azides prepared in the present work all exhibited strong absorptions in the region 2140-2160 cm^{-1} and are believed to be predominantly acyclic.

1.3 Synthesis of Phosphinic Azides

Prior to this work only two simple dialkylphosphinic azides had been reported, namely diethylphosphinic azide (2, R = Et)[2] and di-n-butylphosphinic azide (2, R = Bu^n)[3], but their photochemical decomposition reactions had not been investigated.

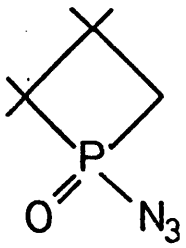
In an extension of the photochemical studies by Harger[12] and Westheimer,[11] di-t-butylphosphinic azide (37), the acyclic analogue of 1-azido-2,2,3,4,4-pentamethylphosphetan-1-oxide, was synthesised.





(37)

The symmetrical acyclic analogue of 1-azido-2,2,3,3-tetramethylphosphetan-1-oxide (19), diethylphosphinic azide (38), was also prepared, together with diisopropylphosphinic azide (39) as the intermediate stage between the di-t-butyl and diethyl compounds.



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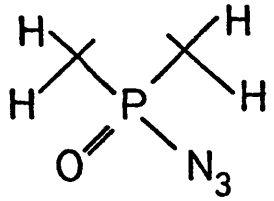

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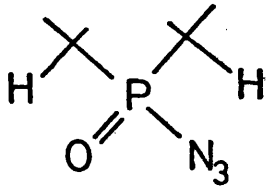


(39)

The acid chloride (41), prepared from the chlorophosphine (40) by oxidation, with either molecular oxygen[4] at 100° or 30% hydrogen

peroxide, was converted into di-t-butylphosphinic azide (37) by reaction with sodium azide and pyridine in dimethylformamide at 80°.

$$Bu^t_2PCl \xrightarrow[\text{or } H_2O_2(aq)]{O_2/100^\circ} Bu^t_2P(O)Cl \xrightarrow[DMF]{NaN_3 \text{ pyridine}} Bu^t_2P(O)N_3$$

(40) (41) (37)

Diisopropyl and diethylphosphinic azides were prepared according to Scheme 1. The phosphinic acids (43),[22] prepared via the bis phosphine bisulphides (42), were converted into the phosphinic chlorides (44) with thionyl chloride. Diisopropylphosphinic azide (39) was obtained by reacting (44, R = Pr) with sodium azide and pyridine in dimethylformamide, whereas the more volatile and sterically less hindered azide (38) was prepared in the lower boiling solvent acetonitrile.

$$6RMgBr + 2PSCl_3 \longrightarrow R_2\overset{S}{\overset{\|}{P}}-\overset{S}{\overset{\|}{P}}R_2 + 6MgBrCl$$

(42)

$$R_2\overset{S}{\overset{\|}{P}}-\overset{S}{\overset{\|}{P}}R_2 \xrightarrow{(O)} R_2P(O)OH \xrightarrow{SOCl_2} R_2P(O)Cl$$

(42) (43) (44)

$$R_2P(O)Cl \xrightarrow[NaN_3 \text{ pyridine}]{} R_2P(O)N_3$$

SCHEME 1

1.4 Photolysis of Phosphinic Azides in Protic Solvents

The photochemical decomposition reactions of the azides (37)-(39) in protic solvents were conducted with a 125W medium pressure mercury lamp in a water-cooled quartz envelope, surrounded by the stirred reaction mixture. Control experiments, in the absence of light, showed that only for diethylphosphinic azide in methanol was there extensive nucleophilic displacement of azide ion by the solvent, with formation of the methyl ester (45).

$$\underset{(38)}{Et_2P(O)N_3} + MeOH \xrightarrow{-HN_3} \underset{(45)}{Et_2P(O)OMe}$$

Steric hinderance to the incoming nucleophile by the t-butyl and isopropyl groups doubtless prevented displacement of the azide ion from the other substrates.

The mode of the photochemical decomposition of the phosphinic azides (37)-(39) in protic solvents is summarised in Scheme 2, and Table I shows the yields of the products.

$$R_2P(O)N_3 \xrightarrow[-N_2]{h\nu} \underset{(46)}{R_2P(O)NH_2} + \underset{(47)}{R_2P(O)NHS} + \underset{(48)}{R-\overset{\overset{O}{\|}}{\underset{\underset{S}{|}}{P}}-NHR}$$

SCHEME 2

In all cases except the decomposition of diisopropylphosphinic azide (39) in dry, peroxide-free, isopropanol, a product was isolated resulting from loss of nitrogen and migration of an alkyl group from

TABLE 1

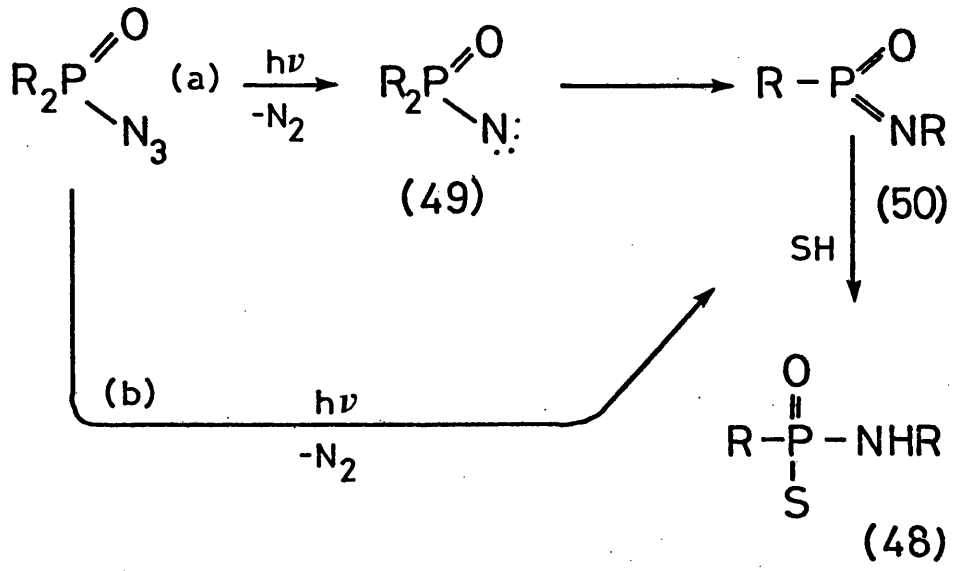
R	SH	Yield of Products % (46)	(47)	(48)
Bu^t	MeOH	[b]	8.1	57
Bu^t	EtOH	23.8		62.3
Bu^t	Pr^iOH	64		27
Bu^t	Bu^tOH	6	[a]	64
Bu^t	Bu^tNH_2			74
Pr^i	MeOH	4.9	36[c]	71
Pr^i	EtOH	46		38
Pr^i	Pr^iOH	86		[b]
Et	MeOH			17

[a] Nmr implied the formation of some (47)

[b] none isolated

[c] crude yield from separate experiment

phosphorus to nitrogen with incorporation of a molecule of solvent.

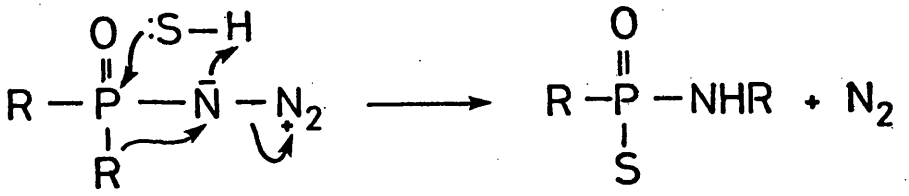


SCHEME 3

These products (48) of rearrangement correspond to the ring-expanded products formed by the azido phosphetan-1-oxides,[11,12] and are probably produced by similar mechanisms, as shown in Scheme 3. Thus, loss of nitrogen from the excited azide may lead to a singlet nitrene (49) (path a) that rearranges to the metaphosphonimidate (50) by alkyl migration from phosphorus onto the electron-deficient nitrogen atom, followed by reaction of (50) with a solvent molecule. Alternatively (path b), alkyl migration may be synchronous with nitrogen loss and result directly in the formation of the intermediate (50).

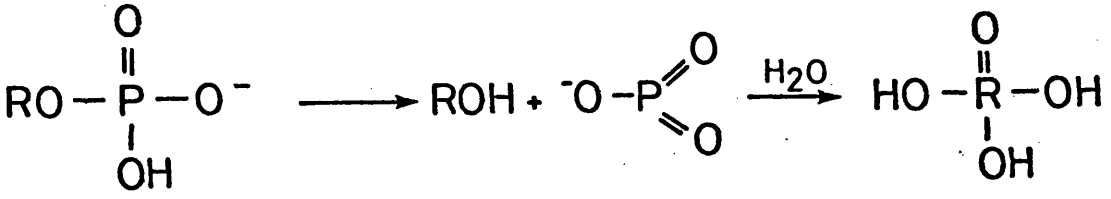
The formation of (48) however need not necessitate the intermediacy of the metaphosphonimidate (50) as it could arise directly from the decomposition of a solvated azide species (51).

Monomeric metaphosphate (52), an oxy analogue of (50), has been postulated as an intermediate in the base-catalysed hydrolyses of the



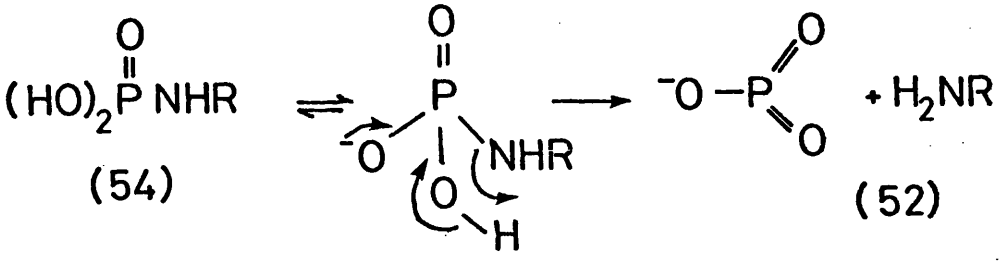
(51) (48)

monoesters (53) of phosphoric acid,[23]



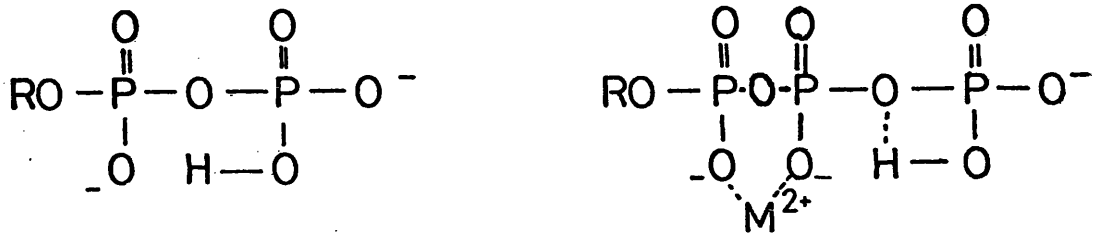
(53) (52)

the N-substituted phosphoramidates[23] (54),



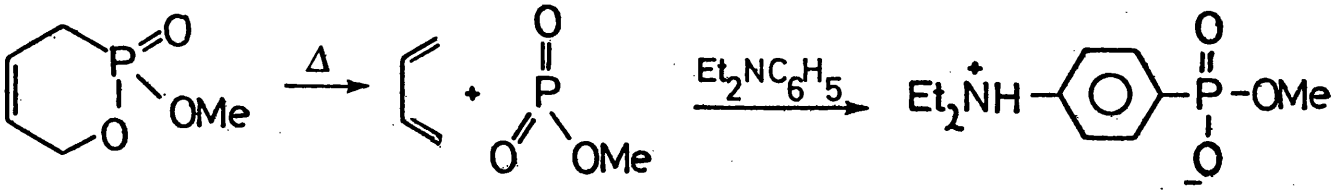
(54) (52)

and the di and triphosphate monoesters (55)[24] and (56)[23].



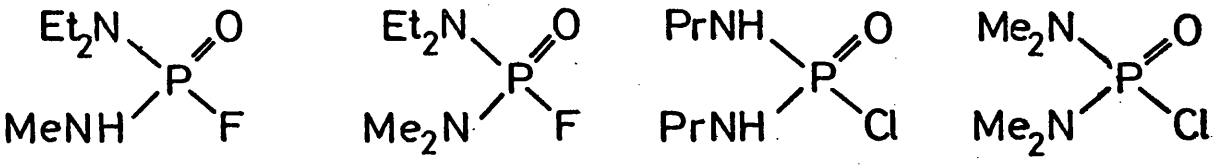
(55) (56)

A convincing demonstration that metaphosphates can be generated comes from a recent report by Westheimer et al.[25] They trapped methyl metaphosphate (58), formed in the thermolytic decomposition of methyl-2-butenylphostonate (57), as (59) by use of N,N-diethylaniline.

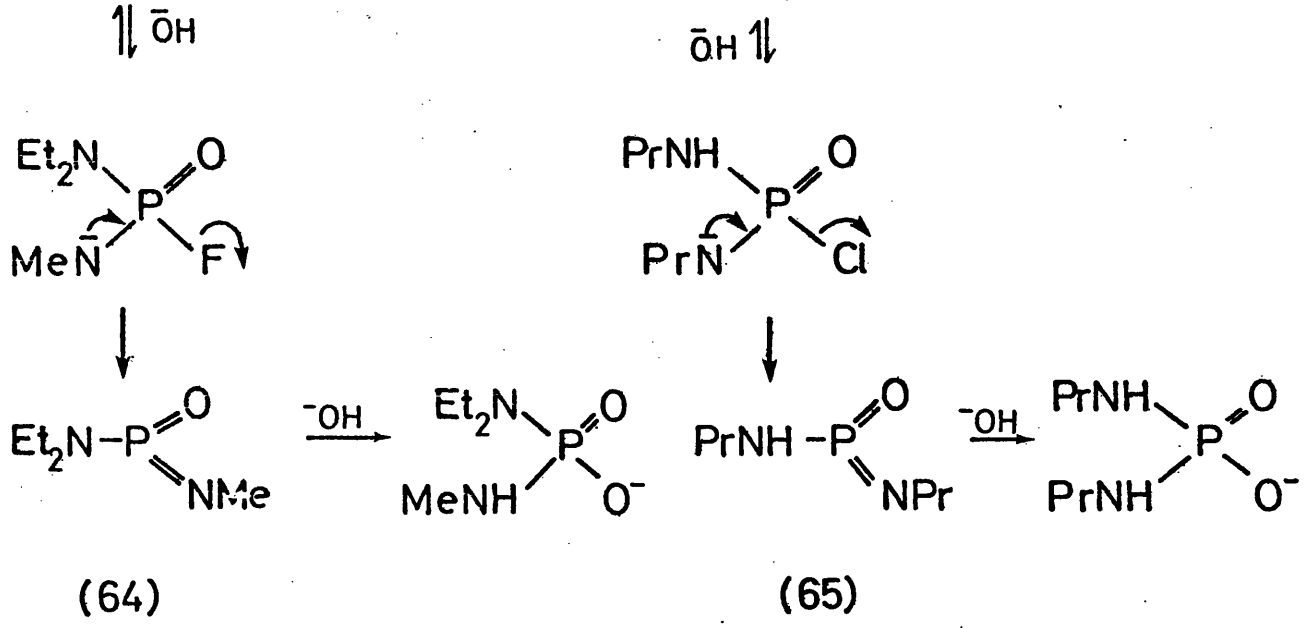


(57) (58) (59)

Metaphosphorimidates have also been postulated as intermediates to account for the fact that (60)[26] and (62)[27,28] are hydrolysed 10^4 and 4×10^6 times faster respectively than their fully alkylated analogues (61) and (63). The mechanism involves removal of a proton



(60) (61) (62) (63)



(64) (65)

from nitrogen followed by rate-determining elimination of the leaving group to yield the metaphosphorimidates (64) and (65) which react with hydroxide ion to give the products.

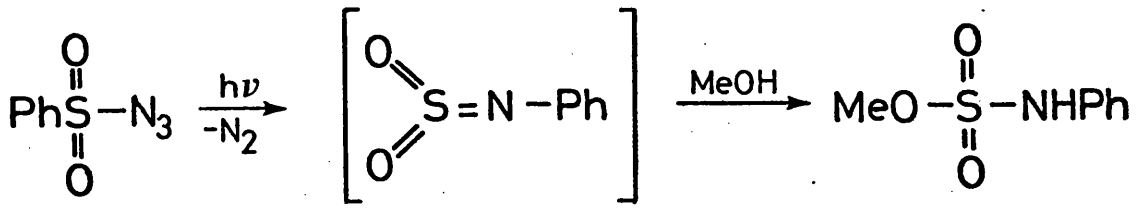
Breslow[29] has shown that migration of a dimethylamino group from phosphorus to nitrogen occurs upon photolysis of the azide $(Me_2N)_2P(O)N_3$ (13) in methanol, whereas photolysis of diethylphosphoryl azide $(EtO)_2P(O)N_3$ in t-butanol leads only to nitrene insertion products and no products arising from the migration of an ethoxyl group. This may result from the enhanced stability of the phosphorus-oxygen bond compared with the phosphorus-nitrogen and phosphorus-carbon bonds.

The rearrangement of phosphinic azides can be compared with the Curtius rearrangement of acyl azides,[30] for which there is strong evidence that discrete nitrenes are not involved.

$$RCON_3 \longrightarrow R-N=C=O + N_2$$

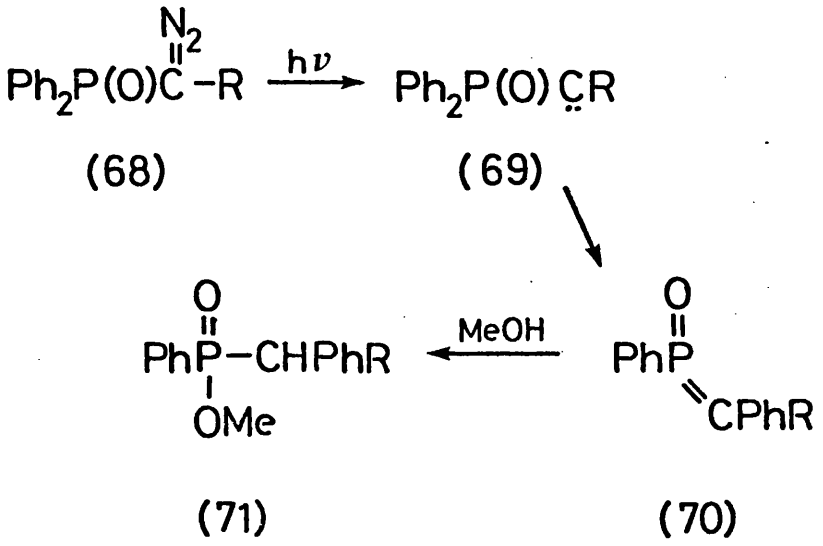
In an acyl azide however the carbonyl carbon atom is trigonal, whereas in the phosphinic azides the phosphorus atom is tetrahedral; the latter would therefore be better compared with the sulphonyl azides (RSO_2N_3) in which the sulphur atom is also tetrahedrally co-ordinated. Indeed Lwowski and co-workers[31,32] found methyl N-phenyl-sulphamate (67) amongst the products of the photochemical decomposition of benzenesulphonyl azide (66) in methanol. Lacking evidence one way or the other, the authors favoured a non-nitrene pathway.

More recently the diazo compounds (68) have been shown to decompose in methanol[33] in a manner similar to the phosphinic azides. The intermediate carbene (69) rearranges by phenyl migration from phosphorus to the electron deficient carbon atom to produce the intermediate (70)



(66) (67)

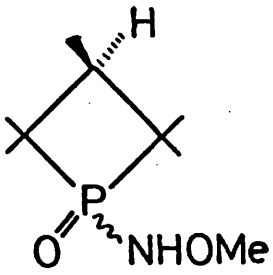
that reacts with methanol to yield the product (71).



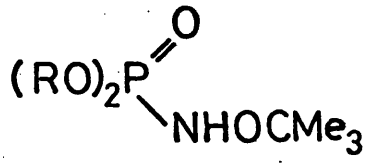
(68) (69) (71) (70)

The reactions of both (37) and (39) with methanol and (37) with t-butanol gave products (47) derived from insertion of a nitrene into the O-H bond of the alcohol. These products are presumably formed from the singlet nitrene. In the photochemical decomposition reactions of the azidophosphetan systems studied by Harger products of this nature were not isolated, although Westheimer, using HPLC, isolated one isomer of (27) in 1% yield from the photolysis of the pentamethyl-azidophosphetan-1-oxides (17, R = Me) and (22) in methanol. The phosphoryl nitrene[29] (9) has also been found to insert into the O-H

bond of t-butanol to yield (11).



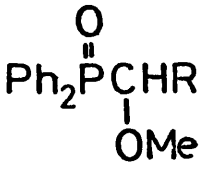
(27)



(11)

In addition Lwowski[32] and Horner[34] have shown that benzenesulphonyl azide and p-toluenesulphonyl azide upon irradiation in methanol give the products (72) derived from insertion of a sulphonyl nitrene into the hydroxyl group of methanol, and analogous products (73) have been obtained by Regitz[33] in the photochemical reactions of phosphoryl carbenes in methanol.

(72)



(73)

R=COPh, H or CO_2Et

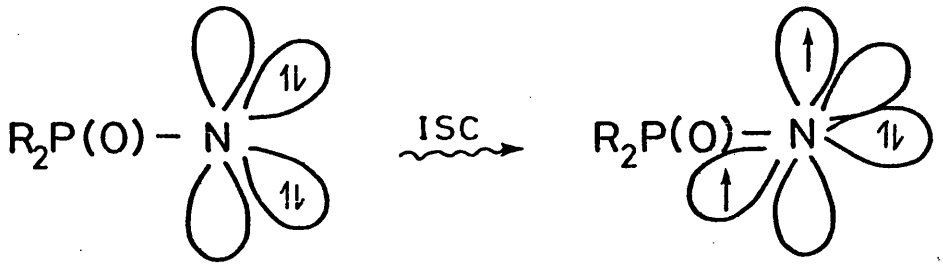
In the majority of the reactions now studied, along with the rearrangement products (48), were obtained the amides (46). The results in Table I show that changing the solvent from methanol to ethanol to isopropanol causes an increase in the amount of phosphinic amide formed in the decomposition reactions of the phosphinic azides. Changing the solvent again from isopropanol to t-butanol results in a dramatic decrease in the yield of the amide, while with t-butylamine as solvent no amides were isolated. The yields of the amides follow

the order of the ease of abstraction of the α-hydrogens to form radicals:

$$(CH_3)_2\,\dot{C}OH > CH_3\dot{C}HOH > \dot{C}H_2OH$$

The amide products can be considered to be formed from a nitrene. The initial reaction possibly involves the decomposition of an excited azide molecule to a triplet nitrene or formation of a singlet nitrene that decays by inter-system crossing (ISC) to the triplet nitrene.

In the singlet nitrene the nitrogen can be thought of as sp^2 hybridised with a vacant p orbital on the nitrogen, the four electrons being spin paired and occupying the two available sp^2 hybrid orbitals.



Singlet Nitrene Triplet Nitrene

In the triplet nitrene the nitrogen is considered to be sp hybridised with two electrons, spin-paired, occupying the available hybrid orbital. The remaining two electrons are accommodated in the two p orbitals with their spins parallel. The triplet nitrene is thus a diradical species and undergoes two successive hydrogen abstractions from the solvent to yield the amide products.

It is interesting to note (Table I) that very high yields of amide products were isolated in the reactions of di-t-butyl and diisopropyl-phosphinic azides with isopropanol and in the latter case it was the

only product isolated; also that the reaction times using isopropanol as solvent were short ($\leq$ 5h) compared with 17-20.5h for the photolyses in other alcohol solvents. These two points suggest that the reactions in isopropanol may proceed by a different mechanism.

Reagan and Nickon[35] have shown that the decomposition of sulphonyl azides in isopropanol gives rise to almost quantitative yields of amide products in the absence of oxygen and that the reaction (Scheme 4) occurs on direct irradiation or selective irradiation of benzophenone added as sensitizer. They concluded from the high quantum yields in

$$RSO_2N_3 + CH_3\overset{\overset{OH}{|}}{\underset{\underset{H}{|}}{C}}CH_3 \rightarrow RSO_2NH_2 + (CH_3)_2CO + N_2$$

SCHEME 4

the reaction of methanesulphonyl azide with isopropanol both in the direct photolysis and in the benzophenone-sensitized process that a radical chain mechanism was operating.

It seems reasonable to suppose that (37) and (39) can decompose in isopropanol solvent by a similar mechanism (equations 1-4).

$$R_2P(O)N_3 \xrightarrow{h\nu} R\,P(O)\dot{\underset{\cdot\cdot}{N}}\cdot + N_2 \qquad \text{eq(1)}$$

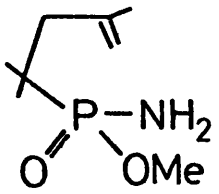
$$R_2P(O)\dot{\underset{\cdot\cdot}{N}}\cdot + Me_2CHOH \longrightarrow R_2P(O)\underset{\cdot\cdot}{\dot{N}}H + Me_2\dot{C}OH \qquad \text{eq(2)}$$

$$R_2P(O)\dot{\underset{\cdot\cdot}{N}}H + Me_2CHOH \longrightarrow R_2P(O)NH_2 + Me_2\dot{C}OH \qquad \text{eq(3)}$$

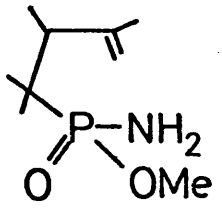
$$R_2P(O)N_3 + Me_2\dot{C}OH \longrightarrow R_2P(O)\ddot{\underset{\cdot}{N}}H + Me_2CO + N_2 \qquad \text{eq(4)}$$

Solvent studies by Nickon et al.[35] have shown that, like the phosphinic azides (37) and (39), methanesulphonyl azide decomposes faster in isopropanol than in methanol and that increasingly complex mixtures are observed on changing the solvent from isopropanol to ethanol to methanol.

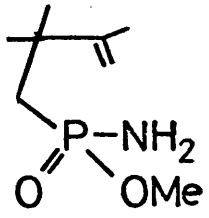
Accompanying ring expanded products, Harger[12] also isolated products (74)-(76) arising from cleavage of the phosphorus-tertiary carbon ring bond.



(74)

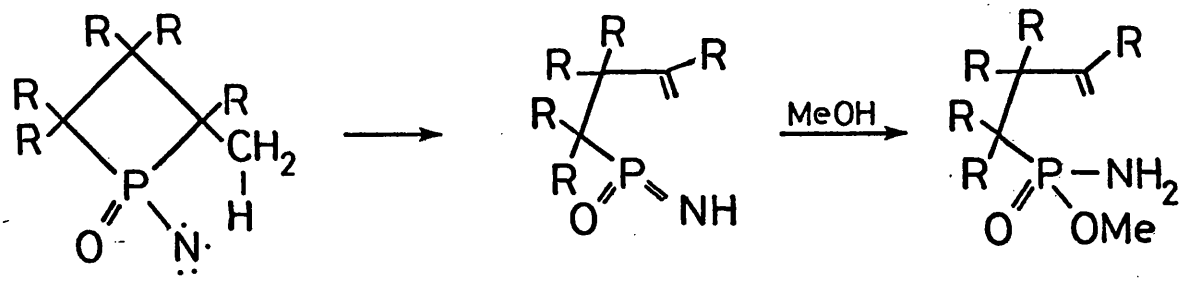


(75)



(76)

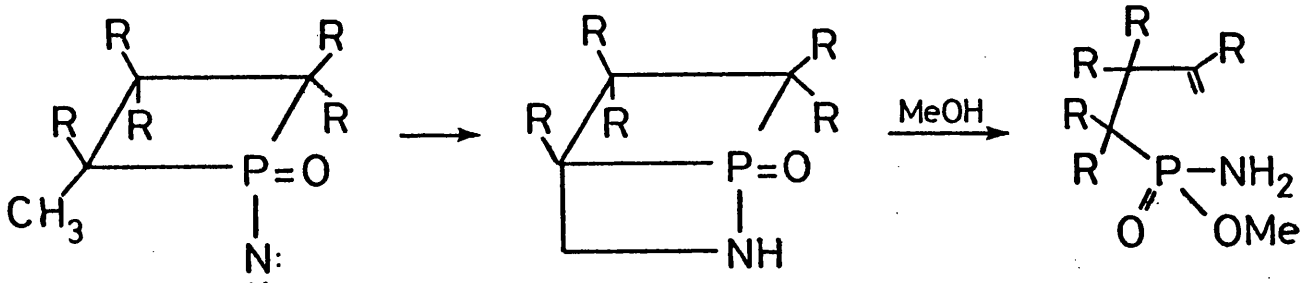
These products may be derived from a triplet nitrene by intramolecular hydrogen abstraction from the 2-methyl group leading to the acyclic metaphosphonimidate (77) which then reacts with the methanol solvent (Scheme 5). A less likely alternative mechanism[11] involves the



(77)

SCHEME 5

insertion of a singlet nitrene into the C-H bond of the 2-methyl group followed by ring cleavage of the bicyclic system (78) by methanol (Scheme 6).

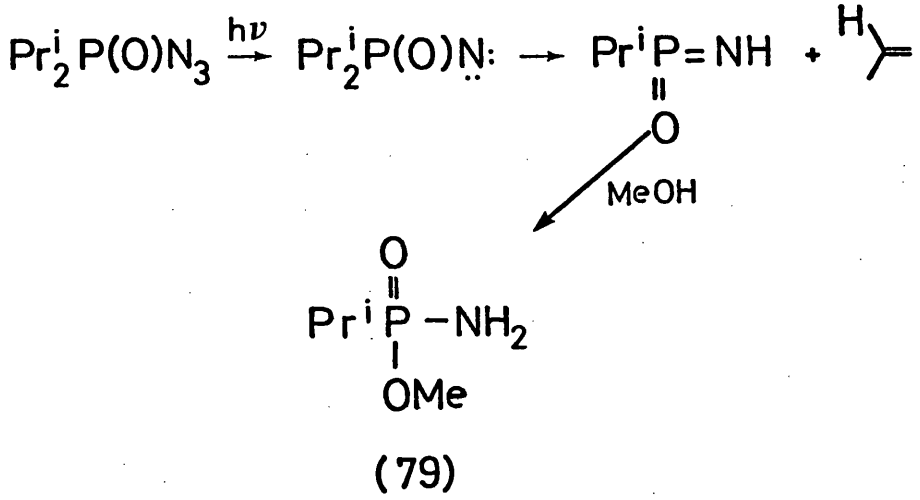


(78)

SCHEME 6

An acyclic phosphinic azide can in principle undergo an analogous reaction, although now fragmentation rather than ring opening will result. For example diisopropylphosphinic azide (39) in methanol would form propene and the phosphonimidate (79) (Scheme 7).

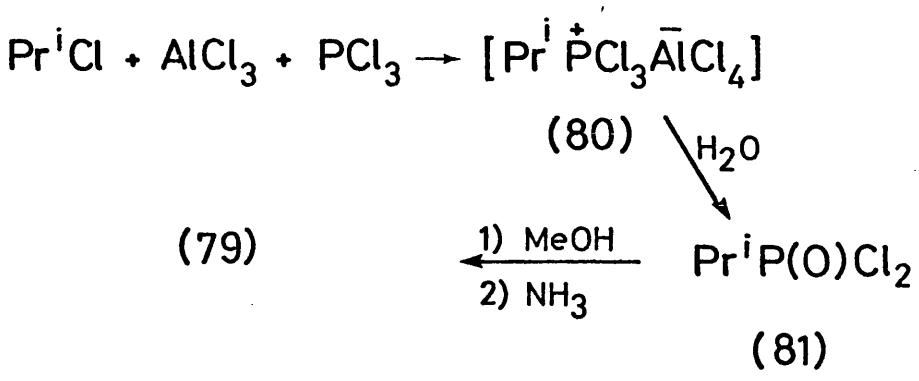
To assist the search for evidence of such fragmentation, an authentic specimen of (79) was synthesised in 48% yield from the phosphonyl chloride (81), obtained from hydrolysis of the aluminium chloride adduct (80), by reaction with one molar equivalent each of methanol and



(79)

SCHEME 7

ammonia. The crude reaction mixture from the photolysis of diisopropylphosphinic azide in methanol was examined by glc. Unfortunately it was found that both diisopropylphosphinic amide (46, R= Pr^i) and the methanol insertion product (47, R= Pr^i) had the same retention time as the authentic product (79) on both of the available glc columns. The presence or absence of the product (79) could not therefore be established.



1.5 Photolysis of Phosphinic Azides in Benzene and Cyclohexane

Investigation of the photolytic decomposition of dialkylphosphinic azides in aprotic solvent was limited to di-t-butylphosphinic azide (37) in benzene and cyclohexane. The photolyses were carried out in a Rayonette reactor using light of wavelength 254 nm, nitrogen was bubbled through the reaction mixtures, and the reactions were monitored by glc by following the disappearance of the azide peak.

Glc analysis of the crude reaction mixture from the photolysis of di-t-butylphosphinic azide in benzene showed biphenyl and di-t-butylphosphinic amide (46, R = Bu^t) to be formed in <1% and ca. 5% yield respectively although neither of these products were isolated. However, chromatography of the crude reaction mixture yielded two isomeric products analysing for $C_{16}H_{38}P_2N_2O_3$.

The 100 MHz proton n.m.r. spectrum (Figure 1) of each isomer consisted of a doublet at δ1.20 (J_{PH} 17 Hz) with the lines separated by a 'hump', and a singlet, at δ1.37 in one case and δ1.34 in the other. The integral ratio of the singlet to doublet was 1:1. The singlet resonances were assigned to the methyl protons of two $PNHBu^t$ groups. No aromatic protons were present.

In the infrared spectrum one isomer (Figure 2) showed a single absorption at 3230 cm^{-1}, assigned to N-H stretching, whereas the other showed several bands in the region 3410-3200 cm^{-1} (Figure 3).

The mass spectra of both of the isomers showed the same ions but in different ratios. No molecular ion corresponding to $C_{16}H_{38}P_2N_2O_3$ (m/e 368) was apparent, but an ion m/e 353 was clearly visible, presumably arising by loss of a methyl group. From this data the anhydride structures (82) and (83) were assigned to the two isomers.

FIGURE 1

N.M.R. Spectra of the Isomeric N, P- di -t- butyl phosphonamidic acid anhydrides.

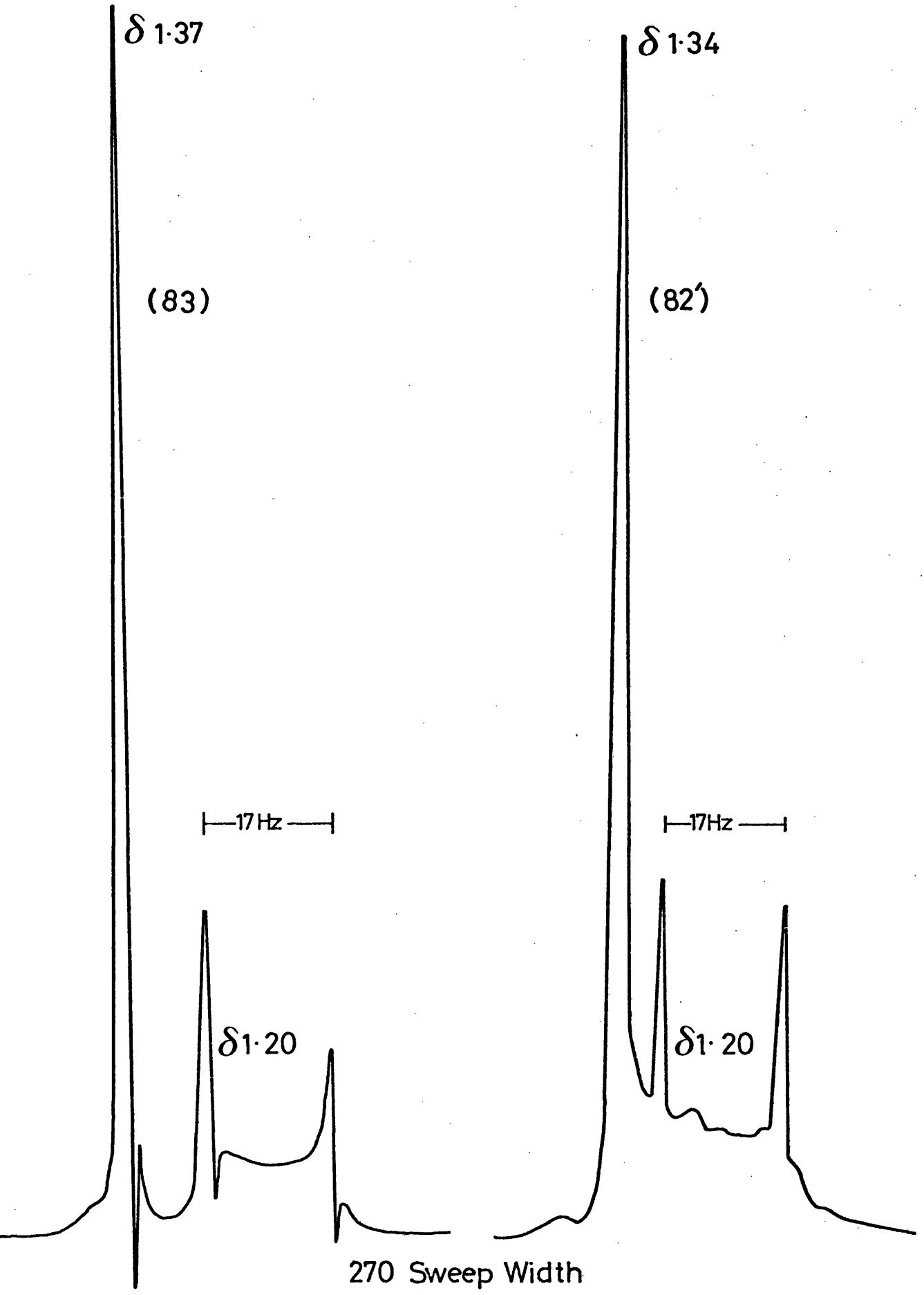
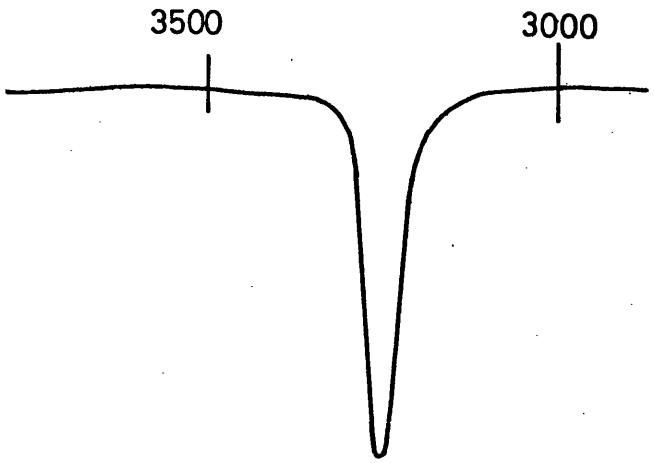
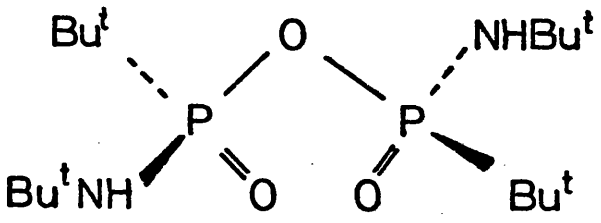


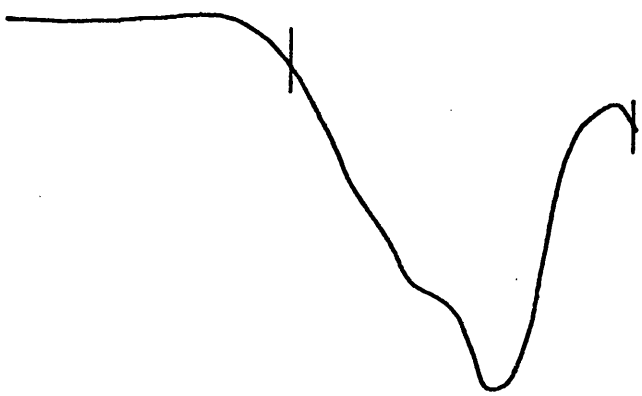
FIGURE 2

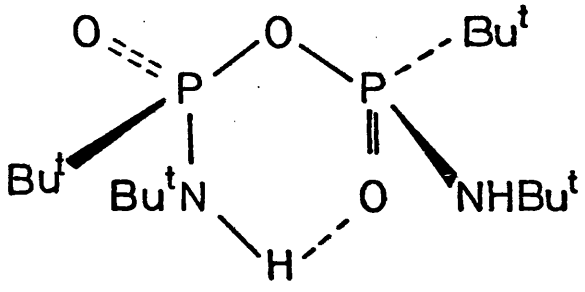




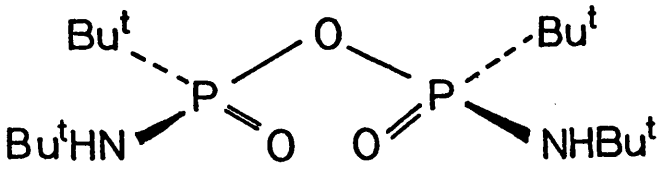
(83)

FIGURE 3

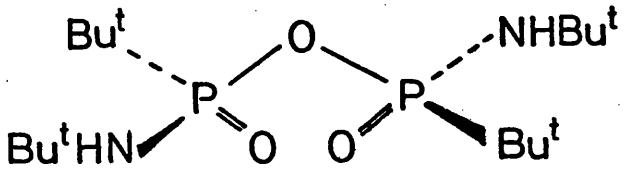




(82')

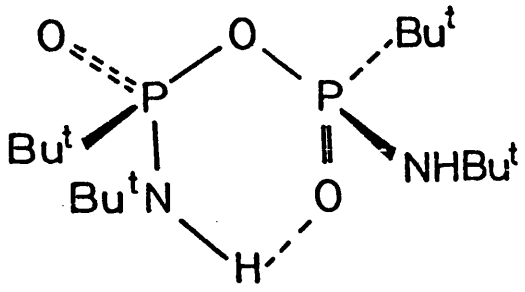


(82)

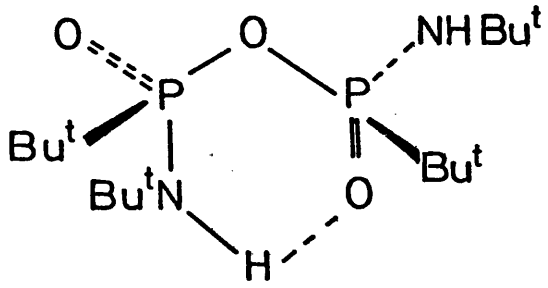


(83)

The existence of more than one band in the infrared spectrum of one of the isomers in the region 3500-3000 cm^{-1} can be attributed to hydrogen bonding within the molecule. Rewriting (82) and (83) gives the conformations (82′) and (83′) respectively in which hydrogen bonding is possible. However steric interactions between the P-t-butyl



(82′)



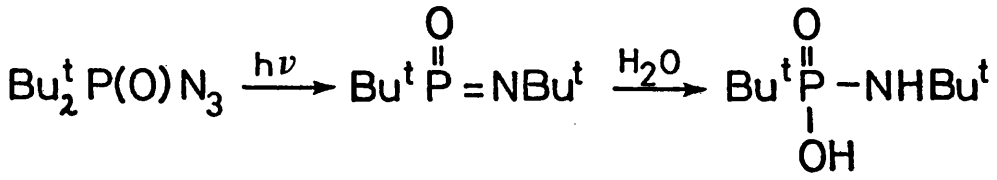
(83′)

groups in (83′) make this an unfavourable conformation for (83) and so precludes intramolecular hydrogen bonding.

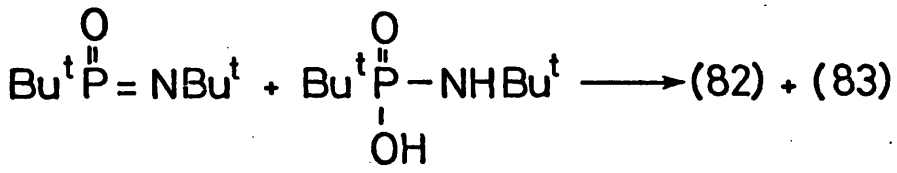
The anhydrides (82) and (83) are derived from two molecules of the azide, with loss of nitrogen, and one molecule of water. The presence of a trace of water in the reaction mixture is not difficult to conceive bearing in mind that elemental analysis of the azide indicated the

presence of water within the molecule [$Bu_2^tP(O)N_3$. 0.37 H_2O].

These anhydrides can be formed in a manner similar to the rearrangement products (48) obtained in the reactions of the dialkylphosphinic azides in protic solvents. The azide (37) can decompose by loss of

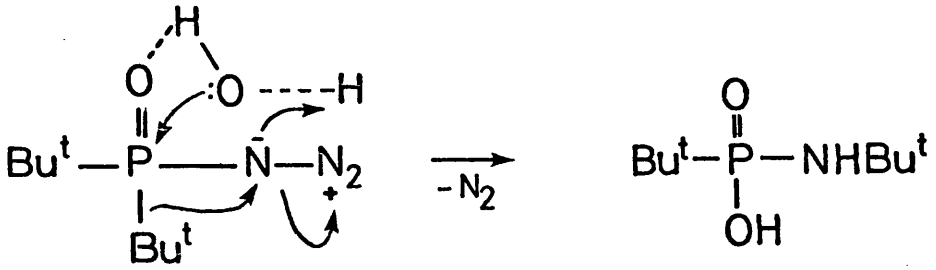


(37) (84) (85)



(84) (85)

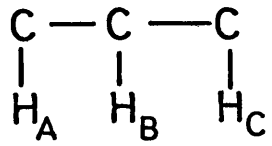
nitrogen and alkyl migration to give the metaphosphonimidate (84) which adds water to give the acid (85). This then reacts with a further molecule of (84) to yield the anhydrides (82) and (83). Alternatively the hydrogen-bonded azide-water species rearranges with synchronous loss of nitrogen to produce the acid (85) directly.



(85)

The apparent complexity of the P-t-butyl resonances in the n.m.r. spectrum can be explained in terms of virtual coupling.[36] In a linear

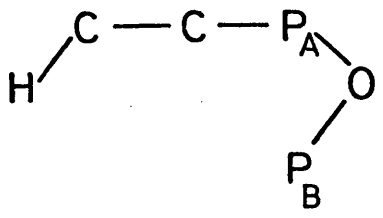
three-proton spin system (86) in which $|\nu_A-\nu_B| \gg J_{AB}$ and $J_{AC} = 0$, protons A and C each give rise to a doublet, and B a quartet ($J_{AB} \neq J_{BC}$) or a triplet ($J_{AB} = J_{BC}$). This situation arises since the nuclei do not interact, and the individual nuclei are characterised by the $\pm\frac{1}{2}$ quantum numbers of their spin states. A multiplicity of $2S + 1 = 2$, or a doublet, is thus predicted for each nucleus as described above.



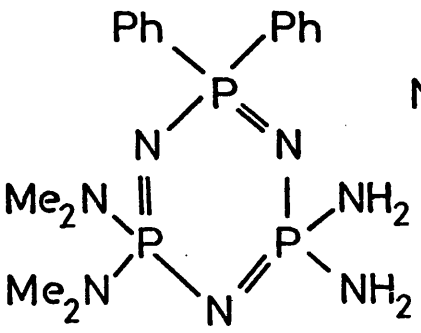
(86)

In a strongly coupled set of nuclei the spins cannot be defined by the quantum numbers $\pm\frac{1}{2}$. A system of N spin $\frac{1}{2}$ nuclei now gives rise to a multiplicity of $2(\frac{1}{2})(N + 1) = N + 1$ for a coupled proton outside the set, and instead of their being only two spin states there are now 2^N states. Another nucleus thus 'sees' all these states and is split into a multiplet containing 2^N peaks, giving rise to a more complex spectrum than predicted from a simple first-order treatment of the interacting nuclei.

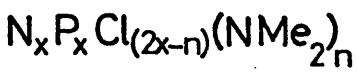
In the case of the anhydrides (82) and (83) the phosphorus atoms P_A and P_B of spin $\pm\frac{1}{2}$ must be strongly coupled and give rise to the complex methyl region of the ^1H n.m.r. spectrum due to virtual coupling.



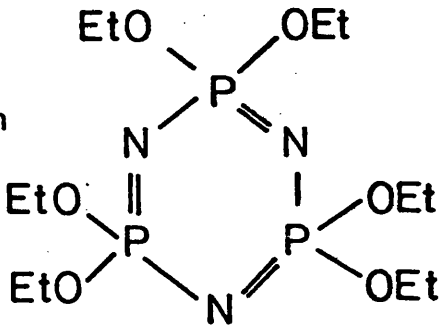
In phosphonitrilic compounds this phenomenon of virtual coupling has been observed for the methyl groups of (87)[37] and (88, x = 3),[38] the methylene protons of (89)[39] and the α-methylene protons of (90).[40] Bullen has made use of this effect in the structural determination of the cyclophosphazatetraenes (88, x = 4).[41] In these compounds the



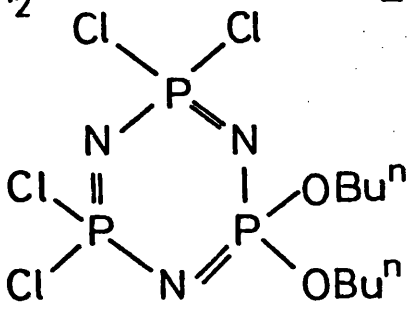
(87)



(88)



(89)



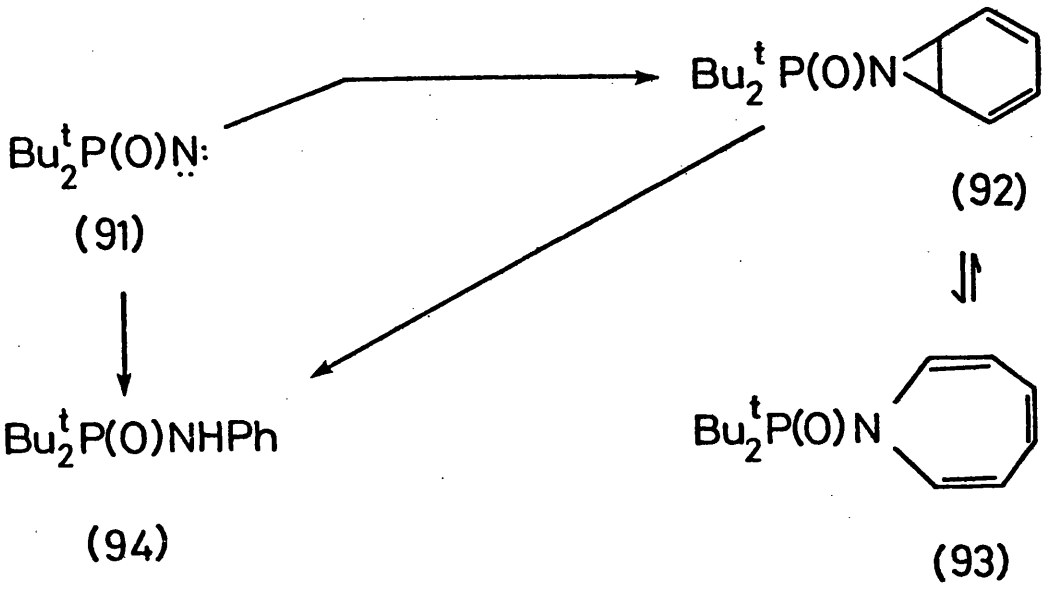
(90)

presence of more than one phosphorus atom in the molecule gives rise to the virtual coupling.

In the anhydrides (82) and (83) direct coupling of the second phosphorus atom P_B to the methyl groups does not occur but interaction of the P_B nucleus with the protons of these groups gives rise to the observed complication of the methyl resonance viz. a doublet with the lines separated by a hump.

Products derived from reaction of a nitrene intermediate with the benzene solvent were not isolated. Conceivably a nitrene, if formed in the singlet state (91) can add to the carbon-carbon bonds of benzene to

yield the azanorcaradiene (92) and this could ring open to the azepine (93) or the phosphinic amide (94). The amide (94) could alternatively be formed by direct insertion of the nitrene into the C-H bonds of benzene.



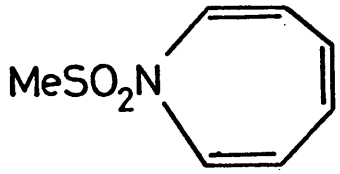
An authentic specimen of the C-H insertion product (94) was required so that using glc its presence or absence from the reaction product could be determined. The amide (94) was synthesised from di-t-butylchlorophosphine by reaction with the potassium salt of aniline followed by oxidation with 30% hydrogen peroxide.

$$PhNH_2 \xrightarrow[-H_2]{KH} Ph\bar{N}H\overset{+}{K} \xrightarrow{Bu^t_2PCl} Bu^t_2PNHPh \xrightarrow{H_2O_2} Bu^t_2P(O)NHPh \quad (94)$$

Using glc it was shown that (94) was formed in not greater than 0.3% yield. The free nitrene if it is formed is thus very unreactive towards insertion into the C-H bonds of benzene.

In the photolysis of methanesulphonyl azide[42] in benzene only a

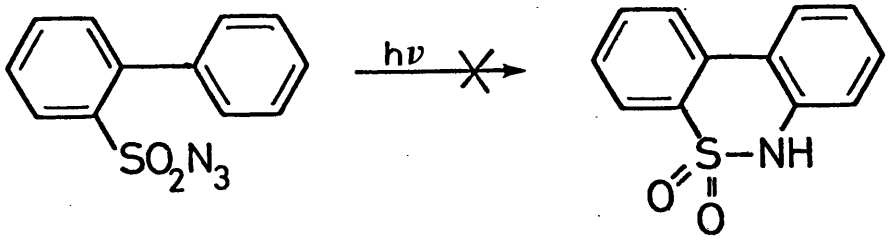
trace of the azepine (95) was obtained but none of the amide (96). Even with biphenyl-2-sulphonyl azide (97)[43] no intramolecular insertion product (98) was obtained upon photolysis in cyclohexane.



(95)

$MeSO_2NHPh$

(96)

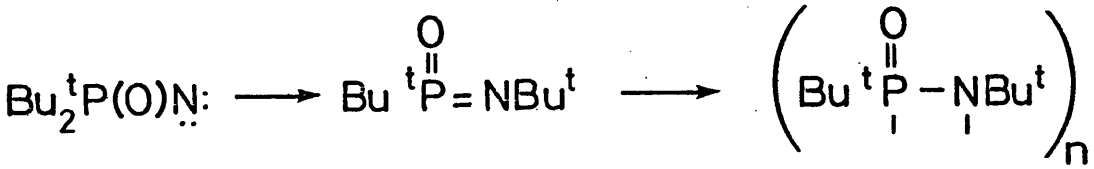


(97) (98)

Alternatively to the reaction with benzene, the nitrene (91) could dimerise to the imide (99) or rearrange by alkyl migration from phosphorus to nitrogen to yield the metaphosphonimidate (84) that would doubtless dimerise or polymerise to (100).

$Bu_2^tP(O)N=N(O)PBu_2^t$

(99)



(91) (84) (100)

The presence or absence of the compounds (92), (93), (99) and (100) in the photolysis of di-t-butylphosphinic azide (37) in benzene

could not be confirmed as authentic samples were not available.

The yield of biphenyl (<1%) formed in the reaction of benzene with di-t-butylphosphinic azide (37) is too small to account for all the amide (46, R = Bu^t) formed (5%). It seems reasonable to assume that at least some of the amide product arises directly by hydrogen abstraction from the benzene solvent by a nitrene, but the source of the remaining hydrogen atoms is unknown. This behaviour is also a puzzling feature of the thermolysis reactions of sulphonyl azides in aromatic solvents.[92]

Photolysis of (37) in cyclohexane gave the amide in 4.5% yield (not greater than 7.5% as determined by glc) and the C-H insertion product (101) in 18% yield together with the anhydride (83). The identity of the amide (101) was confirmed by comparison with an authentic specimen synthesised by reacting di-t-butylchlorophosphine with cyclohexylamine followed by oxidation with 30% hydrogen peroxide.

$$Bu^t_2PCl + 2C_6H_{11}NH_2 \longrightarrow Bu^t_2PNHC_6H_{11} + C_6H_{11}NH_2.HCl$$

$$\downarrow H_2O_2$$

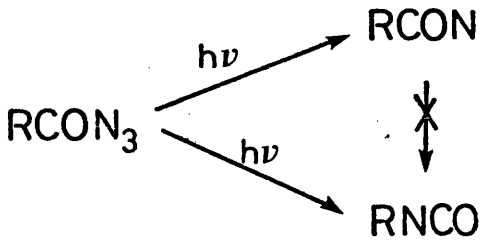
$$Bu^t_2P(O)NHC_6H_{11}$$

(101)

1.6 Comparison of the Photochemical Reactions of Phosphinic and Other Azides

In marked contrast to the photolysis of di-t-butylphosphinic azide (37) in protic solvents, in which the reactions were clean (no discolouration of the solutions and high yields of products), photolysis in aprotic solvents gave highly coloured solutions and relatively low isolated yields of identified products. In protic solvents nitrene and rearrangement products were isolated whereas in aprotic media only the adventitious presence of traces of moisture allowed rearrangement products to be isolated along with nitrene products.

Acyl azides ($RCON_3$) have been shown to decompose in a variety of aprotic solvents to give Curtius rearrangement products in constant yields,[44] although the yields of nitrene insertion products do vary with the nature of the solvent. The rearrangement products do not therefore seem to arise from nitrenes. Work by Eibler et al.[45] showed that benzoyl azide, which in aprotic solvents gave 46-57% yields of phenyl isocyanate, in methanol also gave 44% of isocyanate. Possibly here in protic solvents the benzoyl nitrene and rearrangement products are also produced by independent routes.

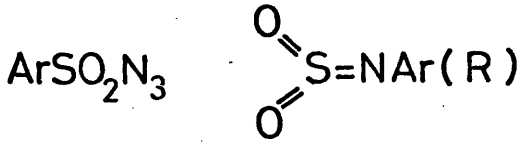


Alkoxycarbonyl azides ($ROCON_3$)[31,46,47,122] in aprotic solvents produce nitrene products with Curtius rearrangement accounting for only a minor part of the reaction. In protic solvents[31,47] both nitrene and

rearrangement products are formed but no evidence exists to suggest that the rearrangement occurs via a nitrene.

With diarylcarbamoyl azides (Ar_2NCON_3)[48] only nitrene products are observed in aprotic solvents whereas in protic solvents both rearrangement and nitrene products are obtained. Dialkylcarbamoyl azides (R_2NCON_3)[49] in all media give Curtius rearrangement products only. Again, there is no evidence to show that the rearrangement products arise from a nitrene.

Photolysis of aliphatic and aromatic (except ferrocenyl[50]) sulphonyl azides (102)[32,34,42,51] in non-protic non-polar solvents (benzene and cyclohexane) produces high-melting materials that have not been characterised. Abramovitch[42] has isolated a trace of the azepine (95) in the photolysis of methanesulphonyl azide in benzene. In protic solvents[31] sulphonyl azides yield both nitrene and rearrangement products. In aprotic solvents the rearrangement product (103), if formed, would probably polymerise. Polymers are indeed formed and, since abstraction and insertion products do not account for all the azide, it could well be that some rearrangement occurs either directly or <u>via</u> a nitrene intermediate.



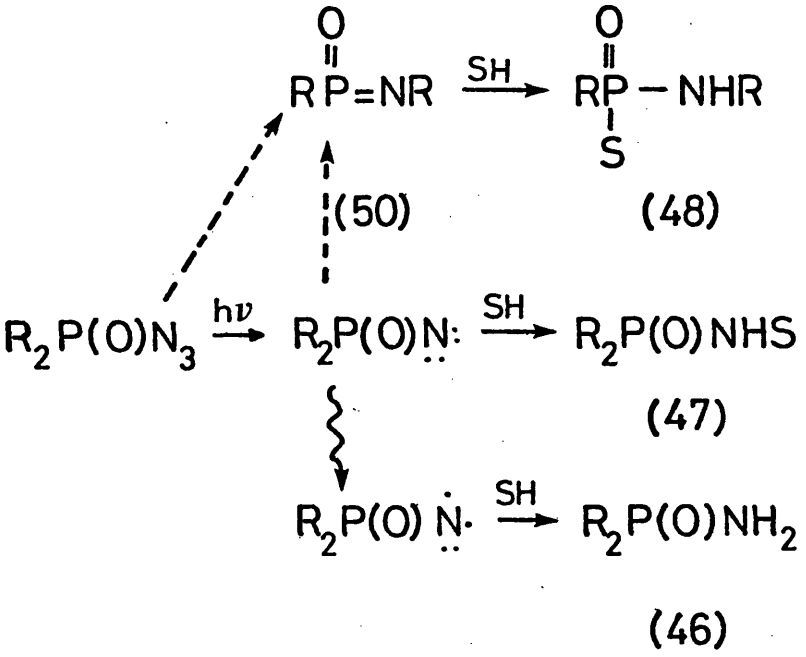
(102) (103)

Since 1914 azides had been classed as 'rigid' - those which do not rearrange upon decomposition - and 'non-rigid' - those which undergo rearrangement. Lwowski and de Mauriac[31] in 1964 took members of each of the three classes of typical rigid azides, namely arylsulphonyl

azides ($ArSO_2N_3$), alkoxycarbonyl azides ($ROCON_3$) and carbamoyl azides (R_2NCON_3), and photolysed them in hydrocarbon solvents and methanol. Each member of the three classes was found to give rearrangement products in methanol but not in the hydrocarbons. From this they concluded that the barrier to rearrangement for rigid azides exists only in non-hydroxylic solvents, and that in protic media it is a hydrogen-bonded azide[31,32] that rearranges. Anselme[48] found no carbazate ($Ph_2NNHCO_2CH_2Bu^t$) among the products of photolysis of diphenylcarbamoyl azide (Ph_2NCON_3) in t-amyl alcohol and attributed this to the bulk of the alcohol preventing it from hydrogen bonding.

Phosphoryl azides, $(RO)_2P(O)N_3$,[29] in both protic and aprotic solvents afford only nitrene products. On the other hand phosphorodiamidic azides, $(R_2N)_2P(O)N_3$,[9,10,29] give largely rearrangement products in protic solvents and polymers in aprotic media, little nitrene product being formed in either case.

In the present work with phosphinic azides there is no definite evidence to suggest that rearrangement products arise from nitrenes. Possibly, as with the acyl azides, phosphinic azides decompose in both protic and aprotic media to singlet nitrenes and metaphosphonimidate intermediates (50) by separate pathways. Only in protic solvents can the metaphosphonimidates be trapped; presumably polymerisation occurs in aprotic media. The singlet nitrenes either insert into the C-H bonds of cyclohexane and the O-H bonds of the alcohols, or cross to triplet nitrenes which abstract hydrogen to yield amide products.



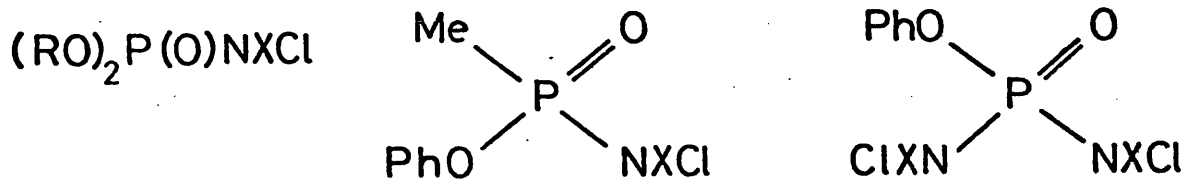
(50) (48) (47) (46)

2 DIALKYLPHOSPHINIC N,N-DICHLOROAMIDES

2.1 Synthesis and Reactions of Quinquevalent Phosphorus N-Chloroamides

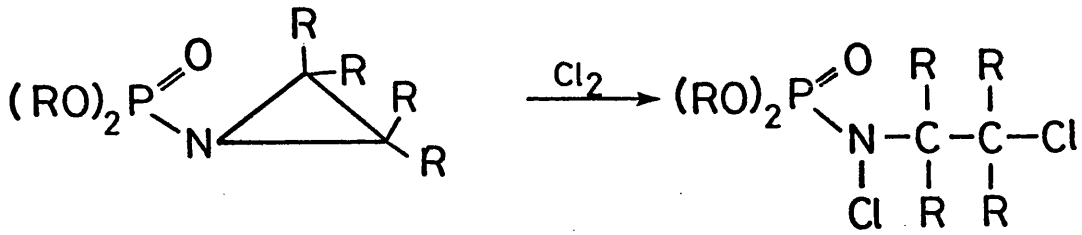
Amides of P(V) acids have been N-chlorinated by a method developed for carbamates.[52] Thus N-chlorophosphoramidates (104, X = Cl, alkyl or alkoxyl) have been prepared, from the parent amides, using chlorine in a sodium acetate-acetic acid buffer solution.[53-57]

Aqueous sodium hypochlorite has proved successful in the preparation of (104) (R = Et and Ph, X = Cl) and (105) and (106) (X = Me and Et).[57]



(104) (105) (106)

In addition Grechkin[58] and Hassner[59] have shown that the N-chlorophosphoramidates (108) are produced when the aziridines (107) undergo ring opening with chlorine.



(107) (108)

The chlorination of only one phosphinic amide, diphenylphosphinic amide, has been reported, (109, R = Ph)[54] being obtained by reaction of the parent amide with t-butyl hypochlorite in carbon tetrachloride.

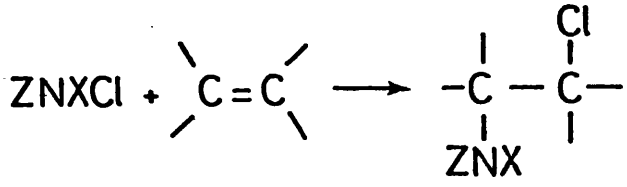
This method has also been found necessary for the synthesis of (104, R = Ph, X = Cl and R = X = Me).[54]

$$R_2P(O)NCl_2$$

(109)

(N,N-Dichloro)dialkylphosphinic amides (109) and monochloro derivatives of primary P(V) amides such as (104)-(106) (X = H or metal) have not hitherto been described.

Interest in the reactions of N-chloroamides with unsaturated compounds has been aroused because of their potential as methods of difunctionalising them. Under conditions known to promote the forma-

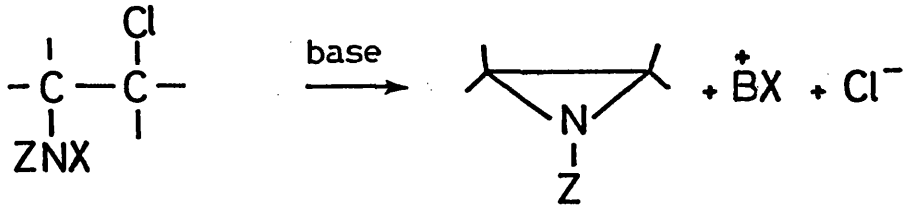


eq.5

(110)

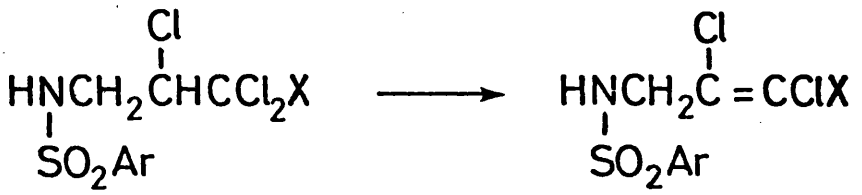
tion of radicals, for example, U.V. irradiation,[56,60] or heating in the presence of chromous chloride[61,62] or dicyclohexyl peroxydicarbonate[63,64] in a nitrogen atmosphere, the reaction shown in equation 5 takes place.

Isolation of the initial N-chloro adduct (110, X = Cl) in most reactions involving N,N-dichloroamides has not been achieved; instead it has been reduced to the NH compound (110, X = H) using aqueous sodium sulphite,[76] sodium metabisulphite[52,53,69,71] or potassium iodide followed by sodium thiosulphate.[60a,b] Treatment of these reduced adducts with base provides a valuable route to N-substituted aziridines (111).[65-68]



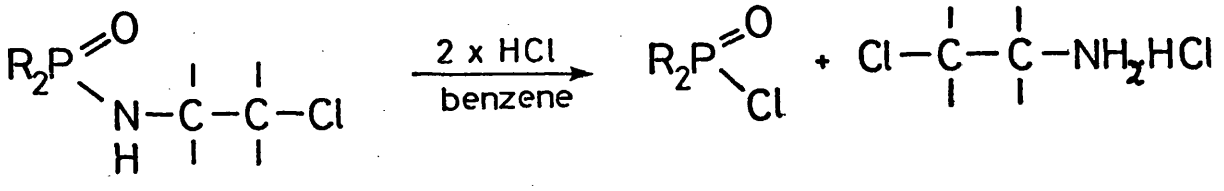
(111)

In only two cases, involving the highly halogenated sulphonamide derivatives (112, X = Cl) and (112, X = H), has a reduced adduct been found to react with alkali by alkene-forming elimination rather than cyclisation.[63]



(112)

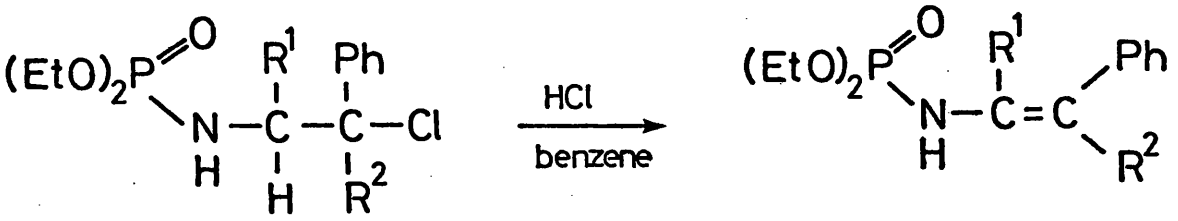
In the situation (113) where phosphorus is directly bonded to nitrogen, the phosphorus-nitrogen bond is readily cleaved by hydrogen chloride in a dry solvent, resulting in a β-chloro amine hydrochloride (114).[55,66,68,69] These, in turn, can be cyclised to yield aziridines (111, R = H).[66,68]



(113) (114)

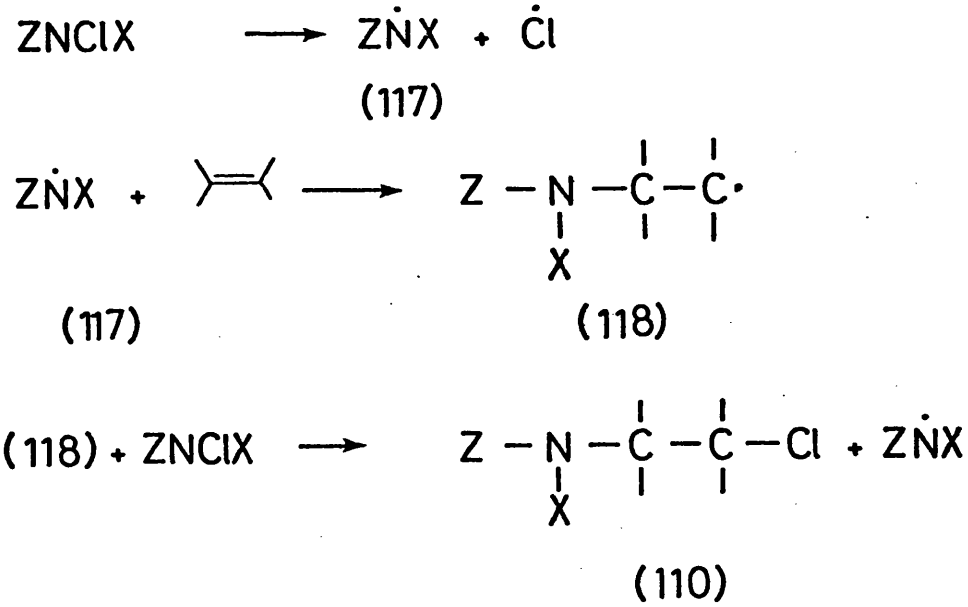
The adduct with trans-stilbene (115, R_1 = Ph, R_2 = H) does not

react with hydrogen chloride, whereas degradation of the adduct (115, $R_1 = H$, $R_2 = Ph$) with the latter follows a different course, eliminating hydrogen chloride and forming the enamide (116).[69a]



(115) (116)

It is generally agreed that the addition products (110, X = Cl) are formed by a radical mechanism since, not only do the reactions require conditions known to produce radicals, but in some cases an induction period has been observed. The formation of these adducts is summarised in Scheme 8. The initial reaction involves homolytic

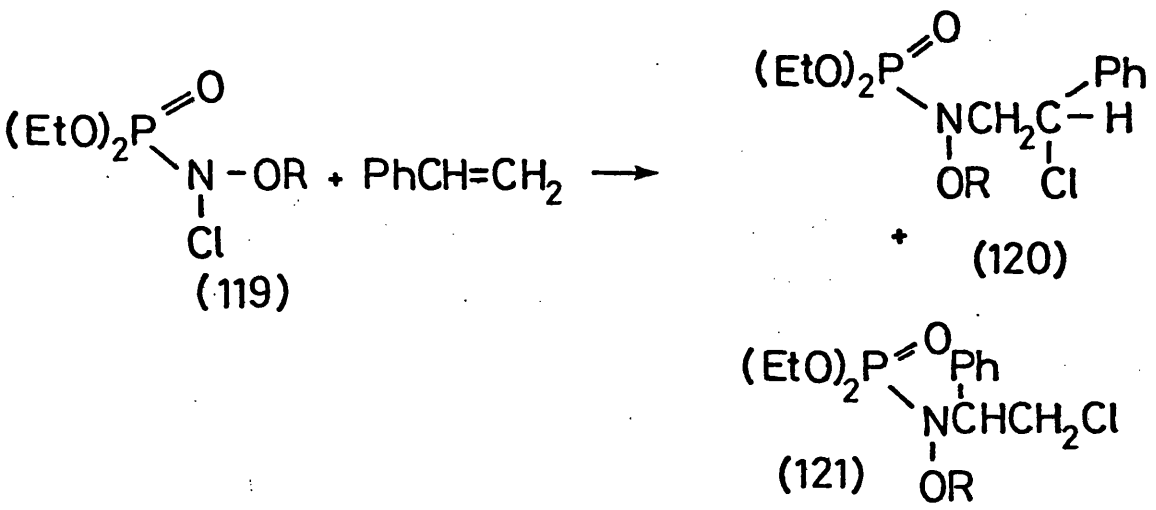


SCHEME 8

cleavage of the nitrogen chlorine bond to produce the amino radical (117) and a chlorine radical. The amino radical then attacks the olefinic substrate to produce the carbon radical intermediate (118)

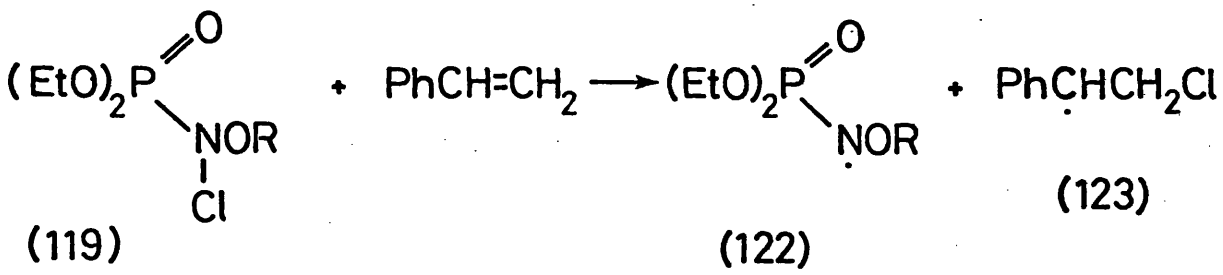
which abstracts chlorine from another molecule of chloroamide to yield the adduct (110).[52,69]

Zwierzak and Brylikowska[56] found that (119) reacted with styrene when heated in benzene and irradiated (U.V.) to yield the isomeric products (120) and (121). They postulated a radical mechanism, but

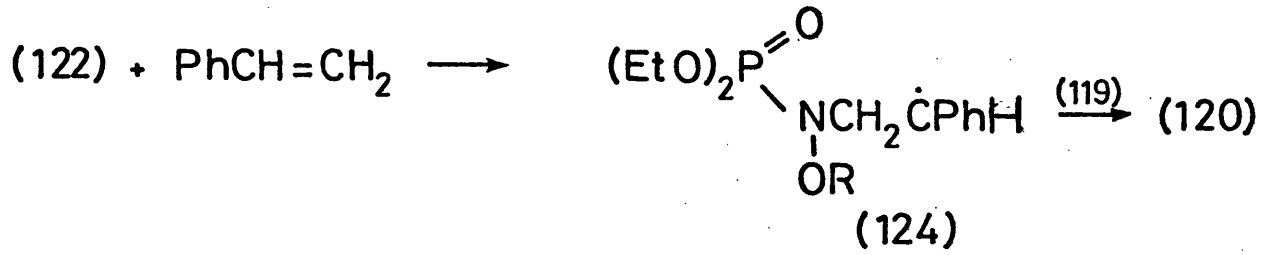


with the amino radical (122) being formed not by homolysis of the nitrogen-chlorine bond in the chloroamide (119), but rather by a bi-molecular reaction of the chloroamide with styrene. In this way the benzylic radical (123) is also produced; so that the amino radical (122) can attack either styrene, leading by way of (124) to the addition product (120), or it can combine directly with the benzylic radical (123) to give the isomeric adduct (121).

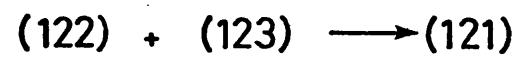
Formation of a Markovnikov addition product by a radical mechanism has been reported by Pinchuk and co-workers.[70] Using different olefinic substrates, namely hex-1-ene and 2-ethyl-hex-1-ene, they claim that diethyl N,N-dichlorophosphoramidate (125) adds to the former to give the 'normal' anti-Markovnikov adduct (126) but to the latter to give the Markovnikov adduct (127). No conclusive proof, however, is



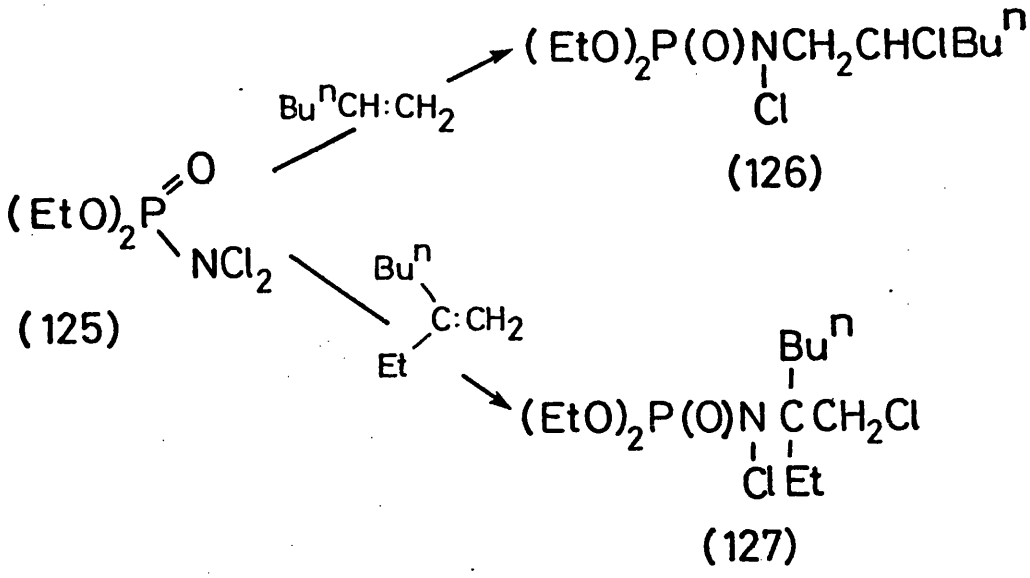
(119) (122) (123)



(124)



presented, and it is contrary to the findings of other workers and the results of this present work.[71]



(125) (126) (127)

Rybakova[64] has reported that (N,N-dichloro)-p-chlorobenzene-sulphonamide adds to hex-1-ene, and Schrage[72] has reported that N-mono-chlorourethane adds to terminal olefins to yield a mixture of Markovnikov and anti-Markovnikov addition products. With the exceptions

noted, radical addition to olefins proceeds to yield the anti-Markovnikov adduct.

It is interesting to note that anti-Markovnikov products have been isolated by Rybakova, from the reactions of certain N,N-dichloro-arylsulphonamides with 1,1-dichloroethylene[73] and 1,1,3-trichloro-propene[67] under conditions known to promote heterolytic addition reactions.

$$ArSO_2NCl_2 + CCl_2 = CHR \xrightarrow[SnCl_4]{AIR} ArSO_2N(Cl)CH(R)-CCl_3$$

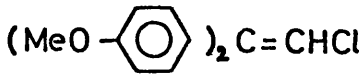
$$R = H \text{ or } CH_2Cl$$

When allylic hydrogens are present in the substrate, substitution can compete with addition.[52,69b,74] Here, abstraction of an allylic

(117) (128)

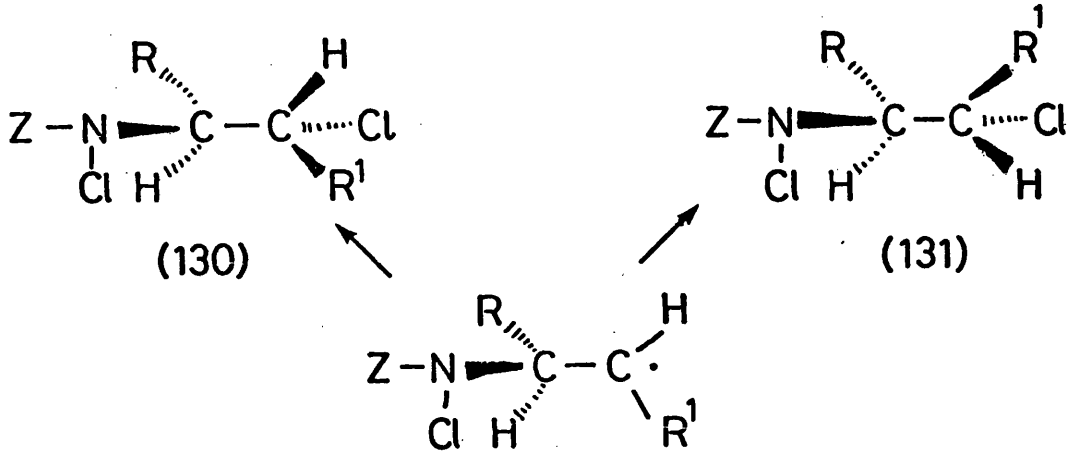
hydrogen by the amino radical (117) or by the chlorine radical produces the delocalised radical intermediate (128).

A vinylic chlorination product (129) was obtained on reacting the chloro-phosphinic amide (125) with 1,1-di-(p-methoxyphenyl)ethylene.[69a]



(129)

Reaction of N-chloroamides with 1,2-disubstituted ethylenes (cis or trans) gives a mixture of erythro (130) and threo (131) isomers.[52,60b,69a] The non-stereospecificity of the reaction is a consequence of the

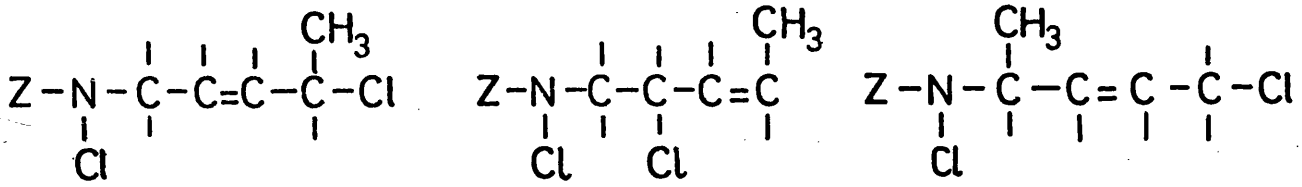


(130) (131)

(132)

intermediacy of the planar radical species (132) in which rotation about the carbon-carbon bond is possible.

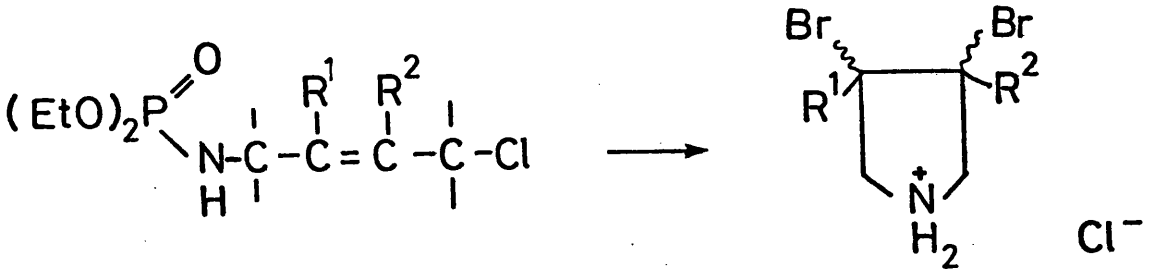
Addition of N-chloroamides to 1,3-dienes may result in 1,4[75,76,77] and 1,2[75,76]-addition. For example, penta-1,3-diene gives the products (133)-(135).[76]



(133) (134) (135)

Zwierzak and Gajda[78] observed solely 1,4-addition of the chloroamide (125) with 1,3-dienes. The resulting adducts (136) were brominated, the phosphorus-nitrogen bonds hydrolysed, and the δ-chloro-

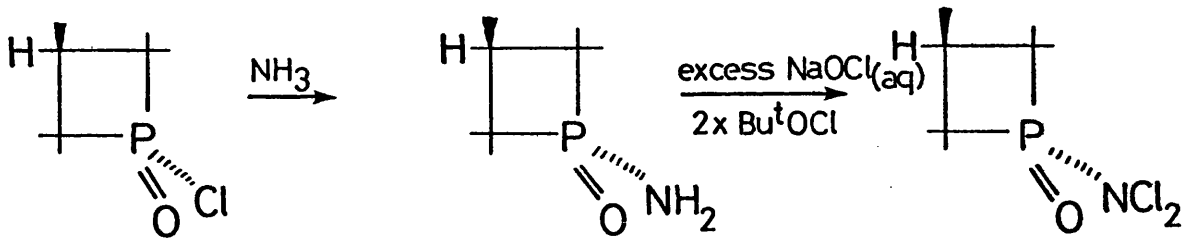
amines heated to yield pyrolidine hydrochlorides (137).



(136) (137)

2.2 Preparation and Disproportionation of Dialkylphosphinic N-Chloro and N,N-Dichloroamides

t-1-Chloro-2,2,r-3,4,4-pentamethylphosphetan-1-oxide (138), prepared by the method of McBride et al.,[79] was converted to the amide (139) by reaction of (138) with ammonia. Attempted preparation of t-1-(N,N-dichloroamino)-2,2,3,4,4-pentamethylphosphetan-1-oxide (140) from the amide (139) using chlorine in a sodium acetate-acetic acid buffer solution gave unsatisfactory results, whereas bubbling chlorine through an aqueous solution of (139) gave (140), but only in 50% yield. Synthesis of (140) was ultimately achieved almost quantitatively by using a two phase system with the amide (139) in dichloromethane and aqueous sodium hypochlorite (containing 8% free chlorine), or by using a small excess of t-butyl hypochlorite in dichloromethane with the amide. The compound (140) represents the first reported cyclic N,N-

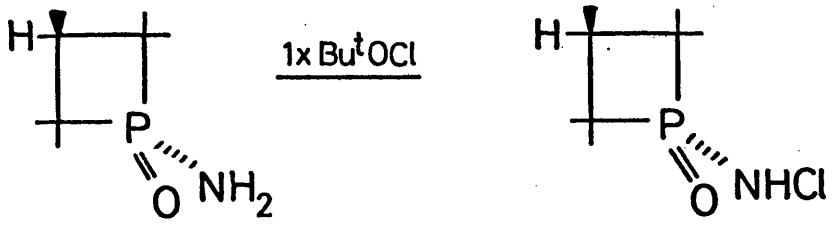


(138) (139) (140)

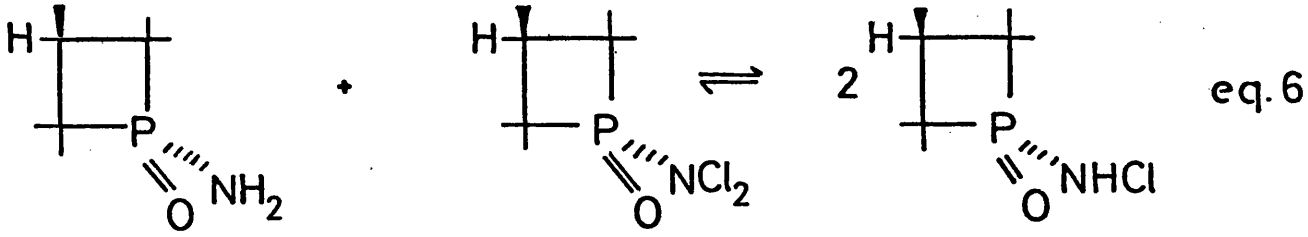
dichloroamino-dialkylphosphinic amide.

The synthesis of the first monochloro derivative of a cyclic P(V) primary amide, namely t-1-(N-chloroamino)-2,2,r-3,4,4-pentamethylphosphetan-1-oxide (141), was effected by reaction of the amide (139) with slightly more than one molar equivalent of t-butyl hypochlorite; alternatively the disproportionation reaction of an equimolar mixture of the amide (139) and the dichloroamide (140) in dichloromethane

afforded the monochloroamide (141). Disproportionation reactions such

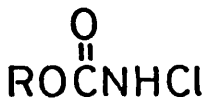


(139) (141)



(139) (140) (141) eq. 6

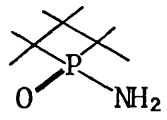
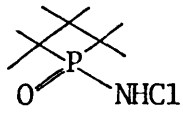
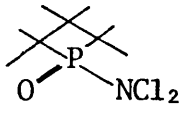
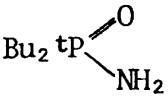
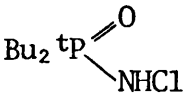
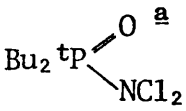
as eq. 6 were originally used by Czapf et al.[80] to synthesise methyl and ethyl N-monochlorocarbamates (142, R = Me or Et).



(142)

The geometry of the phosphinic amide (139), which is apparently (n.m.r.) a single isomer, is unknown. Since, however, the chlorine in the phosphetanic chloride (138) is trans to the C-3[81] methyl and is displaced by various nucleophiles with retention of configuration at phosphorus,[82,119] it is probable that the amino group in (139) is trans to the C-3 methyl group. The geometry of the N,N-dichloroamino and N-chloroamino groups of (140) and (141) respectively are assumed to be trans to the C-3 methyl since they are derived from (139) by reaction

TABLE 2

^{31}P/ppm	Compound	ν_{NH}/cm^{-1}	$\nu_{P=O}/cm^{-1}$	Other prominent absorptions
-50.8		3360 3220 3110	1184 1160	1552(δ_{NH}), 1240, 892 660
-56.6		2680	1176 1167 1158	1376, 1238, 850 616, 602
-77.2			1245 1209	1371, 790, 778
-55.0		3320 3250 3128	1202 1137	1570(δ_{NH}), 902, 814
-63.8		2710	1160	1372, 1360, 1217, 880, 816 660
-80.6	 [a]		1222 1203 1180	1370, 836, 815, 655

[a] Liquid film; others Nujol mulls

at the nitrogen centre and not at the phosphorus.

In solution the monochloroamide (141) exists in equilibrium with the amide (139) and the dichloroamide (140) (eq. 6), but on removal of solvent the relatively insoluble monochloroamide is the only product isolated. No such equilibrium situation was observed by Czapf.[80]

Table 2 shows selected infrared bands for compounds (139)-(141) as Nujol mulls. The product (141) isolated from the reaction shown in equation 6, exhibits a band at 2680 cm^{-1}; by contrast the N-H stretching vibrations of (139) appear as three bands, at 3360, 3220, and 3110 cm^{-1}, whereas (140) contains no N-H band.

In the 100 MHz ^1H nmr spectrum (CH_2Cl_2) the amide (139) shows two doublets for the cis and trans 2,4-methyls at δ1.25 (J_{PH} 17 Hz) and δ1.19 (J_{PH} 18 Hz). The dichloroamide (140) shows a single doublet at δ1.33 (J_{PH} 19 Hz). The spectrum of the mixture formed when the monochloroamide is in solution shows a twelve line pattern for the cis and trans 2,4-methyls, made up of two doublets due to the amide (139) at δ1.25 (J_{PH} 18 Hz) and δ1.21 (J_{PH} 17 Hz), and two doublets at ca. δ1.33 (J_{PH} 19 Hz and 19 Hz) due to the dichloroamide (separation into a four line pattern could be caused by medium effects) together with two doublets at δ1.31 (J_{PH} 19 Hz) and δ1.30 (J_{PH} 19 Hz) attributable to the monochloroamide (141).

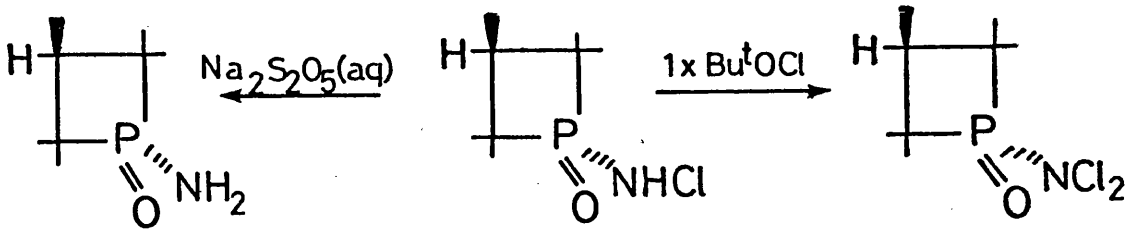
The ^{31}P nmr spectrum of a solution of (141) shows three resonances at (relative to H_3PO_4) -50.8, -56.6 and -77.2 ppm. The signals at -50.8 and -77.2 are those of the amide (139) and the dichloroamide (140) respectively so that the signal at -56.6 ppm is assigned to the monochloroamide (141).

The infrared spectrum of the solid recovered from the nmr solution was as described above, showing just one N-H stretching vibration at

2680 cm^{-1}.

Confirmation that the 100 MHz ^1H nmr spectrum of a solution of the monochloroamide (141) contained signals for both the amide (139) and the dichloroamide (140) was obtained by the addition of a small quantity of the amide to the nmr sample: the high field doublets increased in intensity and, relative to the dichloroamide, the quantity of monochloroamide also increased. Addition of the dichloroamide caused an enhancement of the low field doublet and an increase in the proportion of the monochloroamide with respect to the amide. Thus addition of either amide or dichloroamide to the solution of the monochloroamide shifts the equilibrium (eq. 6) in favour of the monochloroamide.

Lacking satisfactory elemental analyses of the chloroamides (140) and (141), the reactions in Scheme 9 were undertaken to further establish the structures. Thus the monochloroamide (141) was converted in high yield into the dichloroamide (140) upon reaction with a slight excess of t-butyl hypochlorite, and into the parent amide (139) by reduction with aqueous sodium metabisulphite.



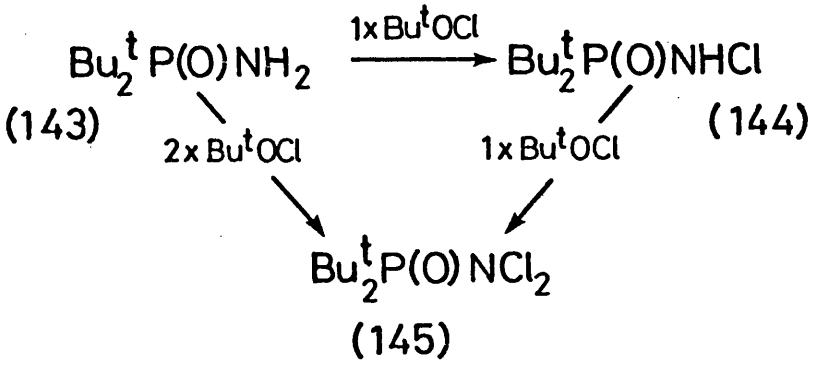
(139) (141) (140)

SCHEME 9

Di-t-butylphosphinic amide (143) was synthesised from di-t-butylchlorophosphine by reaction with ammonia followed by oxidation with 30% hydrogen peroxide (eq. 7).

$$Bu^t_2PCl \xrightarrow{2NH_3} Bu^t_2PNH_2 \xrightarrow{H_2O_2} Bu^t_2P(O)NH_2 \qquad \text{eq. 7}$$
$$+NH_4Cl \qquad (143)$$

(N-chloro)-di-t-butylphosphinic amide (144) was prepared from the amide (143) and t-butyl hypochlorite and by the disproportionation reaction of an equimolar mixture of the amide and the dichloroamide (145) in dichloromethane.[80] The dichloroamide (145) was obtained from the amide and the monochloroamide by reaction with t-butyl hypochlorite.



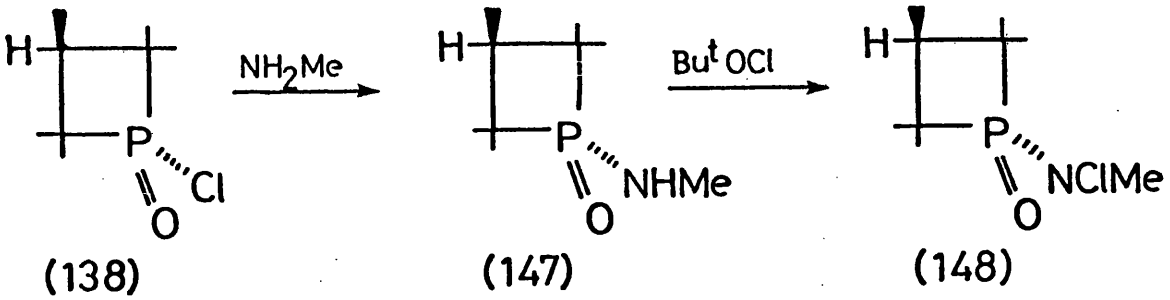
An equilibrium analogous to that shown in eq. 6 was observed with (N-chloro)-di-t-butylphosphinic amide (eq. 8).

$$Bu^t_2P(O)NH_2 + Bu^t_2P(O)NCl_2 \rightleftharpoons 2Bu^t_2P(O)NHCl \qquad \text{eq. 8}$$
$$(143) \qquad (145) \qquad (144)$$

The ^1H nmr spectrum of a solution of the monochloroamide (144) in dichloromethane consisted of three doublets at δ1.48 (J_{PH} 15 Hz), the dichloroamide (145); δ1.25 (J_{PH} 14 Hz), the amide (143); and δ1.35 (J_{PH} 15 Hz), assigned to the monochloroamide (144). Integration showed that (144) is ca. 50% dissociated at 20°C.

The ^{31}P nmr spectrum of a solution of (144) in dichloromethane showed three resonances at -55.0 ppm (relative to H_3PO_4), the amide (143); -80.6 ppm, the dichloroamide (145); and -63.8 ppm, assigned to the monochloroamide (144).

Reaction of the phosphetanic chloride (138) and di-isopropylphosphinic chloride (146) with methylamine and ammonia respectively yielded t-1-(N-methylamino)-2,2,r-3,4,4-pentamethylphosphetan-1-oxide (147) and di-isopropylphosphinic amide (149), and conversion of (147) into t-1-(N-chloro-N-methyl)amino-2,2,r-3,4,4-pentamethylphosphetan-1-oxide (148) and (149) into (N,N-dichloro)-di-isopropylphosphinic amide (150) was achieved using t-butyl hypochlorite. A longer reaction time of 4h



(138) (147) (148)

$Pr^i_2P(O)Cl \xrightarrow{NH_3} Pr^i_2P(O)NH_2 \xrightarrow{Bu^tOCl} Pr^i_2P(O)NCl_2$

(146) (149) (150)

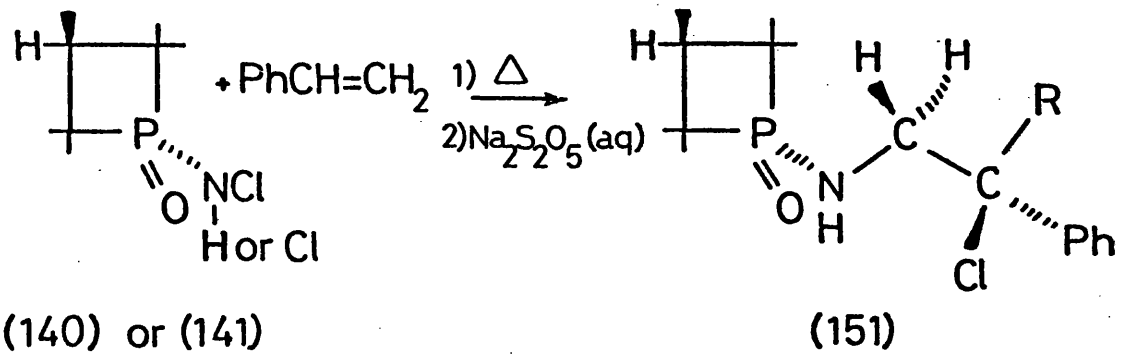
was necessary to bring about the conversion of (147) into (148) compared with <1h for the preparation of the other N-chlorophosphinic amides.

Table 2 contains selected infrared and ^{31}P nmr data for the above amides and chloroamides. The dichloroamides described are pale yellow, low melting, crystalline solids and the monochloroamides are colourless crystalline solids. Compounds (144), (145), and (150) represent the

first reported acyclic (N-chloro) and (N,N-dichloro)-dialkylphosphinic amides.

2.3 Reactions of Phosphinic N-Chloroamides with Phenylethylenes

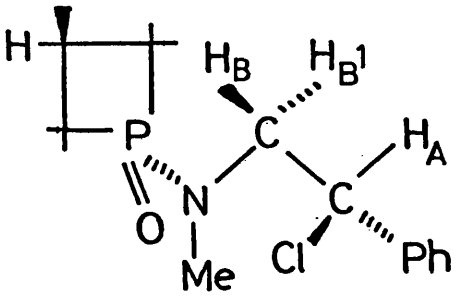
Both t-1-(N,N-dichloroamino)-2,2,r-3,4,4-pentamethylphosphetan-1-oxide (140) and the corresponding N-chloro derivative (141) undergo reaction with styrene in boiling benzene under dry nitrogen. The product, after a reductive work up with aqueous sodium metabisulphite, is the 1:1 adduct (151, R=H) in which the chloroamide has added across the double bond in an anti-Markovnikov fashion. Both the mono and di-



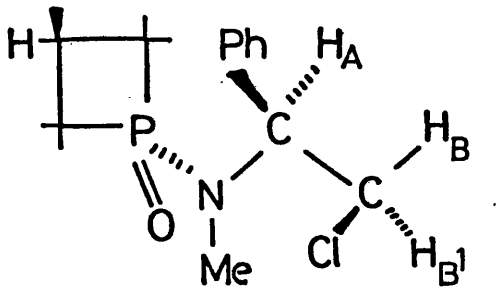
(140) or (141) (151)

chloroamide can thus apparently react with styrene, but since the monochloroamide is in equilibrium with the dichloroamide eq. 6 reaction in both cases could be proceeding via the dichloroamide.

Evidence that the monochloroamide (141) can react with styrene was sought using t-1-(N-chloro-N-methyl)amino-2,2,r-3,4,4-pentamethyl-phosphetan-1-oxide (148). This reacted with styrene to yield, after reductive work up, two isomeric products ($C_{17}H_{27}$ ClNOP) which were separated by chromatography on alumina. Addition of the N-chloroamide (148) across the double bond of styrene might reasonably give rise to two products, the anti-Markovnikov (152) and the Markovnikov (153) adducts. In the proton nmr spectrum of (152) the benzylic proton (H_A) would be expected to appear as a triplet or a double doublet depending upon whether coupling to the non-equivalent protons H_B,$H_B{}^1$ of the methylene group is the same or different. A more complicated pattern



(152)

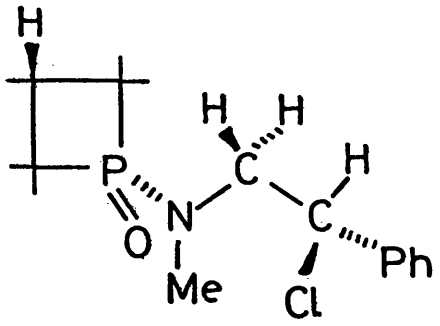


(153)

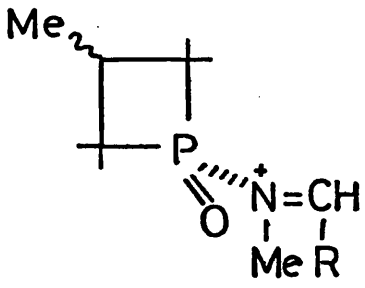
is predicted for H_A in (153) because of the additional coupling of H_A to phosphorus. The methylene protons of (152) and (153) are diastereotopic and will in principle be anisochronous. However, if the chemical shift non-equivalence is very small, for (152) they will appear as either a triplet or a double doublet, by virtue of coupling to phosphorus as well as the benzylic H_A, and for (153) as a doublet due to coupling only to the adjacent benzylic proton H_A.

Both isomers gave spectra containing one-proton resonances at ca. δ5.1, a reasonable chemical shift for H_A in (152) but rather lower field than might be expected for H_A in (153). Moreover, in both spectra these resonances appeared as triplets with no apparent coupling to phosphorus. ^{31}P-Decoupling of the spectra of the two products showed collapse of the methylene signals in both cases. Thus in both isomers, the methylene group seems to be α to the nitrogen, in which case the isomeric product must be (154), where isomerisation across the four-membered ring system has occurred to produce the cis-anti-Markovnikov adduct, rather than the Markovnikov addition product (153). Further evidence that in both isomers the methylene group is α to the nitrogen was obtained from mass spectrometry. For both compounds the most abundant ion has m/e 202 arising from cleavage of the carbon-carbon

bond α to the nitrogen to give the ion (155, R=H).[83] No ion having



(154)



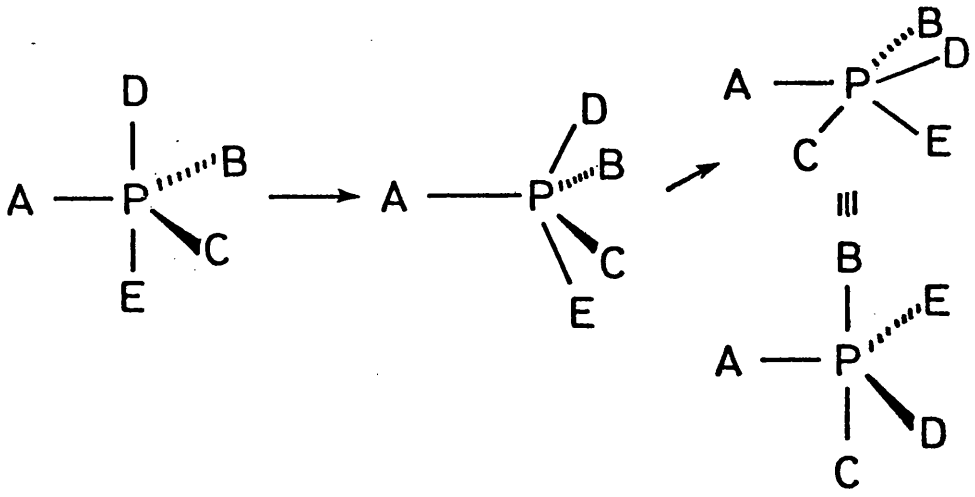
(155)

m/e 278 corresponding to (155, R=Ph) was observed in the mass spectrum of either isomer.

To obtain this type of trans-cis isomerisation a pseudorotation mechanism may be invoked. In the molecule PF_5,[84] one single fluorine resonance split by phosphorus is obtained in the ^{19}F nmr spectrum. Since the molecule has a trigonal bipyramidal arrangement of fluorine atoms about a central phosphorus atom, then the two apical fluorines are equivalent and the three equatorial fluorines are equivalent. To account for the observed total equivalence of the fluorines in the ^{19}F nmr spectrum, then interconversion of apical and equatorial ligands must be occurring and this must be fast on the nmr time scale.

Berry[85] considered a trigonal bipyramidal arrangement of five different ligands (A-E). If a reference ligand A is taken and the two apical ligands (D and E) move towards one another and the two equatorial ligands (B and C) move away from one another, continuation of this motion results in the formation of a new trigonal bipyramid via the intermediacy of a square-based pyramidal arrangement of ligands. In effect the two equatorial ligands and the two apical ligands have interchanged to become apical and equatorial respectively. This interconversion of trigonal bipyramidal arrangements of ligands is known as

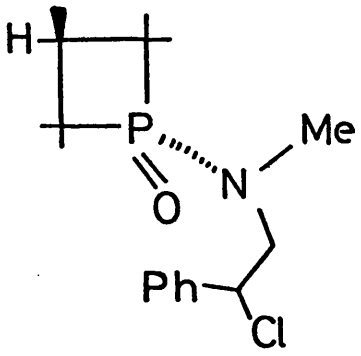
pseudorotation.



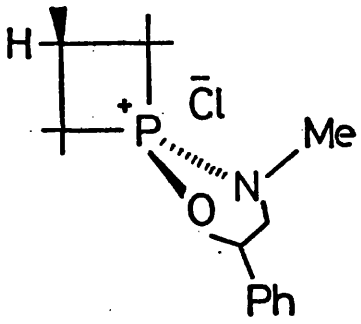
Starting from one trigonal bipyramid three distinct pseudorotations are possible, to give three isomeric trigonal bipyramids. These in turn can pseudorotate to produce in all twenty isomeric trigonal bipyramids (ten enantiomeric pairs). However, when two of the ligands form part of a small ring, those pseudorotations which would place the ring diequatorial may have prohibitively high energy barriers because of ring strain.

The initial adduct (152) is assumed to have the trans configuration and to be in equilibrium with the phosphonium salt (156) formed by intramolecular attack of the nucleophilic phosphinyl oxygen on the exocyclic β carbon atom displacing the labile benzylic chloride anion. If the phosphonium salt (156) is in equilibrium with the phosphorane (157), three pseudorotations can occur to yield the phosphorane (158) in which the nitrogen is now cis to the 3-Me group. The phosphorane (158) is in equilibrium with the phosphonium salt (159) which ring-opens to yield the cis addition product (154).

Support for the first step in the mechanism, involving intramolecular O-alkylation with the formation of the phosphonium salt (156),

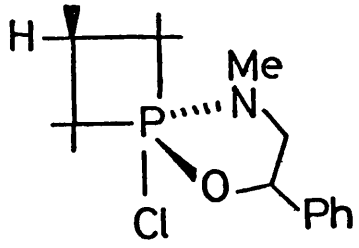


(152)

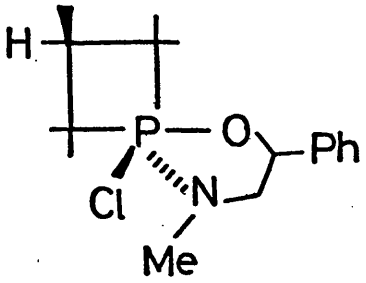


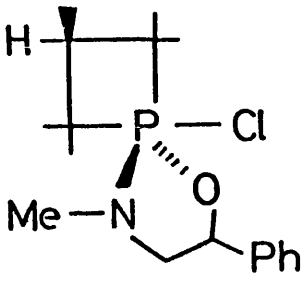
(156)

(156) ⇌

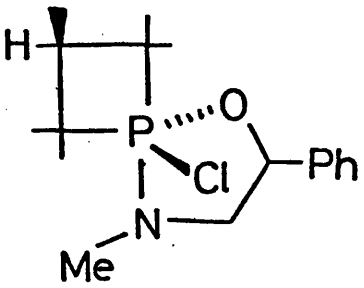


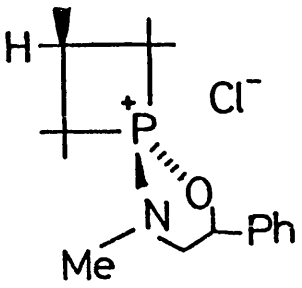
(157)



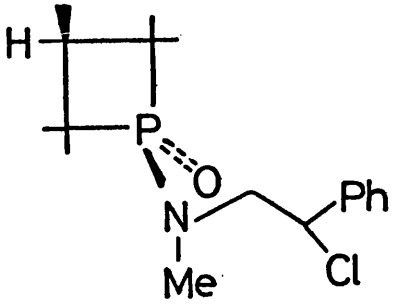


(158)



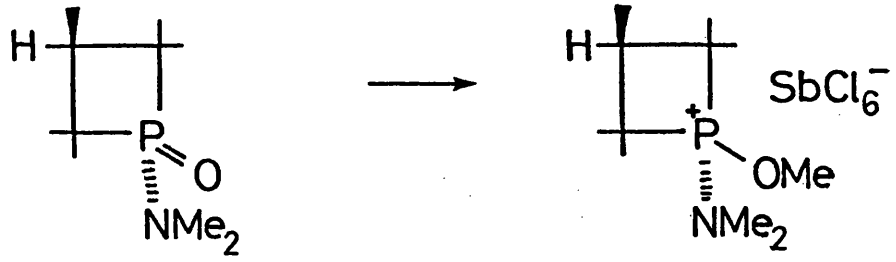


(159)



(154)

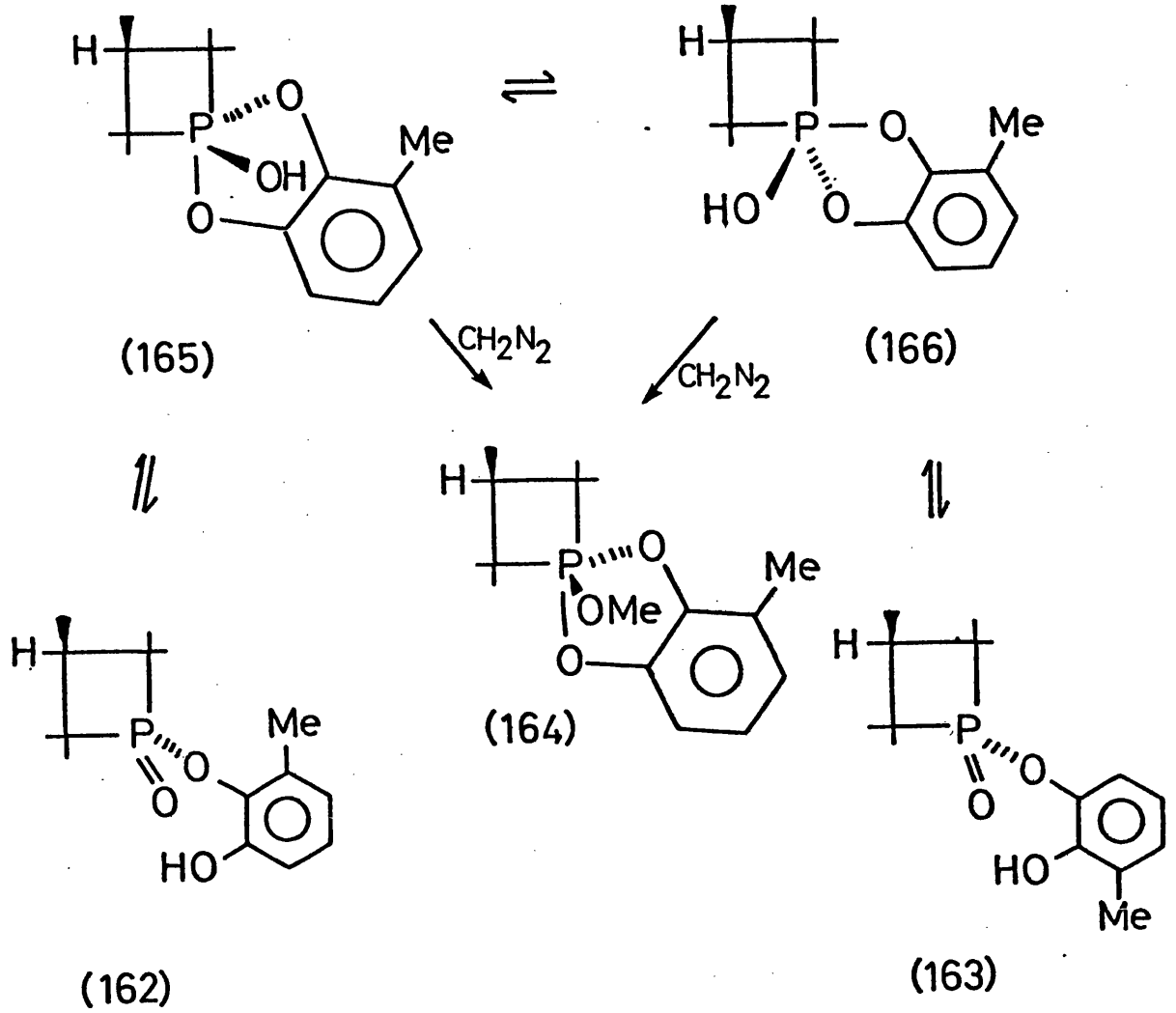
comes from the work by DeBruin et al.[86] who have synthesised the phosphonium hexachloroantimonate (161) from the phosphinic amide (160) using trimethyloxonium hexachloroantimonate.



(160) (161)

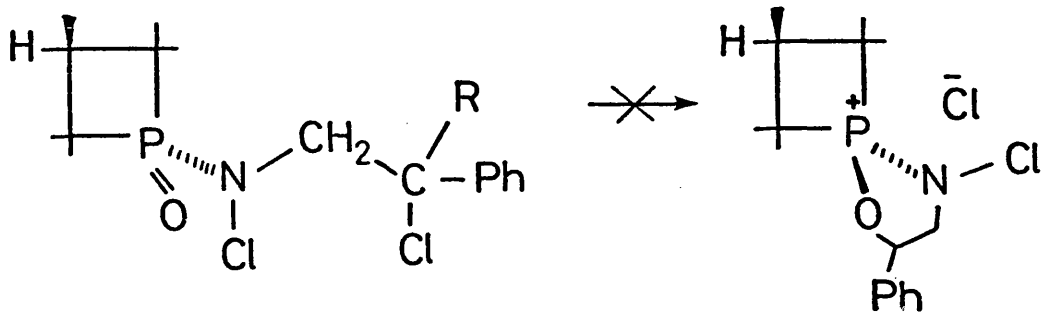
Evidence for the ring closure and ring opening steps and the equilibrium (152)⇌(154) is provided by a recent report by Trippett and Kemp.[87] They showed that the reaction of the trans-pentamethylphosphetanic chloride (138) with 3-methylcatechol in the presence of base gave a single crystalline phosphinate ester which in solution gave an equilibrium mixture of the isomeric esters (162) and (163). Treatment of this equilibrium mixture with diazomethane yielded the methoxy phosphorane (164), suggesting the intermediacy of the hydroxyphosphoranes (165) and (166) in the isomerisation.

A trans-cis isomerism such as (152)⇌(154) was not observed in the reactions of t-1-(N,N-dichloroamino) and t-1-(N-chloroamino)-2,2,-r-3,4,4-pentamethylphosphetan-1-oxides (140) and (141) with styrene. In the reaction medium the adducts exist with an N-chloro substituent and the presence of this electron-withdrawing substituent presumably reduces the nucleophilicity of the phosphinyl oxygen, inhibiting the intramolecular alkylation step. Only on reduction is the electronegative N-chloro substituent removed, and so the adduct (151, R= H) was not subject to the reaction conditions (heat) that brought about the isomer-

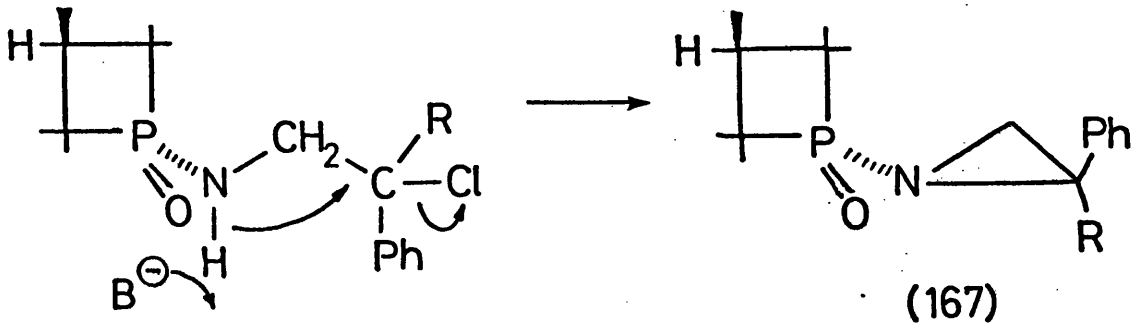


isation (152)⇌(154).

A minor product isolated chromatographically from the reaction of t-1-(N,N-dichloroamino)-2,2,r-3,4,4-pentamethylphosphetan-1-oxide with



styrene was the aziridine (167, R=H). This no doubt arose by alumina-induced elimination of hydrogen chloride from the adduct (151, R=H).

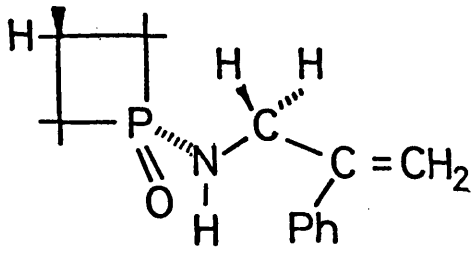


(151) (167)

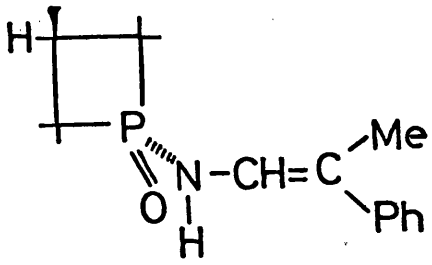
It was identified by comparison of its ^{1}H nmr spectrum with that of an authentic sample, prepared by cyclisation of the adduct (151, R=H) with methanolic sodium methoxide. The spectrum contained a characteristic twelve-line pattern for the three aziridine ring protons.

Adducts (151, R=Me and Ph) were synthesised by the reactions of t-1-(N,N-dichloroamino)-2,2,r-3,4,4-pentamethylphosphetan-1-oxide with α-methylstyrene and 1,1-diphenylethylene respectively. In the former case two minor products were isolated upon chromatography on alumina; the aziridine (167, R=Me), identified by comparison of its ^{1}H nmr spectrum with that of an authentic sample, prepared by base induced elimination of hydrogen chloride from the adduct (151, R=Me), and an olefinic product. The ^{1}H nmr spectrum of the latter is consistent with structure (168) but not the enamide (169) which has only one olefinic proton. A low yield of a product (170), analogous to (168), has been obtained by Lessard et al.[62] from the chromous chloride-promoted addition of ethyl N-chlorocarbamate to tetramethylethylene.

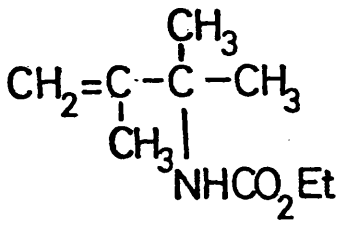
Reaction of the dichloroamide (140) with styrene, α-methylstyrene, and 1,1-diphenylethylene could in each case theoretically yield two isomeric products, corresponding to addition in a Markovnikov (153) and



(168)

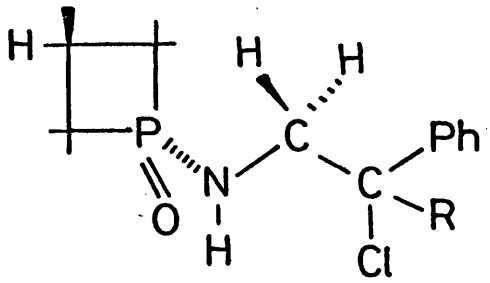


(169)

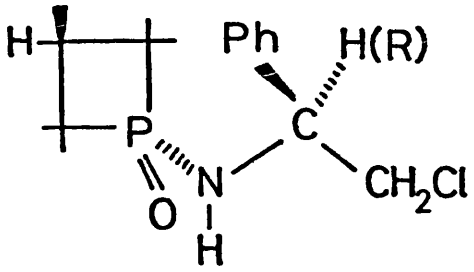


(170)

anti-Markovnikov (151) fashion. However, treatment of the adducts with methanolic silver nitrate gave an immediate white precipitate of silver

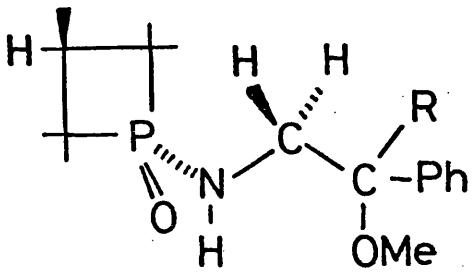


(151)



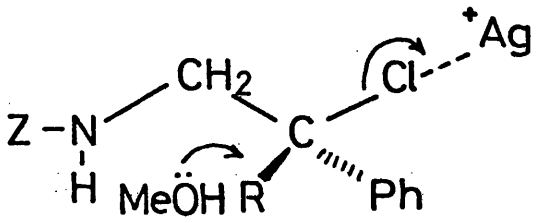
(153)

chloride, suggesting that the chlorine is benzylic as in (151).[52] The products isolated from the reaction with methanolic silver nitrate were the 2′-methoxyl derivatives (171). These adducts are formed either by

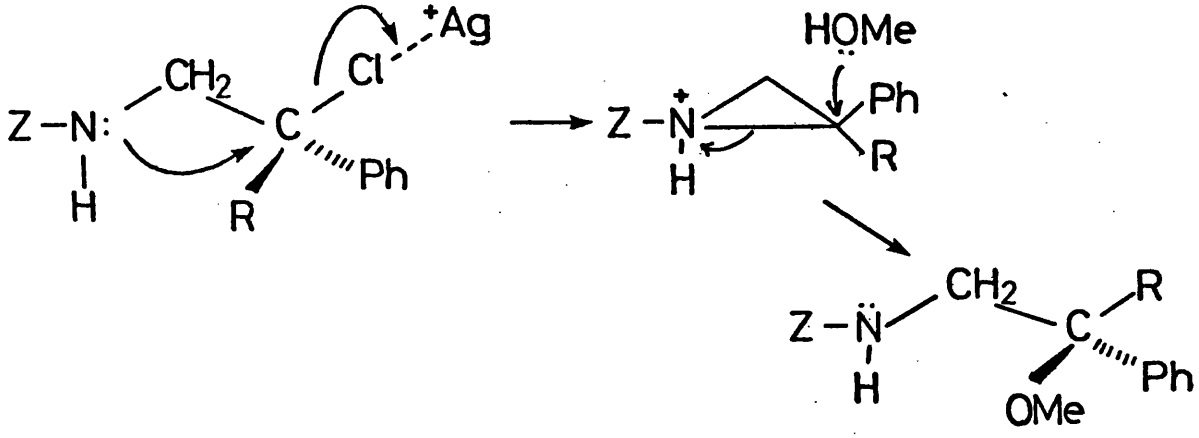


(171)

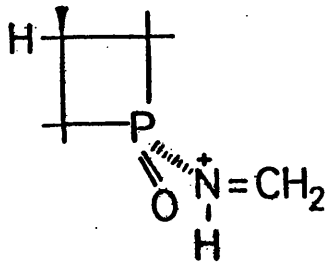
a silver ion promoted SN2 mechanism:



or by an N.G.P mechanism involving an anchimerically-assisted loss of chloride ion by nitrogen, promoted by silver ion, followed by ring opening of the protonated aziridine thus formed.



In the mass spectrometer the adducts (151) and their methanolysis derivatives (171) all gave rise to an ion (172), m/e 188, by cleavage of the carbon-carbon bond next to the nitrogen.[83] The ^{1}H nmr spectra



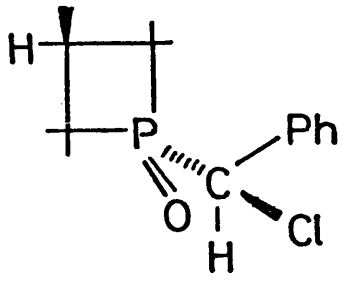
(172)

are also consistent with the structures (151) and (171). The benzylic protons in (151) and (171) (R=H) give rise to triplets and the methylene protons appear as complex patterns. Double doublets are observed

for the methylene protons of (151) and (171) (R= Me and Ph) as a result of coupling to phosphorus and the amide proton. The characteristic pattern of the phosphetan C-2 and C-4 methyl groups, namely two doublets (sometimes superimposed and appearing as just one doublet) from the cis and trans-methyls, was not observed with the adducts (151) and (171) (R= H and Me); these gave eight-line patterns (reduced to six lines in some cases by superimposition) indicating non-equivalence of all four C-2 and C-4 methyl groups. Chirality of the carbon β to the nitrogen in the acyclic chain must be the cause of this non-equivalence. The 1,1-diphenylethylene adducts (151) and (171) (R= Ph) possess no such chiral centre and their symmetry makes the C-2 and C-4 cis and trans methyls appear as a four line pattern (two doublets).

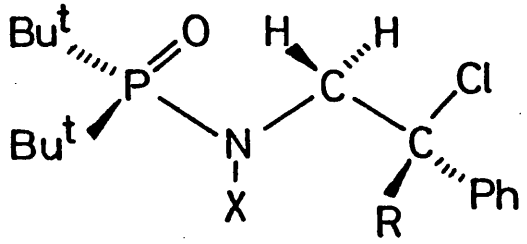
A nitrogen atom to which three unlike groups are attached is potentially a chiral centre but the complex pattern of the phosphetan C-2 and C-4 methyls cannot be attributed to the presence of this centre since the nitrogen in a phosphinic amide is essentially planar.[88]

Recent work by Trippett and co-workers[89] has shown that for t-1-α-chlorobenzyl-2,2,r-3,4,4-pentamethylphosphetan-1-oxide (173) a comparable complex pattern is observed for the C-2 and C-4 methyls as a consequence of the presence of a chiral carbon atom in the molecule.

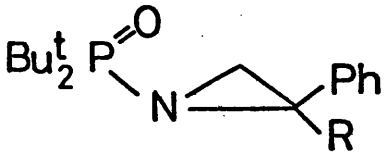


(173)

In an attempt to extend the addition of N-chlorophosphinic amides to phenylethylenes and also to aid spectroscopic interpretation and understanding of the mechanism of the addition reactions, the dichloroamide (145) was allowed to react with styrene and α-methylstyrene to yield the 1:1 adducts (174, R= H or Me, X= Cl) which were reduced with aqueous sodium metabisulphite and the adducts (174, R= H or Me, X= H) isolated. Attempts to isolate the adduct (174, R= Ph, X= H) from the reaction of the dichloroamide (145) with 1,1-diphenylethylene failed, but its formation was confirmed by treatment of the crude reaction product with potassium t-butoxide in t-butanol to yield the aziridine (175, R= Ph).



(174)



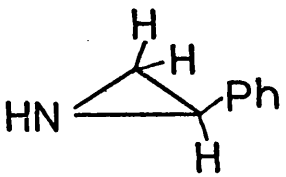
(175)

The initial N-chloro adduct (174, R= H, X= Cl) was also isolated using styrene, and its structure verified by elemental analysis ($C_{16}H_{26}Cl_2NOP$). The infrared spectrum showed no N-H absorptions in the region 4000 - 2000 cm^{-1} whereas the adduct (174, R= H, X= H) absorbed at 3230 cm^{-1}. In (174, R= H, X= Cl; R= H, X= H; R= Me, X= H) the t-butyl groups appear as two doublets (or a triplet if two doublets overlap) because the presence of a chiral centre makes them magnetically non-equivalent. This is analogous to the non-equivalence of the four C-2 and C-4 phosphetan methyls in (151) and (171). The ^1H nmr spectra of (174, R= H, X= Cl and H) are consistent with the proposed structures since the benzylic proton appears as a double doublet or a triplet with no coupling to phosphorus. The non-equivalent methylene protons of

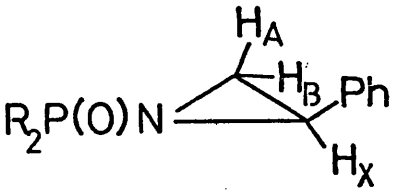
adduct (174, R= H, X= Cl) appear as two eight-line patterns, each proton being coupled to the other methylene proton, to the benzylic proton and to phosphorus. With the reduced adduct (174, R= X= H), additional complexity of the methylene protons is seen because of coupling to the amide proton. The non-equivalence of the methylene protons in the systems $RCH_2CHPhCl$ is well documented.[90]

Cyclisation of the reduced 1:1 adducts (151) and (174, X= H) with methanolic sodium methoxide or potassium t-butoxide in t-butanol yielded aziridines (167) and (175). The styrene adduct (151, R= H) cyclised in high yield, using methanolic sodium methoxide, to (167, R= H) whereas the α-methylstyrene adduct (151, R= Me) gave not only the aziridine (167, R= Me), but also a compound (171, R= Me) resulting from nucleophilic attack of methoxide ion at the benzylic carbon with displacement of the chloride anion.

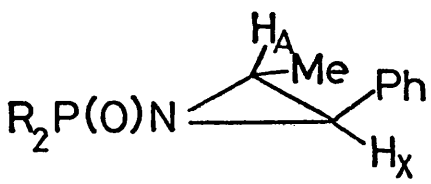
In the ^1H nmr spectra of the aziridines (167) and (175) (R= H), the aziridine protons are shifted downfield relative to the parent aziridine (176), and four types of coupling are observed: geminal, cis, trans, and phosphorus (PNCH), decreasing in the order PNCH > cis > trans > geminal. This is in complete agreement with the work of Berlin[91] on the aziridines (177) and (178) (R= Ph and EtO) and (177, R= NEt_2).



(176)



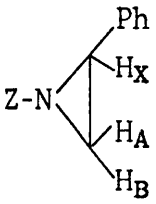
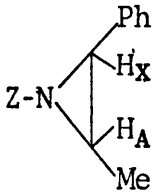
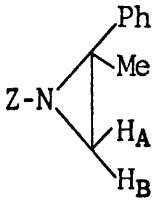
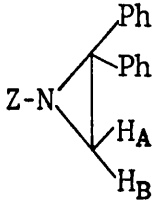
(177)



(178)

Couplings of the aziridine protons to phosphorus decrease in the order $J_{PH_B} > J_{PH_X} > J_{PH_A}$, where H_X refers to the aziridine proton geminal to the phenyl substituent, H_A the proton trans to H_X, and H_B the proton

TABLE 3

	Z	δH_X	δH_B	δH_A		J_{gem}	J_{trans}	J_{cis}	J_{PH_X}	J_{PH_A}	J_{PH_B}
	$Ph_2P(O)$	3.70	2.79	2.12		1.5	3	6	16	13	18
	$(EtO)_2P(O)$	3.40	2.57			1.5	3	6	15.5	15	18
	$Bu_2{}^tP(O)$	3.43	2.72	1.98		2	3	6	13	12	15
	$Pr_2{}^iP(O)$	3.40	2.67	1.97		2	3	6	13	15	15
	$C_8H_{16}P(O)$ [a]	3.55	2.72	2.02		2	3	6	14	13	16
	H[93]	2.83	2.02	1.64		1	3	6			
	$Ph_2P(O)$	3.60		2.67			3		15.5	15	
	$(EtO)_2P(O)$	3.33		3.53			3		15.5	15	
	H	2.47		1.87			3				
	$Bu_2{}^tP(O)$		2.64	2.13		3				14	10
	$C_8H_{16}P(O)$		2.78	2.13		2				14	10
	H[94]		1.72			2					
	$Bu_2{}^tP(O)$		2.94							11	
	$C_8H_{16}P(O)$		2.89							13	

[a] $C_8H_{16}P(O)$ is the pentamethylphosphetan 1-oxide group

cis to H_X. The coupling constants J_{PNCH} are of the order 10-17 Hz for aziridines (167) and (175) (R = H, Me, or Ph) whereas slightly larger values of 13-18 Hz are reported for the aziridines (177) and (178).

Table 3 correlates the chemical shifts and coupling constants of the aziridine protons of the compounds reported in this work and that of Berlin.[91]

In conclusion, the structures of the products (anti-Markovnikov adducts) and the conditions of the reactions (heating in a dry nitrogen atmosphere) suggest that the additions of the (N-chloroamino), (N-methyl-N-chloroamino), and (N,N-dichloroamino)-dialkylphosphinic amides to phenylethylenes follow homolytic mechanisms.

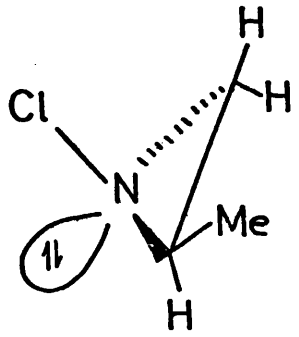
$$R_2P(O)NClX \longrightarrow R_2P(O)\dot{N}X + \cdot Cl$$

$$R_2P(O)\dot{N}X + CH_2{=}CPhR \longrightarrow R_2P(O)\underset{\displaystyle X}{\underset{|}{N}}CH_2\dot{C}PhR$$

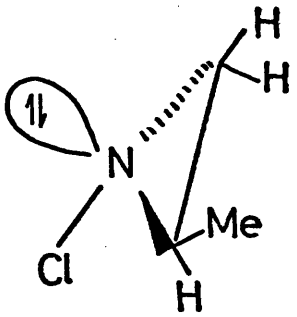
$$R_2P(O)NClX + R_2P(O)\underset{\displaystyle X}{\underset{|}{N}}CH_2\dot{C}PhR \rightarrow R_2P(O)\underset{\displaystyle X}{\underset{|}{N}}CH_2CClPhR + R_2P(O)\dot{N}X$$

2.4 N-Phosphoryl Aziridines

In aziridines, the tetrahedral arrangement of three groups and the lone pair on nitrogen gives rise to the possibility of invertomers in which the group Z attached to nitrogen is either cis or trans to the substituents at positions 2 and 3 in the aziridine ring, e.g. (179) and (180).

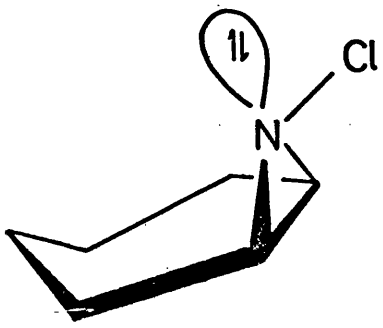


(179)



(180)

With N-chloro-2-methylaziridine the high energy barrier to inversion at nitrogen has enabled Brois[95] to isolate the two invertomers, while Felix et al.[96] have isolated the invertomers (181) and (182) of 7-chloro-7-azabicyclo [4.1.0] heptane, and Atkinson[97] has detected



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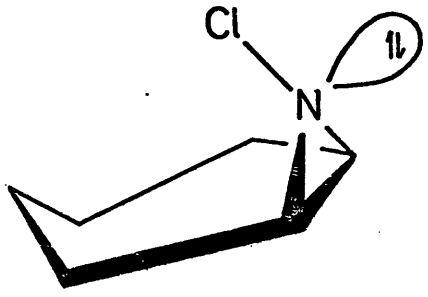

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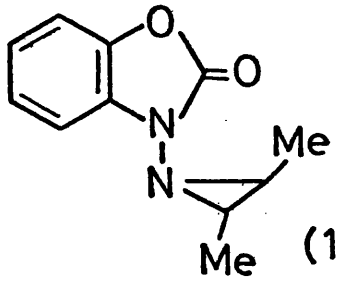
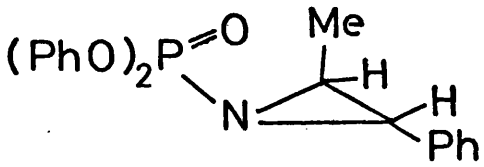


(183)

slow nitrogen inversion by nmr in the benzoxazolinone-substituted aziridine (183).

In N-phosphoryl aziridines Berlin et al.[91] have reported slow inversion at 0° on the nmr time scale for diphenyl-N-(2-phenyl-t-3-

methylaziridinyl)-phosphine oxide (184) as shown by the appearance of two methyl resonances. The evidence, however, is inconclusive since the 100 MHz spectrum at only one temperature (0°) is presented and the apparent small separation (0.64 Hz) of the methyl resonances could in fact arise from coupling of the methyl protons through four bonds to the C-2 aziridine proton. In propylene oxide (185) a coupling constant of 0.36 Hz has been observed between the methyl protons and the cis-hydrogen.[98]



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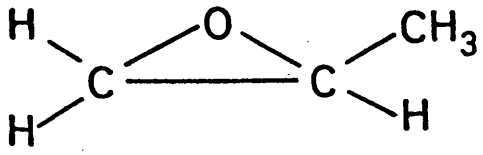
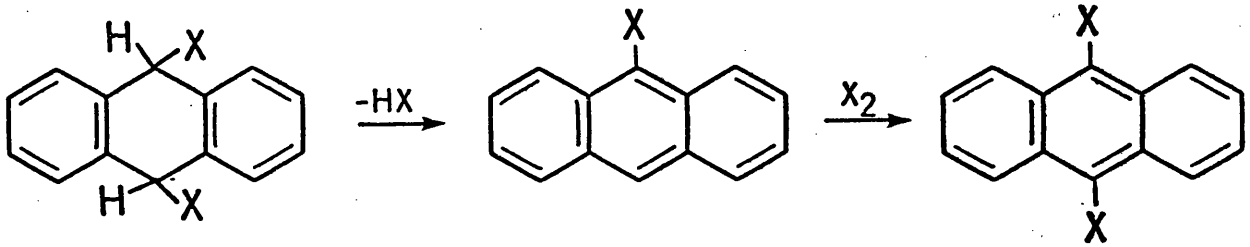


(185)

Nmr (100 MHz) analysis of the aziridine (167, R= Me) at temperatures down to -96° revealed no clear evidence for slow nitrogen inversion. This seems to lend support to the suggestion by Anet and co-workers[99] that, on the nmr time scale, N-phosphoryl aziridines are rapidly inverting even at quite low temperatures. Admittedly, on warming the solution of the aziridine (167, R= Me) to 65° minor changes in the multiplicity of the H_B proton were observed, but these are probably due to small changes in coupling.

2.5 Chlorination of Anthracene and Anisole with Phosphinic N-Chloroamides

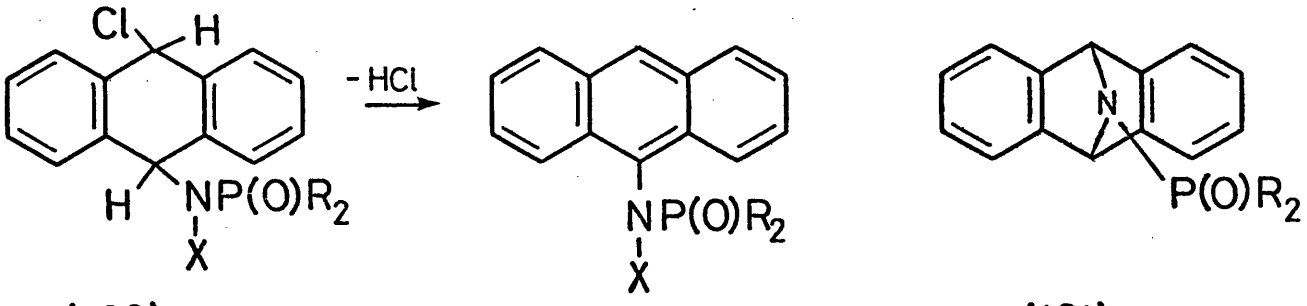
In an extension of the addition reactions of (N-chloroamino), (N-alkyl-N-chloroamino) and (N,N-dichloroamino)-dialkylphosphinic amides to unsaturated systems, anthracene was chosen as substrate. The 9 and 10 positions of anthracene act as the termini of a 1,3-diene system and readily add chlorine and bromine forming the 9,10-substituted dihydroanthracene (186), which loses a molecule of hydrogen halide to form the 9-haloanthracene (187). Further reaction with halogen can lead to the 9,10-dihaloanthracene (188).[100] In Diels Alder reactions



(186) (187) (188)

the addition of dienophiles across the 9 and 10 positions of anthracene is also well documented.[101]

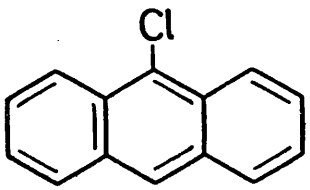
At the outset of this work it was envisaged that, if the 9 and 10 positions act as the termini of a 1,3-diene system, the N-chlorophosphinic amides would add across these positions to give the 9-amino-substituted anthracene (190) after rearomatisation of (189); alter-



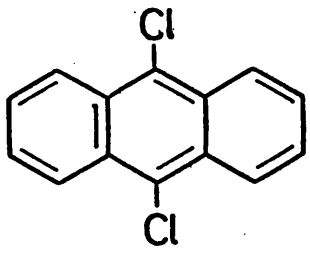
(189) (190) (191)

natively, elimination of chloride ion from the 10-position of (189) could yield the bridged heterocyclic system (191) with the carbon-nitrogen bond still intact.

Heating the dichloroamides (140), (145) and (150) in benzene containing anthracene, followed by reduction with aqueous sodium metabisulphite and chromatography, gave 9-chloro and 9,10-dichloroanthracenes (192) and (193); continuous extraction of the metabisulphite aqueous phase with chloroform yielded the phosphinic amides. No anthracene-amide product was isolated in any of the reactions.



(192)



(193)

Table 4 shows the yields of (192) and (193) and the molar ratios of the chlorophosphinic amides to anthracene used in the reactions.

Since only partial separation of the 9-chloro and 9,10-dichloroanthracenes could be achieved using column chromatography, the yields of these products were calculated according to the following theory. When a mixture of two compounds (1 and 2) is examined by glc, the areas of the peaks recorded will be determined by the amounts of the compounds in the sample and the response of the detector to them.[102]

If A = area of glc peak produced by a compound
W = weight of the compound present in the sample
r = detector response to unit weight of the compound

then $A_1 = W_1 r_1$ and $A_2 = W_2 r_2$

hence $\frac{A_1}{A_2} = \frac{W_1}{W_2} \cdot \frac{r_1}{r_2}$

TABLE 4

Yields of 9-Chloro and 9,10-Dichloroanthracenes
(mol per 100 mol Anthracene)

Chloroamide	Chloroamide : Anthracene	9-Chloroanthracene	9,10-Dichloroanthracene
$C_8H_{16}P(O)NCl_2$ (140)	3 : 1	[a]	49[b]
	1 : 1	31	49.5
$Bu_2{}^tP(O)NCl_2$ (145)	1 : 1	54	27
$Pr_2{}^iP(O)NCl_2$ (150)	1 : 1	50	26
$C_8H_{16}PONHCl$ (141)	2.4 : 1	28	58.5
$C_8H_{16}PONMeCl$ (148)	2 : 1	55	41

[a] None isolated

[b] Isolated yield

For each sample the area ratio (A_1/A_2) was measured by cutting out the glc peaks and weighing them, it being assumed that the areas of the peaks were proportional to their weights.

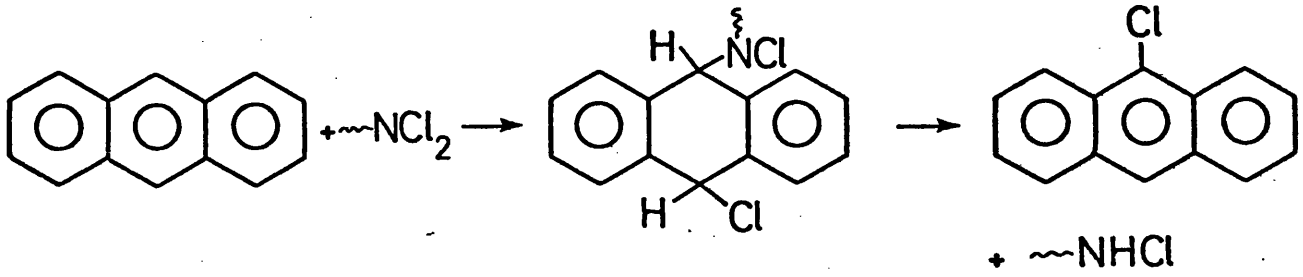
Using a sample containing compounds 1 and 2 in a known weight ratio (W_1/W_2), the relative response (r_1/r_2) of the detector to the compounds was determined. For any other sample, the weight ratio (W_1/W_2) could then be determined by measuring A_1/A_2 and using the above value of r_1/r_2. Combining this information with the knowledge of the combined weight of compounds 1 and 2 isolated by column chromatography, the individual weights of the two compounds formed in the reaction could be determined.

The reaction of t-1-(N,N-dichloroamino)-2,2,r-3,4,4-pentamethyl-phosphetan-1-oxide (140) with anthracene in boiling benzene was followed by glc, by withdrawing samples from the reaction mixture at known time intervals and looking at the variation of the peak areas of anthracene, 9-chloroanthracene, and 9,10-dichloroanthracene with time. When >90% of the anthracene had been consumed, the amount of monochloroanthracene exceeded that of the dichloro compound, but continued reaction caused the proportion of the dichloroanthracene to increase. Clearly the dichloro compound can be formed from the monochloro, although the possibility that some is also formed directly from anthracene cannot be excluded. Comparable results were obtained using t-1-(N-chloroamino)-2,2,r-3,4,4-pentamethylphosphetan-1-oxide (141).

It appears, therefore, that the N-chlorophosphinic amides are acting simply as chlorinating agents in the reactions with anthracene. Since the monochloroamide (141) gave similar results to (140) in its reaction with anthracene, and bearing in mind the equilibrium shown in eq. 6, the question arose as to whether the monochloroamide itself was

acting as the chlorinating species. Evidence that (141) is a possible chlorinating species came from the reaction of t-1-(N-chloro-N-methyl)-amino-2,2,r-3,4,4-pentamethylphosphetan-1-oxide (148) with anthracene which also yielded chlorinated anthracenes, as shown in Table 4.

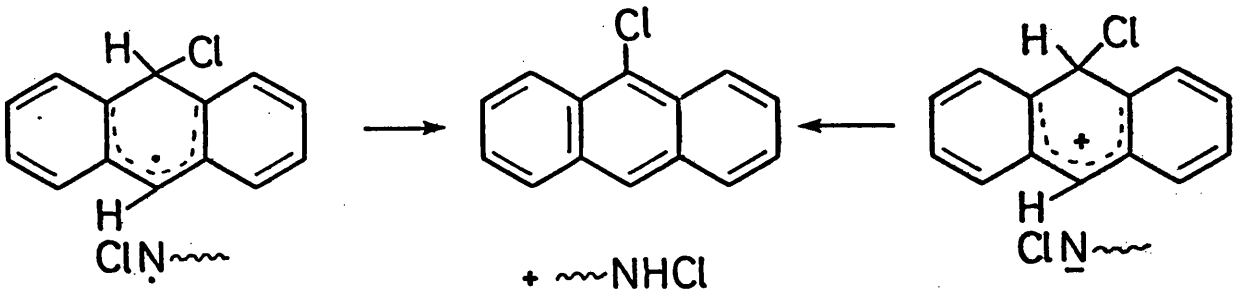
It is well documented that anthracene undergoes reaction at the 9 and 10 positions with both electrophiles[103] and free radicals[104] to produce 9 and 9,10-substituted anthracenes. The mechanism of the present chlorination reactions could also follow an addition-elimination pathway, involving either radicals or ions, with the intermediate dihydroanthracene (194) rearomatising by carbon-nitrogen bond cleavage in preference to chlorine elimination.



(194)

However there is no evidence in the literature to suggest that the intermediate (194) would rearomatise by cleavage of the carbon-nitrogen bond. More likely is that (194), if formed, would rearrange by loss of hydrogen chloride to produce an amino-substituted anthracene. An addition elimination mechanism is therefore unlikely.

The chlorination reactions could involve either a radical pair or ion pair that loses a hydrogen atom or hydrogen ion to produce 9-chloroanthracene. The 9-chloroanthracene would react further to produce 9,10-dichloroanthracene. The fact that phenylethylenes react with N-chlorophosphinic amides by homolytic mechanisms, and that the reactions with anthracene yield no products incorporating a carbon-nitrogen bond seems to suggest that the latter reactions are homolytic



with initial attack of a chlorine radical. There however appears to be no obvious reason why on the one hand the amino radical is the attacking species, in the reactions of N-chlorophosphinic amides with phenylethylenes, whereas on the other hand it is the chlorine radical that attacks the anthracene nucleus.

A third plausible mechanism can be conceived in which the N-chlorophosphinic amides are a source of molecular chlorine, analogous to the reaction of N-chloro and N-bromosuccinimide with alkenes. This mechanism would presumably be ionic, involving a polarised chlorine-chlorine bond.

In an attempt to gain insight into the formation of the chloroanthracenes, the reactions of t-1-(N,N-dichloroamino)-2,2,r-3,4,4-pentamethylphosphetan-1-oxide (140) and the corresponding N-monochloro derivative (141) with anisole were investigated. It was hoped that the ratio of the isomeric o, m, and p-chloroanisoles formed would suggest the type of mechanism operating.

Table 5 shows the ortho : meta : para ratio of the chloroanisoles formed in the chlorination reactions of anisole using molecular chlorine, generated by the reaction of dibenzoyl peroxide with halide salts in the presence of added copper salts (a), from dichloroamine-T in the presence of acetic acid (b) and from t-butyl hypochlorite in a variety of non-acidic solvents (c-f), the chlorinium (Cl^+) ion formed

TABLE 5

	Reagent	Electrophile Radical	Chloroanisole Isomer Ratios (%)			ref.
			o	m	p	
a	$(PhCO_2)_2/LiCl$	Cl_2	24		76	105
b	Dichloroamine-T/HOAc	Cl_2	21		79	106
c	Bu^tOCl/CCl_4	Cl_2	23		77	107
d	Bu^tOCl/Dioxan	Cl_2	20		80	"
e	Bu^tOCl/CH_3CN	Cl_2	20.5		79.5	"
f	Bu^tOCl/Bu^tOH	Cl_2	20.1		79.9	"
g	Cl_2/CCl_4	Cl_2	20.5		79.5	"
h	Bu^tOCl/CH_3COOH	Cl^+	33.5		64.5	"
i	$Bu^tOCl/HOAc/H_2SO_4$	Cl^+	35.5		64.5	"
j	Cl^+/H_2O [a]	Cl^+	34.9		65.1	"
k	$C_6H_5\overset{+}{N}_2BF_4^-$	Ph•	63.7	17.0	16.4	108
l	$PhN(NO)COCH_3$	Ph•	69.3	18.1	12.6	109
m	$Ph\text{-}N{=}N\text{-}CPh_3$	Ph•	69	21	10	110
n	$(PhCO_2)_2$	Ph•	67	18	15	111
o	$(PhCO_2)_2$	Ph•	60	14.7	15.6	108
p		Me•	74	15	11	112
q	$C_8H_{16}P(O)NCl_2$ **(140)**	Cl•	16	6	78	
r	$C_8H_{16}P(O)NHCl$ **(141)**	Cl•	15	5	80	

[a] Generated from hypochlorous acid containing silver perchlorate and perchloric acid.

by the decomposition of t-butyl hypochlorite in acidic media (h-j) and the N-chlorophosphinic amides (140) and (141). In all cases reported using either molecular chlorine or the chlorinium ion as the chlorinating species no m-chloroanisole was produced and the ½ ortho : para ratio of the chloroanisoles was less than one.

The free radical chlorination reaction of anisole appears not to have been investigated, but its free radical phenylation[108-111] has been extensively studied. Table 5 shows the ratio of the o, m, and p isomers formed in the reactions of phenyl radicals generated by the electrolytic reduction of phenyldiazonium tetrafluoroborate (k), N-nitrosoacetanilide (l), from phenylazotriphenylmethane (m) and dibenzoyl peroxide (n and o). It can be seen that upwards of 15% of meta product is obtained in these phenylation reactions and ½ ortho : para ratios >2 are obtained. This pattern was also found in the homolytic methylation reaction of anisole (p).

The ratios of meta to ortho + para isomers in the reaction of (140) and (141) with anisole were determined by glc, which did not adequately resolve the o and p-isomers, assuming that the responses of the isomeric chloroanisoles to the detector were the same. The o and p-chloroanisoles, as a mixture, were isolated by preparative glc (10% SE 30), and nmr analysis of this mixture gave by integration of the respective methoxyl peaks the ortho : para ratio. From this data the ortho : meta : para ratios for the chloroanisoles formed in these reactions were obtained.

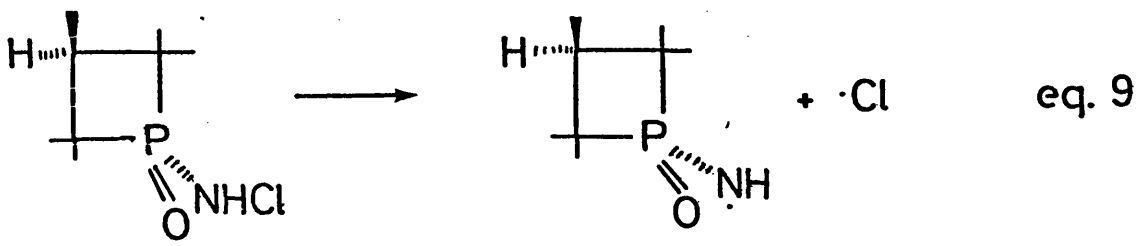
The high para : ortho ratio (ca. 5:1) in the chlorination of anisole with t-1-(N-chloroamino) and t-1-(N,N-dichloroamino)-2,2,r-3,4,4-pentamethylphosphetan-1-oxides seems to suggest that the reaction involves chlorine molecules. However, the formation of substantial amounts of

meta product (5-6%) and the known behaviour of electrophilic radicals[113] whereby the amount of meta product produced is not great points to the reactions proceeding by a homolytic mechanism.

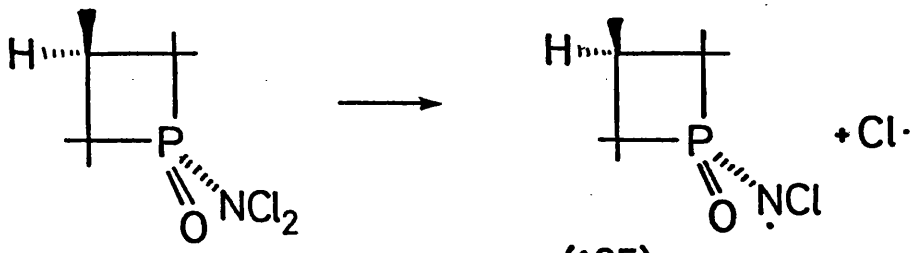
In the chlorination reactions of anthracene the initial step in the mechanism involves homolysis of the nitrogen-chlorine bond of (140) to produce the amino radical (195) and the chlorine radical. Reaction of anthracene with the chlorine radical produces the intermediate radical (196) which either reacts with another chlorine radical to produce 9,10-dichloro-9,10-dihydroanthracene (197) which decomposes by loss of hydrogen chloride to yield 9-chloroanthracene, or hydrogen abstraction by the amino radical from (196) can occur to give 9-chloroanthracene directly and the N-chlorophosphinic amide (141). (141) being in equilibrium with (139) and (140) (eq. 6) accounts for the formation of t-1-amino-2,2,r-3,4,4-pentamethylphosphetan-1-oxide (139) in the reaction.

The 9-chloroanthracene (192) can react in a similar manner to yield the 9,10-dichloroanthracene (193).

The very similar o : m : p ratios in both the reaction of (140) and (141) with anisole seems to confirm that in both cases the reacting species is the same, and the existence of the equilibrium of (141) with (139) and (140) (eq. 6) suggests possibly that the reaction of (141) is via (140) which decomposes to yield the chlorine radical and the reaction shown in eq. 9 does not occur.



eq. 9



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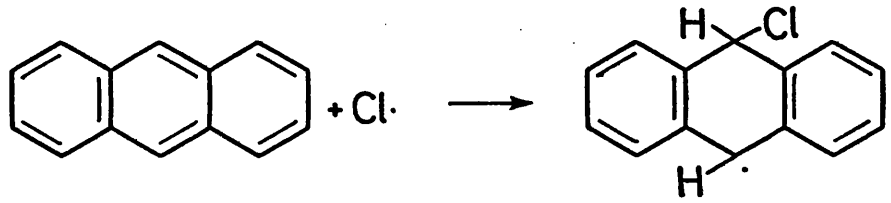

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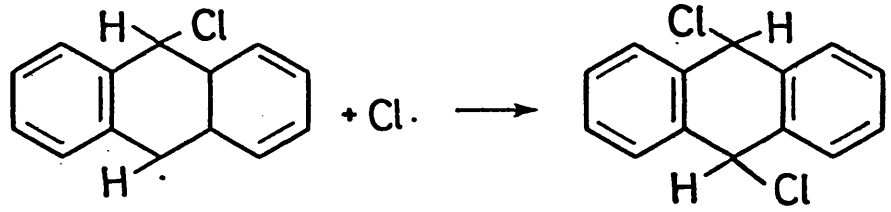
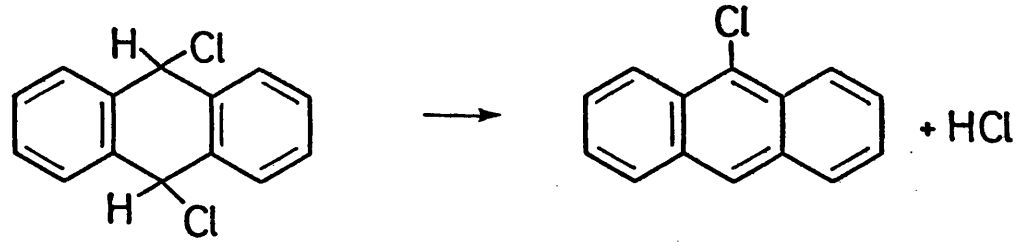
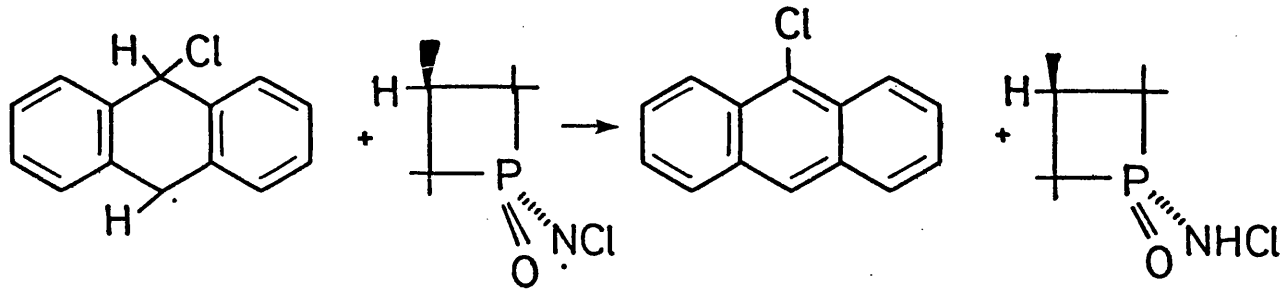


(196) (197)



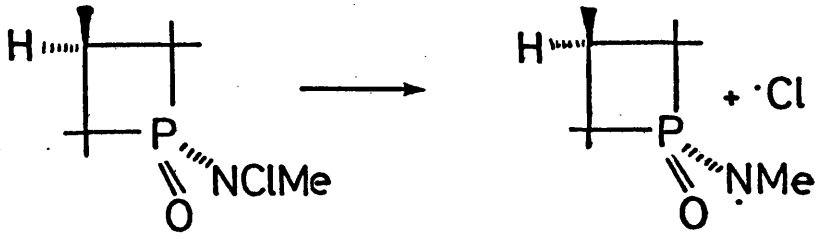
(197) (192)

or



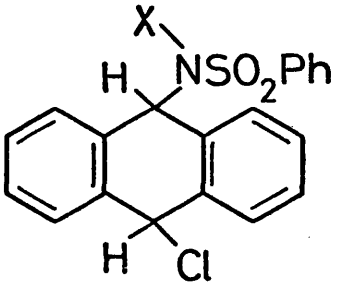
(196) (192) (141)

However, the decomposition of (147) in the presence of anthracene must involve the N-alkyl amino radical (198).



(147) (198)

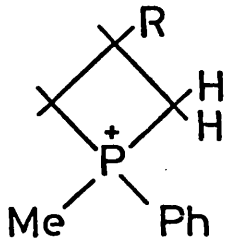
It was later cited in the literature that Kretov et al.[114] had reacted N,N-dichlorobenzenesulphonamide with anthracene. They claimed that the N,N-dichlorosulphonamide added across the 9,10 positions of anthracene to yield the adducts (199) (X = H and Cl). No spectroscopic evidence was, however, presented and the structures (199) were based upon the analysis of oils. Under other conditions this reaction has been shown to give chlorinated anthracenes.[115]



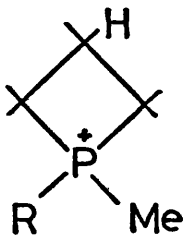
(199)

2.6 Attempted Base-Induced Ring Expansions of N-Chloroamino-phosphetan-1-Oxides

Phosphetan systems have a tendency to react with expansion of the four membered ring, by migration of an α carbon atom onto an exocyclic phosphorus substituent, or with cleavage of a phosphorus-carbon ring bond to yield ring-opened products. Alkaline hydrolysis of the phosphetanium salts (200, R = H),[116] (200, R = Me)[117] and (201, R = Me),[117] and reaction of (201, R = Ph)[117] with cyanide ion followed by oxidation, yield ring-opened products. With (200) the phosphorus-carbon ring bond which breaks is the one that leads to the more stable anion ($-\bar{C}H_2$ more stable than $-\bar{C}Me_2$).

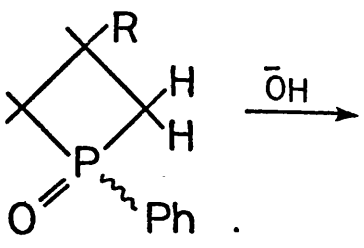


(200)



(201)

The phosphetan oxides (202, R = H and Me) ring open to yield the phosphinic acids (203) upon treatment with base, although both the cis and trans 1-phenyl-pentamethylphosphetan-1-oxides (204) are unaffected by 10 M sodium hydroxide even at 100°.[117]



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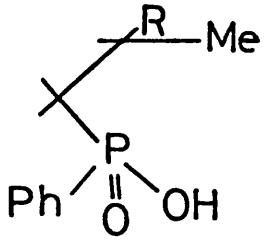
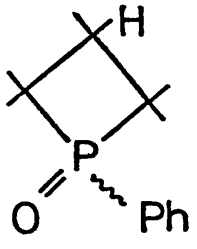
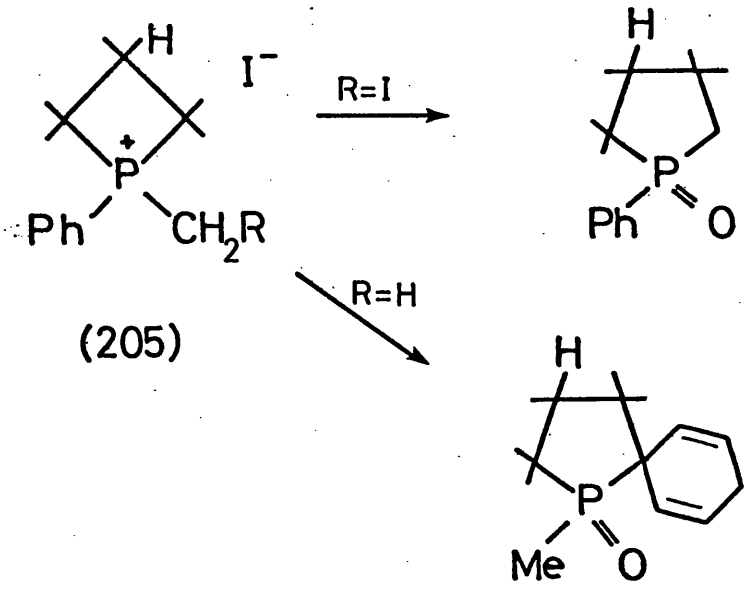


(203)



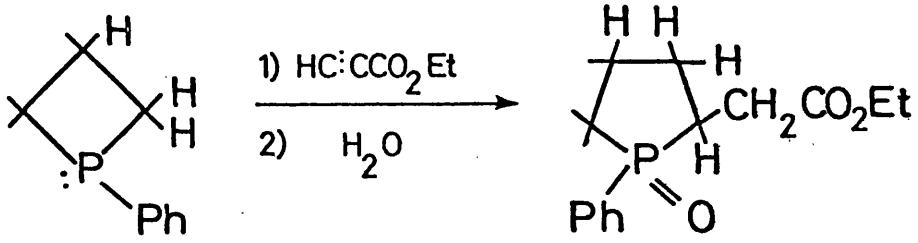
(204)

The alkaline hydrolysis of the phenylmethyl and phenyliodomethyl-phosphetanium salts (205, R=H and I)[118,119] give ring-expanded products, as



(205)

also does the hydrolysis of the adduct of methyl propiolate and 2,2,3-trimethyl-1-phenylphosphetan (206).[119,117]

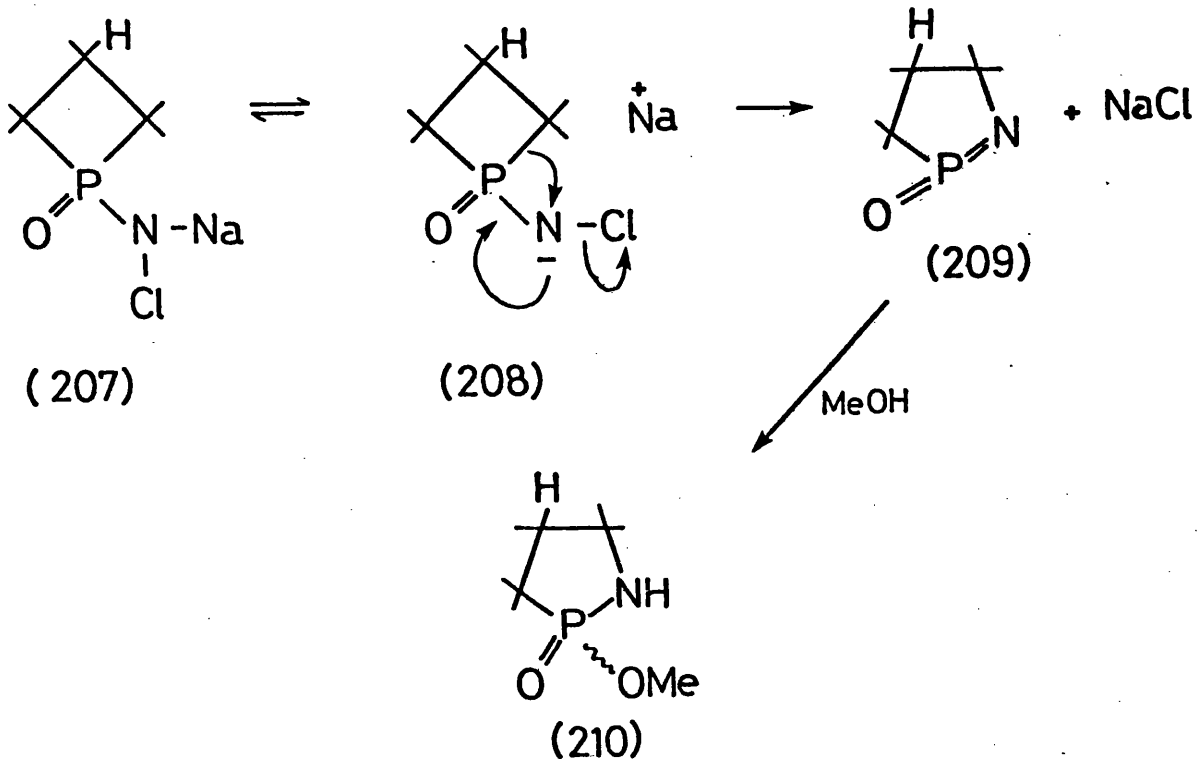


(206)

Ring expansion and ring opening reactions of the azido-phosphetan system have been discussed in Chapter 1 of this work. With the marked ring expansion tendency of the phosphetan system in mind, attempts were made to synthesise the sodium salt of t-1-(N-chloroamino)-2,2,r-3,4,4-pentamethylphosphetan-1-oxide (207).

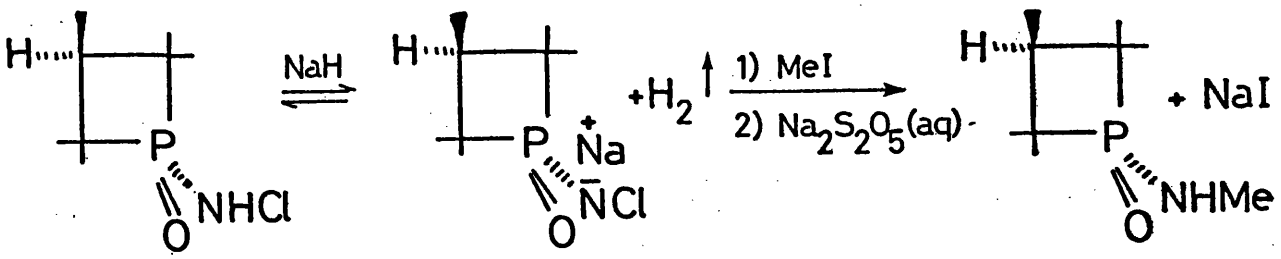
It was envisaged that in methanol the anion (208) might rearrange

by migration of a ring carbon atom to the exocyclic nitrogen and the expulsion of chloride ion; the metaphosphonimidate (209) would react with the methanol solvent to yield the 1,2-azophospholidine derivative (210) (a mixture of geometrical isomers).

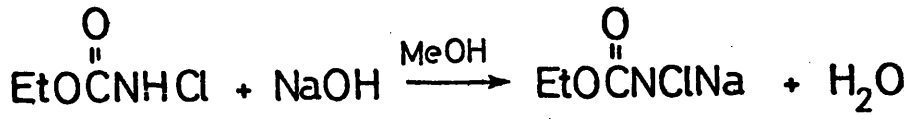


Attempts to prepare the salt (207) by reacting t-1-(N,N-dichloroamino)-2,2,r-3,4,4-pentamethylphosphetan-1-oxide (140) and the corresponding N-monochloro derivative (141) with sodium hydride in benzene gave a low yield of the amide (139). Performing the same reaction with (141) in the presence of methyl iodide afforded t-1-(N-methylamino)-2,2,r-3,4,4-pentamethylphosphetan-1-oxide (147) in 14% yield after reductive work up, consistent with the anion (208) being generated.

Metal salts of ethyl N-chlorocarbamate have been prepared by Saika and Swern;[120] in particular the sodium salt (212), a white, crystalline, non-hygroscopic solid, was prepared by treating ethyl N-chlorocarbamate (211) with sodium hydroxide in methanol at 0°.

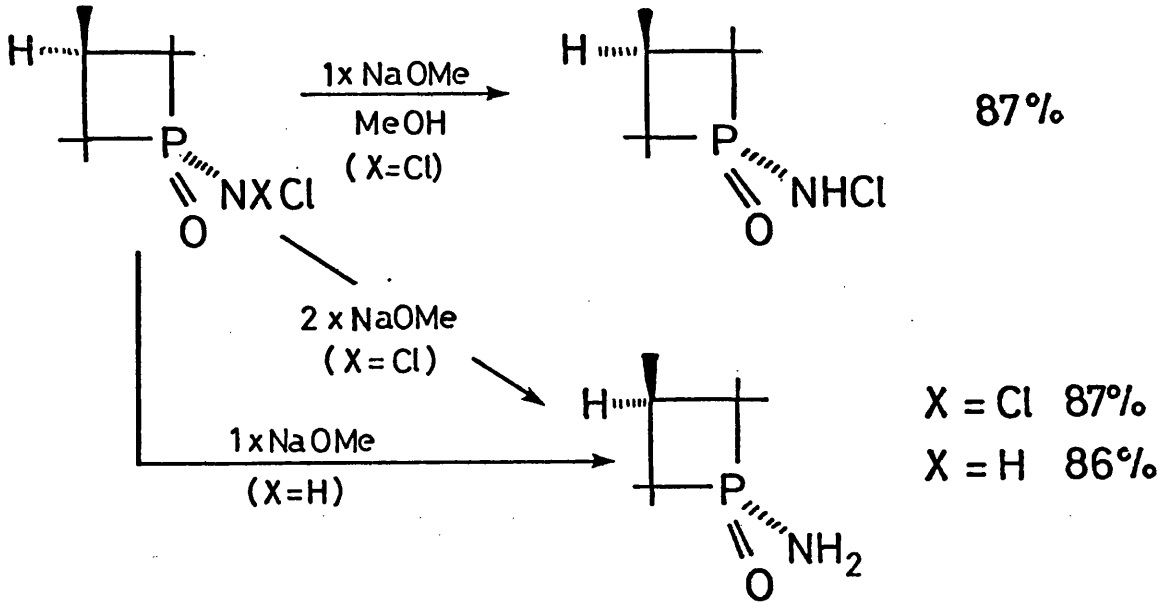


(141) (208) (147)

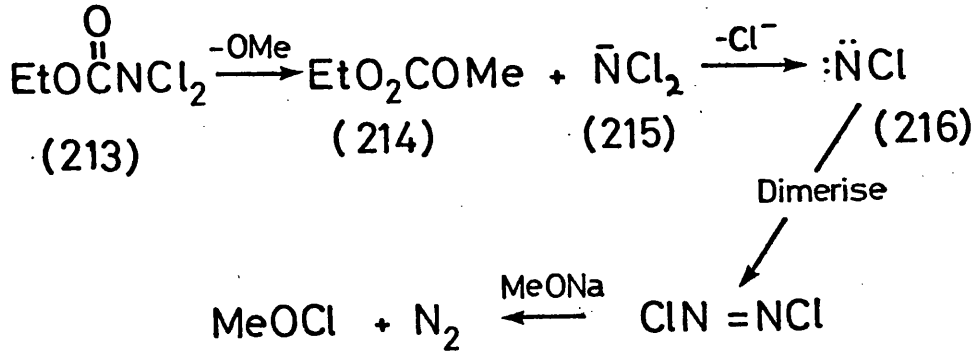


(211) (212)

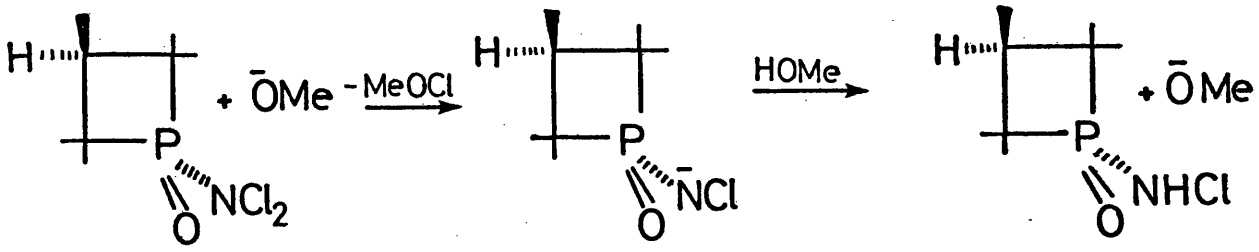
In methanol (140) and (141) reacted with, respectively, 2 moles and 1 mole of sodium methoxide to give the amide (139). The dichloroamide (140) also reacted with 1 mole of sodium methoxide to yield the monochloroamide (141). The sodium salt (207) was not isolated in any of these reactions.



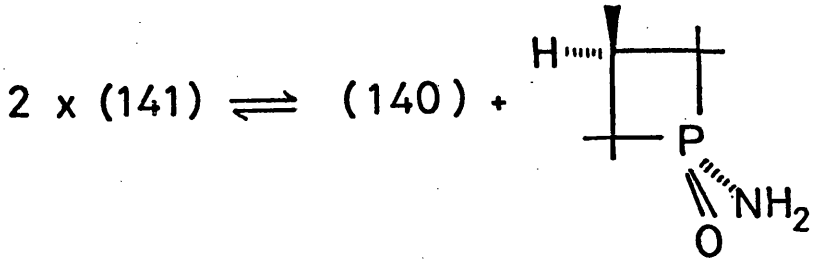
White and Koracic[121] have recently reported the decomposition of diethyl N,N-dichlorocarbamate (213) in methanol containing sodium methoxide. Ethyl methyl carbonate (214) was formed in high yield with consumption of 1.5 molar equivalents of sodium methoxide. They considered several mechanistic schemes including generation of chloronitrene, attack of methoxide on chlorine, and formation of an N-chlorocarbamate radical. Their data points to the first mechanism, which involves initial attack of methoxide on the carbonyl group with expulsion of the dichloroamino anion (215) and formation of ethyl methyl carbonate (214). The loss of chloride ion from (215) gives chloronitrene (216) which dimerises with subsequent loss of chlorine to yield nitrogen.



No product resulting from nucleophilic attack of methoxide ion at the phosphinyl phosphorus of (140) and (141) was observed. Formation of the amide (139) in both the reaction of (140) and (141) with methoxide ion probably only involves the reaction of (140) with methoxide ion.



(140) (141)



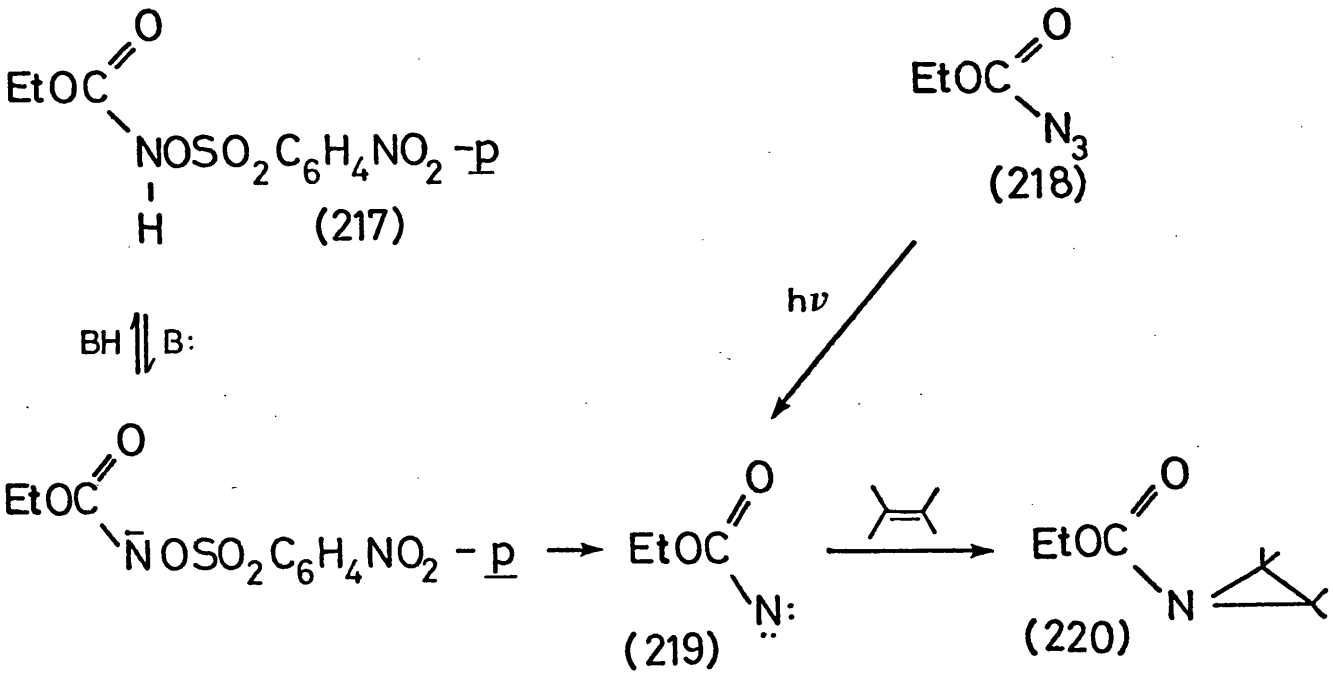
(139)

3 N-PHOSPHINYLTRIPHENYLARSINIMINES

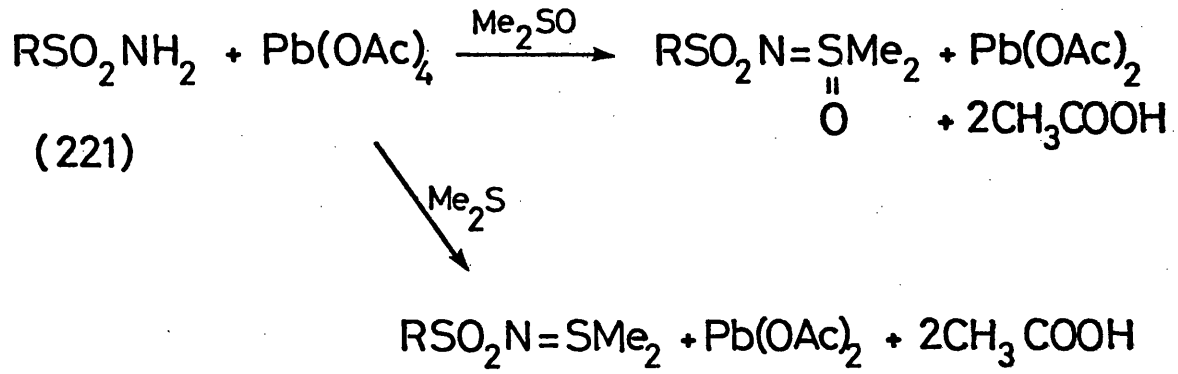
It was of interest to know whether the rearrangement products formed in the photolysis of dialkylphosphinic azides in protic solvents were formed *via* nitrene intermediates. A trap for the nitrenes was therefore required to see if the yield of the rearrangement product would be suppressed.

With nitrogen radicals and anions having been generated in the reactions of phosphinic N-chloroamides with phenylethylenes and base respectively, it was also of interest to see if nitrenes could be generated from these compounds and trapped.

Alkenes are recognised traps for nitrenes and they have been used, for example, to intercept ethoxycarbonyl nitrene (219). The nitrene, generated from N-(p-nitrobenzenesulphonyloxy)urethan (217) in the presence of base and also from the photochemical decomposition of ethoxycarbonyl azide (218), adds to the double bond of an alkene to yield the aziridine product (220).[122]



Sulphonyl nitrenes, generated by the action of lead tetraacetate on the sulphonamide (221) and of a base on the N-arylsulphonoxysulphonamides (222), have been trapped using dimethylsulphide and dimethylsulphoxide;[123] the nitrene generated by the action of copper on sodium



RSO_2NH_2 (221) + $Pb(OAc)_4$ —Me_2SO→ $RSO_2N{=}S(O){=}Me_2$ + $Pb(OAc)_2$ + $2CH_3COOH$

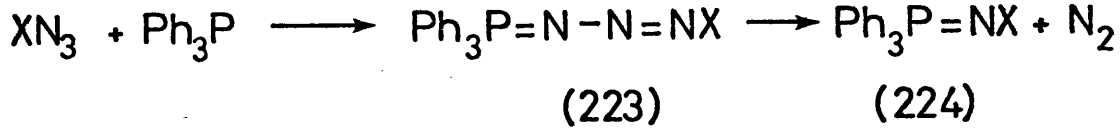
(221) —Me_2S→ $RSO_2N{=}SMe_2$ + $Pb(OAc)_2$ + $2CH_3COOH$

$ArSO_2NHOSO_2Ar$

(222)

N-chlorobenzenesulphonamide has also been trapped using dimethylsulphoxide.[124]

A timely report by Cadogan et al.[125] demonstrated that triphenylarsine is a particularly effective trap for nitrenes generated from azides, unlike triphenylphosphine[126] which reacts directly with the azides to yield intermediates (223) that decompose by loss of nitrogen to the phosphinimines (224). It was thus hoped to use triphenylarsine



$XN_3 + Ph_3P \longrightarrow Ph_3P{=}N{-}N{=}NX \longrightarrow Ph_3P{=}NX + N_2$

(223) (224)

to trap nitrenes generated from the phosphinic azides and phosphinic N-chloroamides.

The expected trapped products from the reactions, the arsinimines (225), were synthesised using the procedure of Cadogan et al.[127] Thus

$$R_2P(O)N = AsPh_3$$
(225)

the amide (139) was converted into (225) by reaction with triphenylarsine in the presence of lead tetraacetate (LTA). In the absence of LTA the reaction did not occur. LTA and triphenylarsine are known to react together to yield diacetoxy triphenylarsorane (226) and reaction of the phosphinic amides (139), (143) and (149) with the arsorane (226) yielded the arsinimines (225).[127]

Nitrenes have been postulated as intermediates in the lead tetraacetate oxidation of amides,[123,128] but in this present reaction a nitrene pathway seems unlikely.

$$Ph_3As + Pb(OAc)_4 \longrightarrow Ph_3As(OAc)_2 + Pb(OAc)_2$$

(226)

$\downarrow R_2P(O)NH_2$

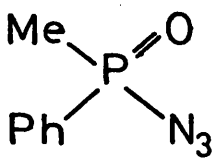
$$Ph_3As{=}NP(O)R_2 + 2AcOH$$

$\uparrow Ph_3As$

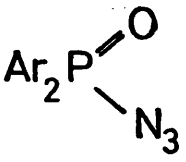
$$R_2P(O)NH_2 \xrightarrow{Pb(OAc)_4} R_2P(O)\ddot{N}:$$

Initially the reaction of the phosphinic azide (37) with triphenylarsine was investigated. Heating the azide with triphenylarsine

to 200°C resulted in no decomposition of the azide. This thermal stability of phosphinic azides has also been observed for the compounds (4)[8] and (227).[16]

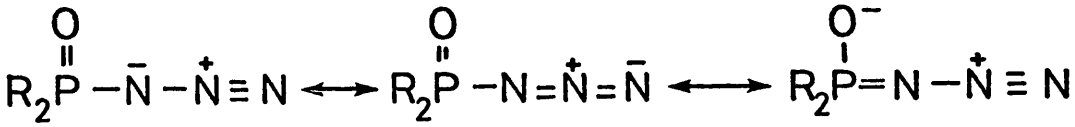


(4)



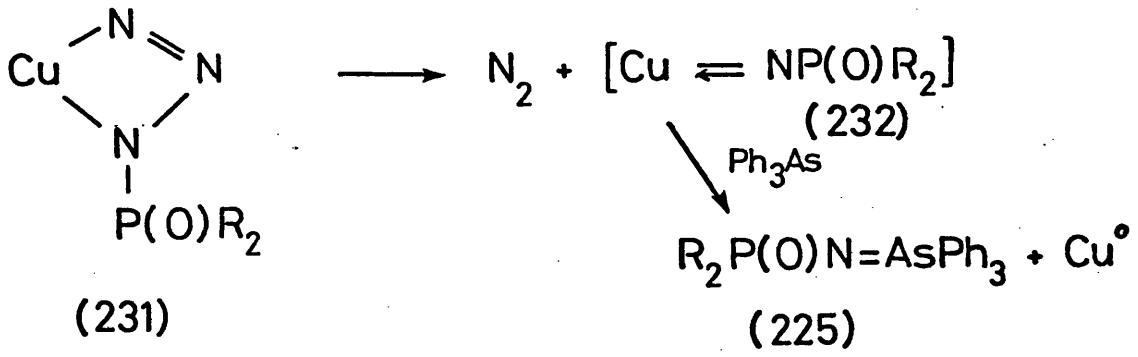
(227)

Resonance structures (228)-(230) can be written for the phosphinic azides and it has been suggested that the existence of the structure (230), which involves pπ-dπ electron delocalisation between phosphorus and the adjacent nitrogen atom accounts for their thermal stability.



(228) (229) (230)

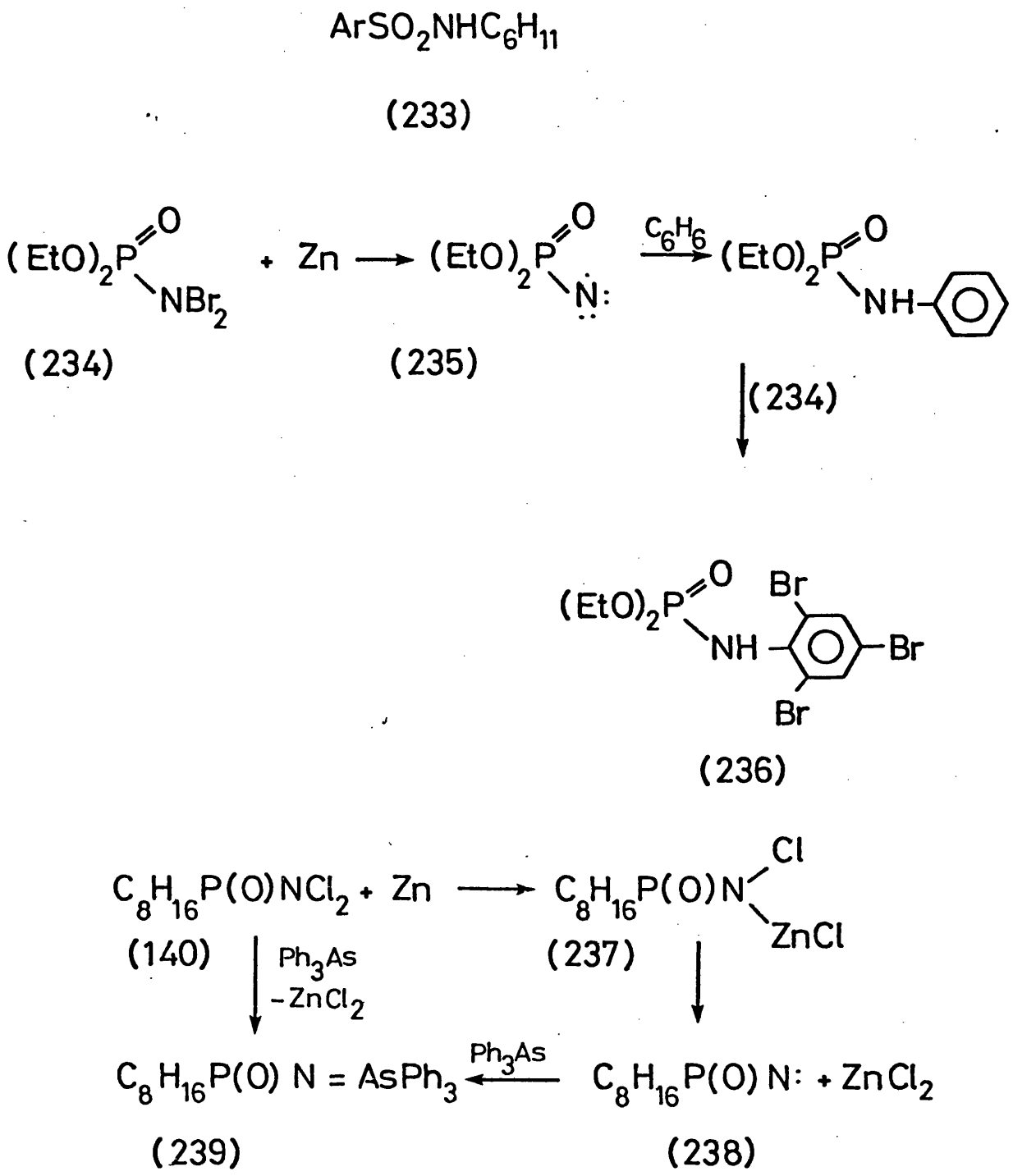
The addition of copper powder to the azide (37) and triphenylarsine lowered the decomposition temperature of the azide to 165°. At the decomposition temperature nitrogen evolution occurred with the formation of the arsinimines (225, R = Bu^t), t-1-azido-2,2,r-3,4,4-pentamethylphosphetan-1-oxide (17) reacted similarly:[129] however the formation of the arsinimine was shown only by tlc, by comparison with the authentic specimen. In the presence of copper the reaction most likely proceeds via the decomposition of an azide-copper complex (231) to an intermediate nitrene-copper species (232), as suggested by Kwart and Khan[130] for the catalysed decomposition of benzenesulphonyl azide.



Attempted photolysis of di-t-butylphosphinic azide (37) in the presence of triphenylarsine in cyclohexane gave a highly coloured solution; no nitrogen evolution was observed, and the azide remained unchanged. It was later noted in the literature[131] that triphenylarsine decomposes photolytically and thus is of little use as a trapping agent in photochemical reactions.

Breslow and Sloan[132] isolated a C-H insertion product (233) from the reaction of N,N-dichloro-p-toluenesulphonamide with zinc in cyclohexane and suggested that its formation could be via a nitrene. Zwierzak and Zawadski[133] have generated diethylphosphoryl nitrene (235) by the reaction of diethyl N,N-dibromophosphoramidate (234) with zinc in boiling benzene, as shown by the isolation of the tribromo-substituted phosphoramidate (236).

It was envisaged that if the nitrene (238) was generated from t-1-(N,N-dichloroamino)-2,2,r-3,4,4-pentamethylphosphetan-1-oxide (140), using zinc in the presence of triphenylarsine it would be trapped as the arsinimine (239). Active zinc,[134] prepared by heating a mixture of zinc bromide and potassium in tetrahydrofuran, reacted with (140) in the presence of triphenylarsine to yield the arsinimine (239). The reaction may proceed via an intermediate zinc complex (237) that decom-



poses to the nitrene (238). However, the reaction was found to proceed even in the absence of zinc, and this casts doubt on the intermediacy of a nitrene.

This type of reaction between N-chloroamides and triphenylarsine has been used by others to prepare arsinimines. Thus the arsinimine (240) has been prepared from both sodium N-chlorotoluene-p-sulphon-

amide[135] and N,N-dichlorotoluene-p-sulphonamide.[136]

$$\underline{p}\text{-}CH_3C_6H_4SO_2N{=}AsPh_3$$

(240)

The questions still remain as to whether the rearrangement products isolated in the photolyses of dialkylphosphinic azides are formed via nitrenes and whether nitrenes can be generated from phosphinic N-chloroamides.

EXPERIMENTAL

Instrumentation

Ir spectra were recorded with Perkin-Elmer 237 and 257 instruments as Nujol mulls except otherwise stated. Mass spectra were recorded with an A.E.I. MS9 instrument ; the results are presented with the molecular ion first unless otherwise stated.

Routine ^{1}H nmr spectra were recorded with a Varian T-60 spectrometer and tetramethylsilane as internal standard and 100 MHz ^{1}H spectra with a Jeol JNM-PS-100 spectrometer.

^{31}P chemical shifts were obtained by decoupling ^{1}H nmr spectra using a HD60 heteronuclear decoupler (NMRSpecialities) and noting the irradiating frequency; they are quoted relative to external 85% phosphoric acid.

Melting points were recorded on a Kofler hot-stage apparatus except where otherwise stated and are uncorrected.

Glc analyses were performed on a Pye 104 flame ionisation chromatograph fitted with 1.5 m x 4 mm i.d. glass columns packed with 3% silicone OV17, 3% NPGS, 3% APL, and 10% E30 on silanised 100-120 mesh diatomite C 'Q'.

Photochemical reactions in protic solvents employed a 125W medium-pressure mercury lamp in a water-cooled quartz envelope, surrounded by the stirred reaction mixture; reactions in aprotic solvents employed a Rayonette reactor with light of wavelength 254 nm.

General Details

Solvents were dried as follows: Diethyl ether and hydrocarbon

solvents over sodium wire; benzene, dichloromethane and acetonitrile were refluxed over and distilled from calcium hydride; dimethylformamide (DMF) was distilled under water pump pressure from calcium hydride; tetrahydrofuran (THF) was refluxed over and distilled from lithium aluminium hydride; t-butylamine and pyridine were refluxed over and distilled from potassium hydroxide pellets; methanol and ethanol were refluxed over their magnesium alkoxides and distilled; dry peroxide-free propan-2-ol was obtained using the method of Vogel.[137] Potassium t-butoxide was sublimed under vacuum.

Alumina refers to Spence type 'H'. Alumina tlc plates were dried in an oven for 24h and left a minimum of 3 days before use.

Evaporation was performed on a rotary evaporator. Gas volumes produced in photochemical and thermal reactions were measured using a gas burette.

All reactions unless otherwise stated were carried out under an atmosphere of dry, oxygen-free nitrogen.

Petroleum refers to the fraction b.p. 60-80°.

t-Butyl Hypochlorite. - Following the procedure of Mintz and Walling,[138] t-butyl hypochlorite was prepared in 73% yield, $\delta(CDCl_3)$ 1.27 (s). The material obtained was used without any further purification.

Synthesis of Phosphinic Azides

Di-t-butylchlorophosphine. - Following the procedure of Scherer and Schieder,[139] di-t-butylchlorophosphine, b.p. 74-78° at 0.5 mmHg (lit.,[139] 48° at 0.3 mmHg), $\delta(CDCl_3)$ 1.18 (d, J_{PH} 12Hz), was obtained in 46% yield.

Di-t-butylphosphinic Chloride. - (i) Di-t-butylchlorophosphine (3.3 g, 18.2 mmol) in dichloromethane (50 ml) was cooled to 0° in an ice bath. Oxidation was achieved by adding dropwise 30% hydrogen peroxide (40 ml), over a period of 1h, with rapid stirring. The organic phase was separated, washed with saturated sodium hydrogen carbonate solution (2 x 15 ml) and water (20 ml), dried ($MgSO_4$), and the solvent evaporated off to yield a colourless solid (2.9 g). Chromatography on silica (100 g) and elution with ether afforded di-t-butylphosphinic chloride (1.8 g, 9.0 mmol, 49%), m.p. 78-81° (lit.,[140] 80.1-80.9°) from petroleum, $\nu_{max.}$ (Nujol) 1231 and 1210 cm^{-1} (P:O), $\delta(CDCl_3)$ 1.35 (d, J_{PH} 16Hz).

(ii) Dry oxygen was bubbled (20h) through a solution of di-t-butylchlorophosphine (5.7 g, 31.6 mmol) in xylene (40 ml) maintained at 100°.[4] The solvent was evaporated off. Chromatography (silica, with ether as eluant) gave di-t-butylphosphinic chloride (2.9 g, 14.8 mmol, 47%) m.p. 78-81° from petroleum with ^1H nmr and ir spectra identical to those of the product previously isolated.

t-1-Chloro-2,2,r-3,4,4-pentamethylphosphetan-1-oxide. - Using the method of Jungermann and co-workers,[79] t-1-chloro-2,2,r-3,4,4-pentamethylphosphetan-1-oxide, m.p. 72-74.5° (lit.,[79] 74-75°) from petroleum, was obtained in 60% yield, $\nu_{max.}$ (Nujol) 1260 and 1220 cm^{-1} (P:O),

$\delta(CDCl_3)$ 1.75 (1H, dxq, J_{HH} 7 and J_{PH} 4Hz), 1.34 (6H, d, J_{PH} 20Hz), 1.31 (6H, d, J_{PH} 20Hz), and 0.93 (3H, dd, J_{HH} 7 and J_{PH} 1.5Hz).

Di-isopropylphosphinic Acid. - An approximately 3M solution of isopropyl magnesium bromide in ether was prepared from 2-bromopropane (246 g, 2.0 mol) and magnesium turnings (48.6 g, 2.0 g atom). To this was added thiophosphoryl chloride (91 g, 0.54 mol) in ether (100 ml) over a period of 3h, the temperature being maintained at 0-5°. The mixture was stirred overnight and then poured slowly onto crushed ice (400 g) and 2M sulphuric acid (650 ml) added cautiously. The organic layer was separated and the aqueous phase extracted with ether (2 × 300 ml). The combined organic extracts were concentrated to a viscous green liquid (crude tetraisopropylbisphosphine-bisulphide), which was oxidised by addition of 30% nitric acid (330 ml), during which time the temperature was kept below 80°, and then heating of the mixture at 100° for 1h. The solution was transferred to an evaporating basin and heated on a steam bath to drive off unreacted nitric acid, water being added repeatedly to replace that lost by evaporation. The material so obtained was dissolved in water (1.0 l) and the solution heated to 80° while lead monoxide (ca. 400 g) was added (to precipitate sulphate ions) until the solution was alkaline to litmus. The precipitated lead sulphate was filtered off and washed with water (1.0 l). Removal of any soluble lead salts was achieved by bubbling hydrogen sulphide through the solution. Complete precipitation could be easily detected by cutting off the hydrogen sulphide supply, allowing the precipitate to settle, to yield a colourless upper solution, then bubbling hydrogen sulphide through again; when no black precipitate formed the reaction was complete. The precipitate was filtered and the filtrate concentrated on a rotary evaporator (3-4h) and finally at 100° under vacuum.

The crude product was distilled to yield di-isopropylphosphinic acid (30.2 g, 0.2 mol, 37%). Crystallisation from petroleum gave the acid m.p. 48-50° (lit.,[141] 47.5-49.5°), $\nu_{max.}$(Nujol) broad absorptions 3000-1900 and 1600 cm^{-1} (OH), $\delta(CDCl_3)$ 12.2 (1H, s, OH), ca. 1.9 (2H, dx septet, J_{PH} 2Hz, J_{HH} 6Hz), and 1.13 (12H, dd, J_{PH} 16Hz, J_{HH} 6Hz).

Diethylphosphinic Acid. - The crude tetraethylbisphosphine-bisulphide prepared from thiophosphoryl chloride (53.0 g, 0.31 mol) and ethyl magnesium iodide (ca. 1.0 mol) was dissolved in water (300 ml) and oxidised at 80° by dropwise addition of 30% hydrogen peroxide (50 ml). After boiling under reflux for 1h, the precipitated sulphur was removed by filtration, a slight excess of freshly precipitated silver oxide added, the suspension heated for 5 min., and the excess silver oxide filtered off. The volume of solution was reduced to 50 ml on a rotary evaporator, 12M hydrochloric acid (50 ml) was added, the mixture stirred vigorously, and the precipitate was filtered off. Removal of water (rotary evaporator) followed by distillation gave diethylphosphinic acid (16.0 g, 0.13 mol, 42%) b.p. 174° at 1.5 mmHg (lit.,[142] b.p. 194-195° at 21 mmHg).

Di-isopropylphosphinic Chloride. - To di-isopropylphosphinic acid (2.7 g, 18 mmol) in benzene (30 ml) was added, dropwise with stirring, thionyl chloride (4.3 g, 36 mmol). The reactants were heated (1.5h) at 92-95°. Volatile material was removed on a rotary evaporator, the last traces of thionyl chloride being removed by addition, and evaporation of, a portion of fresh benzene. The colourless oil obtained was distilled using a bulb-to-bulb distillation apparatus to yield di-isopropylphosphinic chloride (2.85 g, 16.9 mmol, 94%) b.p. (oven temp.) 68-78° at 1.0 mmHg (lit.,[141] 50° at 0.2 mmHg), $\nu_{max.}$(liquid film) 1260

cm^{-1} (P:O), $\delta(CDCl_3)$ 2.28 (2H, 7 lines visible, J_{HH} 6Hz), 1.29 (6H, dd, J_{PH} 19 and J_{HH} 6Hz), and 1.26 (6H, dd, J_{PH} 19 and J_{HH} 6Hz).

Diethylphosphinic Chloride. - In a similar manner diethylphosphinic acid gave the acid chloride (94%), b.p. 54-56° at ca. 0.5 mmHg (lit.,[143] 54° at 0.25 mmHg), $\nu_{max.}$ (liquid film) 1215 cm^{-1} (P:O), $\delta(CDCl_3)$ to a first order approximation 2.17 (4H, overlapping dxq, J_{PH} 10 and J_{HH} 7Hz) and 1.32 (6H, overlapping dxt, J_{PH} 20.5 and J_{HH} 7Hz).

Diethylphosphinic Azide[2]. - Diethylphosphinic chloride (2.8 g, 19.9 mmol) in acetonitrile (30 ml) was added dropwise (4h) to a vigorously stirred, ice-cooled, mixture of pyridine (3.75 g, 47.4 mmol), sodium azide (2.6 g, 40 mmol), and acetonitrile (20 ml). After the addition the mixture was filtered and the solvent evaporated off to give an orange-brown viscous liquid; bulb-to-bulb distillation afforded diethylphosphinic azide (1.8 g, 12.2 mmol, 61%) b.p. (oven temp.) 55-60° at 0.5 mmHg (lit.,[2] b.p. 97° at 8 mmHg), $\nu_{max.}$ (liquid film), 2120 (N_3), and 1270 and 1210 cm^{-1} (P:O), $\delta(CDCl_3)$ to a first order approximation 1.87 (4H, overlapping dxq, J_{PH} 12 and J_{HH} 7Hz) and 1.21 (6H, overlapping dxt, J_{PH} 18 and J_{HH} 7Hz).

Di-isopropylphosphinic Azide. - Di-isopropylphosphinic chloride (2.4 g, 14 mmol) in dimethylformamide (7 ml) was added dropwise (50 min) to a vigorously stirred mixture of pyridine (2.55 g, 28 mmol), sodium azide (1.85 g, 28 mmol), and DMF (10 ml). The reactants were stirred for a further 1h, ether (30 ml) was added, and the mixture was filtered under dry nitrogen. Volatile material was removed and bulb-to-bulb distillation gave di-isopropylphosphinic azide (1.8 g, 10.3 mmol, 74%), b.p. (oven temp.) 72-78° at 0.5 mmHg, $\nu_{max.}$ (liquid film) 2125 and 2115

(N_3) and 1270 and 1210 cm^{-1} (P:O), δ($CDCl_3$) 2.03 (1H, dx septet, J_{HH} ca. 7 and J_{PH} ca. 7Hz), 1.23 (3H, dd, J_{PH} 16 and J_{HH} 4Hz), and 1.16 (3H, dd, J_{PH} 16 and J_{HH} 4Hz) (Found: C, 40.4; H, 8.0; N, 23.8%. $C_6H_{14}N_3OP$ requires C, 41.1; H, 8.1; N, 24.0); this analysis corresponds approximately to $C_6H_{14}N_3OP \cdot 0.17\ H_2O$.

Di-t-butylphosphinic Azide. - Di-t-butylphosphinic chloride (1.7 g, 8.6 mmol), pyridine (1.7 g, 21.5 mmol), and sodium azide (1.3 g, 20 mmol) were added to DMF (15 ml) and the mixture was stirred vigorously and heated (4h) in an oil bath maintained at 95-105°. Ether (30 ml) was added, the mixture filtered, and volatile material removed on a rotary evaporator to give an orange-brown oil. Bulb-to-bulb distillation yielded di-t-butylphosphinic azide (1.4 g, 6.8 mmol, 79%), b.p. (oven temp.) 75-80° at 0.5 mmHg, $\nu_{max.}$ (liquid film), 2140 (N_3) and 1280 cm^{-1} (P:O), δ($CDCl_3$) 1.28 (d, J_{PH} 15Hz) (Found: C, 45.8; H, 8.8; N, 20.0. $C_8H_{18}N_3OP$ requires C, 47.3; H, 8.9; N, 20.7%); this analysis corresponds to $C_8H_{18}N_3OP \cdot 0.37\ H_2O$.

Photolysis of Di-t-butylphosphinic Azide in Protic Solvents

(i) In Methanol. - Di-t-butylphosphinic azide (0.541 g, 2.67 mmol) was photolysed (19h) in methanol (60 ml) and the progress followed using a gas burette and noting the volume of nitrogen evolved (63.6 ml; theoretical volume 59.6 ml). Volatile material was evaporated off to yield 0.585 g of a semi-solid material which on analysis (glc, 3% OV17) showed one major and two minor products. One of the minor peaks was shown to be unreacted azide by comparison with the authentic specimen.

Preparative tlc (alumina) and elution with ether gave two isomeric products; methyl N,P-di-t-butylphosphonamidate (0.313 g, 1.51 mmol, 57%), m.p. 170.5-171.5 from petroleum (b.p. 40-60°), $\nu_{max.}$ (Nujol) 3210 (NH), 1190 and 1185 (P:O), 1050, 1030 and 1020 cm^{-1}, $\delta(CDCl_3)$ 3.51 (3H, d, J_{POCH} 11Hz), ca. 2.03 br (1H, s, NH), 1.30 (9H, s), and 1.09 (9H, d, J_{PH} 15Hz), m/e 192 (M^+-Me), 161, 119, 104 and 78 (Found: C, 52.3; H, 10.8; N, 6.5%. $C_9H_{22}NO_2P$ requires C, 52.2; H, 10.7; N, 6.8%), and (N-methoxy)di-t-butylphosphinic amide (0.045 g, 0.217 mmol, 8.1%), m.p. 98-99° from petroleum, $\nu_{max.}$ (Nujol) 3105 (NH) and 1165 cm^{-1} (P:O), $\delta(CDCl_3)$ 6.10 br (1H, s, NH), 3.53 (3H, s), and 1.28 (18H, d, J_{PH} 13Hz), m/e 207 (M^+), 177 and 121 (100%).
(Found: C, 52.4; H, 10.8; N, 6.5. $C_9H_{22}NO_2P$ requires C, 52.2; H, 10.7; N, 6.8%).

(ii) In Ethanol. - Di-t-butylphosphinic azide (0.542 g, 2.67 mmol) was photolysed (20.5h) in ethanol (100 ml). Volatile material was evaporated off to yield a glassy solid which on analysis (glc, 3% OV17) showed two products, one major and one minor.

Preparative tlc (alumina) on a portion equivalent to 1.07 mmol

starting azide and elution with 6% methanol in ether afforded as the upper band ethyl N,P-di-t-butylphosphonamidate (0.147 g, 0.665 mmol, 62.3%), m.p. 120-122° (sealed tube) from petroleum (b.p. 40-60°), $\nu_{max.}$ (Nujol) 3230 (NH) and 1180 cm^{-1} (P:O), $\delta(CDCl_3)$ 3.90 (2H, m, P-OCH_2), 2.63 br (1H, s, NH), 1.23 (9H, s, -NBu^t), 1.03 (9H, d, J_{PH} 16Hz, Bu^t-P), and signals due to the methyl of the ethoxyl group obscured by the singlet and doublet at δ1.23 and 1.03 respectively, m/e 206 (M^+-Me), 178 and 57. (Found: C, 54.2; H, 10.9; N, 6.0. $C_{10}H_{24}NO_2P$ requires C, 54.3; H, 10.9, N, 6.3%).

The lower band gave di-t-butylphosphinic amide (0.045 g, 0.25 mmol, 23.8%), m.p. 199-200°C from benzene. The ^1H nmr and ir spectra were identical to those of the authentic specimen.

(iii) In Isopropanol. - Di-t-butylphosphinic azide (0.554 g, 2.73 mmol) in isopropanol (100 ml) was photolysed (5h) and the progress of the reaction followed using a gas burette and noting the volume of nitrogen evolved (63.4 ml; theoretical nitrogen volume 61.2 ml). Analysis (glc) of the crude reaction mixture showed one major and one minor product. Preparative tlc (alumina) on a portion equivalent to 1.07 mmol starting azide and elution with 6% methanol in ether gave as the upper band isopropyl N,P-di-t-butylphosphonamidate (0.069 g, 0.29 mmol, 27%), m.p. 148.5-150° from petroleum (b.p. 40-60°), $\nu_{max.}$ (Nujol) 3250 (NH), 1245, 1190 (P:O), and 990 cm^{-1}, $\delta(CDCl_3)$ (100 MHz) 4.70 (1H, m, POCH), 1.97 br (1H, s, NH), 1.36 (9H, s, -NBu^t), 1.30 (3H, d, J_{HH} 6Hz, CH-CH_3), 1.26 (3H, d, J_{HH} 6Hz, CH-CH_3), and 1.12 (9H, d, J_{PH} 16Hz, P-Bu^t), m/e 220 (M^+-Me), 178 (M^+-Bu^t), 120, 105 and 78 (Found: C, 56.0; H, 11.0; N, 5.9. $C_{11}H_{26}NO_2P$ requires C, 56.1; H, 11.1; N, 5.95%).

The lower band yielded di-t-butylphosphinic amide (0.123 g, 0.695 mmol, 64%), m.p. 199-200° from benzene. The ^1H nmr and ir spectra were

identical to those of the authentic sample previously prepared.

(iv) In t-Butanol. - Di-t-butylphosphinic azide (0.554 g, 2.73 mmol) was photolysed (5h) in t-butanol (100 ml). The flow of water through the reaction vessel was adjusted so that the heat of the UV lamp kept the t-butanol in the liquid state. Preparative tlc (alumina) on a portion equivalent to 1.07 mmol starting azide gave as the upper band t-butyl N,P-di-t-butylphosphonamidate (0.17 g, 0.68 mmol, 64%), m.p. 137-139° (sealed tube) from petroleum (b.p. 40-60°), $\nu_{max.}$ (Nujol) 3280 (NH), 1240 and 1190 cm^{-1} (P:O), $\delta(CDCl_3)$ 1.43 (9H, s, OBu^t), 1.30 (9H, s, NBu^t), and 1.07 (9H, d, J_{PH} 16Hz), m/e 234 (M^+-Me), 178 (100%), 78 and 57 (Found: C, 57.4; H, 11.2; N, 5.6. $C_{12}H_{28}NO_2P$ requires C, 57.8; H, 11.3; N, 5.6%).

Glc analysis of the product isolated from the lower band indicated the presence of di-t-butylphosphinic amide by comparison with the authentic specimen.

A further quantity of the crude reaction mixture equivalent to 1.07 mmol starting azide was treated in the above manner in order to isolate the phosphinic amide. The combined portions (from preparative tlc) containing the amide were rechromatographed and eluted with 6% methanol in ether to yield as the lower band di-t-butylphosphinic amide (0.025 g, 0.143 mmol, 6.7%), m.p. 199-200° from benzene, having ^1H nmr and ir spectra identical to those of the authentic specimen.

The second band (from the origin) yielded a product that could not be purified but nmr analysis indicated (N-t-butoxy)-di-t-butylphosphinic amide, $\delta(CDCl_3)$ 1.30 (d, J_{PH} 14Hz, P-Bu^t_2) and 1.22 (s, $NOBu^t$).

(v) In t-Butylamine. - Di-t-butylphosphinic azide (0.50 g, 2.46 mmol) was photolysed (27h) in t-butylamine (100 ml). Volatile material

was removed and chromatography (alumina) and elution with ether gave t-butyl N,N'-di-t-butylphosphonamide (0.451 g, 1.82 mmol, 74%), m.p. 178-180° (sealed tube) (lit.,[144] 181-182°), $\nu_{max.}$(Nujol) 3235 (NH), 1390, 1365, and 1245, 1225, and 1175 cm^{-1} (P:O), $\delta(CDCl_3)$ ca. 1.9 br (2H, s, NH), 1.28 (18H, s, N-Bu^t), and 1.08 (9H, d, J_{PH} 14Hz, P-Bu^t), m/e 248 (M^+), 233 (M^+-Me), 191 (M^+-Bu^t), 177, 135, 120, 118, and 104 (Found: C, 58.3; H, 12.0; N, 11.4. $C_{12}H_{29}N_2OP$ requires C, 58.0; H, 11.8; N, 11.3%).

Photolysis of Di-isopropylphosphinic Azide in Protic Solvents

(i) In Methanol. - Di-isopropylphosphinic azide (0.794 g, 4.53 mmol) was photolysed (17h) in methanol (100 ml). The equivalent of 2.72 mmol starting azide, after removal of all volatile material, was chromatographed (alumina) and eluted with 6% methanol in ether to yield methyl N,P-di-isopropylphosphonamidate (0.345 g, 1.93 mmol, 71%) identified from nmr and ir spectra, ν_{max} (CCl_4) 3180 cm^{-1} (NH), $\delta(CDCl_3)$ ca. 3.87 br (1H, s, NH) exchanges with D_2O, 3.57 (3H, d, J_{PH} 11Hz, P-OMe), ca. 3.25 (1H, m, $NCHMe_2$) ca. 1.67 (1H, m, $P\text{-}CHMe_2$), and 1.12-0.88 (12H, m, $P\text{-}C\text{-}CH_3$ and $N\text{-}C\text{-}CH_3$), and di-isopropylphosphinic amide (0.020 g, 0.134 mmol, 4.9%), m.p. 135-137° from petroleum. The ^1H nmr and ir spectra were identical to those of the authentic specimen.

In a following experiment, from the photolysis of di-isopropylphosphinic azide (0.634 g, 3.622 mmol), the equivalent of 0.543 mmol starting azide yielded from tlc (alumina), and elution (6% methanol in ether) crude (N-methoxy) di-isopropylphosphinic amide (0.035 g, 0.196 mmol, 36%). Crystallisation from petroleum gave a product m.p. 57-59° (sealed tube) with ^1H nmr and ir spectra identical to those of the authentic specimen.

(ii) In Ethanol. - Di-isopropylphosphinic azide (0.515 g, 2.94 mmol) was photolysed (20h) in ethanol (100 ml). Preparative tlc of a portion equivalent to 1.47 mmol starting azide and double elution (3% methanol in ether) gave as the upper band ethyl N,P-di-isopropylphosphonamidate (0.107 g, 0.554 mmol, 38%) identified by nmr and mass spectroscopy, $\delta(CDCl_3)$ (100MHz) 4.0 (2H, m, OCH_2), 3.4 (1H, m, Me_2CHN), 2.4 br (1H, t, NH), 1.84 (1H, m, $Me_2CH\text{-}P$), and 1.37-1.05 [15H, m, $(CH_3)_2CHP$, $(CH_3)_2CHN$, and CH_3CH_2O], m/e 193 (M^+), 178 ($M^+\text{-}CH_3$), 150

(M^+-Pr^i), 148 (M^+-EtO), 135 (M^+-$NHPr^i$), 122, 106, 105, 93, 80, 65, and 58 (Pr^iNH^+).

The lower band gave di-isopropylphosphinic amide (0.100 g, 0.67 mmol, 46%), m.p. 135-138° from petroleum. The ^1H nmr and ir spectra were identical to those of the authentic specimen.

(iii) In Isopropanol. - Di-isopropylphosphinic azide (0.504 g, 2.9 mmol) was photolysed (3h) in isopropanol (100 ml). Chromatography (alumina) and elution (3% methanol in ether) afforded di-isopropylphosphinic amide (0.374 g, 2.5 mmol, 86%), m.p. 136-138° from petroleum, with identical ^1H nmr and ir spectra to those of the authentic specimen.

Methyl Diethylphosphinate. - Diethylphosphinic chloride (1.4 g, 10.0 mmol) in methanol (10 ml) was added dropwise, with stirring to a cooled (0°) solution of sodium methoxide (1.1 g, 20.4 mmol) in methanol (10 ml). The solution was allowed to warm up to room temperature, stirred (1h), filtered, and the solvent evaporated off. Bulb-to-bulb distillation (oven temp. 86-92° at ca. 13 mmHg) gave the title compound (0.40 g, 2.9 mmol, 29%) (lit.,[145] 86° at 12 mmHg), $\nu_{max.}$(liquid film) 1460, 1220 (P:O), 780 and 770 cm^{-1}, $\delta(CDCl_3)$ 3.60 (3H, d, J_{PH} 10Hz, OMe) and 2.0-0.82 (10H, m, Et_2).

Photolysis of Diethylphosphinic Azide in Methanol. - Diethylphosphinic azide (0.640 g, 4.35 mmol) was photolysed (23h) in methanol (100 ml). Chromatography (alumina) on a portion equivalent to 2.18 mmol starting azide (elution with ether containing progressively more methanol) gave methyl diethylphosphinate (0.120 g, 0.88 mmol, 40%), nmr and ir spectra identical to those of the authentic specimen, and methyl N,P-diethylphosphonamidate (0.055 g, 0.36 mmol, 17%) identified only from its ^{1}H nmr spectrum, $\delta(CDCl_3)$ (100MHz) 3.66 (3H, d, J_{PH} 12Hz, P·OMe), 2.97 (2H, m, NH·CH_2Me), 1.94-1.54 (m, 2H, Me·CH_2·P), and 1.37-1.00 (6H, m, CH_3·CH_2·P and CH_3·CH_2N).

Control Experiments for Photochemical Reactions in Protic Solvents

Stirring the appropriate azide in the protic solvent for the same period as used in the photolysis, but without irradiation, resulted in no decomposition of the azide except in the case of:

(i) Diethylphosphinic azide in methanol which eventually gave a quantitative yield of methyl diethylphosphinate; ^{1}H nmr and ir spectra were identical to those of the authentic specimen, and

(ii) Di-t-butylphosphinic azide in t-butylamine, for which the products of decomposition were not investigated.

Photolysis of Di-t-butylphosphinic Azide in Aprotic Solvents

(i) In Benzene. - Di-t-butylphosphinic azide (0.524 g, 2.58 mmol) was photolysed (22h) in benzene (500 ml) and the volatile material removed to yield a red-brown oil. Chromatography (alumina) with ether as eluant gave 0.140 g of a mixture of two compounds as shown by tlc.

Preparative tlc (alumina) of the mixture (elution with ether) gave as the upper band one isomer of N,P-di-t-butylphosphonamidic anhydride (0.0513 g, 0.139 mmol, 10.8%), m.p. 192-195° from petroleum, $\nu_{max.}$ (Nujol) 3260 (NH), 1530, 1253 and 1210 (P:O) cm^{-1}, $\delta(CDCl_3)$ (100MHz) 2.52 br (1H, s, NH), 1.37 (9H, s, N-Bu^t), and 1.20 (9H, d separated by a broad hump, J_{PH} 18Hz), m/e 353 (M^+-CH_3), 297, 240 and 110 (Found: C, 52.2; H, 10.5; N, 7.6. $C_{16}H_{38}N_2O_3P_2$ requires C, 52.2; H, 10.4; N, 7.6%).

The lower band gave a second isomer of N,P-di-t-butylphosphonamidic anhydride (0.059 g, 0.160 mmol, 12.5%) m.p. 106-109° from petroleum, $\nu_{max.}$ (Nujol) 3400, 3300, 3200 (NH), 1700, 1425, 1395, 1368, 1253 and 1210 (P:O), 1045 and 915 cm^{-1}, $\delta(CDCl_3)$ (100MHz) 2.8 br (1H, s, NH), 1.34 (9H, s, NBu^t), and 1.20 (9H, d separated by a broad hump, J_{PH} 16Hz), m/e 353 (M^+-Me), 297, 240, and 184 (Found: C, 52.4; H, 10.5; N, 7.6. $C_{16}H_{38}N_2O_3P_2$ requires C, 52.2; H, 10.4; N, 7.6%).

Using glc (3% OV17) the yield of biphenyl was determined as between 0.5 and 0.75% and that of the parent amide 5%. (N-Phenyl)di-t-butylphosphinic amide was shown to be formed in not greater than 0.3% yield.

(ii) In Cyclohexane. - Di-t-butylphosphinic azide (0.379 g, 1.87 mmol) was photolysed (24h) in cyclohexane (500 ml). Removal of volatile material and chromatography (alumina) gave one isomer of N,P-di-t-butylphosphonamidic anhydride (0.055 g, 0.15 mmol, 16.0%), m.p. 192-195° from

petroleum, nmr and ir spectra identical to those of the product isolated previously. Elution with 3% methanol in ether gave (N-cyclohexyl)di-t-butylphosphinic amide (0.086 g, 0.332 mmol, 18%), m.p. 175-177° from petroleum; the ^{1}H nmr and ir spectra were identical to those of the authentic specimen. Elution with methanol yielded di-t-butylphosphinic amide (0.015 g, 0.085 mmol, 4.5%), m.p. 199-200° after sublimation (oven temp. 75° at 0.75 mmHg); the ^{1}H nmr and ir spectra were identical to those of the authentic specimen.

Synthesis of Phosphinic Amides and N-Chlorinated Derivatives

t-1-Amino-2,2,r-3,4,4-pentamethylphosphetan-1-oxide. - t-1-Chloro-2,2,r-3,4,4-pentamethylphosphetan-1-oxide (50 g, 0.26 mol) in ether (300 ml) was added dropwise to a solution of ammonia (18 g, 1.06 mol) in ethanol (ca. 100 ml) with stirring and cooling in an ice-salt bath. Stirring was continued for a further 2h at room temperature, the precipitate filtered off, the filtrate washed (5% potassium carbonate solution) and dried ($MgSO_4$), and volatile material evaporated off to yield, after crystallisation (benzene), t-1-amino-2,2,r-3,4,4-pentamethylphosphetan-1-oxide (37 g, 0.21 mol, 82%), m.p. 162-163°, $\nu_{max.}$ (Nujol) 3360, 3230 and 3120 (NH_2), 1550 (δ-NH_2), and 1158 cm^{-1} (P:O), ^{31}P-50.8 ppm, $\delta(CDCl_3)$ 3.0 br (2H, s, NH_2) ca. 1.5 (1H, dxq), 1.25 (6H, d, J_{PH} 18Hz), 1.21 (6H, d, J_{PH} 19Hz), and 0.89 (3H, dd, J_{PH} 2 and J_{HH} 7Hz), m/e 175 (M^+), 160 (M^+-CH_3), 143, 112, 105 (M^+-C_5H_{10}), and 97 (Found: C, 54.9; H, 10.0; N, 8.4. $C_8H_{18}NOP$ requires C, 54.8; H, 10.35; N, 8.0%).

t-1-(N-Methylamino)-2,2,r-3,4,4-pentamethylphosphetan-1-oxide. - t-1-Chloro-2,2,r-3,4,4-pentamethylphosphetan-1-oxide (20 g, 0.10 mol) in dichloromethane (100 ml) was added dropwise with stirring to an ethanolic solution of methylamine (30 ml of 30% $^{w}/_{w}$ methylamine). The mixture was stirred for a further 1h, the precipitate filtered off, the filtrate washed (5% sodium carbonate solution) and dried ($MgSO_4$), and the volatile material evaporated off to yield after crystallisation from benzene t-1-(N-methylamino)-2,2,r-3,4,4-pentamethylphosphetan-1-oxide (13.0 g, 0.069 mol, 69%), m.p. 146-148°, $\nu_{max.}$ (Nujol) 3180 (N-H) and 1185 and 1165 cm^{-1} (P:O), $\delta(CDCl_3)$ 2.77 (3H, d, J_{PH} 10Hz), ca. 2.6 br (1H, NH) exchanges with D_2O, ca. 1.58 (1H, dxq, J_{PH} 4Hz, J_{HH} 7Hz),

1.25 (6H, d, J_{PH} 18Hz), 1.19 (6H, d, J_{PH} 19Hz), and 0.89 (3H, dd, J_{HH} 7 and J_{PH} 2Hz), m/e 189 (M^+), 174 (M^+-CH_3), 119 ($M^+-C_5H_{10}$), 112, 97, 78, 72, and 69 (Found: C, 57.3; H, 10.8; N, 7.9. $C_9H_{20}NOP$ requires C, 57.1; H, 10.7; N, 7.4%).

Di-t-butylphosphinic Amide. - Di-t-butylchlorophosphine (27 g, 0.15 mol) in dichloromethane (200 ml) was added dropwise to dried (KOH) liquid ammonia (30 ml) maintained at -40°. The mixture was allowed to warm up to room temperature and stirred for 1h, filtered, and the resulting solution oxidised at 0-10° by the dropwise addition, with stirring, of 30% hydrogen peroxide (50 ml) over a period of 1h. Stirring was continued at room temperature for 1h, the organic layer separated, washed with water (20 ml), dried ($MgSO_4$), and the solvent evaporated off to yield after crystallisation (benzene) di-t-butylphosphinic amide (13.0 g, 0.073 mol, 49%), m.p. 199-200°, $\nu_{max.}$ (Nujol) 3350, 3260, and 3140 (NH_2), 1560 (δ-NH_2), and 1190 cm^{-1} (P:O), $\delta(CDCl_3)$ 2.30 br (2H, NH_2) and 1.09 (18H, d, J_{PH} 13Hz), ^{31}P-55.0 ppm, m/e 177 (M^+), 121 ($M^+-C_4H_8$), 120, 65, and 64 (Found: C, 54.4; H, 11.5; N, 7.9. $C_8H_{20}NOP$ requires C, 54.2; H, 11.4; N, 7.9%).

Di-isopropylphosphinic Amide. - Di-isopropylphosphinic chloride (15.8 g, 0.094 mol) in dichloromethane (100 ml) was added dropwise to liquid ammonia (50 ml) over a period of 1h. The mixture was allowed to warm up to room temperature, stirred for a further 1h, and filtered. The filtrate was washed with water (20 ml), dried ($MgSO_4$), and the solvent evaporated off; crystallisation from petroleum gave analytically pure di-isopropylphosphinic amide (13.8 g, 0.093 mol, 98%), m.p. 135-137.5°, $\nu_{max.}$ (Nujol) 3300, 3230, and 3120 (NH_2), 1575 (δ-NH) and 1170 and 1150 cm^{-1} (P:O), $\delta(CDCl_3)$ 3.03 br (2H, s, NH_2), 2.1-1.6 (2H, m,

Me_2CHP) and 1.13 and 1.09 (12H, two overlapping dd, J_{PH} 15 and J_{HH} 6Hz), m/e 149 (M^+), 107, 106, and 64 (Found: C, 48.2; H, 10.7; N, 9.5. $C_6H_{16}NOP$ requires C, 48.3; H, 10.8; N, 9.4%).

Synthesis of Phosphinic-N,N-dichloroamides

t-1-(N,N-Dichloroamino)-2,2,r-3,4,4-pentamethylphosphetan-1-oxide

a) To a stirred solution of t-1-amino-2,2,r-3,4,4-pentamethylphosphetan-1-oxide (4.5 g, 25.7 mmol) in dichloromethane (135 ml) was added aqueous sodium hypochlorite (180 ml). The mixture was stirred vigorously (0.75h) and the organic layer separated, washed with water (50 ml), dried ($MgSO_4$), and the solvent evaporated to yield a pale yellow crystalline solid. Crystallisation from n-heptane gave long yellow needles of t-1-(N,N-dichloroamino)-2,2,r-3,4,4-pentamethylphosphetan-1-oxide (4.0 g, 16.4 mmol, 64.5%), m.p. 86-89°, $\nu_{max.}$ (Nujol) 1240 and 1205 cm^{-1} (P:O), $\delta(CH_2Cl_2)$ (100MHz) 1.78 (1H, dxq, J_{HH} 7 and J_{PH} 5Hz), 1.33 (12H, d, J_{PH} 20Hz), and 0.97 (3H, dd, J_{HH} 7 and J_{PH} 2Hz), ^{31}P-77.2 ppm (Found: C, 39.6; H, 6.7; Cl, 29.1. $C_8H_{16}Cl_2NOP$ requires C, 39.3; H, 6.6; Cl, 29.05%).

b) To t-1-(N-chloroamino)-2,2,r-3,4,4-pentamethylphosphetan-1-oxide (0.432 g, 2.06 mmol) in dichloromethane (20 ml) was added aqueous sodium hypochlorite (30 ml) and the mixture was stirred vigorously (1.5h). The organic layer was separated, washed with water (15 ml), dried ($MgSO_4$), and the solvent evaporated to yield, after crystallisation from n-heptane, t-1-(N,N-dichloroamino)-2,2,r-3,4,4-pentamethylphosphetan-1-oxide (0.462 g, 1.89 mmol, 92%), m.p. 87-89°. The ^1H nmr and ir spectra were identical to those of the product previously prepared.

c) To t-1-(N-chloroamino)-2,2,r-3,4,4-pentamethylphosphetan-1-oxide (0.50 g, 2.4 mmol) in dichloromethane (2 ml) was added slowly, dropwise, with stirring t-butyl hypochlorite (0.30 g, 2.8 mmol) in dichloromethane (2 ml). The mixture was stirred for 1h, volatile material removed, and the residue triturated with petroleum (b.p. 40-60°) to yield t-1-(N,N-dichloroamino)-2,2,r-3,4,4-pentamethylphosphetan-1-oxide (0.55 g, 2.3 mmol, 96%). Crystallisation from n-heptane gave the product m.p. 86-88° with ^{1}H nmr and ir spectra identical to those of the product previously isolated.

d) To t-1-amino-2,2,r-3,4,4-pentamethylphosphetan-1-oxide (1.3 g, 7.43 mmol) in dichloromethane (20 ml) was added slowly, dropwise, with stirring t-butyl hypochlorite (1.75 g, 16.1 mmol) in dichloromethane (20 ml). The mixture was stirred for 1h, volatile material removed and the crude product triturated with petroleum (b.p. 40-60°); crystallisation from n-heptane gave t-1-(N,N-dichloroamino)-2,2,r-3,4,4-pentamethylphosphetan-1-oxide (1.65 g, 6.76 mmol, 91%) m.p. 87-89°; the ^{1}H nmr and ir spectra were identical to those of the product previously isolated.

Di-t-butylphosphinic-N,N-dichloroamide. - (i) Using the procedure of method (a) above, di-t-butylphosphinic-N,N-dichloroamide was prepared in 83% yield, m.p. 40-41° (sealed tube) from petroleum (b.p. 40-60°) at low temperature, $\nu_{max.}$ (liquid film) 1230, 1210, and 1180 cm^{-1} (P:O), $\delta(CDCl_3)$ 1.45 (d, J_{PH} 15Hz), ^{31}P-80.6 ppm (Found: C, 39.3; H, 7.5; N, 5.8; Cl, 28.7. $C_8H_{18}Cl_2NOP$ requires C, 39.0; H, 7.4; N, 5.7; Cl, 28.8%).

(ii) Using the procedures of methods (c) and (d), di-t-butylphosphinic-N,N-dichloroamide was pre-

pared in 96 and 94% yield respectively, m.p. 40-41° from petroleum (b. p. 40-60°); ^{1}H nmr and ir spectra identical to those of the product previously isolated.

Di-isopropylphosphinic-N,N-dichloroamide. - Using the procedure of method (a) above di-isopropylphosphinic-N,N-dichloroamide, m.p. 32-35° (sealed tube) from petroleum (b.p. 40-60°) at low temperatures, was prepared in 87% yield, δ($CDCl_3$) 2.47 (1H, m, Me_2CHP) and 1.33 (6H, dd, J_{HH} 7 and J_{PH} 16Hz), (Found: C, 33.1; H, 6.7; N, 6.05; Cl, 35.5. $C_6H_{14}Cl_2NOP$ requires C, 33.05; H, 6.5; N, 6.42; Cl, 32.5%).

Synthesis of Phosphinic-N-monochloroamides

t-1-(N-Chloro-N-methylamino)-2,2,r-3,4,4-pentamethylphosphetan-1-oxide. - (i) Using the procedure of method (a) above and a longer reaction time (4h), t-1-(N-chloro-N-methylamino)-2,2,r-3,4,4-pentamethylphosphetan-1-oxide was prepared in 86% yield. Crystallisation from ether-petroleum (b.p. 40-60°) gave colourless crystals that darkened (decomp.) on heating, δ($CDCl_3$) 3.12 (3H, d, J_{PH} 12Hz), 2.77 (1H, dxq, J_{HH} 7 and J_{PH} 5Hz), 1.33 (6H, d, J_{PH} 18Hz), 1.28 (6H, d, J_{PH} 18Hz), and 0.95 (3H, dd, J_{HH} 7 and J_{PH} 2Hz). No satisfactory analysis was obtained.

(ii) Using the procedure of method (d) above, the title compound was obtained in 99% yield. The ^{1}H nmr and ir spectra were identical to those of the product previously isolated.

t-1-(N-Chloroamino)-2,2,r-3,4,4-pentamethylphosphetan-1-oxide. -

a) To a cooled, stirred, solution of t-1-amino-2,2,r-3,4,4-pentamethylphosphetan-1-oxide (1.075 g, 6.14 mmol) in dichloromethane (50 ml)

was added slowly (0.5h), dropwise, t-butyl hypochlorite (0.68 g, 6.27 mmol) in dichloromethane (20 ml). The solution was allowed to warm to room temperature and stirred for a further 0.5h. The solvent was evaporated off and the solid triturated with petroleum to yield t-1-(N-chloroamino)-2,2,r-3,4,4-pentamethylphosphetan-1-oxide (1.2 g, 5.7 mmol, 93%), m.p. 125-130°, $\nu_{max.}$ (Nujol), 2680 (N-H) and 1160 cm^{-1} (P:O), ^{31}P-56.6 ppm, m/e 211 and 209 (M^+), 196, 194, 175 (M^+-Cl+H), 160, 112, 105, 97, 70, 69, 64, 59, and 55 (Found: C, 46.2; H, 8.3; N, 6.6; Cl, 17.3. $C_8H_{17}ClNOP$ requires C, 45.8; H, 8.2; N, 7.15; Cl, 16.9%).

b) t-1-Amino-2,2,r-3,4,4-pentamethylphosphetan-1-oxide (0.174 g, 1.0 mmol) and t-1-(N,N-dichloroamino)-2,2,r-3,4,4-pentamethylphosphetan-1-oxide (0.244 g, 1.0 mmol) were each dissolved in dichloromethane (6 ml), the solutions mixed and stirred (1h) at room temperature. The solvent was evaporated off to yield t-1-(N-chloroamino)-2,2,r-3,4,4-pentamethyl-phosphetan-1-oxide (0.40 g, 1.91 mmol, 95.5%), after trituration with petroleum m.p. 124-130°. The infrared spectrum was identical to that of the product previously isolated.

Di-t-butylphosphinic-N-chloroamide. - (i) Using the procedure of method (a) the title compound was prepared in 97% yield, m.p. 52-54°, $\nu_{max.}$ (Nujol) 2705 (N-H) and 1160 cm^{-1} (P:O), $\delta(CH_2Cl_2)$[see p. 50].

(ii) Using the procedure of method (b) di-t-butylphosphinic-N-chloroamide was prepared in 97% yield, m.p. 52-54°. The ^{1}H nmr and ir spectra were identical to those of the product previously prepared.

(N-Cyclohexyl)di-t-butylphosphinic Amide. - Di-t-butylchlorophosphine (0.0673 g, 0.3 mmol) and cyclohexylamine (0.077 g, 0.8 mmol) were mixed in deuterochloroform (ca. 0.5 ml) contained in an nmr tube. The reaction was complete after 4.5h as shown by the disappearance of the doublet (δ1.18) due to the Bu^t groups of the chlorophosphine. An excess of 30% hydrogen peroxide (0.5 ml) was added with cooling and the tube shaken vigorously. The contents of the tube were allowed to stand (0.5h), diluted with chloroform (10 ml), the organic layer washed with water (ca. 2 ml), dried ($MgSO_4$) and the solvent evaporated off to yield a colourless solid. Preparative tlc (alumina, developed with 3% methanol in ether) gave (N-cyclohexyl)di-t-butylphosphinic amide (0.035 g, 0.135 mmol, 45%), m.p. 175-177° from petroleum, $\nu_{max.}$(Nujol) 3220 (NH), 1160, 1135, and 1100 cm^{-1} (P:O), δ($CDCl_3$) ca. 3.0 br (1H, s, NH), 1.22 (18H, d, J_{PH} 14Hz), broad band due to C_6H_{11} protons partially obscured by doublet at δ1.22, m/e 259 (M^+), 216, 203, 202 (M^+-Bu), 147, 146 and 98 ($C_6H_{11}NH^+$) (Found: C, 64.7; H, 11.7; N, 5.4. $C_{14}H_{30}NOP$ requires C, 64.8; H, 11.7; N, 5.4%).

(N-Phenyl)di-t-butylphosphinic Amide. - A suspension of potassium hydride (10 mmol, 1.8 g of a 22.5% dispersion in paraffin oil) in tetrahydrofuran (THF) (20 ml) was stirred under nitrogen and aniline (0.9 g, 9.8 mmol) in THF (5 ml) was added slowly dropwise. The mixture darkened, liberating a gas (H_2), and eventually solidified. More THF (ca. 20 ml) was added to disperse the solid and di-t-butylchlorophosphine (0.9 g, 4.9 mmol) in THF (5 ml) was added over a period of 0.5h. The resulting solution was stirred (2 days), saturated aqueous ammonium chloride (30 ml) was then added, and the solution stirred for a further 10 min. The THF was evaporated off and the oil that separated was

extracted with dichloromethane (3 × 30 ml). To the organic extracts was added, with stirring, 30% hydrogen peroxide (2 ml) over a period of 0.5h. The organic layer was separated, washed with water (2 × 20 ml), dried ($MgSO_4$), and the solvent evaporated off to yield a dark brown oil. Chromatography on alumina (67 g) and elution with 3% methanol in ether afforded as an orange-brown crystalline solid the crude amide (1.07 g, 4.23 mmol, 86%). Trituration with petroleum (30 ml) and crystallisation from benzene-petroleum followed by sublimation gave analytically pure (N-phenyl)di-t-butylphosphinic amide, m.p. 177.5-178.5°, $\nu_{max.}$ (Nujol) 3220 (NH), 1605, 1500, and 1160 (P:O), $\delta(CDCl_3)$ 7.27-6.77 (5H, m, aromatics), 4.38 br (1H, d, J_{PH} 13Hz, NH) exchanges with D_2O, and 1.27 (18H, d, J_{PH} 14Hz), m/e 253 (M^+), 197, 140, and 57 (Found: C, 66.6; H, 9.6; N, 5.55. $C_{14}H_{24}NOP$ requires C, 66.4; H, 9.65; N, 5.5%).

(N-Methoxy)di-isopropylphosphinic Amide. - Sodium wire (0.34 g, 0.015 g atom) in small pieces was added cautiously to a cooled solution of methoxyamine hydrochloride (1.23 g, 26.2 mmol) in ethanol (10 ml). After ca. 0.5h, the mixture was filtered and the filtrate cooled and stirred while di-isopropylphosphinic chloride (1.0 g, 5.9 mmol) in ethanol (5 ml) was added dropwise over a period of 0.5h. The solution was stirred at room temperature for a further 48h. Preparative tlc (alumina, developed with 6% methanol in ether) on a portion equivalent to 1.6 mmol starting phosphinic chloride gave (N-methoxy)di-isopropylphosphinic amide (0.133 g, 0.75 mmol, 47%). Low temperature crystallisation from petroleum yielded analytically pure material, m.p. 57-58.5° (sealed tube), $\nu_{max.}$ (CCl_4) 3190 (NH), 1215 and 1165 cm^{-1} (P:O), $\delta(CDCl_3)$ 6.2 br (1H, s, NH), 3.55 (3H, s, OMe), ca. 2.12 (2H, m, P·C<u>H</u>Me_2), 1.18

(6H, dd, J_{PH} 16 and J_{HH} 7Hz), and 1.17 (6H, dd, J_{PH} 16 and J_{HH} 7Hz), m/e 179 (M^+), 133 (M^+-NHOMe), 107, 106, 91, 94, and 64 (Found: C, 46.3; H, 10.1; N, 7.55. $C_7H_{18}NO_2P$ requires C, 46.9; H, 10.1; N, 7.8%).

Isopropylphosphonic Dichloride. - Isopropylchloride (11.8 g, 0.3 mol), phosphorus trichloride (17.2 g, 0.25 mol), and aluminium trichloride (33.4 g, 0.5 mol) were shaken mechanically (1h) in a round bottom flask (250 ml). The viscous product obtained was passed down a column (4 ft) packed with crushed ice. The mixture, at the bottom, was extracted with ether (3 × 100 ml), the organic extracts dried ($MgSO_4$), the solvent evaporated off, and the residue distilled to give isopropylphosphonic dichloride (3.8 g, 0.24 mol, 94%), b.p. 71-72° at 11 mmHg (lit.,[146] 35.5° at 1.5 mmHg), $\nu_{max.}$ (thin film) 1465, 1270 and 1240 (P:O), and 680 cm^{-1}, $\delta(CDCl_3)$ 2.63 (1H, m, $Me_2\underline{C}HP$) and 1.28 (6H, dd, J_{PH} 17 and J_{HH} 6Hz).

Methyl P-Isopropylphosphonamidate. - Pyridine (0.315 g, 3.9 mmol) and methanol (0.126 g, 3.9 mmol) in ether (5 ml) was added dropwise with stirring over a period of 0.5h to isopropylphosphonic dichloride (0.641 g, 3.98 mmol). Stirring was continued for a further 1h, the solution filtered, and the filtrate added dropwise to a solution of ammonia (5 ml) in ether (10 ml). The ammonia was allowed to evaporate (ca. 2h), and the remaining volatile material was evaporated off to yield a colourless solid which was extracted with boiling chloroform (2 × 30 ml). The chloroform was evaporated off to yield methyl P-isopropylphosphonamidate (0.038 g, 0.277 mmol, 7%), m.p. 84-86° from petroleum-carbon tetrachloride (1:1), $\nu_{max.}$ (Nujol) 3310, 3240 and 3130 (NH), 1580 (δ-NH_2), and 1200 cm^{-1} (P:O), $\delta(CDCl_3)$ 3.53 (3H, d, J_{PH} 10Hz, P·OMe), 2.83 br (2H, s, NH_2), ca. 1.97 (1H, m, $Me_2\underline{C}H$), and 1.10 (6H, dd,

J_{PH} 18 and J_{HH} 6Hz), m/e 137 (M^+), 122 (M^+-Me), and 95 ($M^+-C_3H_6$) (Found: C, 34.9; H, 8.75; N, 10.2. $C_4H_{12}NO_2P$ requires C, 35.0; H, 8.8; N, 10.2%).

Preparation of o and m-Chloroanisoles

o-Chloroanisole. - To a vigorously stirred, cooled (below 10°), mixture of o-chlorophenol (6.4 g, 0.05 mol), sodium hydroxide (2.5 g, 0.06 mol), and water (20 ml) was added, dropwise, dimethyl sulphate (6.3 g, 0.05 mol) over a period of 1.5h. A mixture of o-chlorophenol (6.4 g, 0.05 mol), sodium hydroxide (2.5 g, 0.05 mol) and water (20 ml), was then added over a period 0.25h and the reactants heated (17h). The organic layer was separated and the aqueous layer extracted with benzene (2 × 20 ml), and the combined organic extracts dried ($MgSO_4$) and distilled to yield o-chloroanisole (5.8 g, 0.044 mol, 44%), b.p. 82-84° at 15 mmHg (lit.,[147] 87-88° at 17 mmHg), $\nu_{max.}$ (liquid film) 1595, 1580, 1490 and 750 cm^{-1}, $\delta(CDCl_3)$ 7.5-6.7 (4H, m) and 3.83 (3H, s).

m-Chlorophenol. - Concentrated sulphuric acid (14 ml, 25 g) was added cautiously with stirring to water (100 ml). To the resulting solution (hot) was added m-chloroaniline (22.5 ml, 16 g, 0.126 mol) and the mixture was warmed to dissolve the chloroaniline sulphate. Water (100 ml) was then added and the mixture stirred and cooled (0°). A cold solution of sodium nitrite (9 g, 0.130 mol) in water (17.5 ml) was added slowly with constant stirring to an end point with potassium iodide-starch paper. After 0.33h the mixture was heated (50°) until nitrogen evolution ceased (0.5h). The mixture was extracted with ether (3 × 75 ml), dried ($MgSO_4$), the ether evaporated off, and the residue distilled to yield m-chlorophenol (3.4 g, 0.0264 mol, 21%) b.p. 78-80° at 15 mmHg (lit.,[148] 214°), $\nu_{max.}$ (liquid film) 3325 cm^{-1} (OH), $\delta(CCl_4)$ 7.39-6.57 (4H, m) and 5.70 (1H, s, OH).

m-Chloroanisole. - Using the procedure as for o-chloroanisole, from m-chlorophenol (3.4 g, 26.4 mmol) was obtained m-chloroanisole (2.7 g, 18.9 mmol, 72%), b.p. 82-84° at 15 mmHg (lit.,[147] 70° at 9 mmHg), $\nu_{max.}$ (liquid film) no absorptions in the region 4000-2000 cm^{-1}, $\delta(CCl_4)$ 7.45-6.70 (4H, m) and 3.83 (3H, s, OMe).

Products Derived from the Reactions of N-Chlorophosphinic Amides with Phenylethylenes

t-1-(2′-Chlorophenethylamino)-2,2,r-3,4,4-pentamethylphosphetan-1-oxide. - t-1-(N,N-Dichloroamino)-2,2,r-3,4,4-pentamethylphosphetan-1-oxide (1.0 g, 4.1 mmol) and styrene (1.0 g, 9.62 mmol) were heated (4h) under nitrogen in benzene (10 ml). The benzene solution was washed with 20% aqueous sodium metabisulphite (20 ml) and water (20 ml), the aqueous layer was extracted with ether (2 × 20 ml), the combined organic extracts dried ($MgSO_4$), and the solvent evaporated off to yield a yellow oil. Chromatography (alumina) and elution with 3% methanol in ether gave the title compound (0.941 g, 3.0 mmol, 73%), m.p. 106.5-107.5° from petroleum, $\nu_{max.}$ (Nujol) 3290 (NH), 1175 and 1160 cm^{-1} (P:O), δ($CDCl_3$) 7.48 (5H, s, aromatics), 5.13 (1H, dd, J_{HH} 8 and J_{PH} 6Hz), 3.58 (2H, m), ca. 3.0 br (1H, NH, exchanges with D_2O), 1.26 (6H, d, J_{PH} 17Hz, P·C·CH_3), 1.22 (3H, d, J_{PH} 18Hz, P·C·CH_3), 1.13 (3H, d, J_{PH} 19Hz, P·C·CH_3), ca. 0.91 (3H, dd, J_{HH} 7 and J_{PH} 2Hz), and the resonance due to P·C·CH obscured, m/e 315 and 313 (M^+, ratio 1:3), 277 (M^+-HCl), and 188 (M^+-PhCHCl, 100%) (Found: C, 61.2; H, 7.9; Cl, 11.3. $C_{16}H_{25}ClNOP$ requires C, 61.25; H, 8.0; Cl, 11.3%).

t-1-(2′-Chloro-2′phenylpropylamino)-2,2,r-3,4,4-pentamethylphosphetan-1-oxide. - t-1-(N,N-Dichloroamino)-2,2,r-3,4,4-pentamethylphosphetan-1-oxide (3.02 g, 12.4 mmol) and α-methyl styrene (1.59 g, 13.5 mmol) were heated (4h) in benzene (70 ml). The benzene solution was washed with 20% aqueous sodium metabisulphite (2 × 30 ml) and water (50 ml), and dried ($MgSO_4$). The volatile material, from a portion of the crude reaction mixture equivalent to 8.28 mmol of the starting N,N-dichloroamide, was evaporated off and crystallisation (carbon tetrachloride) gave the title compound (1.33 g, 4.06 mmol, 49%).

Recrystallisation from petroleum afforded analytically pure material, m.p. 112-115°, $\nu_{max.}$ (Nujol) 3370 (NH), 1190 and 1165 (P:O), 770 and 700 cm^{-1}, $\delta(CDCl_3)$ 7.82-7.38 (5H, m, aromatics), 3.67 br (2H, t, $J_{NH}=J_{PH}=7Hz$), ca. 2.87 br (1H, s, NH), 2.02 (3H, s, Me), 1.28 (3H, d, J_{PH} 17Hz), 1.20 (6H, d, J_{PH} 18Hz), 1.02 (3H, d, J_{PH} 18Hz), ca. 0.90 (3H, dd, J_{HH} 7 and J_{PH} 2Hz), and the resonance due to P·C·CH obscured, m/e 291 (M^+-HCl), 221 (M^+-HCl-C_5H_{10}), 178, 132 (100%), 97, and 57 (Found: C, 61.9; H, 8.0; Cl, 11.2. $C_{17}H_{27}ClNOP$ requires C, 62.3; H, 8.3; Cl, 10.8%).

The combined mother liquors were chromatographed (alumina) and elution with ether containing increasing amounts of isopropanol yielded:

(a) t-1-(2′-methyl-2′-phenylaziridinyl)-2,2,r-3,4,4-pentamethyl-phosphetan-1-oxide (0.048 g, 0.165 mmol, 2%), m.p. 109-115° from petroleum; material of analytical purity was not obtained; $\delta(CDCl_3)$ 7.53-7.27 (5H, m, aromatics), 2.81 (1H, dd, J_{PH} 17 and J_{HH} 2Hz), ca. 2.2 (1H, dd, J_{PH} 10 and J_{HH} 2Hz), 2.02 (3H, s), ca. 1.8 (1H, dxq, J_{HH} 7 and J_{PH} 3Hz), 1.38 (3H, d, J_{PH} 18Hz), 1.29 (3H, d, J_{PH} 19Hz), 1.28 (3H, d, J_{PH} 18Hz), 1.09 (3H, d, J_{PH} 17Hz), and 0.92 (3H, dd, J_{HH} 7 and J_{PH} 2Hz).

(b) t-1-(2′-phenyl-prop-2′-enamino)-2,2,r-3,4,4-pentamethylphos-phetan-1-oxide (0.0364 g, 0.125 mmol, 1.5%) m.p. 122.5-125° from petroleum, $\nu_{max.}$ (Nujol) 3290 (NH), 1520, 1190, 1160 (P:O), 1090, 900, 785, and 715 cm^{-1}, $\delta(CDCl_3)$, 7.67-6.97 (5H, m, aromatics), 5.50 (1H, s), 5.43 (1H, s), 4.17 br (2H, t, $J_{NH}=J_{PH}$ 7Hz), ca. 2.67 br (1H, s, NH), 1.23 (6H, d, J_{PH} 18Hz), 1.10 (6H, d, J_{PH} 18Hz), 0.87 (3H, dd, J_{PH} 2 and J_{HH} 6Hz), resonance due to P·C·CH obscured, m/e 291 (M^+), 221 (M^+-C_5H_{10}), 188, 178, 132, and 97 (Found: C, 70.4; H, 9.1; N, 4.8. $C_{17}H_{26}NOP$

requires C, 70.2; H, 9.1; N, 4.8%).

t-1-(2′-Chloro-2′,2′-diphenylamino)-2,2,r-3,4,4-pentamethylphosphetan-1-oxide. - t-1-(N,N-Dichloroamino)-2,2,r-3,4,4-pentamethylphosphetan-1-oxide (1.12 g, 4.61 mmol) and 1,1-diphenylethylene (1.04 g, 5.78 mmol) were heated (4h) in benzene (30 ml). The solution was washed with 20% sodium metabisulphite solution (20 ml) and water (20 ml), dried ($MgSO_4$), and the volatile material evaporated off to yield after crystallisation (CCl_4) the title compound (0.748 g, 1.92 mmol, 42%), m.p. 128-130°, $\nu_{max.}$ (Nujol) 3310 (NH), 1190, 1165 and 1125 (P:O), 748 and 700 cm^{-1}, $\delta(CDCl_3)$, 7.73-7.27 (10H, m, aromatics), 4.15 br (2H, t, $J_{PH}=J_{NH}=6Hz$), 2.78 br (1H, s, NH), 1.20 (6H, d, J_{PH} 18Hz), 0.98 (6H, d, J_{PH} 19Hz), absorptions due to P•C•CH and P•C•CCH_3 obscured, m/e 353 (M^+-HCl). No satisfactory elemental analysis results were obtained, the best being (Found: C, 67.4; H, 7.5; N, 3.3; Cl, 10.8. $C_{22}H_{29}ClNOP$ requires C, 67.8; H, 7.5; N, 3.6; Cl, 9.1%).

Reaction of t-1-(N-Methyl-N-chloroamino)-2,2,r-3,4,4-pentamethylphosphetan-1-oxide with Styrene. - t-1-(N-methyl-N-chloroamino)-2,2,r-3,4,4-pentamethylphosphetan-1-oxide (0.471 g, 2.11 mmol) and styrene (0.219 g, 2.11 mmol) were heated (20h) under nitrogen in benzene (20 ml) Chromatography (alumina) and elution with 2% methanol in ether afforded 0.185 g of a mixture of two products (as shown by tlc). Preparative tlc (alumina) and elution with 3% methanol in ether gave as the upper band one isomer of 1-(N-methyl-2′-chlorophenethylamino)-2,2,3,4,4-pentamethylphosphetan-1-oxide (0.091 g, 0.278 mmol, 14%), m.p. 149.5-150.5° from benzene-petroleum, $\nu_{max.}$ (Nujol) 1195, 1185 and 1170 (P:O), 980, 960, 760 and 740 cm^{-1}, $\delta(CDCl_3)$ 7.43-7.15 (5H, m, aromatics), 5.07 (1H, t, J_{HH} 7Hz), 3.62 (2H, t, $J_{PH}=J_{HH}$ 7Hz), 2.71 (3H, d, J_{PH} 9Hz),

ca. 1.6 (1H, m, P·C·C·H), 1.23 (6H, d, J_{PH} 18Hz), 1.16 (3H, d, J_{PH} 17Hz), 1.04 (3H, d, J_{PH} 17Hz), and ca. 0.86 (3H, dd, J_{PH} 2, J_{HH} ca. 7Hz), m/e 329, 327 (M^+, ratio 1:3), 291 (M^+-HCl), 203, 202, 179, 159, 145, 141, 132, 104, 97, 91, and 89. Satisfactory elemental analysis was not obtained (Found: C, 61.3; H, 8.3; N, 4.3; Cl, 11.9%. $C_{17}H_{27}ClNOP$ requires C, 62.3; H, 8.3; N, 4.3; Cl, 10.8%).

The lower band gave the other isomer of 1-(N-methyl-2′-chlorophenethylamino)-2,2,3,4,4-pentamethylphosphetan-1-oxide (0.055 g, 0.168 mmol, 8.0%), m.p. 118-120° from petroleum, $\nu_{max.}$ (Nujol) 1190 and 1165 (P:O), 985, 960, 765 and 745 cm^{-1}, δ($CDCl_3$) 7.27 (5H, s, aromatics), 5.02 (1H, t, J_{HH} 7Hz), 3.43 (2H, m, P·N·CH_2), 2.57 (3H, d, J_{PH} 10Hz, P·NMe), ca. 1.8 (1H, m, P·C·CH), 1.08 (6H, d, J_{PH} 17Hz), 1.17 (3H, d, J_{PH} 18Hz), 1.12 (3H, d, J_{PH} 18Hz), and 0.87 (3H, dd, J_{HH} 8 and J_{PH} 2Hz), m/e 329 and 327 (M^+, ratio 1:3), 291, 203, 202, 171, 159, 145, 141, 132, 104, and 97 (Found: C, 62.55; H, 8.4; N, 4.3; Cl, 11.3%. $C_{17}H_{27}ClNOP$ requires C, 62.3; H, 8.3; N, 4.3; Cl, 10.8%).

Continued elution yielded t-1-(N-methylamino)-2,2,r-3,4,4-pentamethylphosphetan-1-oxide (0.180 g, 0.95 mmol, 45%), m.p. 146-148° from petroleum, nmr and ir spectra identical to those of the authentic specimen.

t-1-(2′-Phenylaziridinyl)-2,2,r-3,4,4-pentamethylphosphetan-1-oxide. - To t-1-(2′-chlorophenethylamino)-2,2,r-3,4,4-pentamethylphosphetan-1-oxide (0.316 g, 1.01 mmol) in methanol (5 ml) was added, dropwise with stirring, sodium methoxide (0.30 g, 5.56 mmol) in methanol (5 ml). The mixture was stirred (72h), the solvent removed, and the crude material taken up in dichloromethane (20 ml), washed with water (2 x20 ml), dried ($MgSO_4$), and the solvent evaporated off to yield the title compound (0.207 g, 0.747 mmol, 74%), m.p. 138-140° from petroleum,

$\nu_{max.}$ (Nujol) no absorptions in the region 4000-2000, 1200 and 1190 (P:O), 920, and 780 cm^{-1}, $\delta(CDCl_3)$ (100MHz) 7.2 (5H, s, aromatics), ABXP system of 24 lines (3H) with δ_X 3.55, δ_B 2.72, δ_A 2.02, J_{AB} 2, J_{AX} 3, J_{BX} 6, J_{PH_A}13, J_{PH_B}16, and J_{PH_X} 14 Hz (aziridine ring protons), 1.83 (1H, dxq, J_{PH} 3 and J_{HH} 7Hz), 1.37 (3H, d, J_{PH} 18Hz), 1.27 (3H, d, J_{PH} 19Hz), 1.22 (3H, d, J_{PH} 19Hz), 0.99 (3H, d, J_{PH} 18Hz) and 0.85 (3H, dd, J_{PH} 2 and J_{HH} 8Hz), m/e 277 (M^+), 262 (M^+-CH_3), 207 (M^+-C_5H_{10}), 174, 171, 166, 160, 139, 118, 104, 101, 97, and 91 (Found: C, 69.4; H, 8.8; N, 5.2. $C_{16}H_{24}NOP$ requires C, 69.3; H, 8.7; N, 5.05%).

t-1-(2′-Methyl-2′-phenylaziridinyl)-2,2,r-3,4,4-pentamethylphosphetan-1-oxide. - t-1-(N,N-Dichloroamino)-2,2,r-3,4,4-pentamethylphosphetan-1-oxide (0.408 g, 1.67 mmol) and α-methyl styrene (0.208 g, 1.76 mmol) were heated (1h) in benzene (10 ml). The solvent was evaporated off and the crude material taken up in methanol (5 ml). To this solution was added, dropwise with stirring, a solution of sodium methoxide (0.60 g, 11.1 mmol) in methanol (5 ml) and the mixture was stirred (60h) at room temperature. The solvent was evaporated and dichloromethane (20 ml) added. The solution was washed with water (2 ×20 ml), dried ($MgSO_4$), and chromatographed (alumina). Elution with 3% methanol in ether gave the title compound (0.112 g, 0.384 mmol, 23%), m.p. 110-113° from petroleum, $\nu_{max.}$ (Nujol) 1465, 1190 (P:O), 1025, 935, and 770 cm^{-1}, $\delta(CDCl_3)$ (100MHz) 7.5-7.24 (5H, m, aromatics), 2.64 (1H, dd, J_{PH} 14 and J_{HH} 2Hz), 2.13 (1H, dd, J_{PH}10 and J_{HH} 2Hz), 1.98 (3H, s), 1.86 (1H, dxq, J_{HH} 7 and J_{PH} 3Hz), 1.35 (3H, d, J_{PH} 18Hz), 1.27 (3H, d, J_{PH} 18Hz), 1.25 (3H, d, J_{PH} 18Hz), 1.07 (3H, d, J_{PH} 18Hz) and 0.89 (3H, dd, J_{HH} 7 and J_{PH} 2Hz), m/e 291 (M^+), 221 (M^+-C_5H_{10}), 178, 171, and 132 (100%) (Found: C, 70.2; H, 9.1; N, 4.6. $C_{17}H_{26}NOP$ requires C, 70.1; H, 9.0; N, 4.8%).

Continued elution gave t-1-(2′-methoxy-2′-methylphenethylamino)-2,2,r-3,4,4-pentamethylphosphetan-1-oxide (0.124 g, 0.383 mmol, 23%), m.p. 191-193° from petroleum, characterised only by comparison of its ^{1}H nmr spectrum with that of the authentic specimen.

t-1-(2′,2′-Diphenylaziridinyl)-2,2,r-3,4,4-pentamethylphosphetan-1-oxide. - t-1-(N,N-Dichloroamino)-2,2,r-3,4,4-pentamethylphosphetan-1-oxide (0.544 g, 2.23 mmol) and 1,1-diphenylethylene (0.735 g, 4.08 mmol) were heated (1h) in benzene (20 ml). The solvent was evaporated off from a portion equivalent to 1.125 mmol of the starting N,N-dichloroamide and the residue stirred (16h) in t-butanol (10 ml) containing potassium t-butoxide (0.475 g, 4.24 mmol). The solvent was evaporated off and the crude product taken up in dichloromethane (20 ml), washed with water (2 x 15 ml), dried ($MgSO_4$) and chromatographed (alumina); elution with 3% methanol in ether gave the title compound (0.214 g, 0.606 mmol, 54%), m.p. 150-154° from petroleum, $\nu_{max.}$ (Nujol) 1210 (P:O), 965, 780, 765, 710, and 700 cm^{-1}, $\delta(CDCl_3)$ 7.28 (10H, s, aromatics), 2.89 (2H, d, J_{PH} 13Hz), 1.90 (1H, m, P·C·CH), 1.33 (6H, d, J_{PH} 17.5Hz), 1.10 (6H, d, J_{PH} 17.5Hz) and 0.89 (3H, dd, J_{HH} 6 and J_{PH} ca. 1Hz), m/e 353 (M^+), 283 ($M^+-C_5H_{10}$), 282, 241, 240, 224, 195, 194 ($C_{14}H_{12}N^+$), 167, 165, 97, and 91 (Found: C, 74.8; H, 8.0; N, 3.9. $C_{22}H_{28}NOP$ requires C, 74.8; H, 8.0; N, 4.0%).

t-1-(2′-Methoxyphenethylamino)-2,2,r-3,4,4-pentamethylphosphetan-1-oxide. - To t-1-(2′-chlorophenethylamino)-2,2,r-3,4,4-pentamethylphosphetan-1-oxide (0.220 g, 0.701 mmol) in methanol (10 ml) was added silver nitrate (0.40 g, 2.36 mmol) and the mixture was stirred (16h) vigorously. Dichloromethane (15 ml) was added, the mixture filtered, the solvent evaporated off, and chromatography (alumina with 3%

methanol in ether) afforded the title compound (0.193 g, 0.624 mmol, 89%), m.p. 94-97° after repeated crystallisations from petroleum, $\nu_{max.}$ (Nujol) 3270 (NH), and 1190 and 1165 cm^{-1} (P:O), $\delta(CDCl_3)$ (100 MHz) 7.33 (5H, s, aromatics), 4.31 (1H, dd, J_{HH} 8 and J_{HH} 4Hz), 3.28 (3H, s, OMe), 3.18 (2H, m), 1.48 (1H, dxq, J_{HH} 7 and J_{PH} 4Hz, signal partly obscured by P·CMe_2 resonances), 1.23 and NH not observed (3H, d, J_{PH} 18Hz), 1.21 (3H, d, J_{PH} 18Hz), 1.19 (3H, d, J_{PH} 17Hz), 1.10 (3H, d, J_{PH} 17Hz) and 0.85 (3H, dd, J_{HH} 8 and J_{PH} 1Hz), m/e 309 (M^+), 294 (M^+-Me), 277 (M^+-MeOH), 239 (M^+-C_5H_{10}), 206, 188 (100%, $C_8H_{16}PONHCH_2^+$), 159, 136, 121, 104, and 97. No satisfactory elemental analysis results could be obtained; the best were (Found: C, 65.4; H, 9.05; N, 4.8. $C_{17}H_{28}NO_2P$ requires C, 66.0; H, 9.1; N, 4.5%).

t-1-(2′-Methoxy-2′-methylphenethylamino)-2,2,r-3,4,4-pentamethylphosphetan-1-oxide. - t-1-(N,N-Dichloroamino)-2,2,r-3,4,4-pentamethylphosphetan-1-oxide (0.471 g, 1.93 mmol) and α-methyl styrene (0.238 g, 2.02 mmol) were heated (1h) in benzene (12 ml). Volatile material was removed and the resulting yellow oil taken up in methanol (15 ml). Silver nitrate (1.2 g, 6.6 mmol) was added and the mixture vigorously stirred (12h). Dichloromethane (15 ml) was added and the mixture was filtered; chromatography (alumina with 1% methanol in ether as eluant) gave the title compound (0.330 g, 1.02 mmol, 53%), m.p. 131-134° from carbon tetrachloride-petroleum, $\nu_{max.}$ (Nujol) 3260 (NH), 1237, 1185 and 1165 (P:O), 1080, 835, and 710 cm^{-1}, $\delta(CDCl_3)$ (100MHz) 7.41-7.28 (5H, m, aromatics), 3.22 (2H, dd, J_{PH} 7 and J_{HNCH} 6Hz, P·N·CH_2), 3.12 (3H, s, OMe), 2.76 br (1H, m, NH) exchanges with D_2O, 1.62 (3H, s), 1.23 (3H, d, J_{PH} 18Hz), 1.19 (3H, d, J_{PH} 18Hz), 1.18 (3H, d, J_{PH} 17Hz), 1.03 (3H, d, J_{PH} 17Hz) and resonance due to P·C·CH obscured partially, 0·87(3H, d, J_{HH} 7Hz), m/e 323 (M^+), 319, 318 (M^+-Me), 291 (M^+-MeOH), 253, 206, 189, 188, 160,

159, 148, 141, 136, 135 (100%), and 97 (Found: C, 66.1; H, 9.3; N, 4.3. $C_{18}H_{30}NO_2P$ requires C, 66.9; H, 9.35; N, 4.3%).

t-1-(2′-Methoxy-2′,2′-diphenylethylamino)-2,2,r-3,4,4-pentamethylphosphetan-1-oxide. - t-1-(N,N-Dichloroamino)-2,2,r-3,4,4-pentamethylphosphetan-1-oxide (0.497 g, 2.04 mmol) and 1,1-diphenylethylene (0.373 g, 3.45 mmol) were heated (1h) in benzene (12 ml). Volatile material was evaporated off, the crude product taken up in methanol (5 ml) and to this was added, dropwise with stirring, a solution of sodium methoxide (0.80 g, 14.8 mmol) in methanol (10 ml). Stirring was continued (16h), the solvent evaporated off, and the solid obtained taken up in dichloromethane (20 ml). The solution was washed with water (2 × 20 ml) and dried ($MgSO_4$); chromatography (alumina, elution with 3% methanol in ether) gave the title compound (0.337 g, 0.989 mmol, 49%), m.p. 192-193° from petroleum, $\nu_{max.}$ (Nujol) 3315 (NH), 1409, 1192 and 1165 (P:O), 1100, 1085, 1076, 780, 755, 705, and 695 cm^{-1}, $\delta(CDCl_3)$ 7.3-7.0 (10H, m, aromatics), 3.87 (2H, dd, J_{PH} 7 and J_{NH} 5Hz), 3.08 (1H, s, OMe), 2.4 br (1H, m, NH), 1.14 (6H, d, J_{PH} 18Hz), 0.87 (6H, d, J_{PH} 17Hz), 0.77 (3H, dd, J_{HH} 7 and J_{PH} 2Hz), m/e 385 (M^+), 370 (M^+-Me), 353 (M^+-MeOH), 198 (100%), and 188 ($C_8H_{16}PONHCH_2^+$) (Found: C, 71.0; H, 8.4; N, 3.5. $C_{23}H_{32}NO_2P$ requires C, 71.6; H, 8.4; N, 3.6%).

(N-Chloro-N-2-chlorophenethyl)di-t-butylphosphinic Amide. - (N,N-Dichloro)di-t-butylphosphinic amide (0.516 g, 2.1 mmol) and styrene (0.228 g, 2.2 mmol) were heated (3 days) in benzene (12 ml). Chromatography (alumina) on a portion equivalent to 1.05 mmol starting amide and elution with 3% methanol in ether gave the title compound (0.285 g, 0.81 mmol, 77.4%), m.p. 121-123° from petroleum, $\nu_{max.}$ (Nujol) no absorptions in the region 4000-2000, 1460, 1170 (P:O), 868, 715, and

658 cm^{-1}, δ($CDCl_3$) 7.40-7.12 (5H, m, aromatics), 5.13 (1H, t, J_{HH} 7Hz, $-CH_2\underline{C}HPhCl$), ABMX system of 16 lines with δ_A 4.08, δ_B 3.78, J_{AB} 14, $J_{AM} \simeq J_{BM}$ 7 and $J_{AX} \simeq J_{BX}$ 3Hz, 3.97 (2H, m, $-\underline{CH}_2CHPhCl$), 1.34 (9H, d, J_{PH} 17Hz), and 1.10 (9H, d, J_{PH} 16Hz), m/e 349 (M^+ for ^{35}Cl, ^{35}Cl; small), 315 and 313 (M^+-HCl), 279 (M^+-Cl_2), 223, 190, 166, 161, 148, 118, 105, and 91 (Found: C, 54.8; H, 7.6; N, 4.1; Cl, 20.3. $C_{16}H_{26}Cl_2NOP$ requires C, 54.9; H, 7.5; N, 4.0; Cl, 20.2%).

(N-2-Chlorophenethyl)di-t-butylphosphinic Amide. - (N-chloro-N-2-chlorophenethyl)di-t-butylphosphinic amide (0.085 g, 0.243 mmol) was stirred (18h) in benzene (3 ml) with saturated aqueous sodium metabisulphite (6 ml). The organic layer was separated, washed with water, dried ($MgSO_4$) and the solvent evaporated to yield the title compound (0.071 g, 0.225 mmol, 93%), m.p. 152-155° from petroleum, $\nu_{max.}$ (Nujol) 3230 (NH), 1155 (P:O), 1110, 852, 820, 775, 712, 692, and 665 cm^{-1}, δ($CDCl_3$) 7.2 br (5H, s, aromatics), 4.98 (1H, dd, J_{HH} 8 and J_{HH} 5Hz), 3.5 (2H, m, P·N·CH_2), 2.6 br (1H, s, NH), 1.23 (9H, d, J_{PH} 14Hz), 1.15 (9H, d, J_{PH} 14Hz), m/e 317, 315 (M^+, ratio 1:3), 279 (M^+-HCl), 260, 258 (M^+-Bu^t), 223, 202, 191, 190, 168, 167, 166, 161, 148, 120, 118, 105, 104, and 91. No satisfactory analysis was obtained (Found: C, 60.2; H, 8.5; N, 4.4; Cl, 12.2%. $C_{16}H_{27}ClNOP$ requires C, 60.8; H, 8.6; N, 4.4; Cl, 11.2%).

N-(Di-t-butylphosphinyl)-2-phenylaziridine. - A fraction, equivalent to 0.525 mmol starting N,N-dichloroamide, of the crude reaction product from the reaction of (N,N-dichloro)di-t-butylphosphinic amide with styrene was cyclised (NaOMe/MeOH). Chromatography (alumina, elution with 3% methanol in ether) gave the title compound (0.125 g, 0.45 mmol, 86%), m.p. 99.5-101° from petroleum, $\nu_{max.}$ (Nujol) 1165

(P:O), 930, 775, and 695 cm^{-1}, $\delta(CDCl_3)$ (100MHz) 7.28 (5H, s, aromatics) ABXP system of 24 lines (3H) with δ_X 3.43, δ_B 2.72, δ_A 1.98, J_{AX} 3, J_{BX} 6, J_{AB} 2, J_{PH_A}13, J_{PH_B}12, and J_{PH_X}15Hz (aziridine ring protons), 1.35 (9H, d, J_{PH} 16Hz), and 1.22 (9H, d, J_{PH} 16Hz), m/e 279 (M^+), 223, 167, 166 (100%), 148, 118, 105, 104, and 91 (Found: C, 68.3; H, 9.4; N, 4.9. $C_{16}H_{26}NOP$ requires C, 68.8; H, 9.4; N, 5.0%).

N-(Di-t-butylphosphinyl)-2-methyl-2-phenylaziridine. - (N,N-Dichloro)di-t-butylphosphinic amide (0.933 g, 3.79 mmol) and α-methyl styrene (0.546 g, 3.86 mmol) were heated (5.5h) in benzene (30 ml). The benzene solvent was evaporated off and the crude material dissolved in t-butanol (20 ml) at 50°. To the stirred (2h) solution was added potassium t-butoxide (0.850 g, 7.59 mmol); the solvent was evaporated off and chromatography (alumina) on a portion equivalent to 1.90 mmol starting N,N-dichloroamide afforded the title compound (0.255 g, 0.87 mmol, 46%) identified only from its ^1H nmr spectrum, $\delta(CDCl_3)$ 7.43 (5H, s, aromatics), 2.64 (1H, dd, J_{PH} 14 and J_{HH} 3Hz), ca. 2.13 (1H, dd, ca. J_{PH} 10 and J_{HH} 3Hz), 1.77 (3H, s), 1.33 (9H, d, J_{PH} 13Hz), and 1.18 (9H, d, J_{PH} 13Hz).

N-(Di-t-butylphosphinyl)-2,2-diphenylaziridine. - Using the same procedure as above, the title compound (impure) was obtained in 32% yield and identified only from its ^1H nmr spectrum, $\delta(CDCl_3)$ 7.37-7.00 (10H, m, aromatics), 2.94 (2H, d, J_{PH} 11Hz), and 1.18 (18H, d, J_{PH} 14 Hz).

N-(Di-isopropylphosphinyl)-2-phenylaziridine. - Using the procedure above the title compound was obtained in 42% yield and identified only from its ^1H nmr spectrum, $\delta(CDCl_3)$, 7.20 (5H, s, aromatics) ABXP system

of 24 lines (3H) with δ_X 3.40, δ_B 2.67, δ_A 1.97, J_{AX} 3, J_{AB} 2, J_{BX} 6, J_{PH_X}13, J_{PH_A}15, and J_{PH_B}15Hz (aziridine ring protons), ca. 2.08 (2H, m, $Me_2C\underline{H}P$), and 1.48-0.90 (12H, m, $(C\underline{H}_3)_2CHP$).

Reactions of N-Chlorophosphinic Amides with Anthracene and Anisole

Isolation of 9-Chloro and 9,10-Dichloroanthracene from the Reaction of t-1-(N,N-Dichloroamino)-2,2,r-3,4,4-pentamethylphosphetan-1-oxide with Anthracene. - t-1-(N,N-Dichloroamino)-2,2,r-3,4,4-pentamethylphosphetan-1-oxide (1.53 g, 6.8 mmol) and anthracene (1.22 g, 6.8 mmol) were heated (4h) at reflux temperature in benzene (45 ml) under nitrogen. The cooled solution was filtered and volatile material evaporated off to yield a yellow crystalline solid, which after three crystallisations (acetone) gave 9,10-dichloroanthracene (0.07 g, 0.28 mmol, 4.1%), m.p. 209-211° (lit.,[149] 210°) $\delta(CDCl_3)$ 8.8 (4H, m) and 8.7 (4H, m), $\nu_{max.}$ (Nujol) 1320, 1270, 950 and 750 cm^{-1}, m/e 250, 248, and 246 (1:6:9) (M^+) and 176 (100%, M^+-Cl_2).

Chromatography of the mother liquors (kieselghur; 250:1) and elution with petroleum (b.p. 40-60°) afforded 9-chloroanthracene (0.03 g, 0.14 mmol, 2.1%) m.p. 103-104° (lit.,[150] 104-106°) from ethanol, $\nu_{max.}$ (Nujol) 1270, 940, 880, 727, and 725 cm^{-1}, $\delta(CDCl_3)$ 8.67-8.42 (3H, m), 8.22-7.97 (2H, m), and 7.78-7.28 (4H, m), m/e 214 and 212 (ratio 1:3, M^+), 176 (M^+-HCl), 151, 150, and 106.

9,10-Dichloroanthracene. - t-1-(N,N-Dichloroamino)-2,2,r-3,4,4-pentamethylphosphetan-1-oxide (0.619 g, 2.54 mmol) and anthracene (0.148 g, 0.83 mmol) were heated (21h) in benzene (7 ml). The crude reaction mixture was washed with 20% aqueous sodium metabisulphite (2 × 40 ml) and the aqueous phase extracted with benzene (2 × 30 ml). The combined organic extracts were dried ($MgSO_4$), the solvent evaporated and chromatography (silica; elution with petroleum) gave 9,10-di-

chloroanthracene (0.100 g, 0.405 mmol, 49%) m.p. 209-211° (lit.,[149] 210°) from acetone, with ^{1}H nmr and ir identical to those of the product previously isolated.

Quantitative Study of the Chlorination of Anthracene

(i) With t-1-(N,N-Dichloroamino)-2,2,r-3,4,4-pentamethylphosphetan-1-oxide. - t-1-(N,N-Dichloroamino)-2,2,r-3,4,4-pentamethylphosphetan-1-oxide (0.503 g, 2.05 mmol) and anthracene (0.350 g, 1.94 mmol) were heated (3.5h) in benzene (25 ml). Samples (0.5 ml) were withdrawn from the reaction mixture at known time intervals and analysed by glc (3% APL, 250°). The variation of the ratio of the areas of the peaks due to 9-chloroanthracene (R_T 7.3 min) and 9,10-dichloroanthracene (R_T 13.1 min) was followed:

Time(h)	9-Chloroanthracene : 9,10-Dichloroanthracene
0.5	1 : 0.5
1.0	1 : 0.4
1.25	1 : 0.8
1.30	1 : 1.3
2.75	1 : 1.4
3.30	1 : 1.3

The crude reaction mixture was shaken with 20% aqueous sodium metabisulphite (2 x 20 ml) and water (10 ml), and the organic layer separated, dried ($MgSO_4$) and chromatographed (Kieselghur). Elution with petroleum (b.p. 40-60°) afforded 0.348 g of a mixture of 9-chloro and 9,10-dichloroanthracene.

From the relative peak areas of 9-chloroanthracene and 9,10-dichloroanthracene (1 : 1.3) in the reaction mixture prior to work up,

the known relative detector response of 9-chloroanthracene : 9,10-dichloroanthracene (1.3 : 1 $^{w}/_{w}$), and the total isolated yield of 9-chloro and 9,10-dichloroanthracene, the yields of 9-chloroanthracene (0.129 g, 0.601 mmol, 31%) and 9,10-dichloroanthracene (0.239 g, 0.96 mmol, 49.5%) were calculated.

The aqueous phase was extracted with chloroform (4 × 25 ml) to yield t-1-amino-2,2,r-3,4,4-pentamethylphosphetan-1-oxide (0.041 g, 0.234 mmol, 11.4%) m.p. 162-164° from benzene. The ^{1}H nmr and ir spectra were identical to those of the authentic specimen.

(ii) With t-1-(N-Chloroamino)-2,2,r-3,4,4-pentamethylphosphetan-1-oxide. - t-1-(N-Chloroamino)-2,2,r-3,4,4-pentamethylphosphetan-1-oxide (0.475 g, 2.27 mmol) and anthracene (0.167 g, 0.94 mmol) were heated (20h) in benzene (40 ml) and the reaction followed by glc as in (i) above:

Time(h)	9-Chloroanthracene : 9,10-Dichloroanthracene
0.25	1 : 0.1
0.75	1 : 0.1
2.00	1 : 0.15
3.00	1 : 0.3
4.50	1 : 1.1
5.00	1 : 1.5
6.30	1 : 1.8
7.30	1 : 1.9
20.00	1 : 1.9

Chromatography (Kieselghur) and elution with petroleum (b.p. 40-60°) afforded 0.193 g of a mixture of 9-chloro and 9,10-dichloroanthracene.

From the glc (3% APL) peak areas of the reaction mixture before chromatography and the known relative detector responses, the yields of 9-chloroanthracene (0.056 g, 0.261 mmol, 28.0%) and 9,10-dichloroanthracene (0.137 g, 0.55 mmol, 58.5%) were calculated.

(iii) With t-1-(N-Chloro-N-methylamino)-2,2,r-3,4,4-pentamethylphosphetan-1-oxide. - In a similar manner to (i) using t-1-(N-chloro-N-methylamino)-2,2,r-3,4,4-pentamethylphosphetan-1-oxide (0.461 g, 2.06 mmol) and anthracene (0.178 g, 1.0 mmol), a combined yield of 9-chloro and 9,10-dichloroanthracene of 0.200 g was obtained from a portion of the reaction mixture equivalent to 0.92 mmol starting anthracene.

Using glc (3% APL) with the relative detector response of 9-chloro : 9,10-dichloroanthracene (1.24 : 1) and the relative peak areas of 9-chloro : 9,10-dichloroanthracene (1.42 : 1) the yields of 9-chloroanthracene (0.1068 g, 0.503 mmol, 55%) and 9,10-dichloroanthracene (0.0932 g, 0.38 mmol, 41%) were calculated.

Continuous extraction of the aqueous phase with chloroform afforded t-1-(N-methylamino)-2,2,r-3,4,4-pentamethylphosphetan-1-oxide (0.276 g, 1.46 mmol, 77%) m.p. 146-148° from benzene. The ^{1}H nmr and ir spectra were identical to those of the authentic specimen.

(iv) With (N,N-Dichloroamino)di-t-butylphosphinic Amide. - In a similar manner to (iii) the combined yield of 9-chloro and 9,10-dichloroanthracene was 0.168 g, from anthracene (0.177 g, 1.0 mmol) and (N,N-dichloro)di-t-butylphosphinic amide (0.243 g, 0.99 mmol), on a portion of the reaction mixture equivalent to 0.92 mmol starting anthracene.

Using glc the yields of 9-chloroanthracene (0.106 g, 0.494 mmol, 54%) and 9,10-dichloroanthracene (0.062 g, 0.249 mmol, 27%) were

calculated.

(v) With (N,N-Dichloro)di-isopropylphosphinic amide. - Similarly yields of 9-chloroanthracene (0.109 g, 0.508 mmol, 50%) and 9,10-dichloroanthracene (0.067 g, 0.269 mmol, 26%) were calculated from an isolated yield of 9-chloro and 9,10-dichloroanthracene of 0.176 g.

Chlorination of Anisole by N-Chloroamides

(i) With t-1-(N-Chloroamino)-2,2,r-3,4,4-pentamethylphosphetan-1-oxide. - t-1-(N-Chloroamino)-2,2,r-3,4,4-pentamethylphosphetan-1-oxide (1.054 g, 4.8 mmol) and anisole (0.54 g, 5.0 mmol) were heated (39h) in benzene (80 ml). The benzene solution was washed with water (2 × 30 ml) and dried ($CaCl_2$). To 10 ml of the solution was added p-dichlorobenzene (0.196 g, 1.33 mmol) as an internal standard. From the relative detector response of p-dichlorobenzene : p-chloroanisole (1:1) the yield of the chloroanisoles (0.0964 g, 0.667 mmol, 13.5%) was obtained assuming the response of the detector to the isomeric chloroanisoles was the same.

From the peak areas of m-chloroanisole and o + p-chloroanisoles the proportion of m-chloroanisole (5%) was calculated.

Preparative glc (10% E 30) on the crude reaction mixture gave as a mixture o and p-chloroanisoles, which on analysis (nmr) by integration of the methoxyl peaks δ3.88 and 3.77 respectively in the ratio 9:49, gave an ortho : meta : para ratio of 15 : 5 : 80.

Extraction of the aqueous phase with chloroform (3 × 50 ml) gave t-1-amino-2,2,r-3,4,4-pentamethylphosphetan-1-oxide (0.065 g, 0.37 mmol, 7.7%) m.p. 162-163° from benzene. The ^1H nmr and ir spectra were identical to those of the authentic specimen.

(ii) t-1-(N,N-Dichloroamino)-2,2,r-3,4,4-pentamethylphosphetan-1-oxide. - t-1-(N,N-Dichloroamino)-2,2,r-3,4,4-pentamethylphosphetan-1-oxide (0.488 g, 2.0 mmol) and anisole (0.226 g, 2.09 mmol) were heated (41h) in benzene (30 ml). In a similar manner to (i) the proportion of m-chloroanisole was 6.0%. The total yield of chloroanisoles (0.120 g, 0.843 mmol) was 42%, and the ortho : para ratio was 13 : 62 corresponding to an ortho : meta : para ratio 16 : 6 : 78.

Attempted Ring Expansion of N-Chlorophosphinic Amides

(i) t-1-(N,N-Dichloroamino)-2,2,r-3,4,4-pentamethylphosphetan-1-oxide. - To t-1-(N,N-dichloroamino)-2,2,r-3,4,4-pentamethylphosphetan-1-oxide (0.246 g, 1.01 mmol) in methanol (10 ml) was added, dropwise with stirring, sodium methoxide (0.055 g, 1.02 mmol) in methanol (5 ml). Stirring was continued (6.5h), the solvent evaporated off, and the resulting solid dissolved in chloroform, filtered, washed with water (10 ml), and dried ($MgSO_4$) to yield t-1-(N-chloroamino)-2,2,r-3,4,4-pentamethylphosphetan-1-oxide (0.184 g, 0.89 mmol, 87%), m.p. 126-130° from petroleum, ir identical to that of the product previously prepared.

Using a 2:1 molar ratio of sodium methoxide to t-1-(N,N-dichloroamino)-2,2,r-3,4,4-pentamethylphosphetan-1-oxide, t-1-amino-2,2,r-3,4,4-pentamethylphosphetan-1-oxide was obtained in 87% yield, m.p. 162-163° from benzene. The ^1H nmr and ir spectra were identical to those of the product previously prepared.

(ii) t-1-(N-Chloroamino)-2,2,r-3,4,4-pentamethylphosphetan-1-oxide. - Using the same procedure as in (i) and a molar ratio of sodium methoxide to N-chloroamide of 1:1, t-1-amino-2,2,r-3,4,4-pentamethylphosphetan-1-oxide was isolated in 86% yield, m.p. 162-163° from benzene. The ^1H nmr and ir spectra were identical to those of the product previously prepared.

(iii) Trapping of the N-Chloroamide Anion (208) with Methyl Iodide. - Sodium hydride (0.122 g, 5.04 mmol) as a 50% suspension in paraffin was washed with benzene (3 × 15 ml) and suspended by vigorously stirring in benzene (20 ml) and methyl iodide (0.721 g, 5.08 mmol) was added. t-1-(N-Chloroamino)-2,2,r-3,4,4-pentamethylphosphetan-1-oxide

(0.50 g, 2.39 mmol) was added in small portions and stirring continued (12h) to yield a pale yellow solution. The solution was shaken with 20% aqueous sodium metabisulphite (20 ml) and the organic layer was separated and dried ($CaCl_2$); chromatography (alumina, elution with 3% methanol in ether) gave t-1-(N-methylamino)-2,2,r-3,4,4-pentamethyl-phosphetan-1-oxide (0.062 g, 0.34 mmol, 14%), m.p. 146-148° from benzene, with ^1H nmr and ir spectra identical to those of the authentic specimen.

Arsinimines

N-[t-(2,2,r-3,4,4-Pentamethylphosphetinyl)]triphenylarsinimine. - t-1-Amino-2,2,r-3,4,4-pentamethylphosphetan-1-oxide (0.176 g, 1.0 mmol), lead tetraacetate[151] (0.891 g, 2.0 mmol), and triphenylarsine (0.617 g, 2.0 mmol) were heated (22h) in dichloromethane (25 ml). The reactants were filtered, washed with water (20 ml) and sodium bicarbonate solution (2 × 20 ml), and dried (Na_2SO_4). Chromatography (alumina, elution with 2% methanol in ether) gave the title compound (0.339 g, 0.708 mmol, 71%), m.p. 199.5-201.5° from petroleum, $\nu_{max.}$ 1150 (P:O), 1088, and 1065 cm^{-1}, $\delta(CDCl_3)$ 7.73-7.23 (15H, m, aromatics), 1.63 (1H, m, P·C·CH), 1.09 (6H, d, J_{PH} 17Hz), 1.03 (6H, d, J_{PH} 17Hz), and 0.79 (3H, dd, J_{HH} 7 and J_{PH} 2Hz, P·C·C·CH_3), m/e 479 (M^+), 409 (M^+-C_5H_{10}), 306 (Ph_3As^+), 226, 152, and 134 (Found: C, 64.9; H, 6.35; N, 3.1. $C_{26}H_{31}AsNOP$ requires C, 65.2; H, 6.5; N, 2.9%). In the absence of lead tetraacetate, t-1-amino-2,2,r-3,4,4-pentamethylphosphetan-1-oxide was found not to react with triphenylarsine, as shown by no change in the nmr after heating (36h).

Reaction of Di-t-butylphosphinic Azide with Triphenylarsine in the Presence of Copper. - Di-t-butylphosphinic azide (0.127 g, 0.63 mmol), triphenylarsine (0.378 g, 1.2 mmol) and copper powder (0.605 g, 0.0095 g atom) were heated (8h) at 165° until nitrogen evolution ceased. To the crude reaction mixture was added dichloromethane (20 ml), the mixture was filtered, and chromatography (alumina, elution with 3% methanol in ether) gave N-(di-t-butylphosphinyl)triphenylarsinimine (0.140 g, 0.29 mmol, 46%), m.p. 174-176° from petroleum, $\nu_{max.}$ (Nujol) 1135 (P:O), 1080 and 1065 cm^{-1}, $\delta(CDCl_3)$ 7.77-7.62 (6H, m), 7.38-7.23 (9H, m), and 1.08 (18H, d, J_{PH} 13Hz), m/e 424 (M^+-Bu^t), 365, 347, 332,

306 (Ph_3As^+), 290, 275, 229, 228, 227, 214, 154, 152, and 121 (Found: C, 64.9; H, 6.95; N, 2.9. $C_{26}H_{33}AsNOP$ requires C, 64.8; H, 6.9; N, 2.9%).

Heating the azide (165°) alone resulted in no decomposition, as shown by no change in the ^1H nmr and ir spectra before and after heating. Heating the azide (165°) in the presence of added triphenylarsine also resulted in no decomposition, as shown by the ^1H nmr spectrum and by tlc (by comparison with the authentic specimen of N-(di-t-butylphosphinyl)triphenylarsinimine).

N-[t-(2,2,r-3,4,4- entamethylphosphetinyl)]triphenylarsinimine. - The formation of the title compound in the reaction of t-1-azido-2,2,r-3,4,4-pentamethylphosphetan-1-oxide with triphenylarsine in the presence of copper was shown using tlc.

Arsinimines by Condensation of Amides with Diacetoxytriphenylarsorane:

(i) N-[t-(2,2,r-3,4,4- entamethylphosphetinyl)]triphenylarsinimine. - t-1-Amino-2,2,r-3,4,4-pentamethylphosphetan-1-oxide (0.175 g, 1.0 mmol) and diacetoxytriphenylarsorane[127] (0.634 g, 1.50 mmol) were heated (2h) in benzene (10 ml). Chromatography (alumina, elution with 2% methanol in ether) gave the title compound (0.337 g, 0.704 mmol, 70%), m.p. 199-201° from petroleum, ^1H nmr and ir identical to those of the authentic specimen.

(ii) N-(Di-t-butylphosphinyl)triphenylarsinimine. - A similar procedure, but using toluene as solvent, gave the title compound (25%), m.p. 174-175.5° from petroleum, with ^1H nmr and ir spectra identical to those of the product previously isolated.

(iii) N-(Di-isopropylphosphinyl)triphenylarsinimine. - Using the procedure as in (i) above, from di-isopropylphosphinic amide, the title compound was obtained (73%) m.p. 100.5-102° from petroleum, δ($CDCl_3$) 7.75-7.60 (6H, m), 7.43-7.27 (9H, m), 2.13-1.63 (2H, m, Me_2CHP), 1.10 (6H, dd, J_{PH} 16 and J_{HH} 7Hz), and 0.98 (6H, dd, J_{PH} 15 and J_{HH} 7Hz) (Found: C, 63.8; H, 6.6; N, 3.05. $C_{24}H_{29}AsNOP$ requires C, 63.6; H, 6.45; N, 3.1%).

Reaction of t-1-(N,N-Dichloroamino)-2,2,r-3,4,4-pentamethylphosphetan-1-oxide with Triphenylarsine in the Presence of Active Zinc. - Anhydrous zinc bromide (11.5 g, 0.05 mol) was dissolved in tetrahydrofuran (40 ml), potassium (3.8 g, 0.1 mol) added, the mixture heated (4h), and the solvent evaporated off to yield a dark grey powder (15.3 g) containing ca. 0.05 g atom of active zinc.[134]

t-1-(N,N-Dichloroamino)-2,2,r-3,4,4-pentamethylphosphetan-1-oxide (0.976 g, 4.0 mmol) and triphenylarsine (1.225 g, 4.0 mmol) were dissolved in dichloromethane (35 ml). To this solution was added active zinc (0.539 g mixture, equivalent to 0.0017 g atom zinc) and the mixture was heated (15h), filtered, washed with 20% aqueous sodium metabisulphite (40 ml) and water (3 × 30 ml) and dried (Na_2SO_4). Chromatography (alumina, elution with 3% methanol in ether) on a portion equivalent to 1.33 mmol starting N,N-dichloroamide yielded N-[t-(2,2,r-3,4,4-pentamethylphosphetinyl)]triphenylarsinimine (0.294 g, 0.6 mmol, 46%), m.p. 199-201° from petroleum. The ^1H nmr and ir spectra were identical to those of the authentic specimen.

Reaction of t-1-(N,N-dichloroamino)-2,2,r-3,4,4-pentamethylphosphetan-1-oxide with Triphenylarsine. - t-1-(N,N-Dichloroamino)-2,2,r-3,4,4-pentamethylphosphetan-1-oxide (0.486 g, 1.99 mmol) and triphenyl-

arsine (0.611 g, 2.0 mmol) were dissolved in dichloromethane (20 ml) and heated (12h). The crude reaction product was washed with 20% aqueous sodium metabisulphite (15 ml) and water (2 × 15 ml), and dried (Na_2SO_4). Chromatography (alumina; elution with 2% methanol in ether) on a portion equivalent to 0.97 mmol starting N,N-dichloroamide afforded N-[t-(2,2,r-3,4,4-pentamethylphosphetinyl)]triphenylarsinimine (0.237 g, 0.49 mmol, 50.5%), m.p. 199-201° from petroleum, with ^1H nmr and ir spectra identical to those of the product previously isolated.

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SUMMARY

Azido, N-chloroamino, and N,N-dichloroamino derivatives of dialkylphosphinic acids have been synthesised.

The azides upon photolysis in alcohols (except isopropanol) or t-butylamine give products derived from alkyl migration from phosphorus to nitrogen with incorporation of a molecule of solvent. Diisopropyl and di-t-butylphosphinic azides also give amides and products derived from insertion of a formal nitrene into the O-H bond of the alcohol. Diethylphosphinic azide undergoes predominantly nucleophilic substitution by the methanol solvent. Anhydrides formed in the photolysis of di-t-butylphosphinic azide in cyclohexane and benzene arise from the presence of adventitious moisture and accompany nitrene products. The formation of these products is discussed in terms of independent routes involving either a metaphosphonimidate intermediate (only trapped in protic solvents) or a singlet nitrene that decays to a triplet nitrene.

An equilibrium has been shown to exist between amides, N-chloroamides, and N,N-dichloroamides. The chloroamides add to phenylethylenes to yield anti-Markovnikov products after reduction, these cyclise with base to aziridines. The formation of cis and trans adducts in the reaction of t-1-(N-chloro-N-methylamino)-2,2,r-3,4,4-pentamethylphosphetan-1-oxide with styrene is discussed in terms of a pseudorotation mechanism. The initial N-chloro adduct has been isolated in the reaction of (N,N-dichloro)di-t-butylphosphinic amide with styrene.

Attempts to form ring expanded products in the reaction of t-1-(N-chloroamino)- and t-1-(N,N-dichloroamino)-2,2,r-3,4,4-pentamethylphosphetan-1-oxides (141) and (140) respectively yielded only the parent amide. The formation of an anionic species in these reactions was shown by trapping with methyl iodide.

The N-chloroamides with anthracene give 9-chloro and 9,10-dichloroanthracenes. The o:m:p ratio of chloroanisoles formed in the reaction of the chloroamides (140) and (141) is used to elucidate the nature of the mechanism of the chlorination reactions.

Triphenylarsine has been tried as a trap for nitrenes generated from N,N-dichloroamides and azides, without success.