ASPECTS OF THE CHEMISTRY OF PHOSPHORANES

by

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THESIS PRESENTED FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

University of Edinburgh May 1981

DECLARATION

I declare that this thesis is my own composition, that the work of which it is a record has been carried out by myself, and that it has not been submitted in any previous application for a higher degree.

This thesis describes results of research carried out in the Department of Chemistry, University of Edinburgh, under the supervision of Professor J.I.G. Cadogan and Dr. I. Gosney since 1 October 1977, the date of my admission as a research student.

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LECTURE COURSES

Postgraduate courses attended include: Chemistry at its Most Colourful (8 lectures - Staff of I.C.I. Organics Division); Catalysis and Chemical Productivity (7 lectures - Staff of I.C.I. Petrochemicals Division); Mass Spectrometry (5 lectures - Prof. J.H. Beynon); Zeolites (5 lectures - Dr. B.M. Lowe); The Bio-organic Chemistry of Drugs, Toxins and other Xenobiotics (5 lectures - Dr. A.G. Rowley); Strategy in Organic Synthesis (5 lectures - Dr. I. Gosney); Basic and Advanced Stereochemistry (5 lectures - Dr. H. McNab); Attendance for three years at organic research group seminars.

ABSTRACT

The reaction of tervalent phosphorus reagents with o-azidophenol in ether at room temperature is shown to give pentacoordinate phosphorus derivatives of the 1,3,2-benzoxazaphospholine ring system *via* an intermolecular reaction. This simple and mild reaction is capable of extension and was used to synthesise a series of heterocyclic phosphoranes with various substituents at phosphorus and in the endocyclic ring, including benzdiazaphospholines.

In certain cases, reaction of a bifunctional azido compound with tervalent phosphorus reagents leads to the alternative formation of a tetracoordinate iminophosphorane. It is argued that the coordination state of the reaction product can be correlated with the influence of electronic effects at phosphorus and the small-ring effect. Thus, pentacoordinate phosphorane formation is favoured over iminophosphorane formation when an electropositive phosphorus atom is enclosed within a small-ring.

The utilisation of these findings has led to the design of a successful intermolecular synthesis of tetraoxyphosphoranes and other spirobicyclic phosphoranes from azidobenzene, 2-phenyl-1,3,2-dioxaphospholan and alcohols.

The pentacoordinate phosphoranes, 2,2-dimethoxy-2-phenyl-1,3,2-benzoxazaphospholine and 2,2-dimethoxy-2,5-diphenyl-1,3,2-oxazaphospholan have been examined by variable temperature ^{1}H and ^{31}P n.m.r. spectroscopy and the results rationalised in terms of regular pseudorotational processes.

These studies have culminated in attempts to prepare and isolate a chiral monocyclic pentacoordinate phosphorane. In this respect a single racemic diastereoisomer of 2,5-diphenyl-2-methoxy-2-α-naphthyl-1,3,2-oxazaphospholan, which is stable towards stereomutation at room temperature, has been isolated. Other attempts to isolate a single chiral diastereoisomer from the reaction of (S)-(+)-2-azido-1-phenyl-1-ethanol with a range of racemic phosphinites have been unsuccessful.

CONTENTS

SECTION I - INTRODUCTION		Page
1.	Iminophosphoranes	1
1.1	Preparation of alicyclic iminophosphoranes	2
	(i) Reaction of azido compounds with tervalent phosphorus reagents: The Staudinger Reaction	2
	(ii) Reaction of chloramines with phosphines	7
	(iii) Reaction of amines with dihalophosphoranes: The Kirsanov Reaction	7
	(iv) Reaction of primary amines with phosphines and tetrahalomethanes	10
	(v) Miscellaneous preparations	10
1.2	Preparation of cyclic iminophosphoranes containing less than six atoms	11
1.3	Reactions of iminophosphoranes	14
	(i) Reaction with compounds containing the functional groups C=O or C=S	14
	(ii) Reaction with triple bonds	19
	(iii) Formation of heterocycles by intermolecular reactions	21
	(iv) Intramolecular reactions	21
	(v) Hydrolysis	28
	(vi) Phosphonium salt formation	29
	(vii) Formation of pentacoordinate phosphoranes	30
2.	Pentacoordinate Phosphoranes	31
2.1	Bonding	33
2.2	Pseudorotation	36

		Page
2.3	Factors determining pseudorotational barriers and ligand positions in pentacoordinate phosphoranes	41
	(i) Apicophilicity	41
	(ii) Ring Strain	45
2.4	Preparation of pentacoordinate phosphoranes	48
2.4.1	Reaction of tervalent phosphorus reagents with α,β-unsaturated systems	48
2.4.2	Reaction of tervalent phosphorus reagents with monocarbonyl compounds	54
2.4.3	Reaction of tervalent phosphorus reagents with compounds containing a weak sigma bond	55
2.4.4	Reaction of tervalent phosphorus reagents with diols and related compounds	55
2.4.5	Reaction of tervalent phosphorus reagents with aryl 2-nitroaryl ethers and sulphides	56
2.4.6	Preparations of pentacoordinate phosphoranes involving phosphorus ylides	57
2.4.7	Preparation from phosphonium salts and metal alkyls	66
3.	The Small-Ring Effect	68
3.1	Origins and manifestations	68
	(i) Ring strain	68
	(ii) Entropy	73

		Page
3.2	The small-ring effect in synthesis; reactions which involve pentacoordinate phosphorus	76
Section II - Experimental		
1.	Abbreviations and Symbols	83
2.	Instrumentation	84
3.	Solvents	87
4.	Preparation of Tervalent Phosphorus Compounds	87
5.	Preparation of Phosphoryl Compounds	97
6.	Preparation of Azido Compounds	98
7.	Preparation of Iminophosphoranes and Pentacoordinate Phosphoranes: Reaction of Azido Compounds with Tervalent Phosphorus Reagents	110
7.1	Reaction of o-Azidophenol with Tervalent Phosphorus Reagents	111
7.2	Reaction of o-Azidophenylbenzoate with Tervalent Phosphorus Reagents	117
7.3	Reaction of o-Azidophenyl tosylate with Tervalent Phosphorus Reagents	117
7.4	Reaction of o-Azidobenzyl alcohol with Tervalent Phosphorus Reagents	118
7.5	Reaction of o-Hydroxybenzylazide with Tervalent Phosphorus Reagents	120
7.6	Reaction of trans-2-Azidocyclohexanol with Tervalent Phosphorus Reagents	121
7.7	Reaction of 2-Azido-1-phenyl-1-ethanol with Tervalent Phosphorus Reagents	122

		Page
7.8	Reaction of (S)-(+)-2-Azido-1-phenyl-1-ethanol with Tervalent Phosphorus Reagents	125
7.9	Reaction of N-(o-Azidophenyl)phthalimide with Tervalent Phosphorus Reagents	127
7.10	Reaction of o-Azidoaniline with Tervalent Phosphorus Reagents	128
7.11	Reaction of N-(o-Azidophenyl)benzamide with Tervalent Phosphorus Reagents	130
7.12	Reaction of N-(o-Azidophenyl)-p-toluene-sulphonamide with Tervalent Phosphorus Reagents	131
7.13	Reaction of azidobenzene with Tervalent Phosphorus Reagents	135
8.	^{31}P N.m.r. Studies of the Reaction of Azido Compounds with Tervalent Phosphorus Reagents	135
9.	Preparation of Pentacoordinate Phosphoranes: Reaction of Iminophosphoranes with Alcohols	139
9.1	Reaction of N-Phenylimino-2-phenyl-1,3,2-dioxaphospholan with Alcohols	139
9.2	Reaction of N-Phenylimino-2-phenyl-1,3,2-dioxaphosphepan with Alcohols	149
10.	^{31}P N.m.r. Studies of the Reaction of Iminophosphoranes and Pentacoordinate Phosphoranes with Alcohols	150
11.	Variable Temperature N.m.r. Studies on 1,3,2-Oxazaphosphoranes	151
12.	The Acidic Hydrolysis of Pentacoordinate Oxazaphosphoranes	154

		Page
13.	Thermal Reactions of some Iminophosphoranes	157
14.	Preparation of Phosphatriazenes: Reaction of Tervalent Phosphorus Compounds with Azido Compounds	160
15.	Miscellaneous Reactions	162
Section III - Discussion		
	Preamble	167
1.	Reaction of bifunctional azides with tervalent phosphorus reagents; formation of pentacoordinate phosphoranes	168
1.1	o-Azidophenol with methyl diphenylphosphinite	168
1.2	Mechanism	172
1.3	General reaction of o-azidophenol with tervalent phosphorus reagents	176
1.4	Reaction of other azido alcohols with tervalent phosphorus reagents	181
1.4.1	trans-2-Azidocyclohexanol; 2-azido-1-phenyl-1-ethanol	181
1.4.2	o-Hydroxybenzyl azide; o-azidobenzyl alcohol	183
1.5	Reaction of o-azidoanilines with tervalent phosphorus reagents; formation of benzdiazaphospholines	185
1.5.1	o-Azidoaniline	185
1.5.2	o-Azidoaniline derivatives	187
1.6	Reaction of o-azidophenyl tosylate with tervalent phosphorus reagents	
1.7	Conclusions	191

		Page
2.	Factors influencing pentacoordinate phosphorane formation vs. iminophosphorane formation	194
2.1	Electronic effects at phosphorus	195
2.2	Small-ring effect	197
2.3	Other factors	199
3.	Formation of pentacoordinate phosphoranes by reaction of iminophosphoranes with alcohols	200
3.1	Reaction of N-phenylimino-2-phenyl-1,3,2-dioxaphospholan with 1,2-dihydroxybenzene	201
3.2	General reaction of N-phenylimino-2-phenyl-1,3,2-dioxaphospholan with alcohols	202
3.3	Mechanism	209
3.4	Conclusions	211
4.	Variable temperature n.m.r. studies of oxazaphosphoranes	212
4.1	2,2-Dimethoxy-2-phenyl-1,3,2-benzoxazaphospholine	214
4.2	2,2-Dimethoxy-2,5-diphenyl-1,3,2-oxazaphospholan	216
5.	Attempted synthesis and isolation of a chiral monocyclic pentacoordinate phosphorane	221
5.1	Reaction of racemic 2-azido-1-phenyl-1-ethanol with racemic phosphinites	223
5.2	Reaction of (S)-(+)-2-azido-1-phenyl-1-ethanol with racemic phosphinites	225

		Page
	Appendix	230
	Miscellaneous Studies	230
1.	Hydrolysis of selected pentacoordinate oxazaphosphoranes	230
2.	Phosphatriazene studies	232
3.	Intramolecular carbonyl-iminophosphorane reactions	233
4.	Reaction of 2,2-di(dimethylamino)-benzoxazaphosphole with dimethyl acetylene dicarboxylate	235
	Publications	237
	References	238

SECTION I

INTRODUCTION

INTRODUCTION

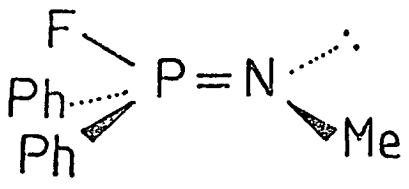
1. Iminophosphoranes

Iminophosphoranes are phosphorus nitrogen ylides and can be represented by the resonance hybrid forms (1a) and (1b). The phosphorus nitrogen bond character is thought to be determined by the degree of overlap between the filled nitrogen 2p orbitals and the vacant phosphorus 3d orbitals.[1]

$$R_3P{=}NR' \longleftrightarrow R_3\overset{+}{P}{-}\overset{-}{N}R'$$

(1a) (1b)

The phosphorus-nitrogen bond length of 1.641×10^{-10}m derived from the crystal structure of N-methyliminodiphenylfluorophosphine (2)[2] indicates the presence of d_π-p_π bonding as it is much less than the expected single bond length, 1.78×10^{-10}m, and closer to the double bond length, 1.64×10^{-10}m.[3] The bond angles of 119°, PNC, and FPN, 118.7°, FPC, 110.9°, NPC, 104.2°, and CPC, 107.1°, suggest that nitrogen is sp^2 hydridised and that phosphorus is tetragonally hybridised.



(2)

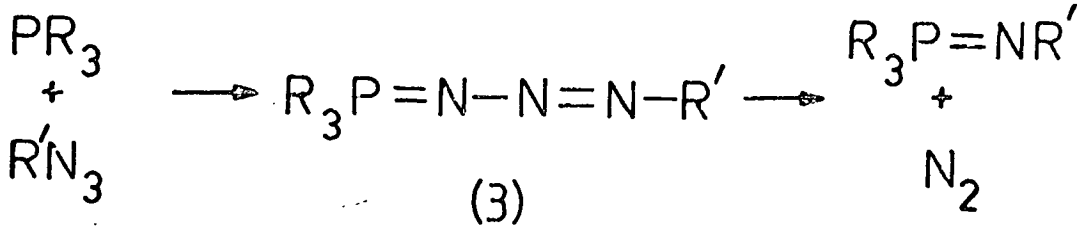
The polarity of the phosphorus-nitrogen bond depends on the degree of charge separation in the ylide, i.e. the relative contribution from form (1b), which in turn depends on the inductive, mesomeric and steric properties of the groups attached to phosphorus and nitrogen.

Iminophosphoranes can act as both electrophiles and nucleophiles. Generally, however, the more directional filled orbitals of nitrogen can intereact more effectively with electrophiles than can the more diffuse 3d orbitals of phosphorus with nucleophiles. Accordingly, iminophosphoranes behave more like bases than acids.

1.1. Preparation of alicyclic iminophosphoranes

(i) Reaction of azido compounds with tervalent phosphorus reagents: The Staundinger Reaction

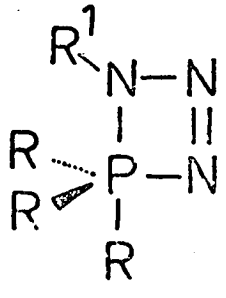
Iminophosphoranes were first prepared in 1919 by Staudinger and Meyer,[4] by the action of azido compounds on tertiary phosphines (Scheme 1). They proposed that the reaction proceeded *via* a linear phosphatriazene intermediate (3).



Scheme 1

Many phosphatriazenes have been subsequently isolated[5-8] and Mosby and Silva[9] have noted that the general conditions for adduct stability are that R' should be electron withdrawing, and R should be an electron donor.

Three different structures have been proposed for phosphatriazenes *viz* (4), (5) and (6); however, Franz and Osuch[10] and Goldwhite *et al.*[11] have excluded the cyclic pentacoordinate structure (4) on the basis of the low field ^{31}P chemical shifts observed for these compounds. Infra-red studies on the ^{15}N labelled adduct formed from tosyl azide and triphenylphosphine (5) support a linear structure for this phosphatriazene.[12] By contrast, Thayer and West[13] have observed an absorption at 2018 cm^{-1} (in both solid and solution) for the phosphatriazene formed from triphenylsilyl azide and triphenylphosphine which they explain on the basis of a non-linear structure (6). Johnson[1] has suggested that formation of the non-linear adduct (6) may be facilitated by delocalisation of the lone pair of electrons on nitrogen into the 3d orbitals of both phosphorus and silicon.



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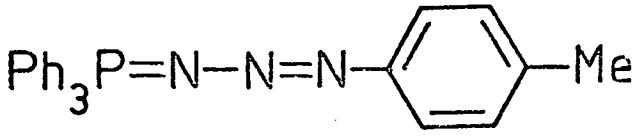

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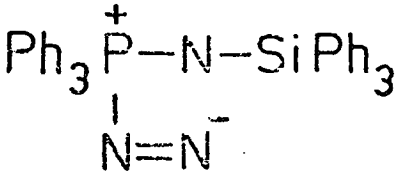
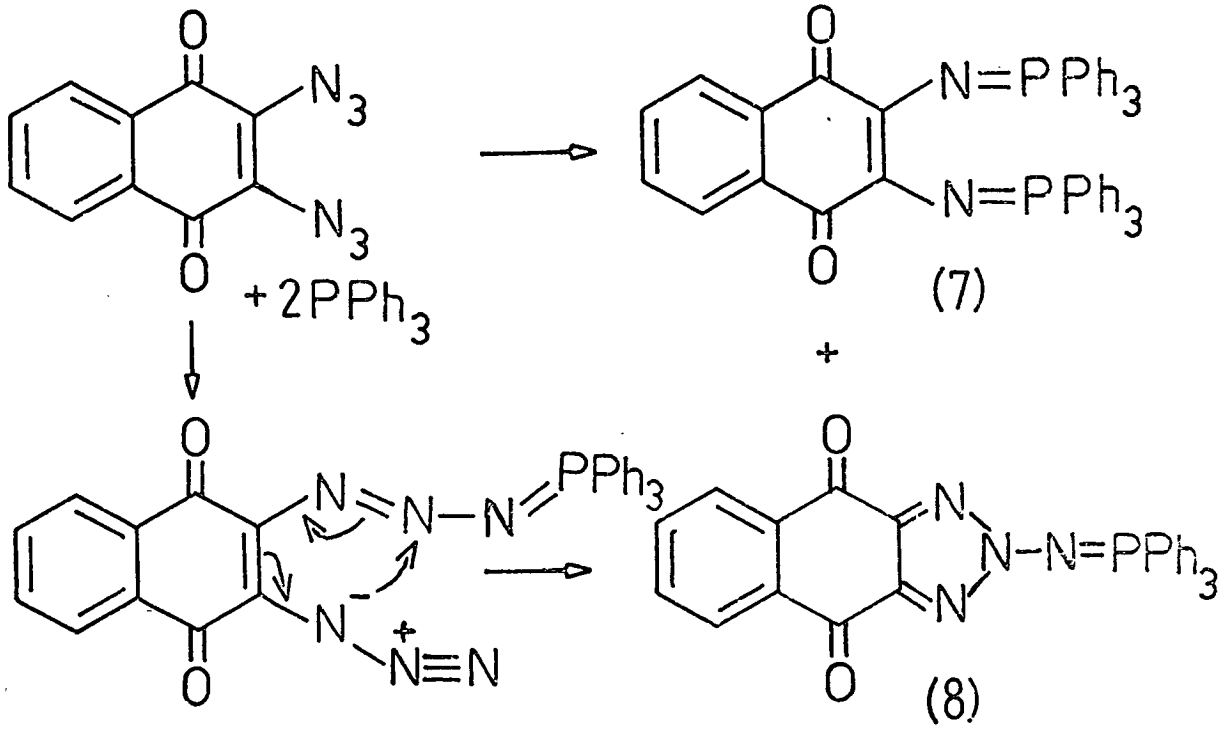


(6)

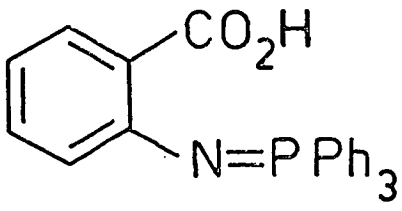
Mosby and Silva[9] have shown that reaction of 2,3-bisazido-naphthoquinone with triphenylphosphine gives, in addition to the expected bisiminophosphorane (7), a phosphinyl derivative of naphtho(2,3-d)triazoledione (8). This result can only be rationalised by assuming a linear phosphatriazene intermediate as shown in Scheme 2.



Scheme 2

Phosphatriazenes can be stabilised by interaction of the chain nitrogens with an adjoining group, as with the adduct derived from o-azidobenzoic acid and triphenylphosphine. This adduct is exceptionally stable, but decomposes in boiling toluene to give the corresponding iminophosphorane (9).

By comparison, the reaction of p-azidobenzoic acid with triphenylphosphine proceeds smoothly at 20°C with loss of nitrogen. The I.R. spectrum of the adduct shows the OH stretching frequency to have moved to longer wavelength, indicating hydrogen bonding. These observations are consistent with an intramolecular phosphatriazene structure probably best represented as (10).



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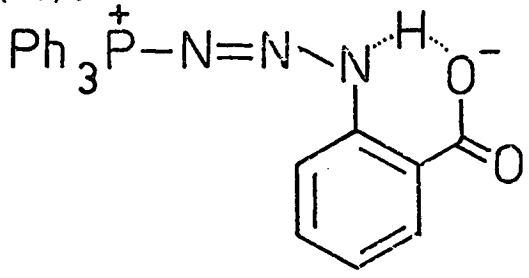
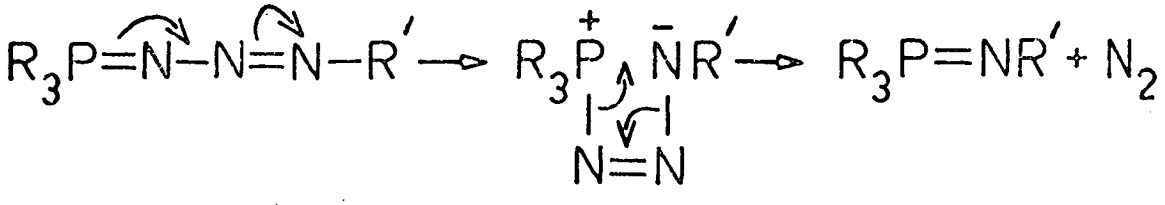


(10)

Leffler and Temple[14] have postulated a mechanism for the Staudinger reaction involving a four centre rearrangement as shown in Scheme 3.



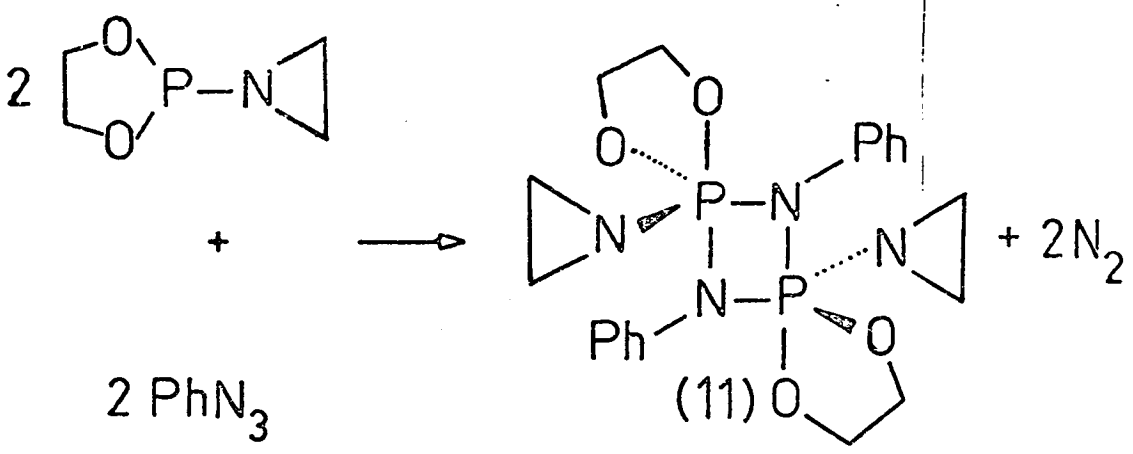
Scheme 3

In connection with the above mechanism Bock and Schnöller[12] have demonstrated by ^{15}N labelling that the two terminal azide nitrogens are always lost on iminophosphorane formation.

Kinetic studies[11,15,16,17] of the reaction have shown that phosphatriazene formation is second order, the rate of formation depending upon the nucleophilicity of the phosphorus reagent, $(C_5H_{10}N)_3P > Et_3P > Ph_3P > (EtO)_3P > (PhO)_3P > PCl_3$ (phosphorus trichloride giving no reaction), and the electrophilicity of the azide, $\underline{p}$-$NO_2Ar > Ar > \underline{p}$-MeOAr (Ar = PhN_3). Decomposition of the adduct to the iminophosphorane is first order, the rate determined by the stability of the phosphatriazene.

The Staudinger reaction has been used to prepare a wide range of iminophosphoranes (1) with R = alkyl, aryl, aryloxy, alkoxy, thioalkoxy and R' = alkyl, aryl, acyl, aroyl, sulphonyl, organophosphorus,[18] organometallic.[19] The reaction is limited only by the availability of azido compounds and low nucleophilicity of some tervalent phosphorus reagents.

If the phosphorus atom of an iminophosphorane is contained within a small ring dimerisation may occur. For example, Bellan *et al.*[20] have observed that reaction of 2-aziridino-1,3,2-dioxaphospholan with phenylazide gives a diazadiphosphetidine (11), as shown in Scheme 4, and not the expected iminophosphorane.



Scheme 4

(ii) Reaction of chloramines with phosphines

Reaction of chloramine and its derivatives in the presence of base gives iminophosphoranes (Scheme 5).[21]

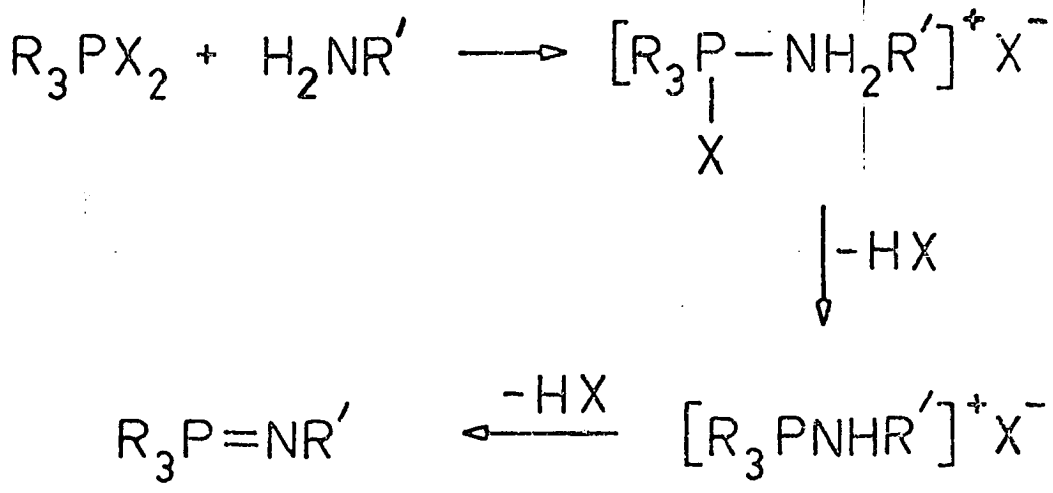
$$Ar_3P + ClNHR \rightarrow [Ar_3PNHR]^+Cl^- \xrightarrow{-HCl} Ar_3P{=}NR$$

Scheme 5

If the sodium salt of the chloramine is used the addition of base is unnecessary.[22]

(iii) Reaction of amines with dihalophosphoranes: The Kirsanov Reaction

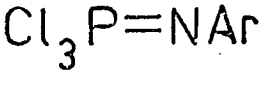
The utility of this reaction for the preparation of iminophosphoranes has been reviewed by Kirsanov.[23] Generally, reaction as in Scheme 6 leads to the formation of an iminophosphorane and two molar equivalents of hydrogen halide. Base is often required to liberate the iminophosphorane from the intermediate salts.



Scheme 6

A wide range of iminophosphoranes have been prepared by this method with R = alkyl, aryl, halide and R' = hydrogen, hydroxy, alkyl, aryl, amido, sulphonyl.

Iminophosphoranes (12) prepared from reaction of anilines with phosphorus pentachloride may dimerise to form diaza-diphosphetidines (13).[24] The tendency to dimerise has been correlated with pK_a data for the parent aniline; the most weakly basic anilines give only iminophosphoranes.



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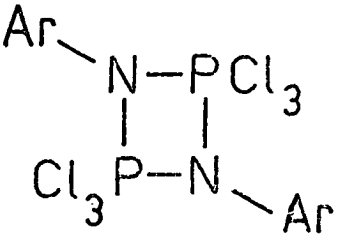

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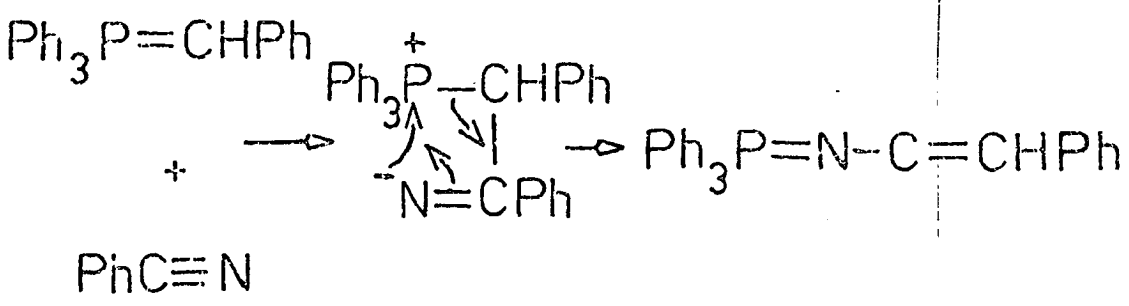
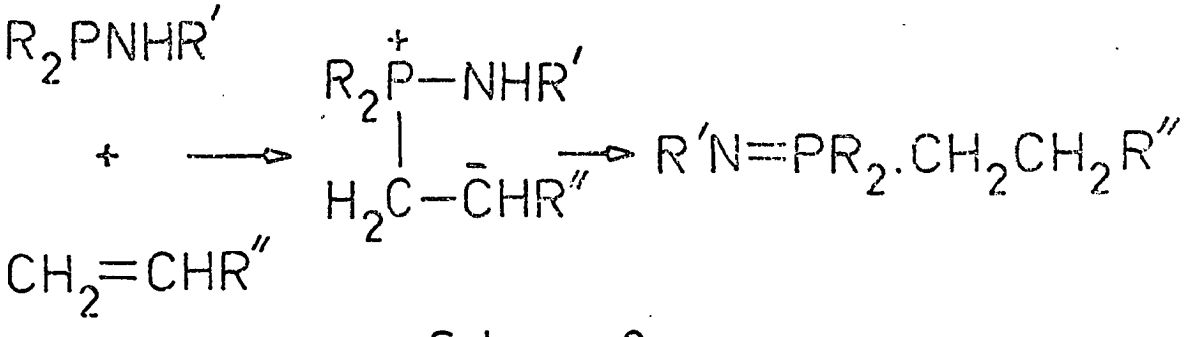
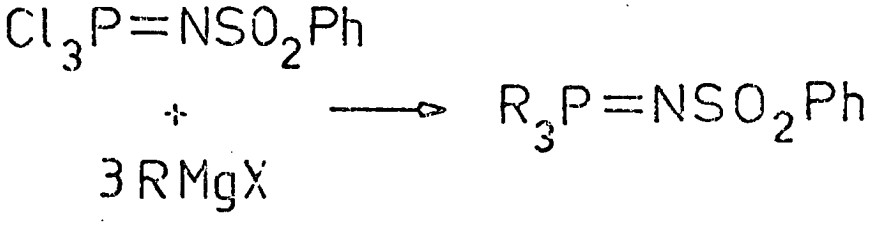
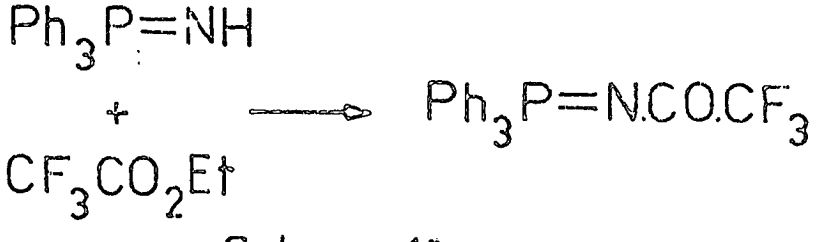


Scheme 8



Scheme 9





Scheme 10

(iv) Reaction of primary amines with phosphines and tetrahalomethanes

Appel[25] has recently reviewed this reaction and the proposed mechanism is outlined in Scheme 7.

$$R_3P + CX_4 + R'NH_2 \longrightarrow \underset{(14)}{[R_3PNHR']^+X^-} + CHX_3$$

$$[R_3PNHR']^+X^- \xrightarrow{-HX} R_3P{=}NR'$$

Scheme 7

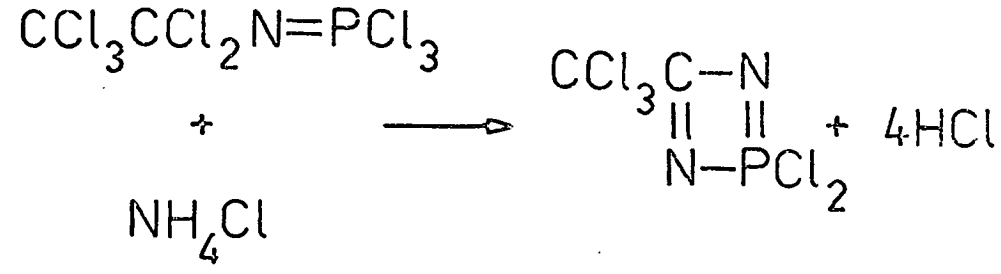
The related reaction of an aminophosphine with a tetrahalomethane is also believed to involve the intermediacy of a phosphonium salt (14).[26]

(v) Miscellaneous preparations

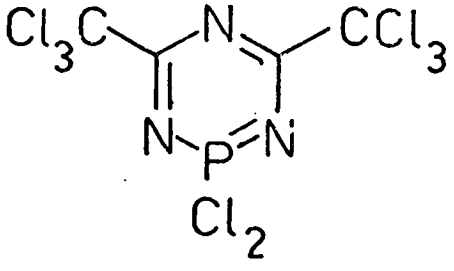
Several other less general methods for the preparation of iminophosphoranes are known, including reaction of phosphonium ylides with nitriles (Scheme 8),[27] reaction of electrophilic olefins with aminophosphines (Scheme 9),[28,29] and modification of iminophosphoranes by replacement of phosphorus[30] and nitrogen[31] substituents with alternative ligands (Scheme 10).

1.2 Preparation of cyclic iminophosphoranes containing less than six atoms

No authentic examples of four-membered cyclic iminophosphoranes have been recorded in the literature. Kukhar *et al.*[32] have reported the synthesis of such a compound (Scheme 11) but later it was shown to be a mixture of two six-membered ring phosphorus heterocycles, (15) and (16).[33]



Scheme 11



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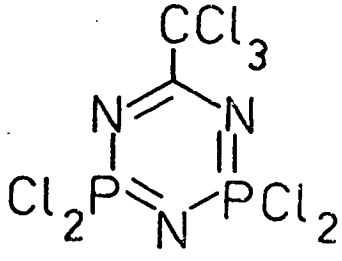
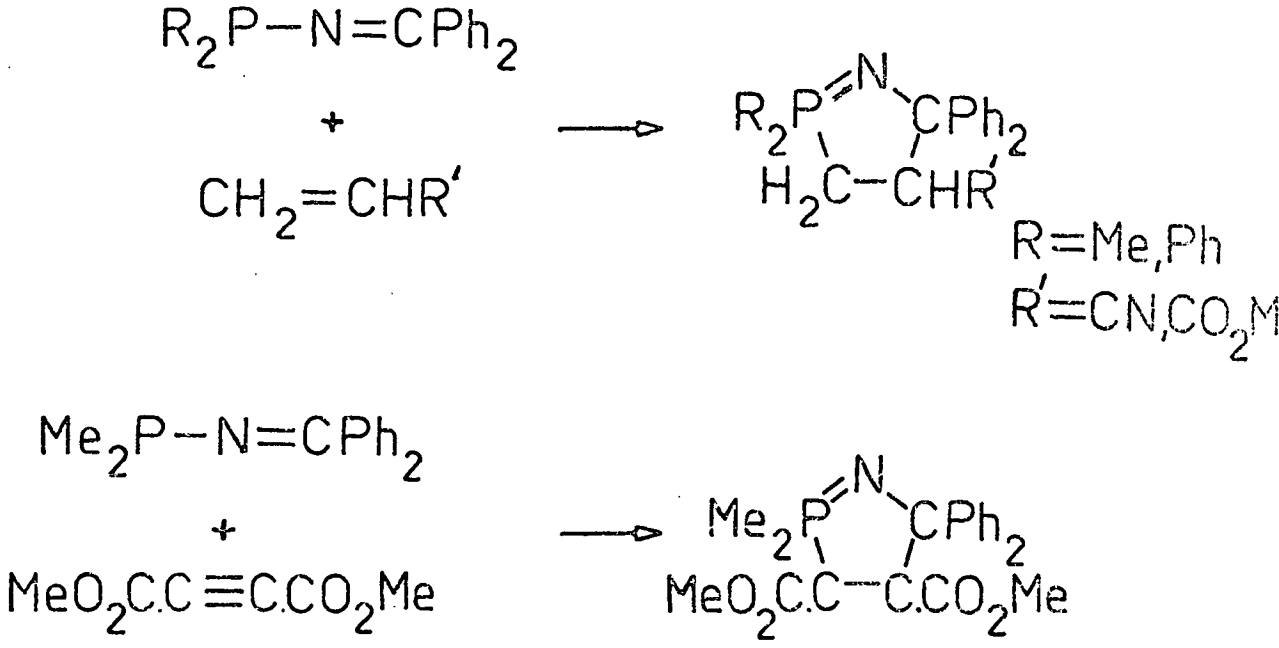


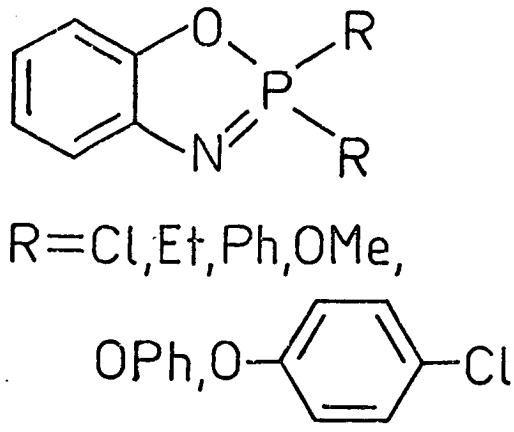
(16)

The first cyclic iminophosphorane was prepared in 1971 by Schmidpeter and Zeiss[34] by the 1,3-dipolar cycloaddition of electrophilic olefins or diacetylene dicarboxylate to dialkyldiphenylmethyleneaminophosphane (Scheme 12).

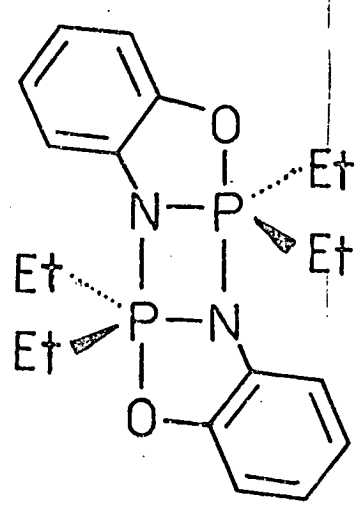


Scheme 12

Both Kabachnik *et al.*[35] and Stegmann *et al.*[36] have reported the synthesis of several 2,2-substituted-1,3,2-benzoxazaphospholes (17) using the Kirsanov and Staudinger reactions. However, an X-ray crystal structure determination in the case of (17, R = Et) revealed a dimeric diazadiphosphetidine structure (18).[37] High field ^{31}P chemical shifts were observed for all these compounds in benzene solution, indicating the presence of a dimeric structure.

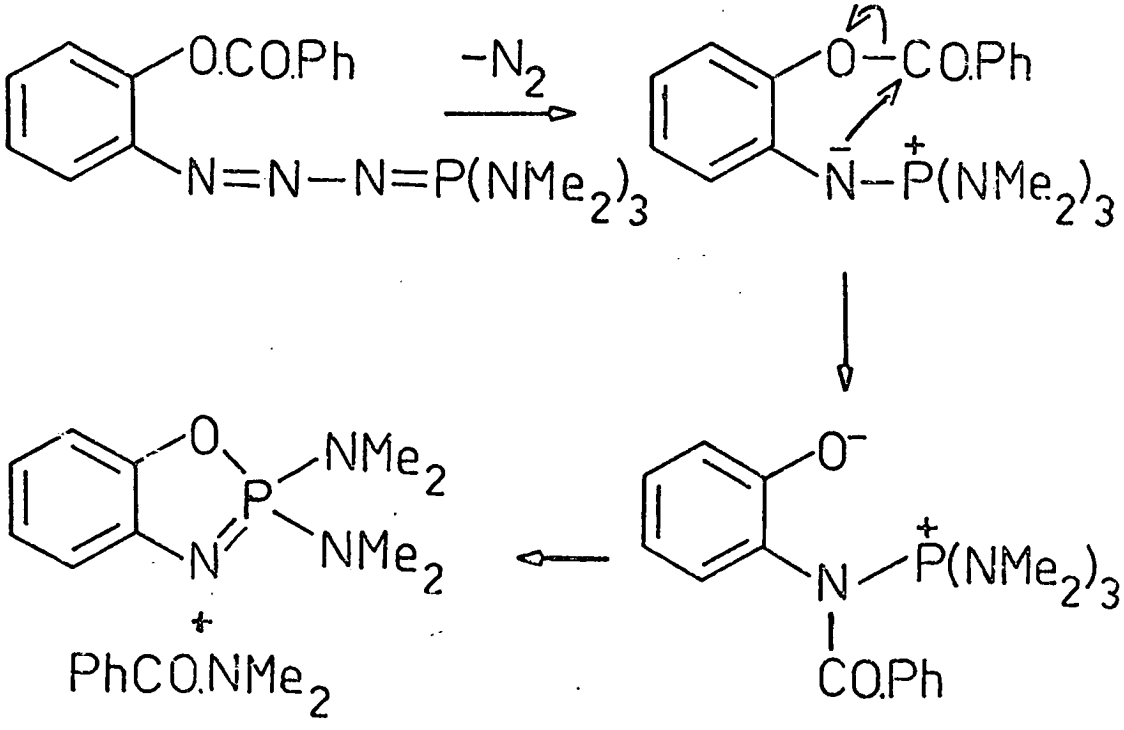


(17)



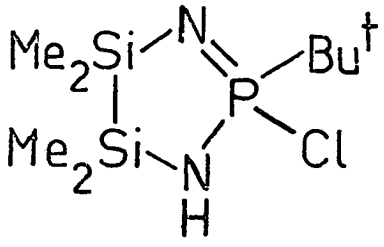
(18)

Recently, a monomeric benzoxazaphosphole (17, R=NMe_2) has been prepared by the author,[38] details of which are published in the Appendix. The proposed mechanism of formation is outlined in Scheme 13.

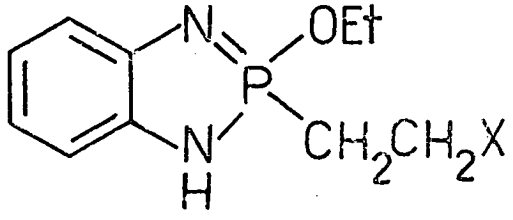


Scheme 13

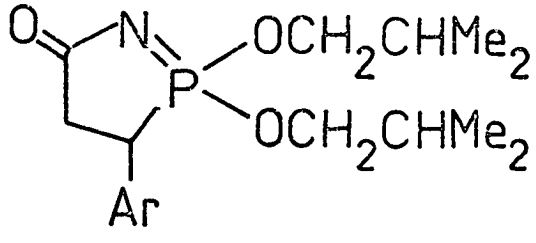
Other examples of cyclic iminophosphoranes containing five atoms have been reported by Scherer *et al.*[39] (19), Pudovik *et al.*[40] (20), and Tarasova *et al.*[41] (21) although no ^{31}P chemical shifts were reported to support a monomeric structure.



(19)



(20)



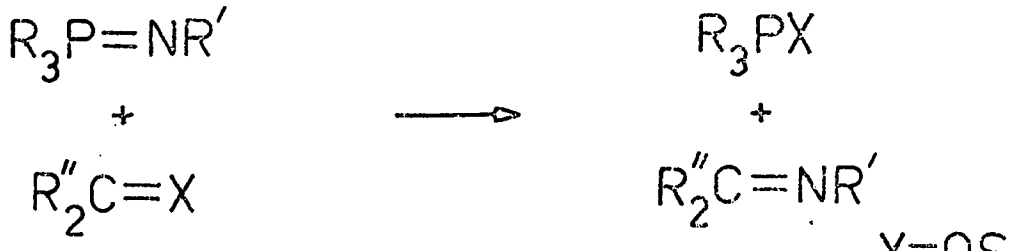
(21)

1.3 Reactions of iminophosphoranes

The chemistry of iminophosphoranes is governed by three major factors. Firstly, the degree of negative charge on nitrogen which determines the nucleophilicity of the iminophosphorane. Secondly, the ability of phosphorus to expand its octet thus allowing the formation of pentacoordinate intermediates, and finally, the strong bonds that phosphorus forms with certain atoms, particularly oxygen.

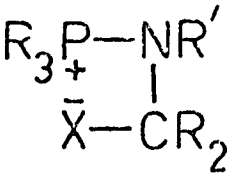
(i) Reaction with compounds containing the functional groups C = O or C = S

Iminophosphoranes react with compounds containing a C = O or a C = S group, in a reaction analogous to the Wittig reaction, to form imines (Scheme 14). The driving force for this reaction is the formation of the strong P = O or P = S, double bond. A wide range of compounds have been employed in this reaction including carbon dioxide, aldehydes, ketones, ketenes, isocyanates, carbon disulphide and isothiocyanates.[4,5,42]

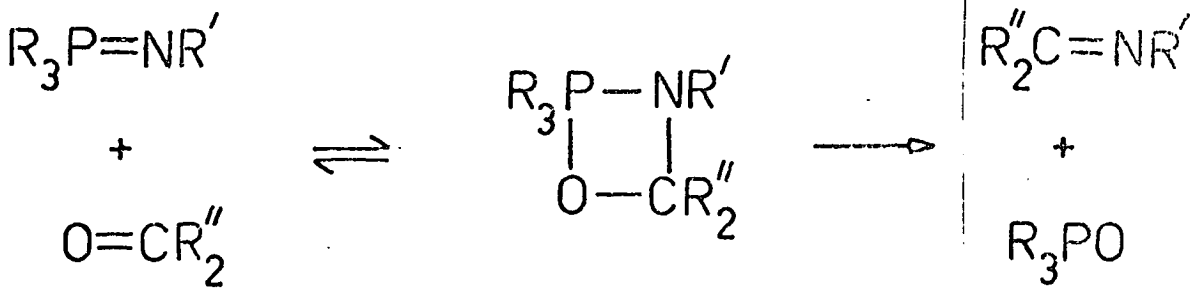


Scheme 14

Johnson and Wong[43] have suggested that the reaction proceeds *via* a betaine intermediate (22) as in the Wittig reaction. However, Frøyen[44] has concluded, from a kinetic study of the reaction between p-nitrobenzaldehyde and a series of N-phenyliminophosphoranes, that the intermediate is a pentacoordinate phosphorane which eliminates phosphine oxide in a concerted fashion (Scheme 15).

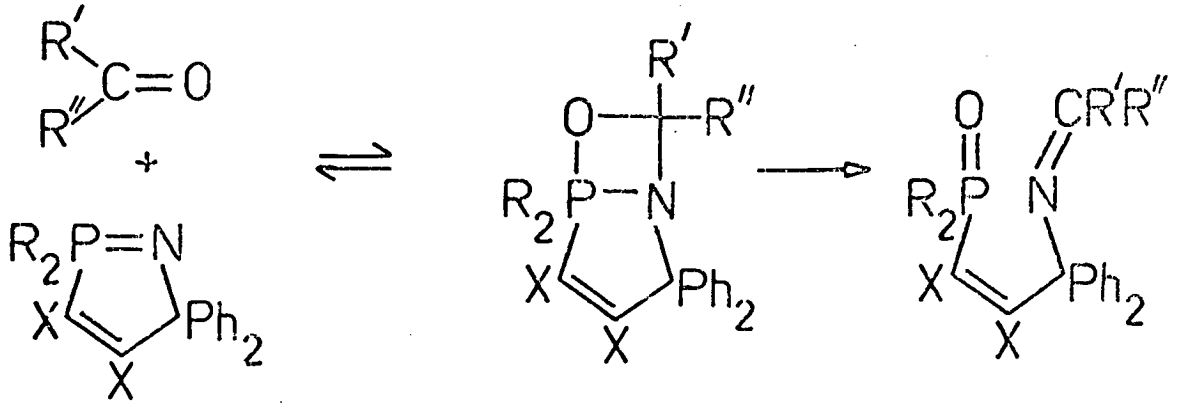


(22)



Scheme 15

Recently, Schmidpeter and Criegen[45] have isolated pentacoordinate phosphoranes from the reaction of cyclic iminophosphoranes (23) with ketones. The cycloadducts were formed reversibly and decomposed on heating to give the expected imines (Scheme 16).



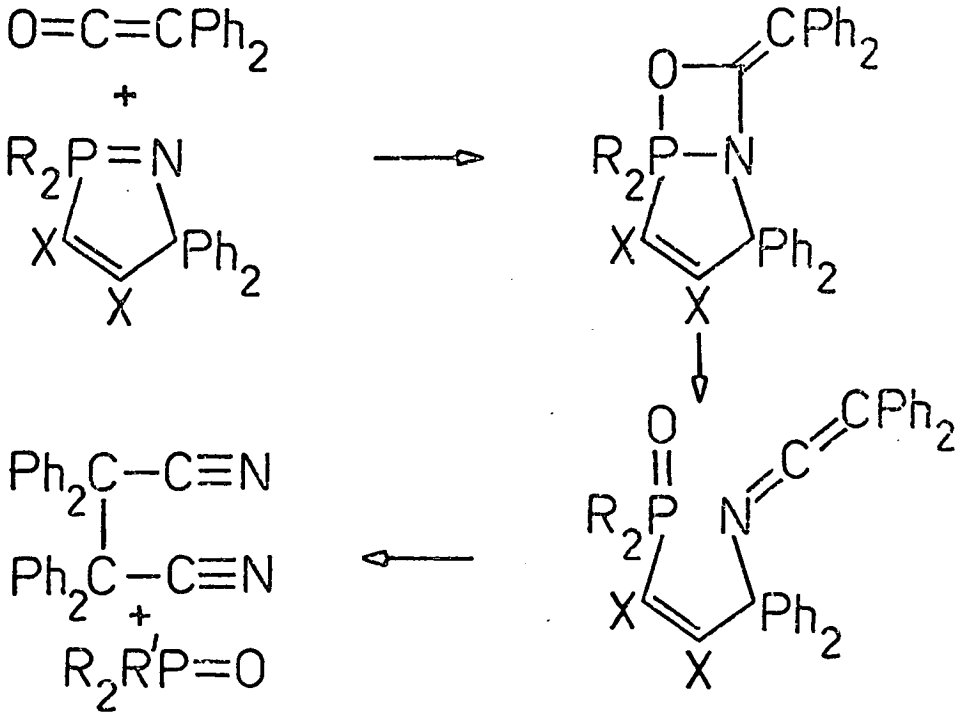
(23)

X=CO_2Me R=Me,Ph

R′,R″=H,Me,Ph,CF_3,CCl_3

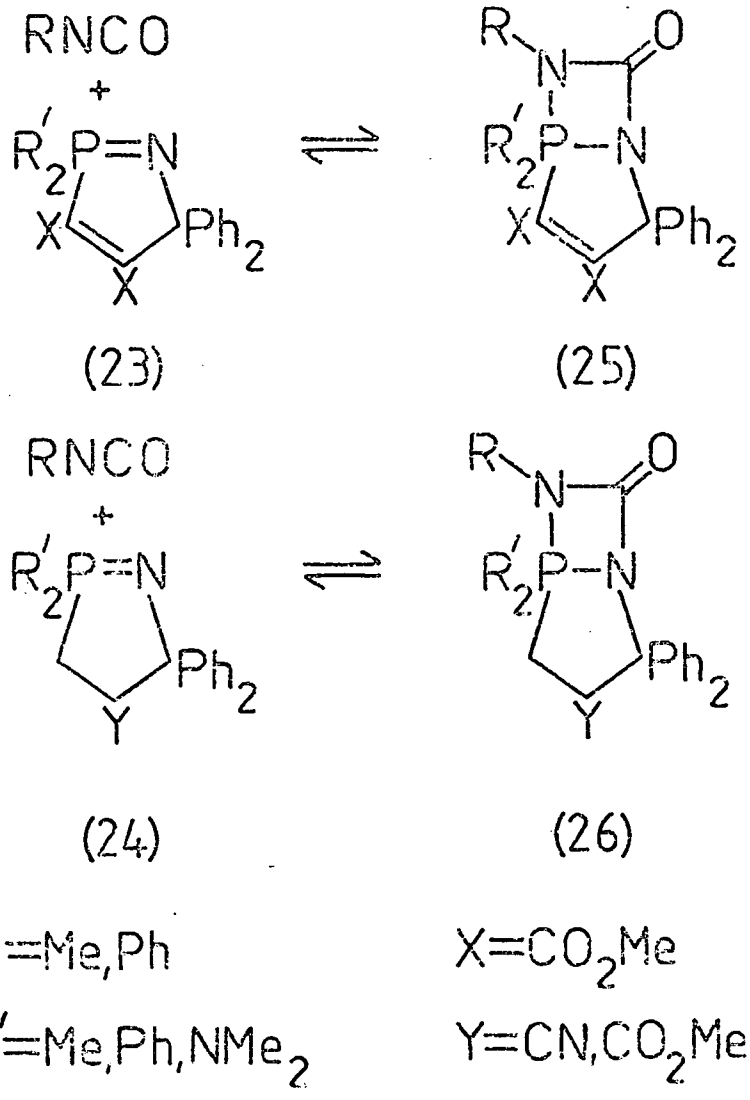
Scheme 16

These workers also found that the azaphospholes (23, R = Me,Ph) reacted with diphenylketene[46] to form isolable but unstable adducts which decomposed in solution, presumably *via* an imine, to give tetraphenylsuccinic dinitrile and a mixture of phosphoryl compounds (Scheme 17). They concluded from these results that the reactions involved a four-centre cyclic intermediate rather than a betaine thus supporting Frøyens mechanism.[4]



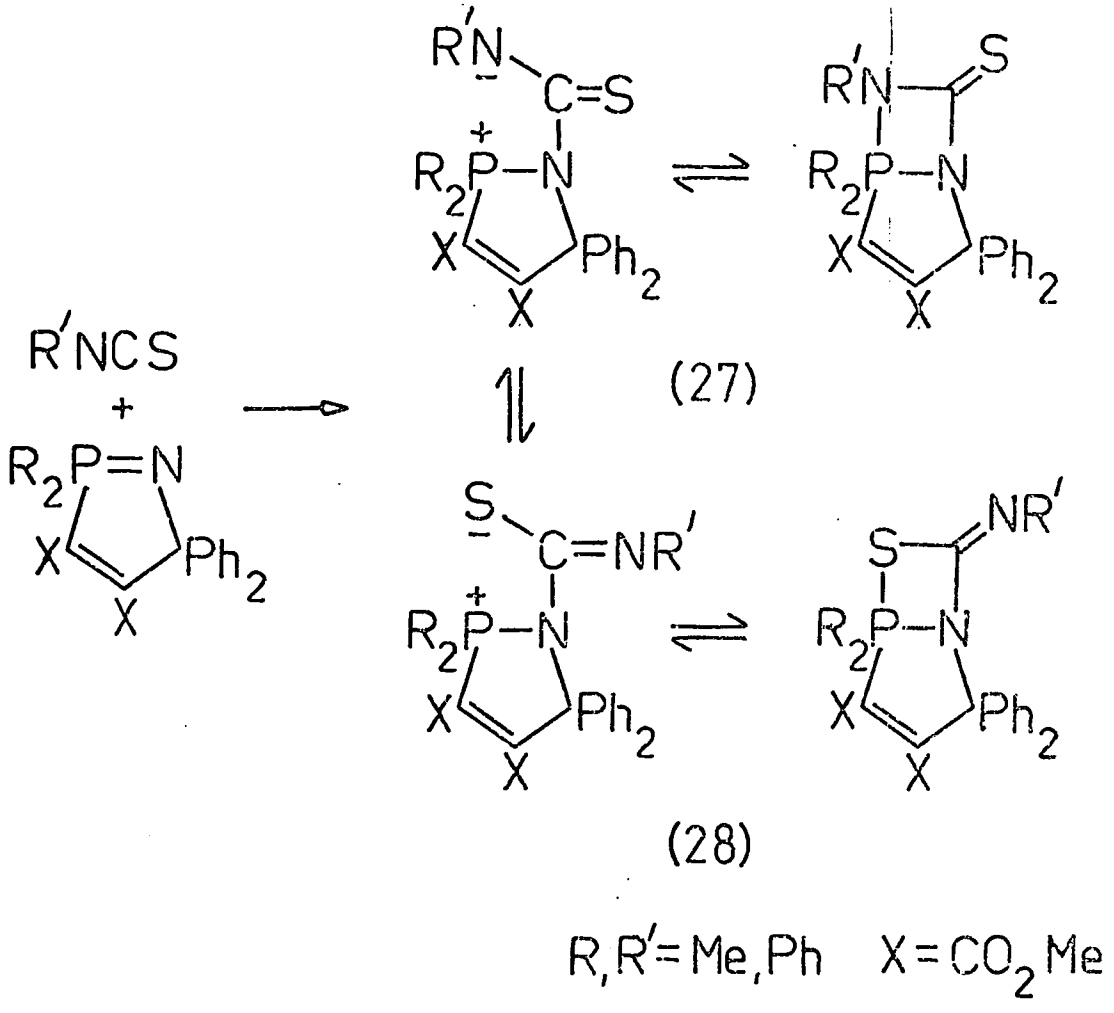
Scheme 17

Schmidpeter and Criegen have also investigated the reaction of cyclic iminophosphoranes (23) and (24) with isocyanates[47] and isothiocyanates.[48] In the case of isocyanates, addition occurred across the C = N double bond to give relatively stable adducts (25) and (26) which existed in partial equilibrium with undefined zwitterionic forms (Scheme 18).



Scheme 18

By comparison, isothiocyanates added across both the C = N and C = S double bonds to give adducts (27) and (28), respectively, which were in equilibrium with ring opened zwitterionic forms (Scheme 19).



(27)

(28)

R, R′ = Me, Ph X = CO_2Me

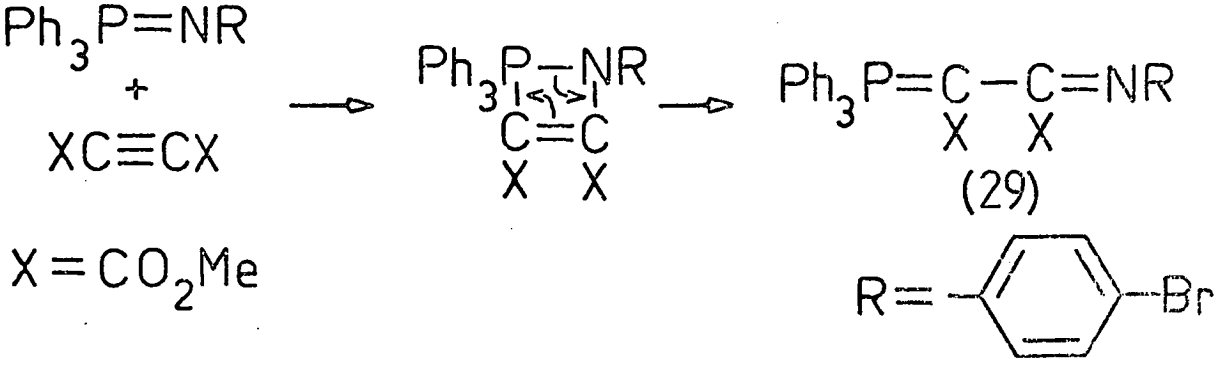
Scheme 19

The observation of a zwitterionic product in the latter reaction provides some support for the proposal by Johnson and Wong[43] for the formation of a betaine intermediate in the C = S/P = N reaction as discussed earlier. However, it is possible that the chemistry of cyclic iminophosphoranes is different from that of their acyclic analogues.

(ii) Reaction with triple bonds

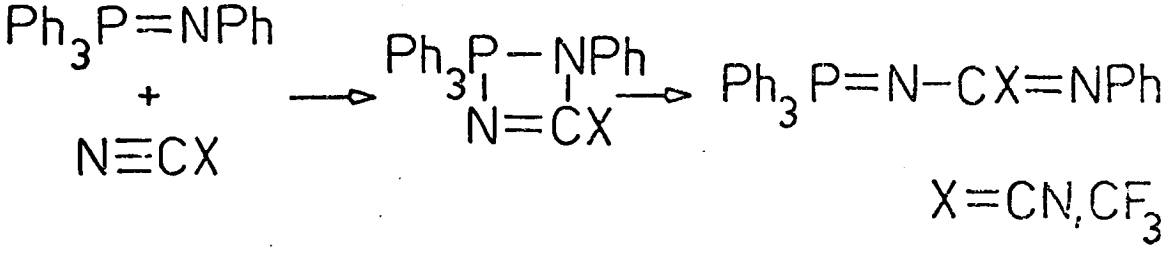
Brown *et al.*[49] have shown that reaction of N-(p-bromophenyl)iminotriphenylphosphine with dimethylacetylenedicarboxylate leads to the formation of a stabilised phosphonium ylide (29). When electron withdrawing groups such as

2,4-dinitrophenyl, carboethoxy, benzoyl and p-toluenesulphonyl were attached to nitrogen no reaction was observed. They proposed a mechanism involving nucleophilic attack by nitrogen and the formation of a four-centre pentacoordinate phosphorane intermediate which rearranged to (29) as shown in Scheme 20.[50]



Scheme 20

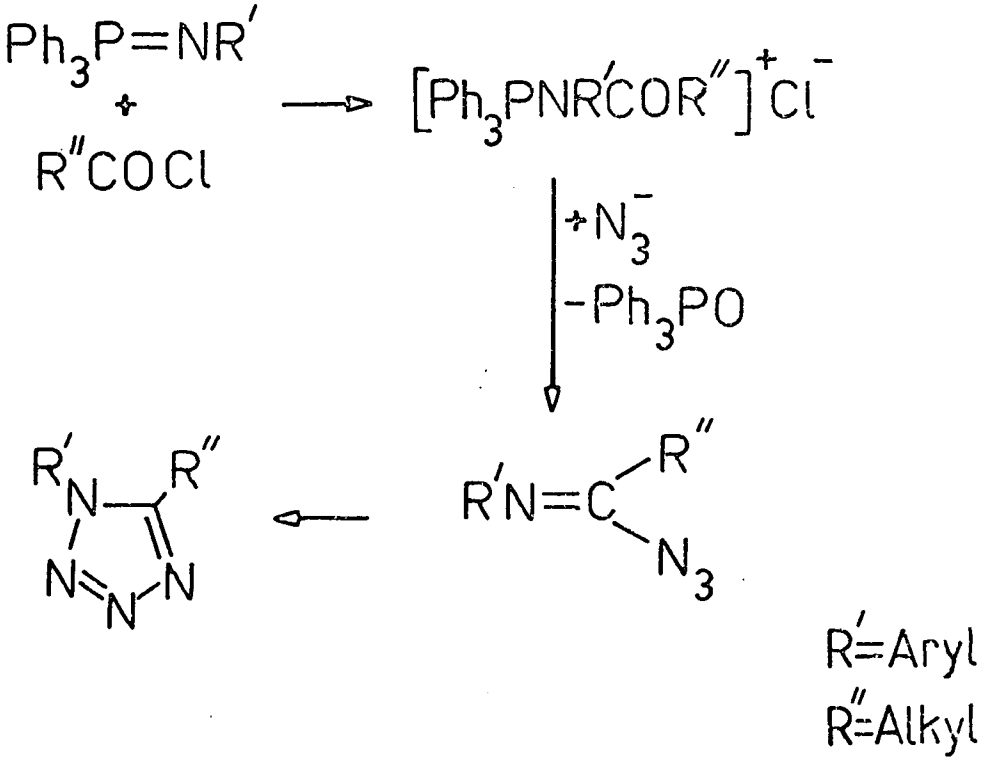
Electrophilic nitriles react in a similar manner to form a new iminophosphorane (Scheme 21).[51]



Scheme 21

(iii) Formation of heterocycles by intermolecular reactions

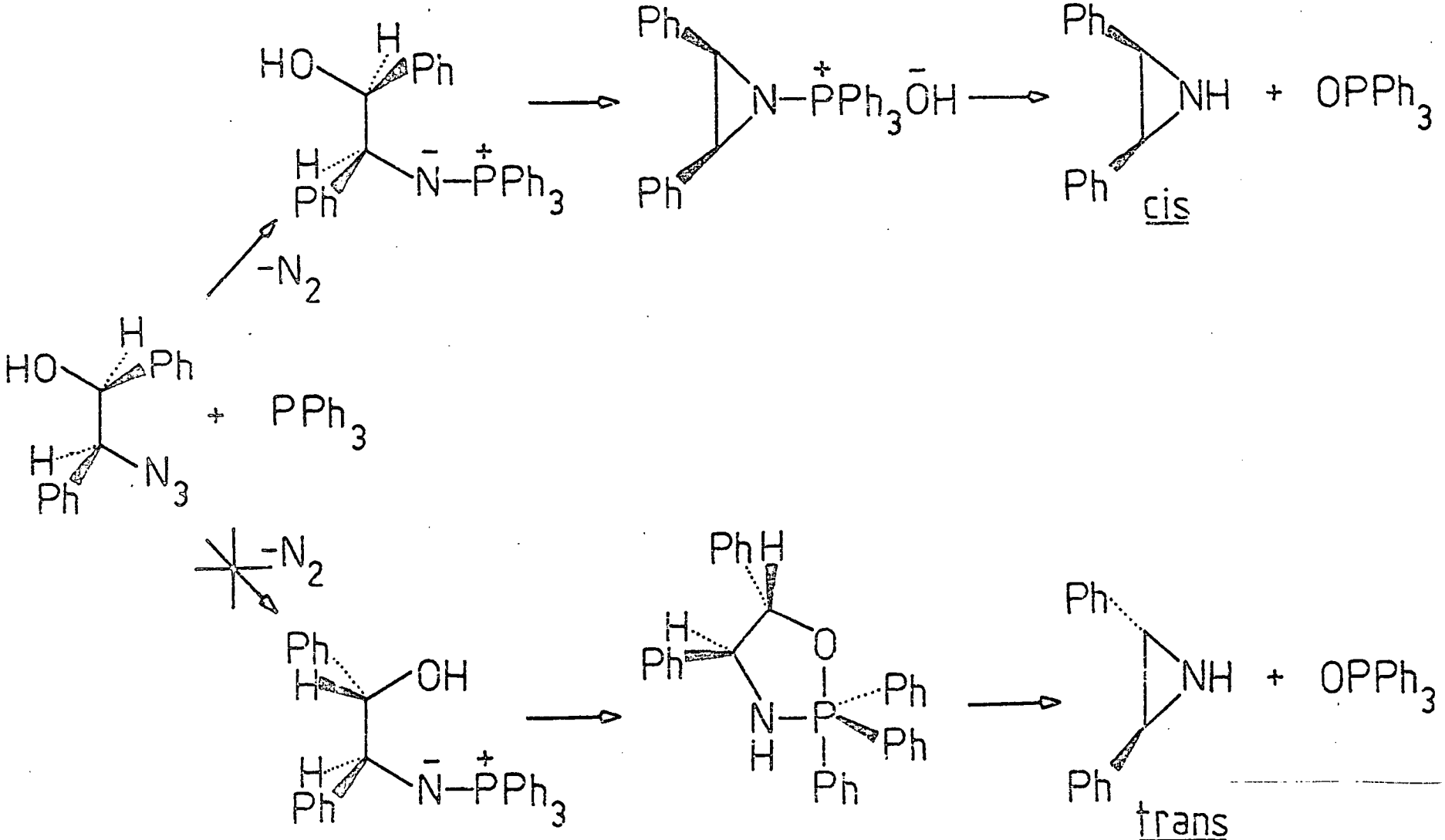
The utility of iminophosphoranes in the synthesis of heterocyclic compounds has been fully reviewed by Zbiral.[52] The reactions often proceed *via* the intermediacy of a phosphonium salt and subsequent loss of the phosphorus moiety as its oxide. A typical example is shown in Scheme 22 for the formation of tetrazoles from the reaction of iminophosphoranes with acyl halides and sodium azide.[53]



Scheme 22

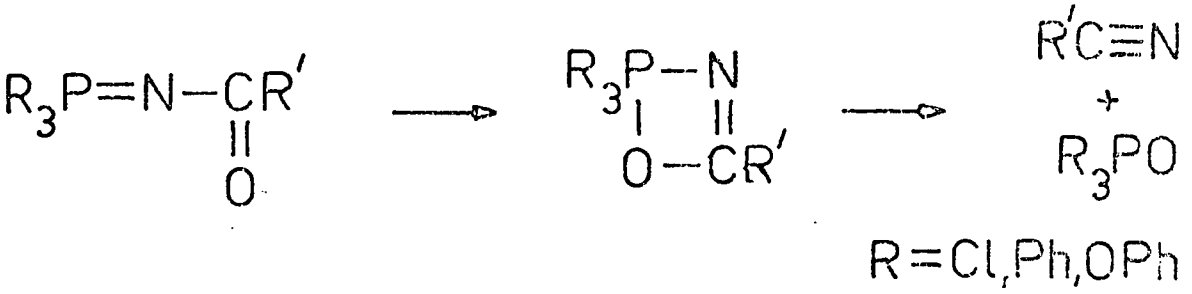
(iv) Intramolecular reactions

Staudinger *et al.*[4] and Kirsanov *et al.*[54,55] have reported the formation of nitriles upon thermolysis of N-acyl or N-aryl iminophosphoranes. The decomposition presumably occurs


HO
H
Ph
H
Ph
N–PPh3
-N2
Ph
N–PPh3OH
NH
+ OPPh3
cis
+ PPh3
N3
OH
PhH
O
N–P
trans

Scheme 24

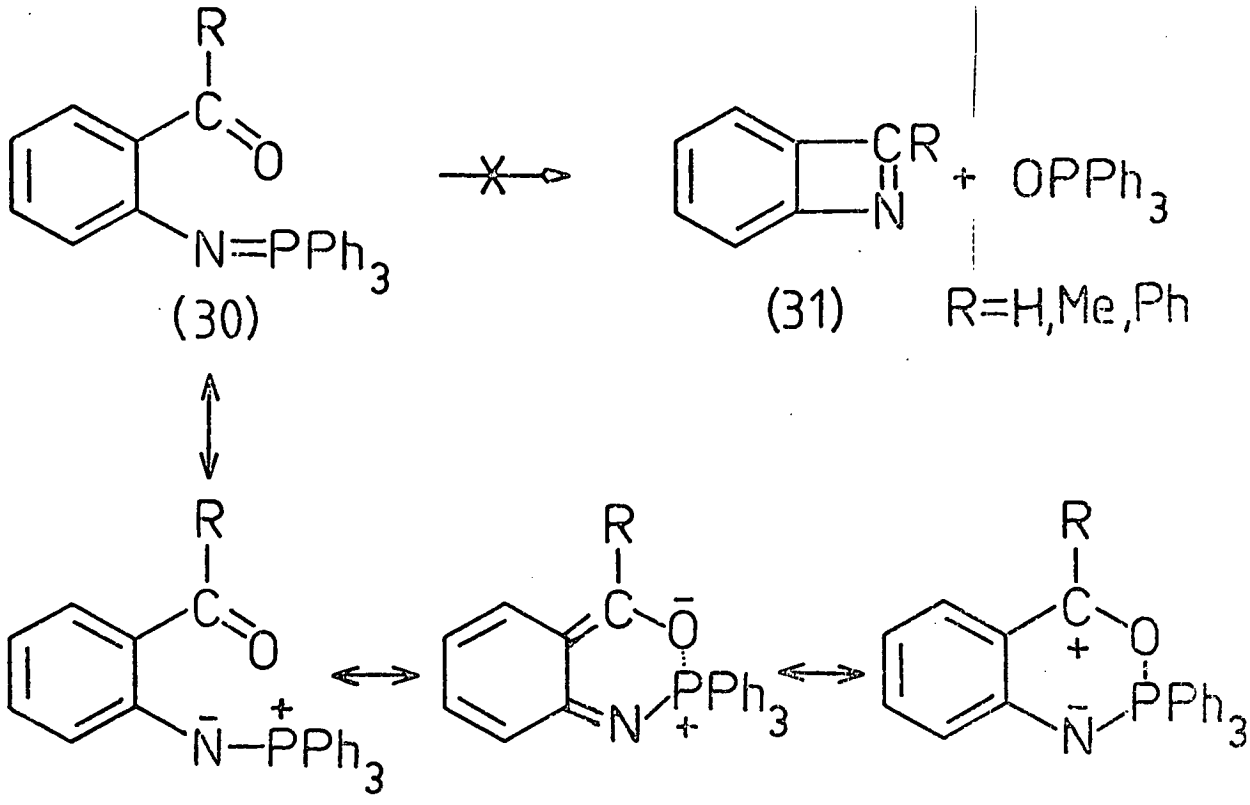
via a four-membered ring intermediate as shown in Scheme 23. A similar mechanism has been invoked to rationalise the formation of alkylisocyanates and alkylisocyanurates upon thermolysis of N-alkoxycarbonyl iminophosphoranes.[56]



Scheme 23

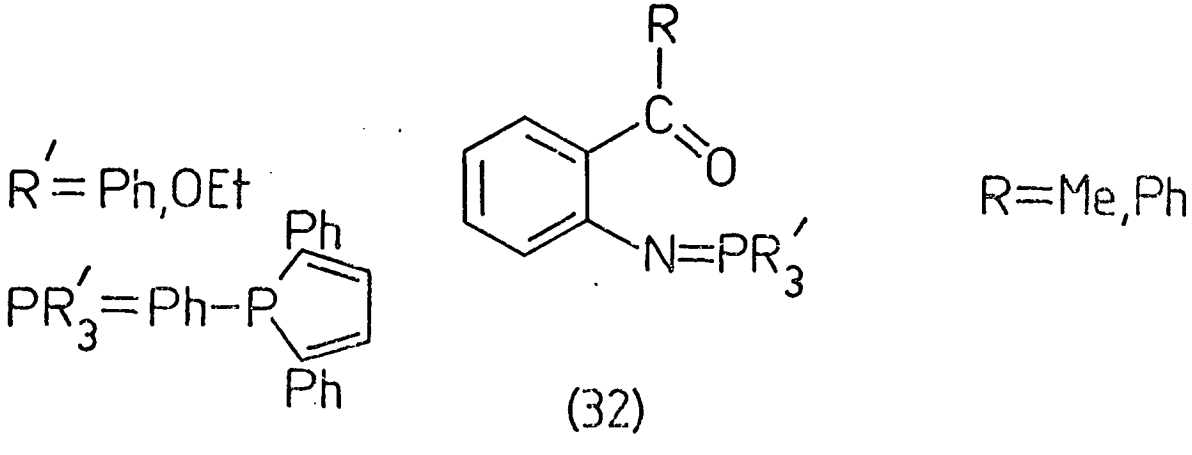
Aziridines have been prepared by Blum *et al.*[57,58] from the reaction of 2-azido alcohols with tertiary phosphines. For example, (±)-threo-2-azido-1,2-diphenylethanol and triphenylphosphine gave cis-2,3-diphenylaziridine. The authors explained the stereospecificity of this reaction by the mechanism shown in Scheme 24. The preparation of aziridines by the reaction of 2-amino-alcohols with dibromotriphenylphosphorane probably proceeds *via* a similar mechanism.[59]

Two groups of workers have attempted to synthesise benzazetes (31) using an intramolecular carbonyl/iminophosphorane reaction, but without success. In one instance, Nomura *et al.*[60] thermolysed a series of N-(2-acylphenyl) iminophosphines (30) in boiling toluene but observed no decomposition (Scheme 25). They attributed the unexpected thermal stability of (30) to resonance stabilisation.



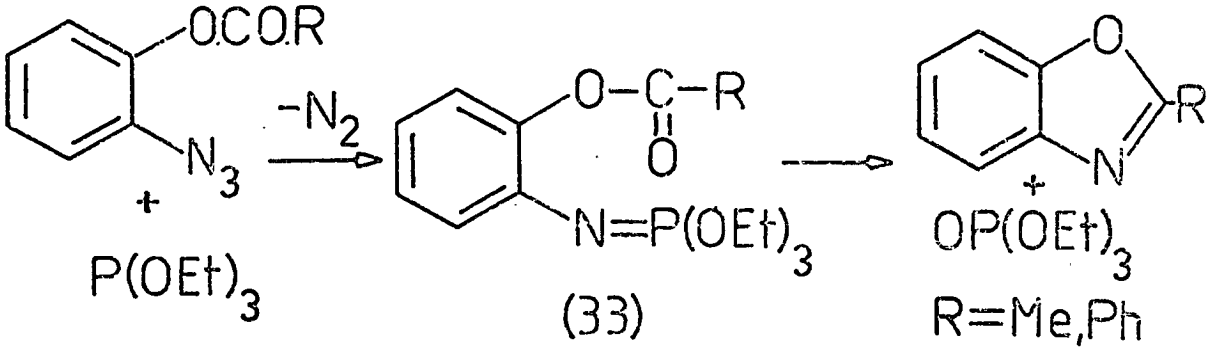
Scheme 25

Independently, Scott[61] attempted to decompose the related compounds (32) at temperatures up to 450°C, but observed only isomerisation of the starting material or products derived from intermolecular reactions.



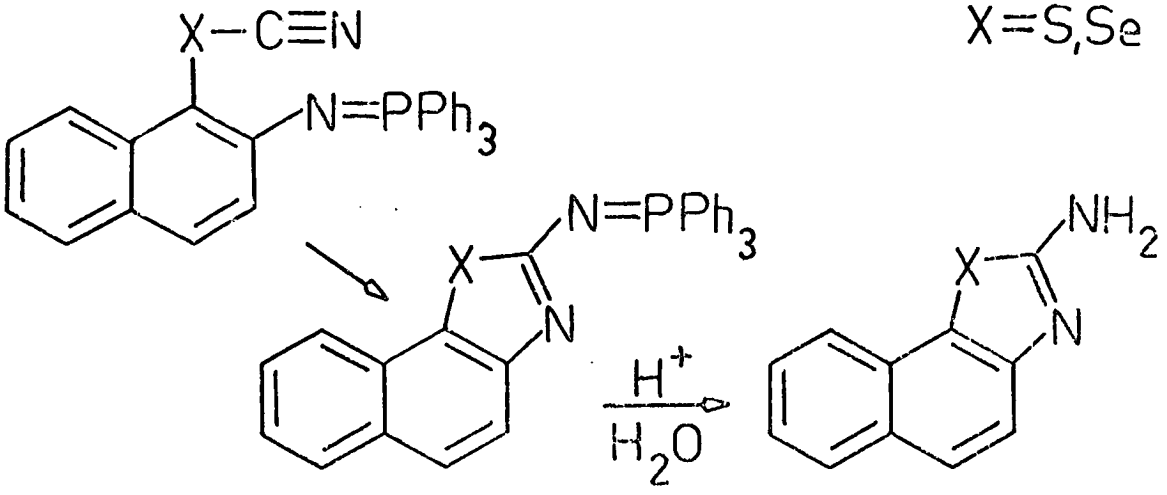
(32)

In contrast to these failures, five membered ring heterocyclic compounds have been prepared by three different intramolecular iminophosphorane reactions. Leyshon and Saunders[62] have reported the synthesis of 2-substituted benzoxazoles by the action of triethylphosphite on 2-azidophenyl esters (Scheme 26). Although an iminophosphorane (33) was not actually isolated its intermediacy was detected by ultraviolet and ^1H n.m.r. spectroscopy.



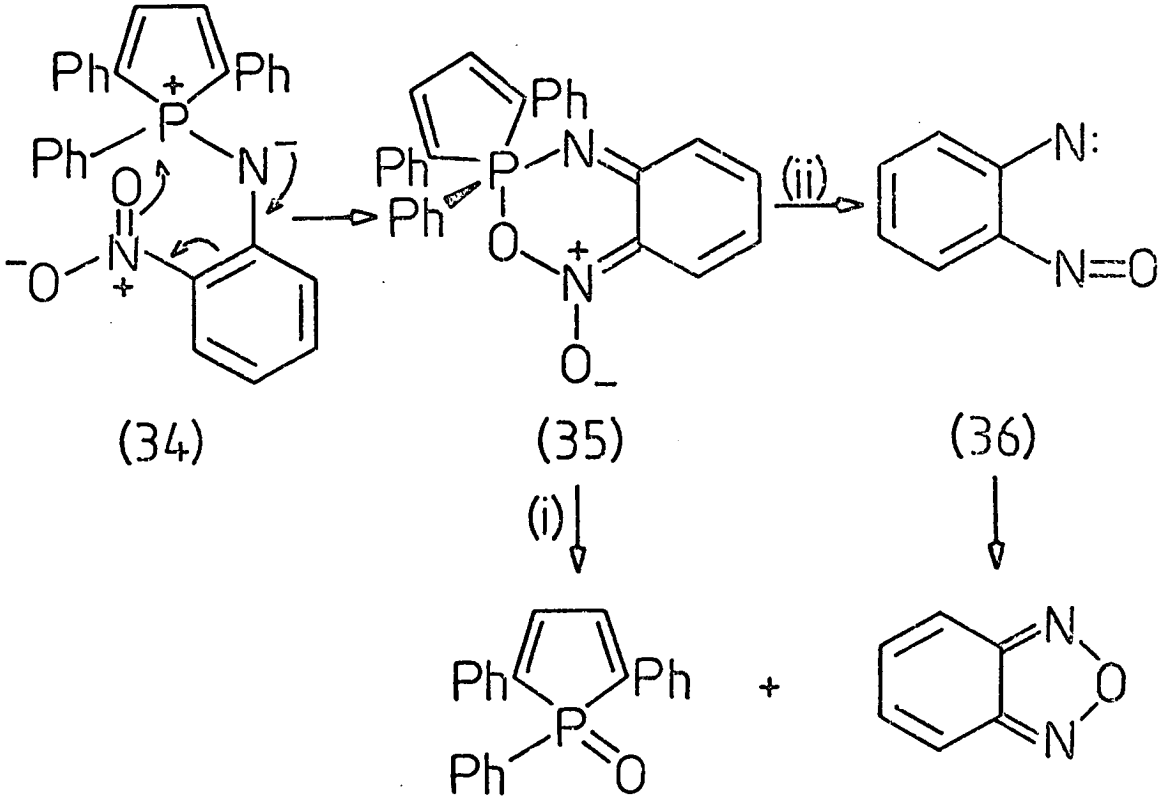
Scheme 26

Zbiral[63] has utilised the reaction of iminophosphoranes with triple bonds to prepare naphtho-1,3-thiazoles and naphtho-1,3-selenazoles as shown in Scheme 27.



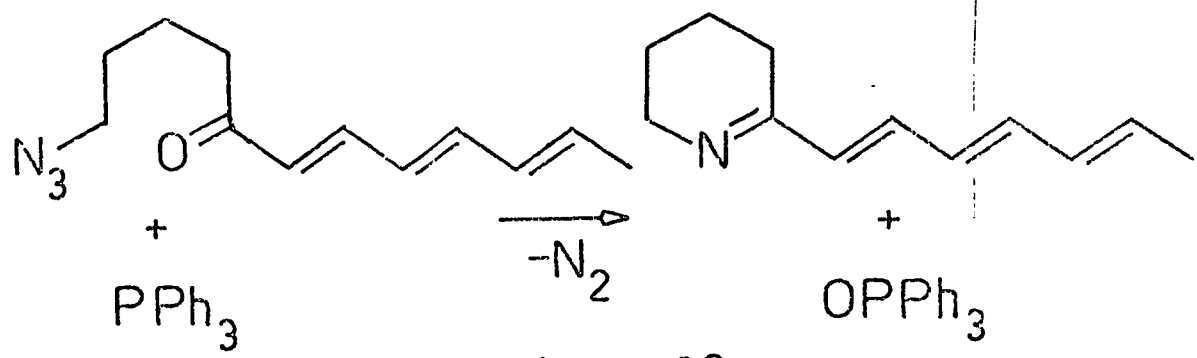
Scheme 27

Benzofurazan[64] has also been prepared by the thermal decomposition of N-o-nitrophenylimino-1,2,5-triphenylphosphole (34). The proposed reaction mechanism involved the formation of a pentacoordinate phosphorane (35) as an intermediate which decomposed either in a concerted step (i) or stepwise (ii) *via* o-nitrenonitrosobenzene (36) (Scheme 28).

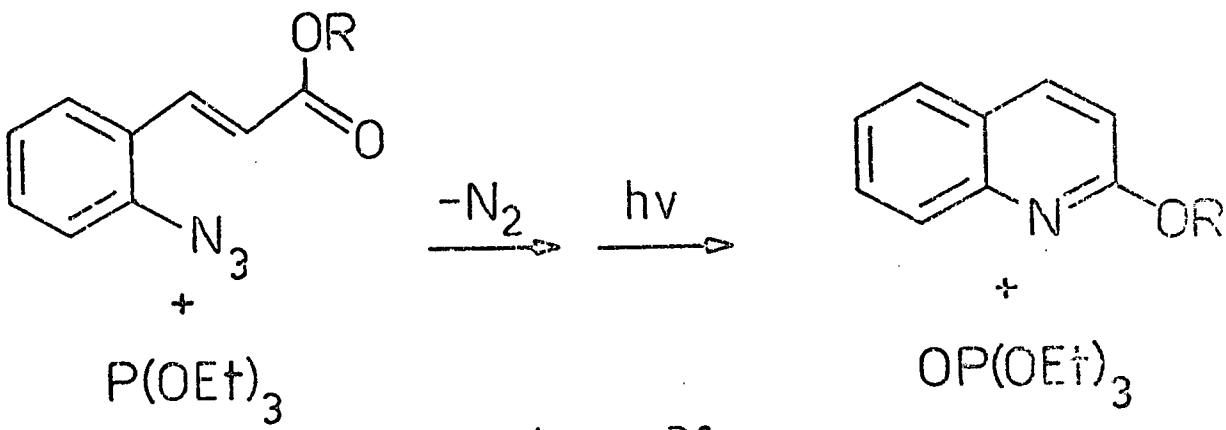


Scheme 28

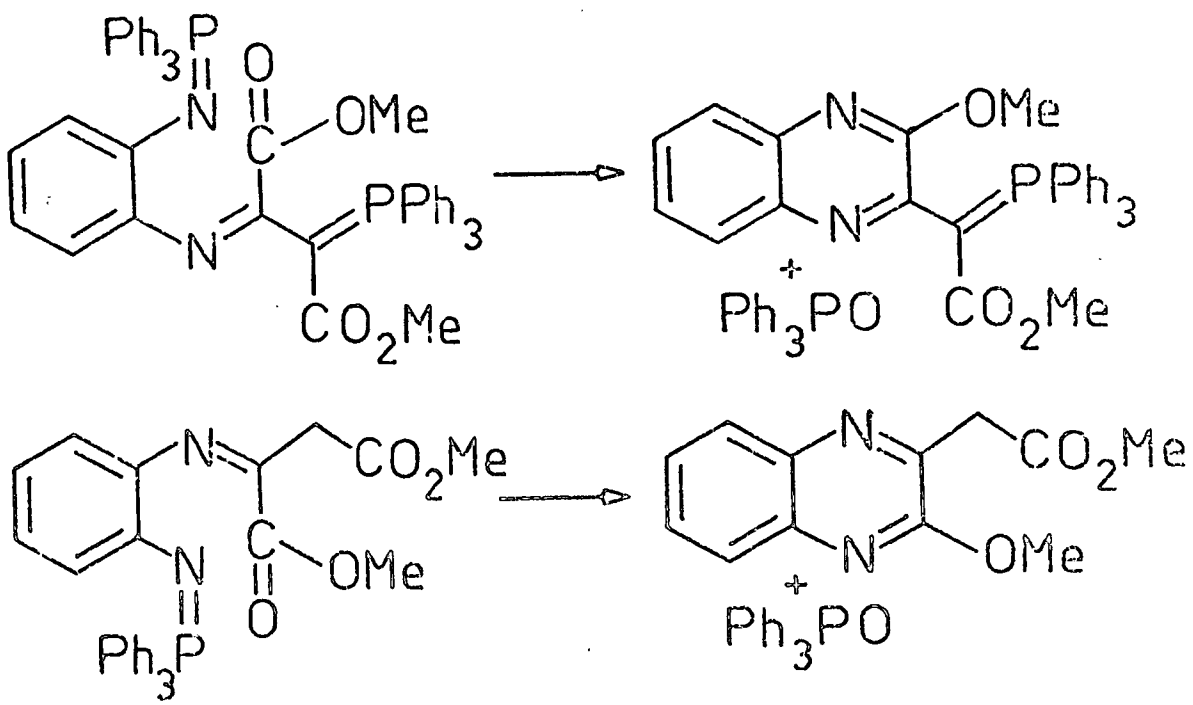
Three examples of intramolecular carbonyl/iminophosphorane reactions to form six-membered rings have been reported in the literature. Pailer and Haslinger[65] have synthesised the alkaloid nigrifactine (Scheme 29), Saunders *et al.*[66] have prepared 2-substituted quinolines (Scheme 30), and Brown



Scheme 29



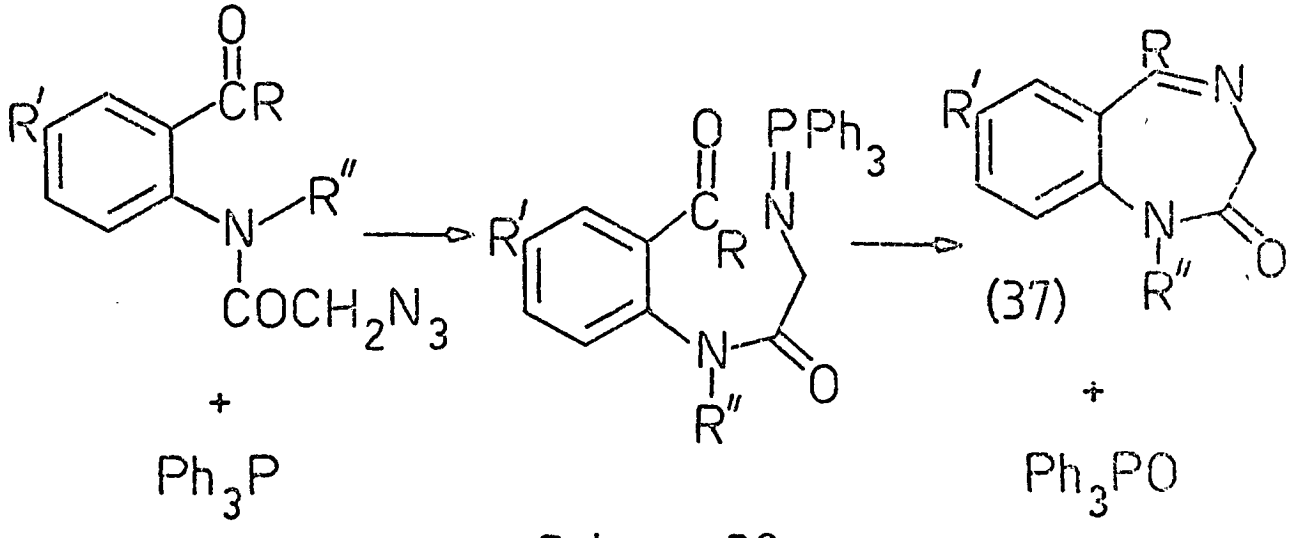
Scheme 30



Scheme 31

et al.[67] have isolated two 2,3-disubstituted benzopyrazines from the reaction of N-2-substituted iminophosphoranes with dimethylacetylene dicarboxylate (Scheme 31).

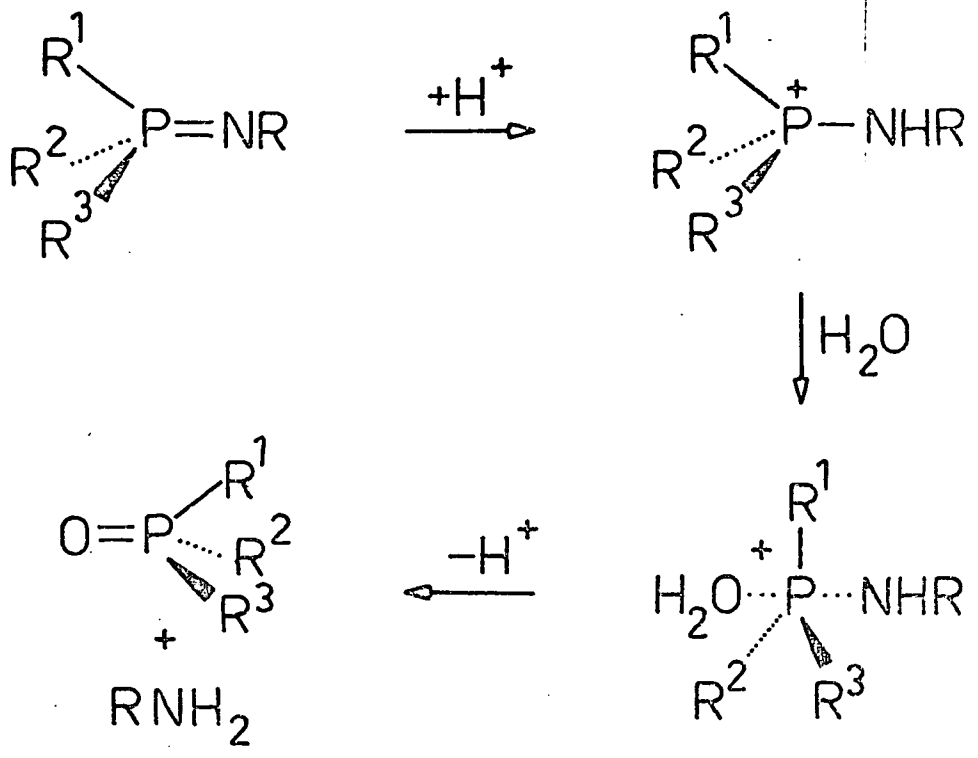
Ackrell *et al.*[68] have recently described the preparation of benzo-1,4-diazepin-2-ones (37) *via* the intermediacy of an iminophosphorane as shown in Scheme 32. This is the first example of an intramolecular carbonyl/iminophosphorane reaction leading to a seven-membered ring.



Scheme 32

(v) Hydrolysis

The hydrolysis of iminophosphoranes is thought to occur by protonation of nitrogen to form a phosphonium salt followed by attack of a water molecule at phosphorus to give a pentacoordinate phosphorane which decomposes to phosphine oxide and amine (Scheme 33).[1] Evidence in support of this mechanism has come from the acidic hydrolysis of (+)-N-p-nitrophenyliminomethylphenylpropylphosphine which affords mainly, but not exclusively, inverted phosphine oxide.[69]



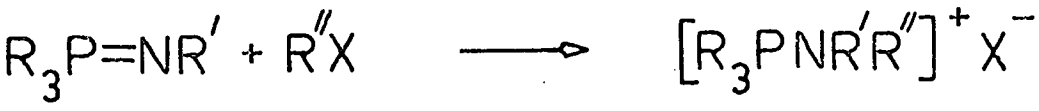
Scheme 33

The ease of hydrolysis appears to be related to the basicty of the nitrogen atom. Electron withdrawing groups attached to nitrogen tend to stabilise the iminophosphorane and lead to a decrease in reactivity. For example, N-ethyl-iminotriphenylphosphine hydrolyses instantaneously in neutral solution, whereas N-carboethoxyiminotriphenylphosphine hydrolyses slowly in boiling acidic solution.[70]

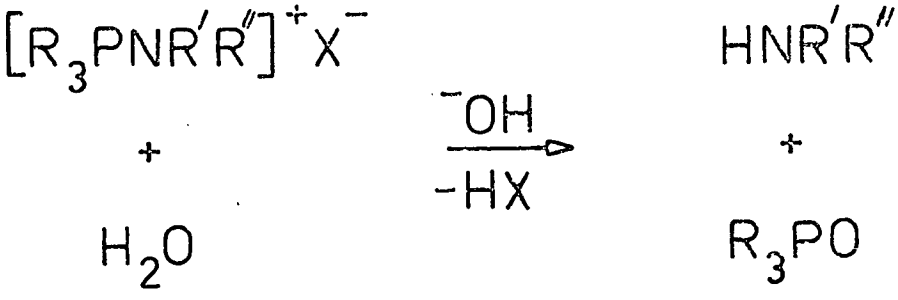
(vi) Phosphonium salt formation

Iminophosphoranes readily form salts upon treatment with alkyl halides (Scheme 34) although they are generally less nucleophilic than the isoelectronic phosphonium ylides.[14,15] This reaction possesses considerable synthetic utility for the preparation of N-alkyl-N-arylamines since hydrolysis of these phosphonium salts leads to the formation of phos-

phine oxides and pure disubstituted amines in high yield (Scheme 35).[71]



Scheme 34

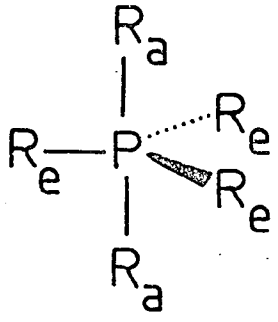


Scheme 35

(vii) Formation of pentacoordinate phosphoranes - See 2.4.6 (iii), (v) and (vi)

2. Pentacoordinate Phosphoranes

It is impossible to arrange five ligands symmetrically around a central phosphorus atom such that all bond lengths and bond angles are equal. However, it has been predicted theoretically that a trigonal bipyramidal (TBP) geometry should be energetically the most favourable configuration for acyclic PR_5 compounds (38).[72-80] X-Ray and electron diffraction studies have generally confirmed this prediction although deviations from TBP geometry are frequently observed.[81]

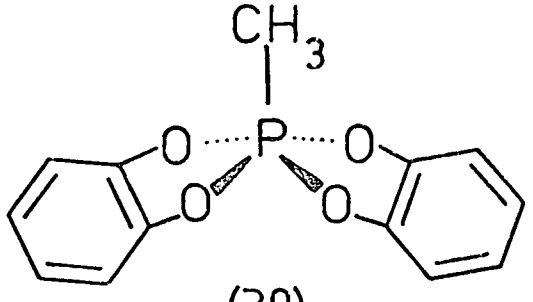


(38)

A consequence of the trigonal bipyramidal structure (38) is that there are two types of ligands; three equatorial ligands (R*e*) at an angle of 120° to each other and at right angles to two colinear apical ligands (R*a*). The apical (*a*) substituents are relatively sterically crowded as they have three 90° neighbours whereas the equatorial (*e*) substituents have only two. It might therefore be expected that the apical bond length would be longer, and hence the bond strength weaker, relative to an equatorial bond. These properties

have been demonstrated for pentafluorophosphorane (38, R = F) where the P-F*a* distance is 1.577(5)Å and the P-F*e* distance is 1.534(4)Å and the P-F*a* vibrational symmetrical stretching frequency is 177 cm^{-1} lower than the P-F*e* frequency.[82]

Pentacoordinate phosphoranes can adopt a square pyramidal (SP)[81] structure if the phosphorus atom is enclosed in a small ring and also bonded to a particular arrangement of ligands with different electronegativities, for example, compound 39.[83] This SP geometry leads to non-equivalent ligands with four basal ligands at an angle of 87° to each other and at 104° to a single apical ligand. Generally, however, it has been estimated that the TBP configuration is energetically more favourable than the SP configuration by approximately 20-40 kJ mol^{-1}.[78,84-87]



(39)

Two important characteristics of pentacoordinate phosphoranes, which profoundly influence their properties, are that electronegative elements tend to occupy apical sites and that the ligands can undergo intramolecular reorganisation by a process generally referred to as pseudorotation. These characteristics will be discussed in some detail in later sections.

2.1 Bonding

Zeeman[72] has investigated, in terms of electrostatic repulsion forces, the shape of AB_5 complexes with fixed AB distances and found that the TBP is more favourable than the SP configuration. Introduction of non-Coulombic repulsion terms into the calculations led to a further increase in the relative energetic stabilisation of the TBP.

The valence shell electron pair repulsion model developed by Gillespie,[73,74] where pairs of bonding or non-bonding electrons are always arranged so as to minimise electrostatic repulsion, also predicts that a TBP rather than a SP configuration is more favourable. This approach has been used to explain successfully the observed trends in molecular geometry of the series of compounds $PF_{5-n}Me_n$, n = 0-3.[74]

Likewise, Rundle[75,76] has constructed a semilocalised three-centre electron-rich model which gives a good first order representation of the structures of PR_5 compounds. He neglected d-orbitals in the basis set, viewed the equatorial bonds as normal and constructed the apical bonds from three-centre orbitals which were comprised of the phosphorus $3p_z$ and the axial ligand s and p functions. Rundle successfully predicted, from this model, that the apical bonds should be longer and that electronegative ligands should preferentially occupy these positions. In this connection, Bartell[77] has demonstrated that Rundle's model can also explain the trends observed in the fluorophosphorane series $PF_{5-n}Me_n$, n = 0-3.[88]

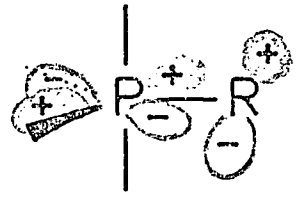
More recent molecular orbital studies[78-80] of the bonding in the hypothetical model compound PH_5 have led to the conclusions that apical bonding is weaker and that the apical hydrogens are more electronegative than the corresponding equatorial hydrogens in a TBP configuration.

It is interesting to note that the above theoretical studies, although adopting different approaches, all lead to the same general conclusions concerning the structure of pentacoordinate phosphoranes and apical ligand properties.

Since five σ bonds are required to bind ligands to phosphorus in PR_5 compounds it has been assumed that a fifth atomic orbital must be involved in the formation of the σ framework. In 1961 Cotton[89] described the bonding in terms of a simple sp^3d hybridisation model, but as already mentioned, Rundle has constructed a successful model which neglects d-orbitals. The role of d-orbitals in σ bond formation is still in doubt. Recently, Ramirez *et al.*[85,90,91] have predicted from CNDO/2 studies a substantial participation by 3d-orbitals in the molecular bonding. However, the results of semi-empirical Hückel calculations suggest that d-orbitals make only minor contributions to the σ bond framework.[79,92]

The d-orbitals are, however, thought to be involved in π bonding in pentacoordinate phosphorus compounds. Hindered rotation has been observed about the P-N or P-S bond in pentacoordinate phosphoranes containing an equatorial

thio or amino substituent.[93-95] This effect has been rationalised on the basis of P_{π}-d_{π} bonding. Molecular orbital calculations[78,85] have predicted that orbital overlap is greatest for π acceptors in an apical position. Conversely, π donors will achieve greater orbital overlap in an equatorial position. As a consequence equatorial substituents with a donor orbital will tend to orientate it in the equatorial plane, thereby giving rise to a barrier to free rotation (see 40).



(40)

Generally, pentacoordinate phosphoranes adopt a TBP configuration with the apical bonds longer and weaker than the equatorial bonds. The molecular bonding is formed predominantly from a σ-bond framework composed of S- and p-orbitals with a secondary contribution from d_{π}-p_{π} bonding, particularly in the case of equatorial substituents.

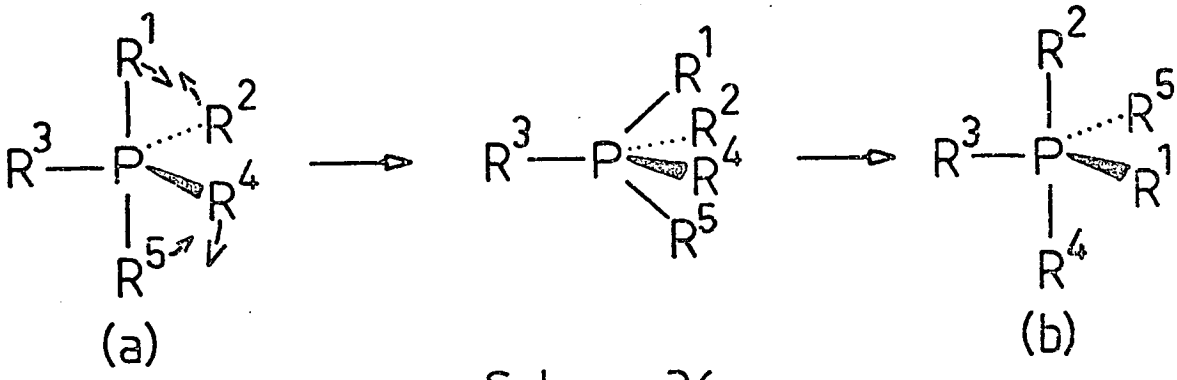
2.2. Pseudorotation

Pseudorotation is an intramolecular process by which the TBP orientation of groups arranged about a pentacoordinate central atom may be changed without the cleavage of bonds, that is a so-called regular process. This phenomena has been demonstrated for many pentacoordinate phosphoranes including PF_5.[96] The ^{19}F n.m.r. spectrum of this compound at room temperature contains only one fluorine resonance thereby indicating that the apical and equatorial sites are scrambled. However, the I.R. spectrum[97] distinguishes different sites in the molecule with different apical and equatorial bond lengths. The rationale of these observations is that ligands interchange between the apical and equatorial sites at a rate between 10^2 and $10^8 s^{-1}$, thus appearing equivalent on the slow n.m.r. time scale but not on the relatively faster I.R. time scale.

Berry[98] has explained this process using a mechanism in which two equatorial ligands exchange pairwise for two apical ligands, while the fifth ligand remains stationary and acts as a pivot. The process, generally referred to as Berry Pseudorotation (BPR), is outlined in Scheme 36.

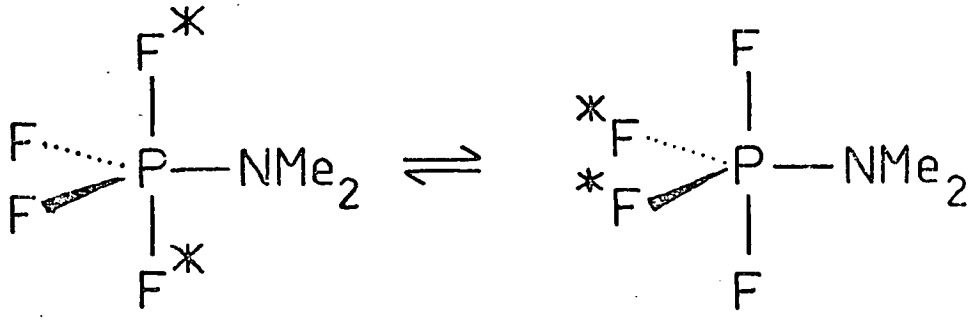
The two apical ligands (1,5) of TBP(a) are bent(by 15^o each) in the plane occupied by ligands (1,3,5); simultaneously, two equatorial ligands (2,4) are bent (by 15^o each) in the equatorial plane while ligand (3) acts as the pivot. The result is a square pyramidal intermediate with ligands (1,2,4,5) at the basal positions

and the apicel position occupied by ligand (3). This is the high energy point of the process, and gives an activation energy to the reorganisation. Continuation of the bending process by another 15° leads to the generation of the isomeric TBP (b).

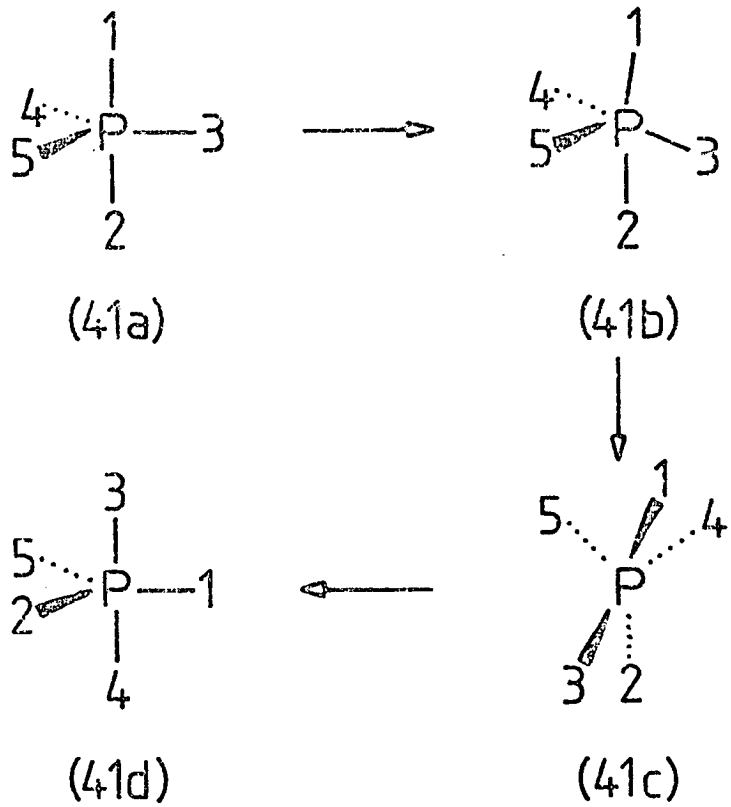


Scheme 36

Whitesides and Mitchell[99] have demonstrated that the interchange of apical and equatorial fluorines in the molecule Me_2NPF_4 proceeds *via* a concerted and pairwise interchange of the two equatorial fluorines with the two apical fluorines (Scheme 37). These observations are consistent with the BPR mechanism.



Scheme 37



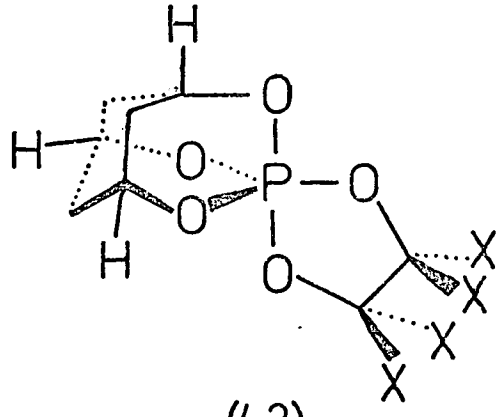
Scheme 38

Ramirez and Ugi *et al.*[84-86] have proposed an alternative pseudorotation process, the so-called turnstile rotation (TR) mechanism, which satisfies the criteria necessitated by the Whitesides and Mitchell experiment. Turnstile rotation may be visualised as a combination of three independent motions which begin simultaneously and occur synchronously as shown in Scheme 38. Thus, the diequatorial angle of 41a, 4-P-5, contracts from 120° to 90° and the ligand pair 1 and 3 tilts in the plane P-1-3-2 towards the apical ligand 2, to yield 41b. The ligand pair 1 and 3 then rotates against the trio 2-4-5 leading to 41c which is the halfway intermediate between the two isomeric TBP geometries 41a and 41d and is known as the 30° TR barrier. The rotation continues for a further 30° with a synchronous 9° tilting of the pair 3-1, and expansion of the angle 5-P-2 to 120°, to generate the new TBP41d

The energy barrier to pseudorotation in acylic pentacoordinate phosphoranes by the BPR mechanism has been calculated to be 1.4 kcal mol^{-1} (Hückel MO),[78] 4.8 kcal mol^{-1} (*ab initio*),[8] and 3.5 kcal mol^{-1} (CNDO/2).[84] Similarily, calculation of the energy barrier encountered in the TR mechanism has yielded values of 10.0 kcal mol^{-1} (Hückel MO),[78] 18.1 kcal mol^{-1} (*ab initio*),[87] and 9.1 kcal mol^{-1} (CNDO/2).[84] On the basis of these calculations it would appear that BPR would be the preferred mechanism but, Ramirez *et al.*[84,85] have concluded on the basis of their CNDO/2 calculations that neither mechanism is quantum mechanically impossible. Furthermore, they note that there are four possible TR pathways which lead to the same

isomerisation as one BPR. As a result the former process becomes relatively more likely from a statistical point of view.

The TR mechanism has been invoked to explain the facile ligand reorganisation observed in the polycyclic oxyphosphorane 42; $\Delta G \leqslant 5$ kcal mol^{-1}.[91] The authors argued that a prohibitively high energy barrier would have to be traversed if a BPR mechanism was operating. However, the experimental data can be rationalised in terms of a TR mechanism if the five-membered ring oxygens are considered as the pair and the adamantoid oxygens as the trio.



(42)

X=CF_3

In this thesis no attempt will be made to distinguish between the two different mechanisms for ligand reorganisation in pentacoordinate phosphoranes. However, for consistency all experimental observations will be explained in terms of BPR processes.

Finally, it is worth noting that reorientation of groups around a pentacoordinate central atom may also occur *via* irregular processes whereby bonds are broken and reformed.

These may involve a hexacoordinate transition state or intermediate, usually a base-catalysed reaction,[100] or a tetracoordinate intermediate generated by an acid-catalysed[101] or thermal[102] reaction. The operation of these processes can usually be detected by n.m.r. spectroscopy and differentiated from regular processes by the anomalous loss of coupling to phosphorus arising from bond fission, and the abnormal solvent dependence due to the intermediacy of ionic species.

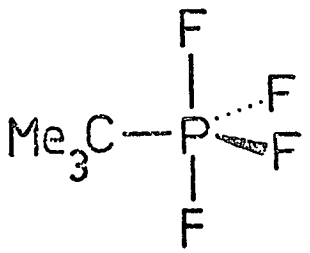
2.3 Factors determining pseudorotational barriers and ligand positions in pentacoordinate phosphoranes

In the preceding section (2.2) it was noted that molecular orbital calculations[78,84,87] predicted a free-energy barrier to ligand reorganisation in pentacoordinate phosphoranes, the magnitude of which has been determined experimentally for many pentacoordinate phosphoranes usually by n.m.r. spectroscopy,[103] but in some cases by polarimetry.[104] The data obtained has been rationalised mainly in terms of (i) apicophilicity and (ii) ring strain, although steric factors may be important, especially in structurally crowded phosphoranes. These factors will now be considered in some detail.

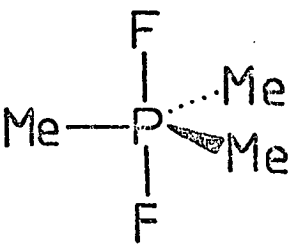
(i) Apicophilicity

On the basis of theoretical calculations Trippett[103] has suggested that apicophilicity is a function of three variables: (a) electronegativity, (b) π-donor ability and (c) π-acceptor ability.

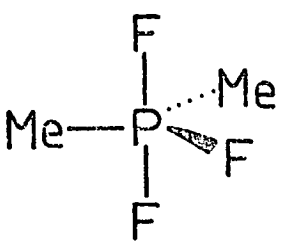
(a) Electronegativity. From experimental studies, it appears that the most electronegative atoms or groups attached to phosphorus prefer to occupy the apical sites in



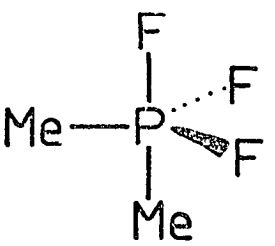
(43)



(44)



(45)



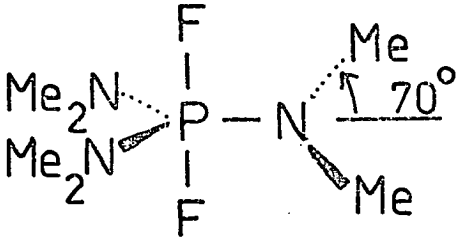
(46)

a TBP structure. This effect has been demonstrated, for example, in a series of alkylfluorophosphoranes R_nPF_{5-n}, n = 1-3. Thus, compound 43 exhibited only one fluorine resonance in the ^{19}F n.m.r. spectrum at temperatures down to -120°C.[105] However, upon introduction of a second alkyl group as in 45, the spectrum showed[106] two distinct fluorine environments at temperatures below +5°C. When three alkyl groups were present, (44), a single fluorine signal was observed with a characteristic PF_a coupling constant of 545 Hz. This spectrum exhibited no temperature dependence.[107]

These results, although qualitative, indicated a progressive increase in the barrier to pseudorotation upon substitution of fluorine by an alkyl group. This can be explained by assuming a greater apicophilicity for fluorine than for an alkyl group. Thus in compound 43 the fluorines undergo rapid interchange between apical and equatorial positions using the alkyl group as pivot. However, with compound 45 interchange can only occur *via* the intermediate structure 46 in which an alkyl group and a fluorine atom adopt unfavourable apical and equatorial positions respectively. An even greater barrier to rotation occurs in compound 44 in which both the alkyl groups and fluorine atoms are located in their favoured positions.

Sheldrick[81] has also noted that all structural determinations for static acyclic pentacoordinate phosphoranes have shown that the ligand distribution over apical and equatorial sites of the TBP is in accordance with electronegativity predictions.

(b) π-Donor ability has already been discussed with respect to bonding in Section 2.1. Briefly, an atom with a lone pair of electrons bound to phosphorus will preferentially occupy an equatorial site with the donor orbital in the equatorial plane. However, this effect may be compromised by steric interactions as, for example, in $(Me_2N)_3PF_2$.[108] In this compound the dimethylamino groups make a dihedral angle of only 70° with the equatorial plane (47) which presumably represents a compromise between the steric repulsion of the atom cores and the electronic energy.



(47)

(c) π-Acceptor ability. Theoretical studies[78,85] predict that an atom or group with a vacant low lying orbital will preferentially occupy an apical position.

Consideration of these variables has led Trippett[103] to propose a tentative apicophilicity scale (Figure 1) which he states is in accord with much of the published experimental data.

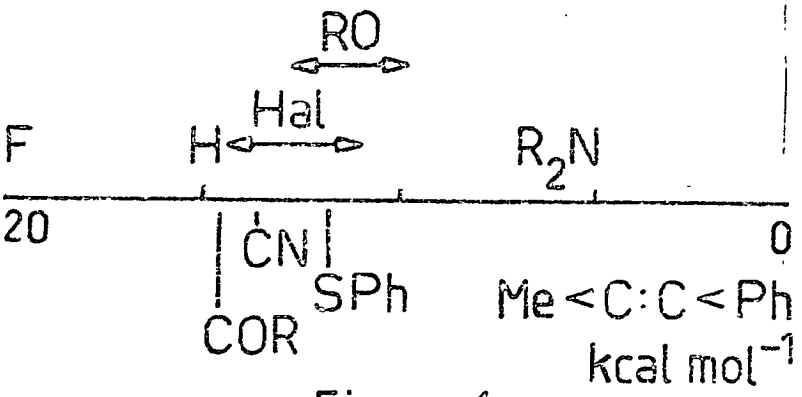
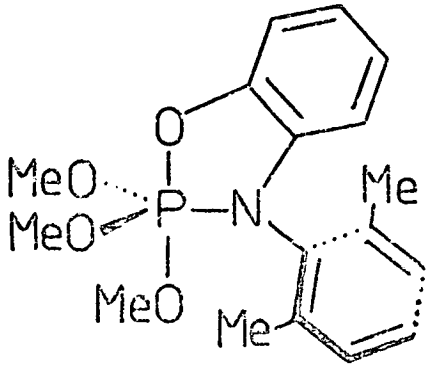


Figure1

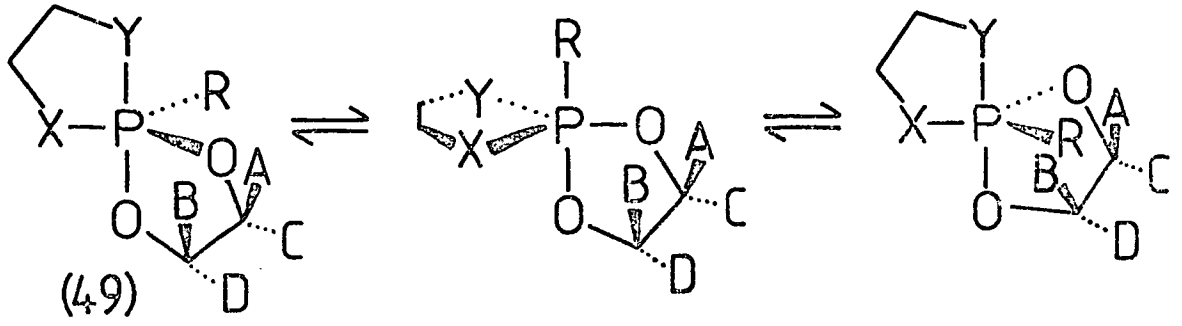
(ii) Ring strain

The origin of ring strain in pentacoordinate phosphoranes and the small ring effect generally will be discussed more fully later, in Section 3.1. In summary, however, it is generally accepted that four- and five-membered rings,[85,86] in phosphoranes with TBP structures, will preferentially adopt the more favourable conformation which spans the *ae* rather than the *ee* positions due to relief of ring strain. In addition, the more apicophilic ring atom, bound to phosphorus, assumes an apical placement. For example in compound 48. Thus, X-ray analysis shows that the almost planar five-membered ring spans the *ae* sites with oxygen, the more apicophilic atom, in the apical position.[109] It should be noted that small and medium sized rings are incapable of diapical placement.



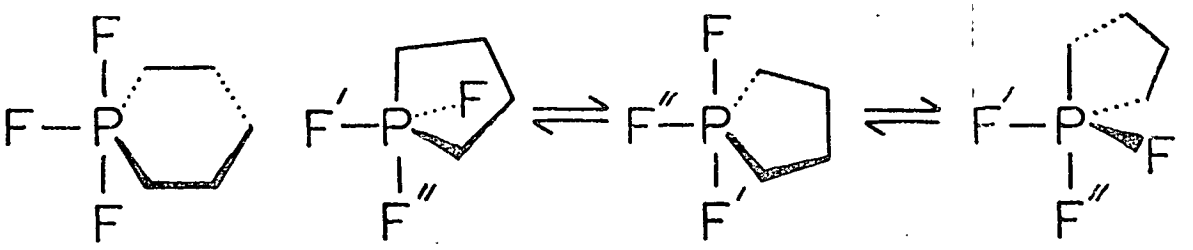
(48)

The presence of small rings in pentacoordinate phosphoranes can restrict the pseudorotation processes which involve diequatorial placement of the ring. Thus, Trippett[103] has calculated that the energy required to change the dioxaphospholan ring in the bicyclic compound (49) from the *ae* to *ee* conformation is of the order of 17 kcal mol^{-1} (Scheme 39).



Scheme 39

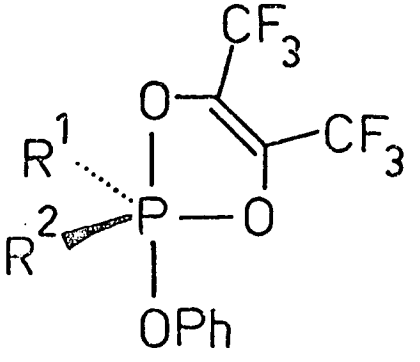
In certain cases competition can occur between ring strain and apicophilicity effects. For example, the six-membered cyclic compound (50) exhibits a temperature invariant ^{19}F n.m.r. spectrum up to at least 100°C indicating that the structure is essentially frozen with the ring located in the strain-free diequatorial conformation. By contrast, the spectrum of the five-membered cyclic phosphorane (51) shows equivalent fluorine atoms above -70°C indicating rapid interchange of these atoms between *a* and *e* sites as shown in Scheme 40. Such a pseudorotation process places the ring in an unfavourable diequatorial position, but at the same time two fluorine atoms can assume favourable apical positions.



(50) (51)

Scheme 40

Trippett has demonstrated[110] that steric effects may also affect the barrier to pseudorotation. Thus, the series of compounds (52) show a steady increase in ΔG as both R^1 and R^2 change from Me to Bu^t. This change is attributable to the increasing relative steric compression at the apical position as the equatorial group increases in size.



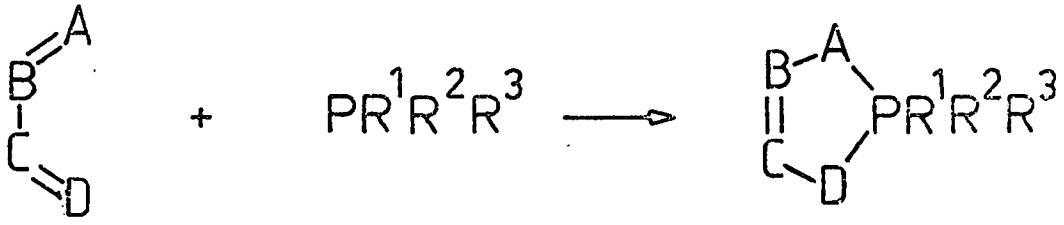
(52)

2.4 Preparation of pentacoordinate phosphoranes

Pentacoordinate phosphoranes vary widely in stability, ranging from short-lived intermediates, found in a number of reactions of nucleophiles with pentavalent tetracoordinate phosphorus compounds,[101] to thermally stable compounds, the topic of this section.

2.4.1 Reaction of tervalent phosphorus reagents with α,β-unsaturated systems.

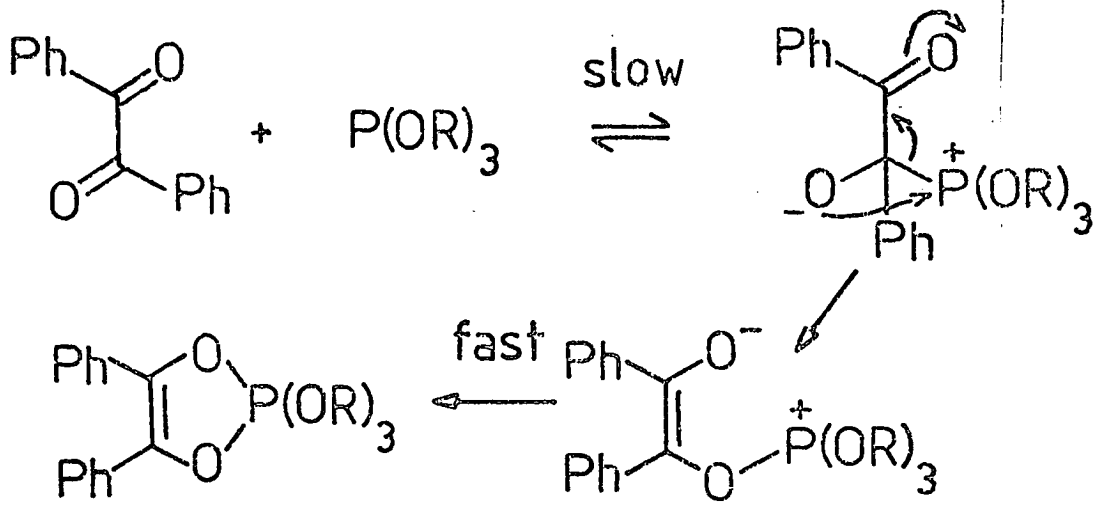
The general reaction is shown in Scheme 41 and formely involves Michael addition of a tervalent phosphorus reagent to an α,β-unsaturated system.



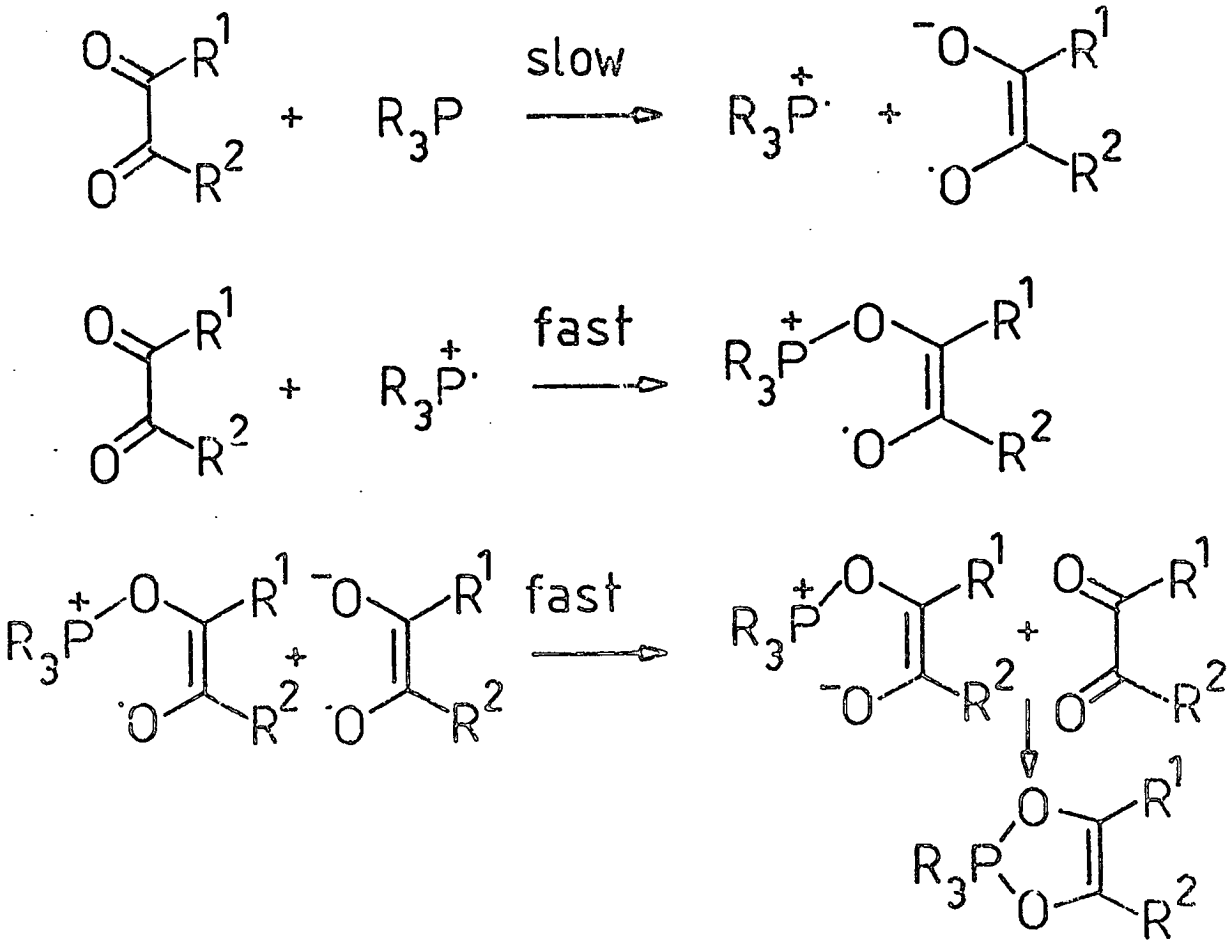
Scheme 41

(i) with dicarbonyl compounds.

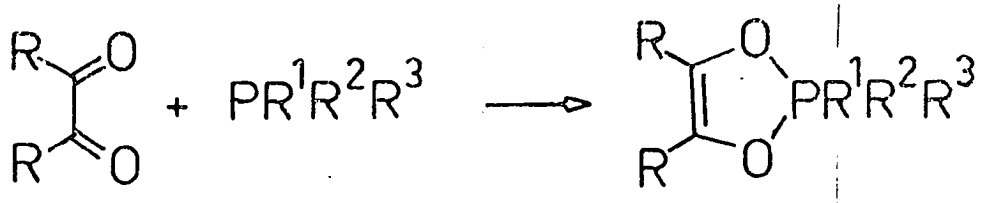
Kukhtin[111] first isolated a pentacoordinate phosphorane in 47% yield from the reaction of biacetyl with triethyl phosphite under mild conditions. The scope of this reaction has bee subsequently extended to acylic and cyclic phosphites, phosphonites, phosphinites and their amino and thio analogues and a variety of dicarbonyl compounds[112-114] and provides a general route to phosphoranes containing a 1,3,2-dioxaphospholene ring (Scheme 42).



Scheme 43



Scheme 44



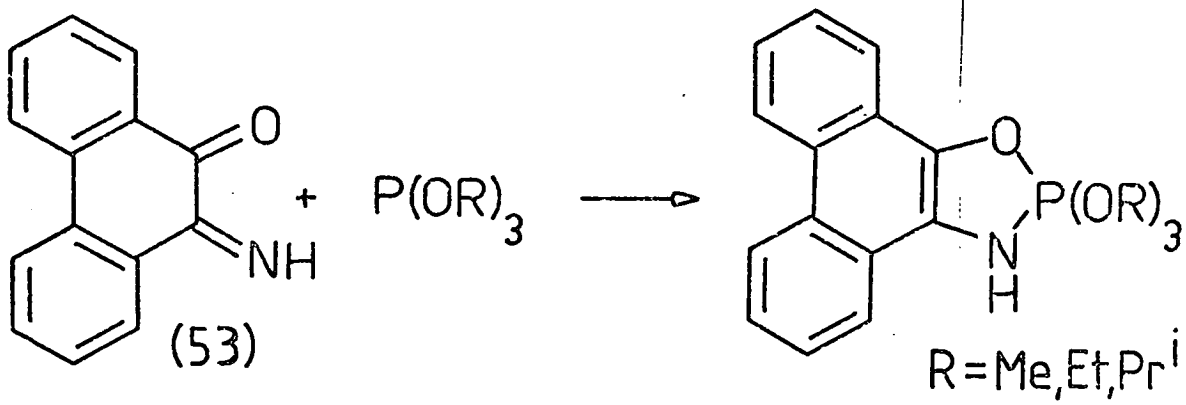
Scheme 42

There has been some debate concerning the mechanism of the Kukhtin reaction. Kinetic studies[115,116] support a process involving nucleophilic attack by phosphorus on a carbonyl carbon atom followed by rearrangement and rapid ring closure as shown in Scheme 43, and exclude a concerted cycloaddition reaction which requires attack at oxygen. However, in conflict with these results electron spin resonance measurements[117] indicate the involvement of radical intermediates whereby an initially formed phosphinium radical reacts rapidly with a neighbouring carbonyl group (Scheme 44).

Pentaoxyphosphoranes prepared in this way can be subsequently modified by ligand exchange reactions with aminoalcohols[118] or diols[119] thus extending the scope of the synthesis.

(ii) with α-keto imines.

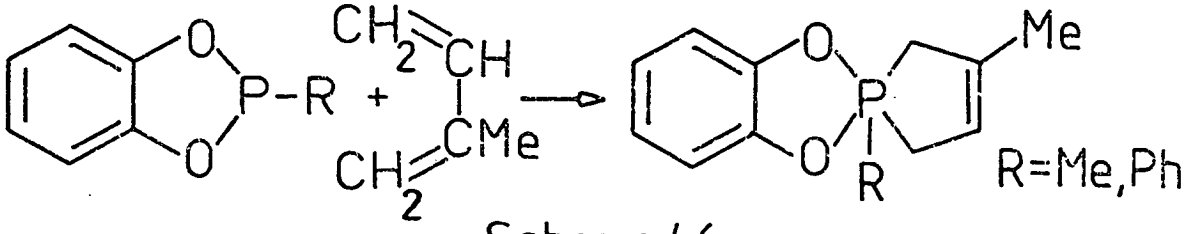
Trialkylphosphites react with α-keto imines in an analogous manner to the formation of the dicarbonyl adducts. Thus, phenanthrenequinonemonoimine (53) reacts with trialkyl phosphites as shown in Scheme 45, to give pentacoordinate phosphoranes.[120]



Scheme 45

(iii) with 1,3-dienes.

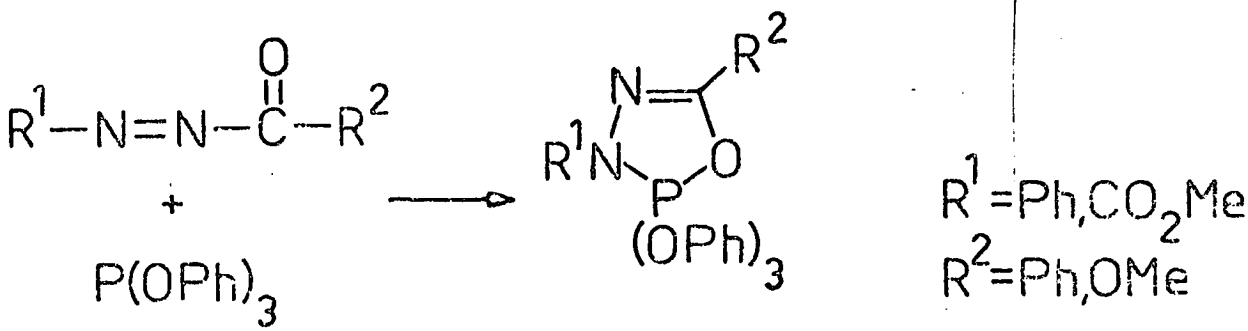
Pentacoordinate phosphoranes have also been prepared by the reaction of 1,3-dienes with tervalent phosphorus reagents.[121,1] For example, isoprene reacts with 2-substituted-1,3,2-benzodioxaphospholans to give pentacoordinate phosphoranes in greater than 85% yield (Scheme 46).



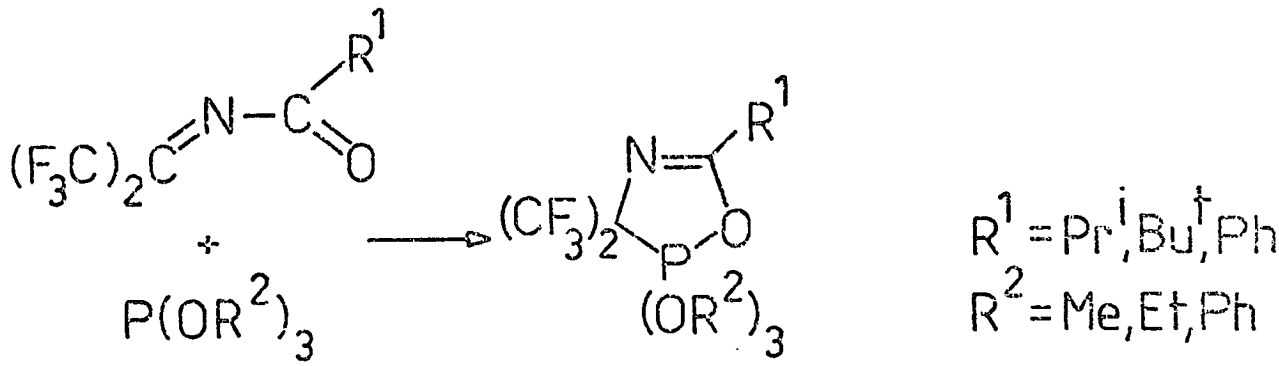
Scheme 46

(iv) with α,β-unsaturated carbonyl compounds.

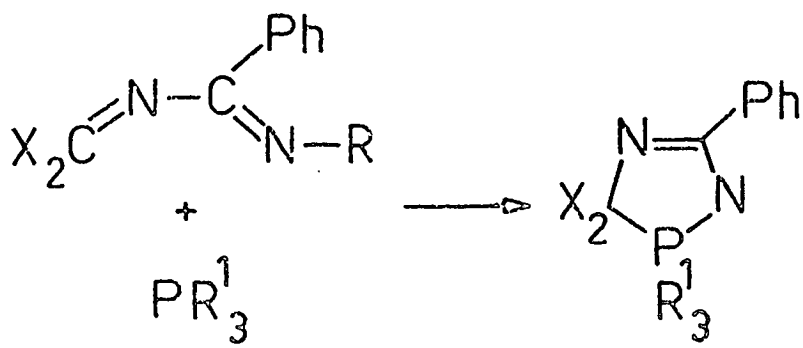
The title compounds react with tervalent phosphorus compounds to form 1,2-oxaphospholenes in fair to good yields (Scheme 47).[123-126] The reaction mechanism appears to be analogous to that described in Section 2.4.1 (i). Thus, kinetic studies[127] have provided evidence that phosphorus acts as a nucleophile, although electron spin resonance studies indicate the intermediacy of free radicals.[117]



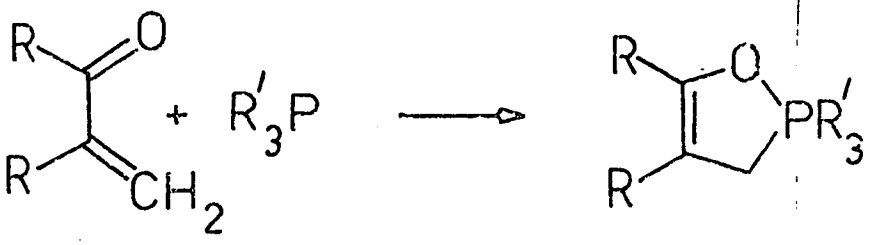
Scheme 49



Scheme 50

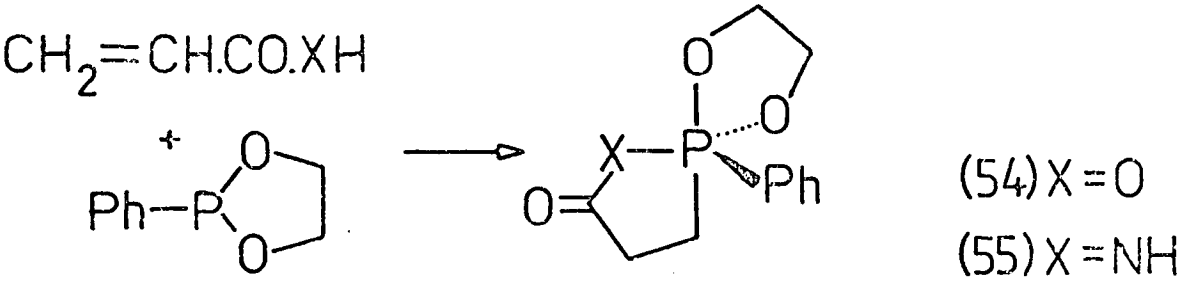


Scheme 51



Scheme 47

In contrast to the foregoing syntheses, the reaction of 2-phenyldioxaphospholan with acrylic acid and acrylamide leads to the formation of phosphoranes (54) and (55) as shown in Scheme 48.[128] These were claimed to be the first examples of stable pentacoordinate acyloxy- and acylamido-phosphoranes. Less stable acyloxyphosphoranes have also been prepared by reaction of acyclic tervalent phosphorus reagents with α-keto acids.[129]



Scheme 48

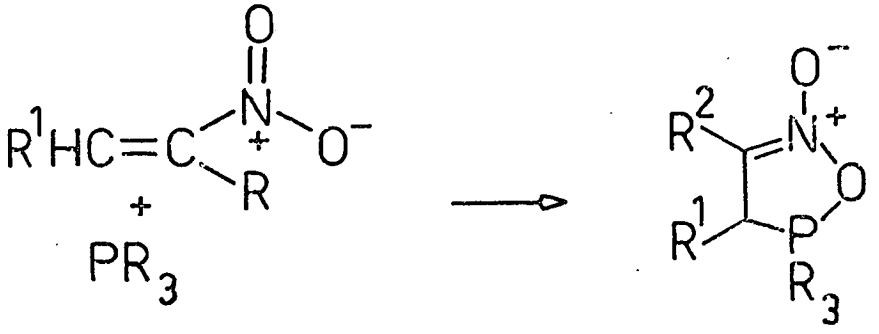
(v) with other conjugated systems.

Several miscellaneous examples have been reported in the literature including reaction of tervalent phosphorus reagents with azocarbonyl compounds (Scheme 49),[130-132] 1,1,1,3,3,3-hexafluoro-2-(acylimino)-propanes (Scheme 50),[133] and N-(hexafluoro-2-propyliden)-N′-arylbenzamidines (Scheme 51).[134]

(vi) with nitroalkenes.

The N = O double bond of the nitroalkene can be formally considered to be part of a conjugated system which reacts with

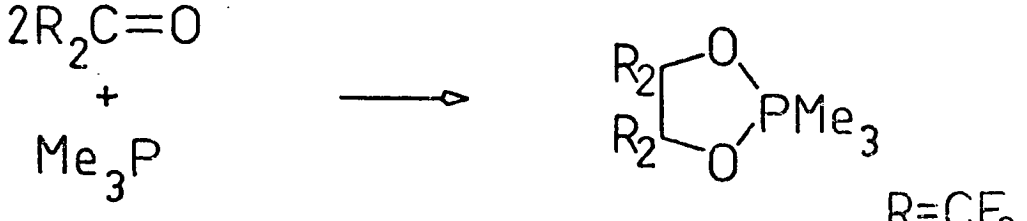
tervalent phosphorus reagents to form pentacoordinate phosphoranes as shown in Scheme 52.[135,136] Substitution of the nitroalkene with aryl groups (R_1,R_2 = Ar) has been found to increase the stability of the phosphorane adduct.[137]



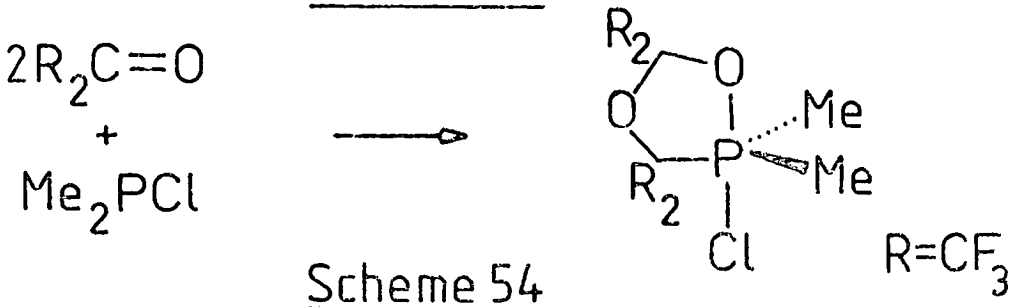
Scheme 52

2.4.2 Reaction of tervalent phosphorus reagents with monocarbonyl compounds.

Tervalent phosphorus reagents react with two equivalents of a carbonyl compound to form pentacoordinate phosphoranes containing either a 1,3,2-dioxaphospholan ring[138] or a 1,4,2-dioxaphospholan ring[139] as shown, for example, in Scheme 53 and Scheme 54 respectively.



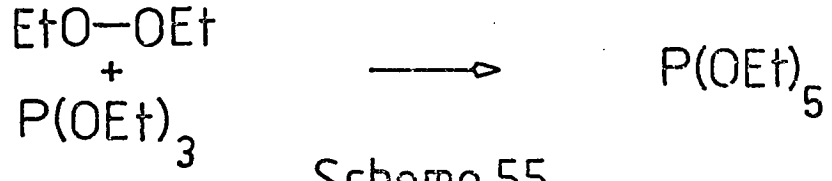
Scheme 53



Scheme 54

2.4.3. Reaction of tervalent phosphorus reagents with compounds containing a weak sigma bond.

The first reported example of this type of reaction was the preparation of pentaethoxyphosphorane by reaction of triethylphosphite with diethylperoxide (Scheme 55).[140]

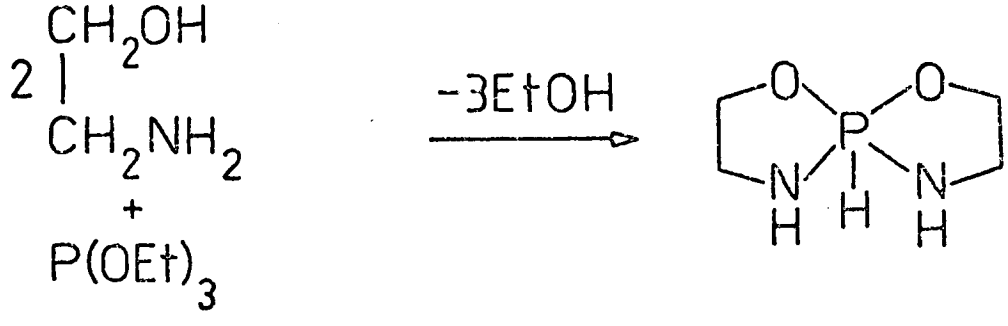


Scheme 55

Cyclic phosphoranes have been similarily prepared from dioxetanes[141] and dithietes.[142] Notably, a mixture of unstable three-membered ring phosphoranes have been prepared by reaction of 3,3,4-trimethyl-1,2-dioxetane with phenyl-phosphiran at low temperature.[143]

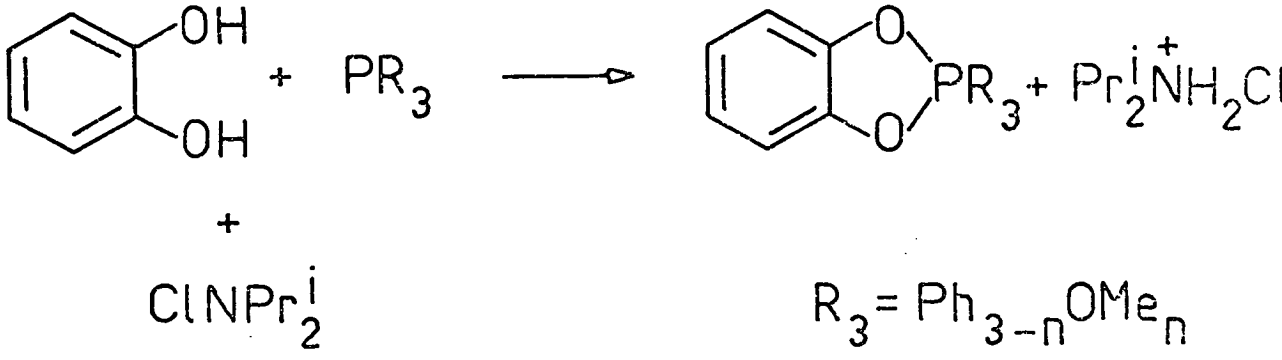
2.4.4 Reaction of tervalent phosphorus reagents with diols and related compounds.

This type of reaction is commonly used in the preparation of pentacoordinate phosphoranes. For example, Grechkin *et al.*[1
have reacted ethanolamine with triethylphosphite to form three equivalents of ethanol and a phosphorane containing a P-H bond (Scheme 56).



Scheme 56

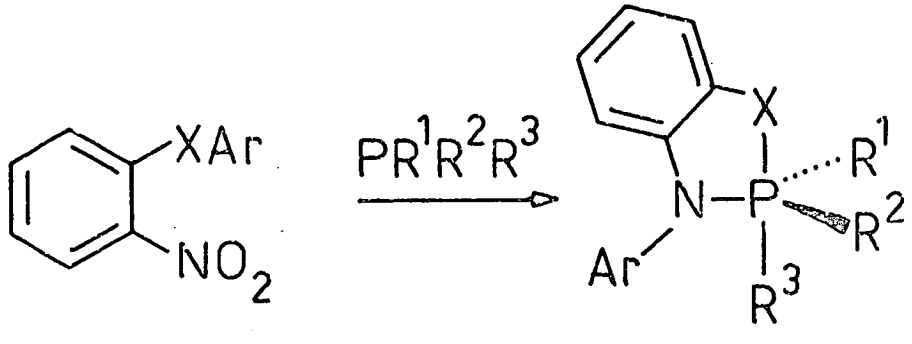
Trippett *et al.*[145,146] have developed a general synthesis of pentacoordinate phosphoranes involving condensation of acyclic tervalent phosphorus reagents with, for example, catechol in the presence of N-chlorodiisopropylamine at -78°C (Scheme 57).



Scheme 57

2.4.5 Reaction of tervalent phosphorus reagents with aryl 2-nitroaryl ethers and sulphides.

Cadogan *et al.* have prepared pentacoordinate phosphoranes containing a benzoxazaphospholine[147,148] or a benzthiazaphospholine[149,150] ring by the reductive cyclisation of aryl 2-nitroaryl ethers and sulphides with tervalent phosphorus reagents as shown in Scheme 58. The structures of (56, X = O,S) have been confirmed by X-ray crystallography.[149,151]



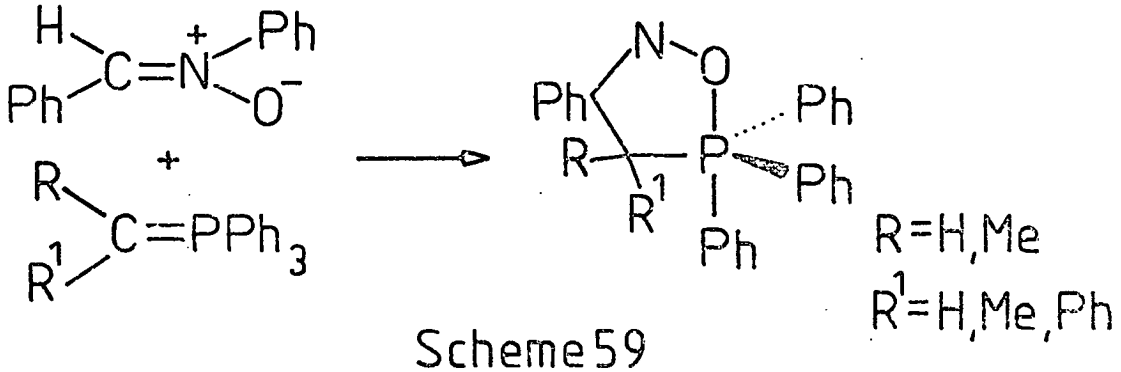
(56)

Scheme 58

2.4.6 Preparations of pentacoordinate phosphoranes involving phosphorus ylides.

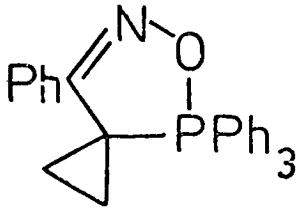
(i) Reaction with 1,3-dipoles

Wulff and Huisgen[152] have isolated pentacoordinate phosphoranes from the reaction of C,N-diphenylnitrone with substituted methylenephosphoranes in fair to good yields as shown in Scheme 59.



Scheme 59

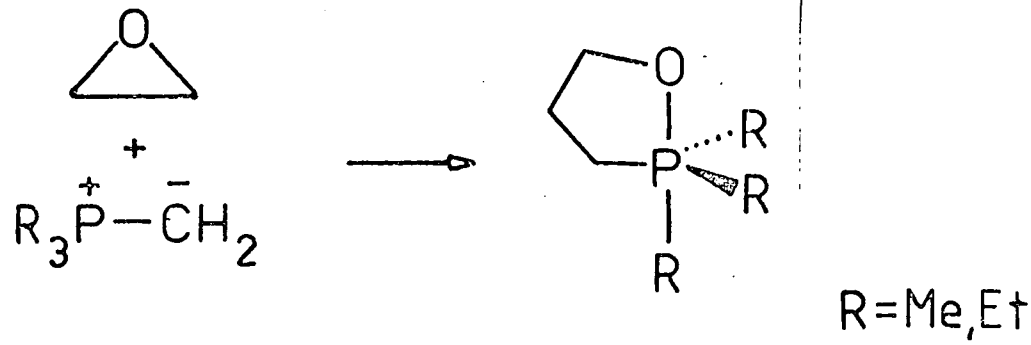
Nitrile oxides also react with phosphonium ylides. For example, Bestmann and Kunstmann[153] have prepared the cycloadduct (57) from the reaction of benzonitrile oxide with cyclopropylenetriphenylphorane in 61% yield.



(57)

(ii) Intermolecular reaction with epoxides

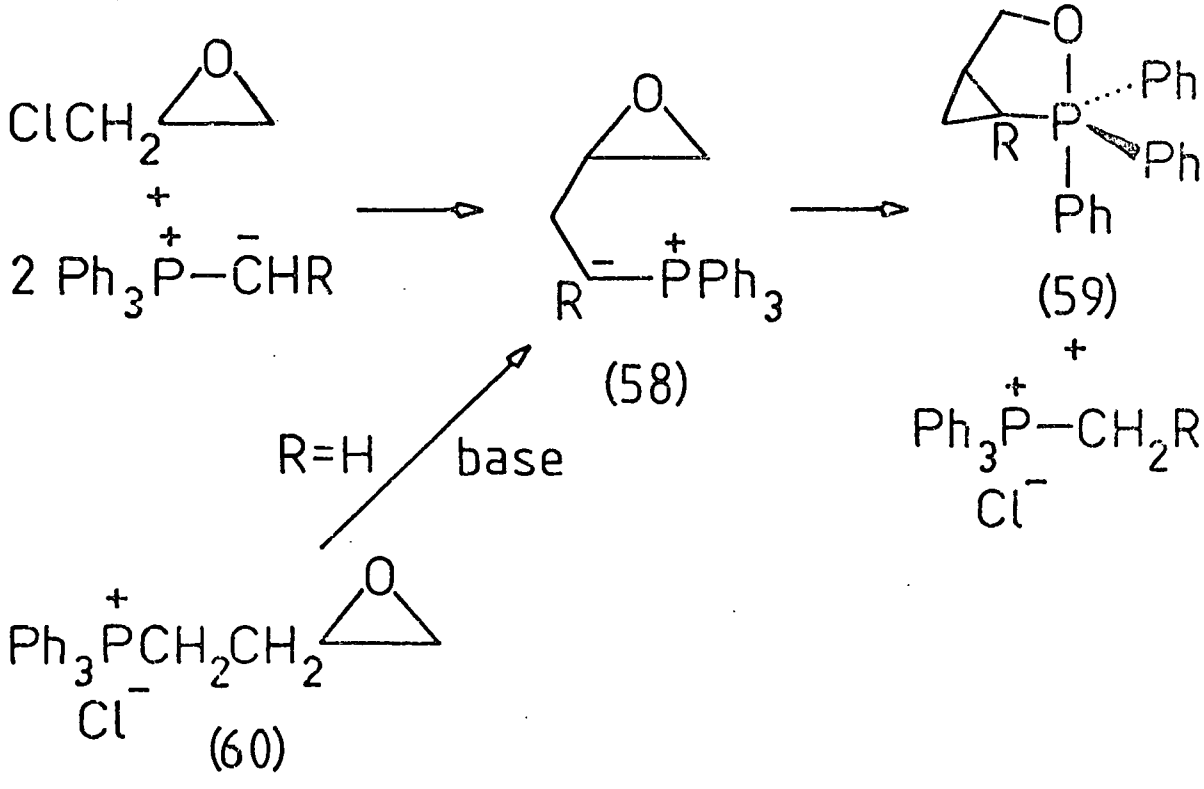
Schmidbauer and Holl[154] have isolated distillable pentacoordinate phosphoranes from the reaction of methylene-phosphoranes with ethylene oxide (Scheme 60). The adducts were shown to have TBP structures using variable temperature ^{1}H, ^{13}C and ^{31}P n.m.r. spectroscopy.



Scheme 60

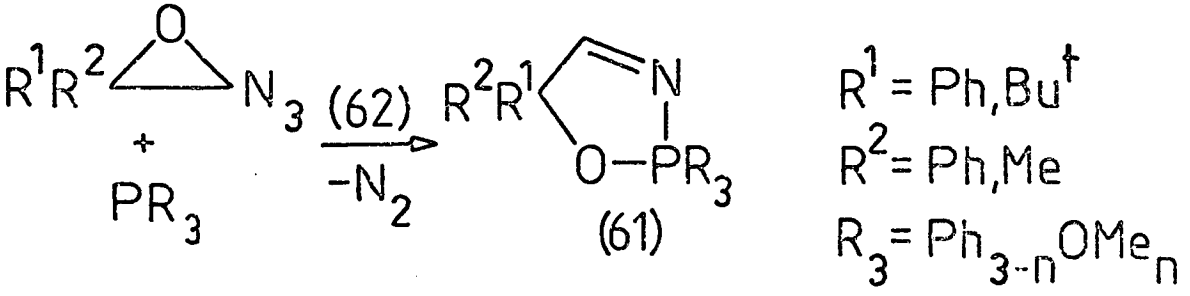
(iii) Intramolecular reaction with epoxides

Stable pentacoordinate phosphoranes have been prepared by the reaction of methylenephosphorane with epichlorohydrin (Scheme 61).[155] Evidence for the intermediacy of the ylide (58) was obtained by the alternative synthesis of (59) by treatment of the ω-epoxyphosphonium salt (60) with base.



Scheme 61

A related synthesis has been reported by Kyba and Alexander[156] involving the reaction of tervalent phosphorus reagents with 2-azido-oxirans to afford pentacoordinate phosphoranes of type (61), apparently *via* a phosphorus-nitrogen ylide (62) as shown in Scheme 62. X-Ray crystallography showed that the product contained an apical sp^2 nitrogen atom.



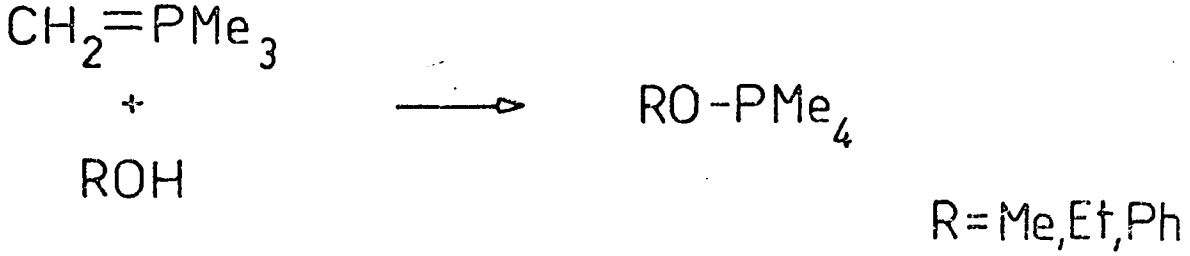
Scheme 62

(iv) Reaction with carbonyl containing compounds

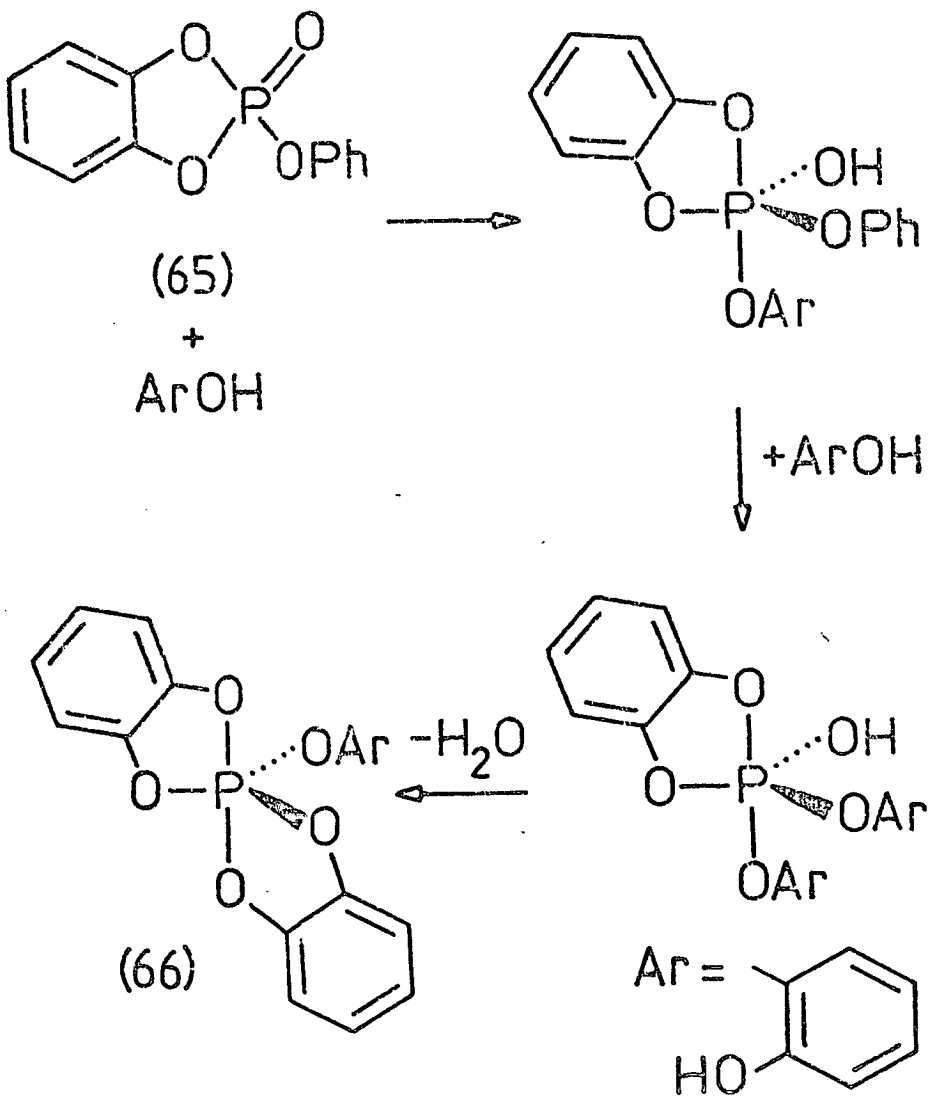
This method of preparation has been discussed earlier in Section 1.3 (i).

(v) Intermolecular reactions with alcohols

Reaction of alcohols with trimethyl methylenephosphorane leads to the formation of pentacoordinate phosphoranes as shown in Scheme 63.[157,158] This type of reaction has also been used to prepare monocyclic phosphoranes containing a phospholan or a phosphorinan ring.[159]

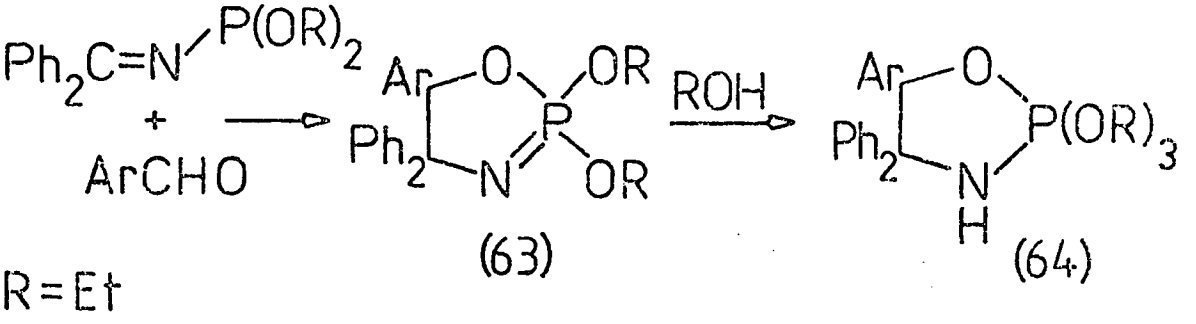


Scheme 63



Scheme 65

Cyclic iminophosphoranes (63), prepared by the 1,3-dipolar cycloaddition of a diethyl phosphoramidite to an aromatic aldehyde, have also been shown to react with ethanol to produce the oxazaphosphorane (64) as shown in Scheme 64.[160]



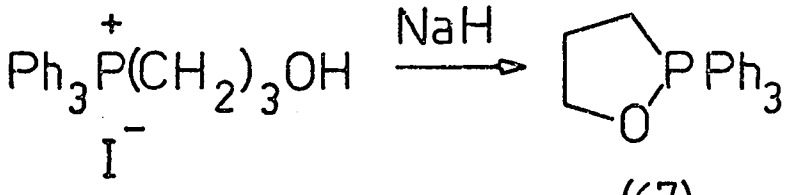
Scheme 64

The related reaction of a phosphoryl compound with a diol has been reported by Koizumi *et al.*[161] Thus, reaction of 2-phenoxy-benzodioxaphosphole-2-oxide (65) with catechol in the presence of triethylamine yields the spirobicyclic phosphorane (66) in 37% yield. The proposed mechanism is shown in Scheme 65. The authors suggest that the oxide (65) also acts as a dehydrating agent in this reaction.

(vi) Intramolecular reactions with alcohols and related compounds

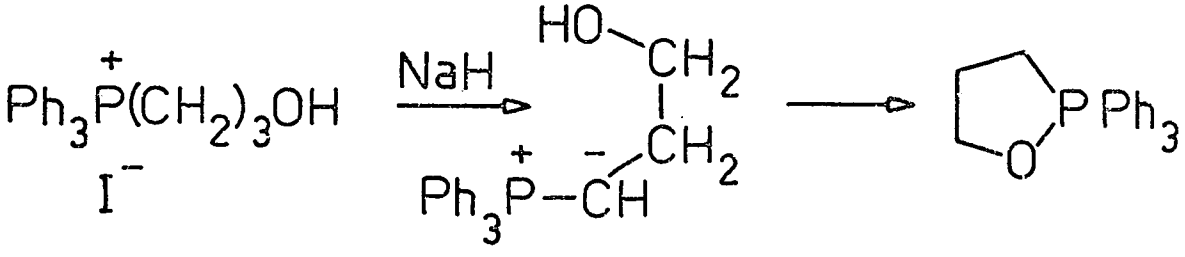
The preparation of pentacoordinate phosphoranes, such as (67), from hydroxy phosphonium salts by treatment with base has been rationalised in terms of a cyclisation involving attack of an oxyanion at a phosphonium centre.[162] Thus, treatment of 3-hydroxy-propyltriphenylphosphonium iodide with

sodium hydride leads to formation of the monocyclic phosphorane (67) as shown in Scheme 66. However, an alternative explanation, pertinent to this thesis, involves the intramolecular addition of an hydroxy group to an intermediate ylide (Scheme 67).



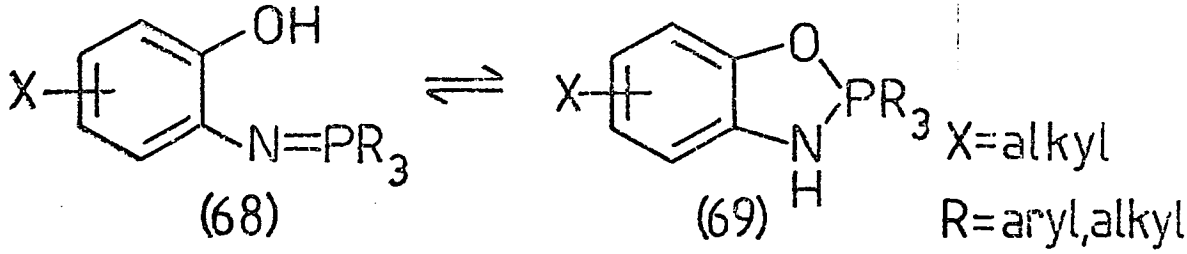
(67)

Scheme 66



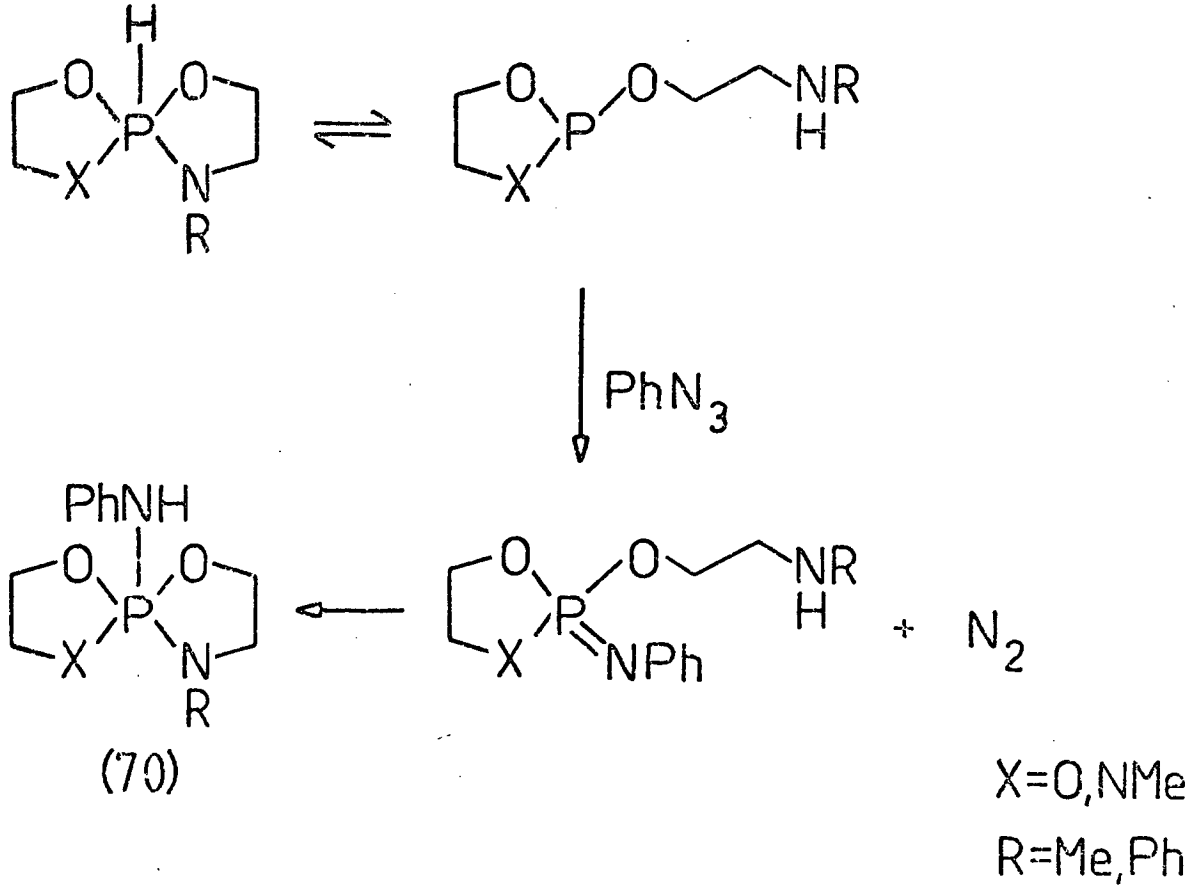
Scheme 67

An analogous reaction has been observed for phosphonium salts containing an ω-oxime group.[163] Stegmann *et al.*[164] have also observed the intramolecular cyclization of a range of substituted N-o-hydroxyphenyl iminophosphoranes (68). A thermodynamic equilibrium was found to exist between the iminophosphorane (68) and pentacoordinate phosphorane (69) forms (Scheme 68), dependent on substituents, solvent and temperature.

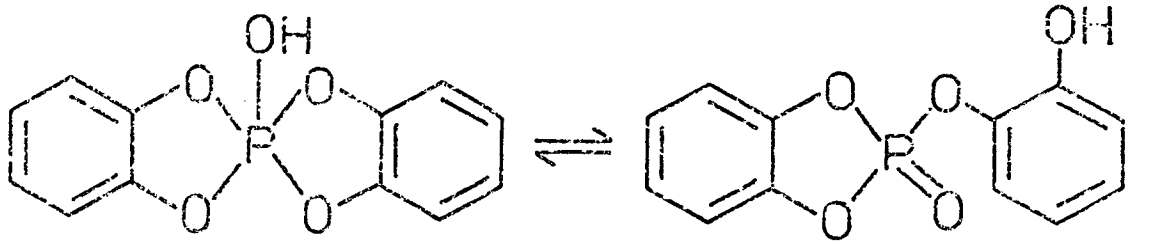


Scheme 68

Spirobicyclic phosphoranes of type (70) have been prepared by Wolf *et al.*[165] from a related reaction of phenyl azide with phosphorus containing compounds existing as a P^{III}-P^{V} tautomeric equilibrium mixture (Scheme 69).

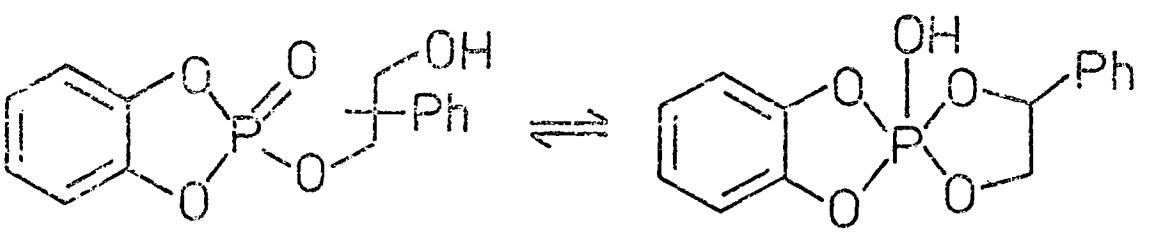


Scheme 69



(72)

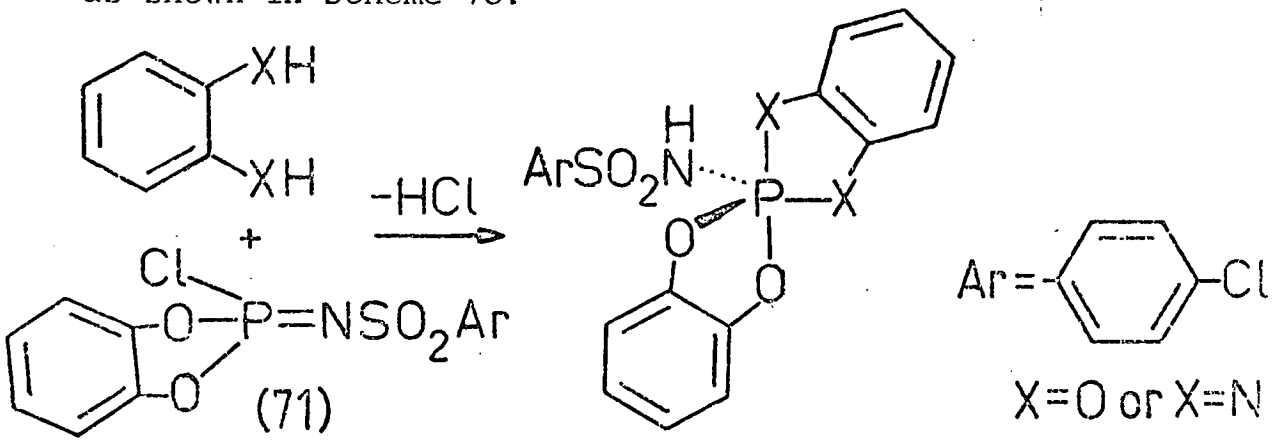
Scheme 71



(73)

Scheme 72

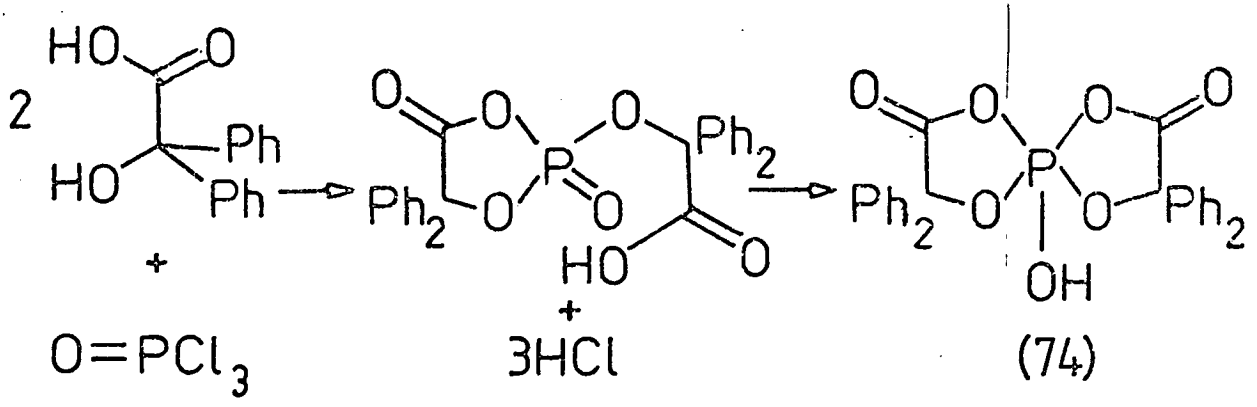
Another reaction which may fall in this category is due to Kukhar *et al.*[166] and involves the condensation of iminophosphorane (71) with catechol or o-phenylenediamine as shown in Scheme 70.



Scheme 70

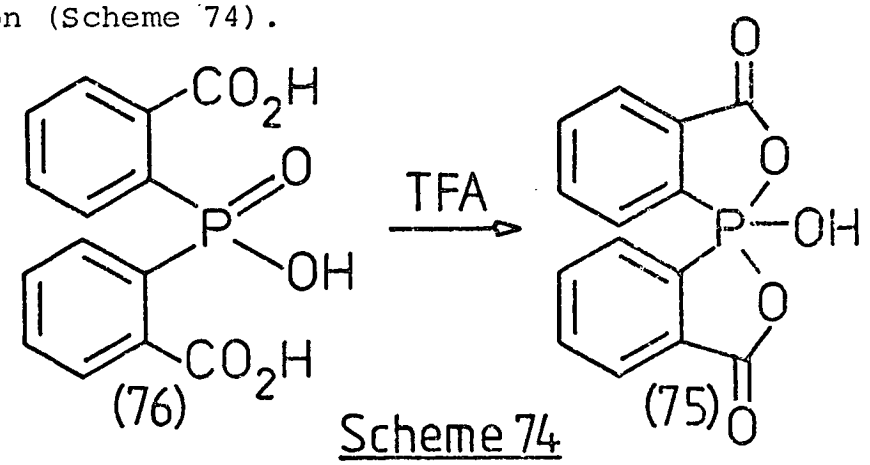
The foregoing reactions involving phosphorus-carbon and phosphorus-nitrogen ylides may be extended to include phosphoryl compounds which contain a hydroxy function. For example, both Munoz *et al.*[167] and Ramirez *et al.*[168] have reported the preparation of hydroxyphosphoranes by the intramolecular reaction of a phosphoric ester (72) and a phosphate ester (73) respectively as shown in Schemes 71 and 72. As in the case of the benzoxazaphosphoranes (69) prepared by Stegmann *et al.*[164] the products existed in tautomeric equilibrium with the open-chain forms.

In a later paper Munoz *et al.*[169] reported the similar preparation of the hydroxyphosphorane (74), which could be isolated as its triethylamine and N,N-dimethylformamide salts (Scheme 73).



Scheme 73

Segall and Granoth[170] have also isolated compound (75), as a 1:1 crystalline adduct with trifluoroacetic acid, in 75% yield from the acid (76) *via* an intramolecular condensation reaction (Scheme 74).

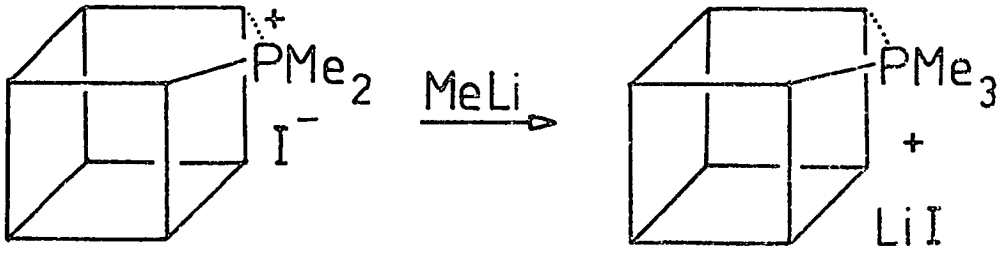


Scheme 74

2.4.7 Preparation from phosphonium salts and metal alkyls.

Pentaaryl phosphoranes are most commonly prepared by treatment of phosphonium salts with metal aryls. For example, pentaphenylphosphorane has been prepared in 60% yield by the addition of phenyl lithium to tetraphenylphosphonium iodide in dry ether.[171]

A similar procedure has been used by Katz and Turnblom[172] to prepare the first stable pentaalkylphosphorane from dimethylphosphoniahomocubane iodide as shown in Scheme 75. Spirobicyclic phosphoranes have also been prepared in an analogous manner.[173,174]



Scheme 75

The chemistry and synthetic use of pentacoordinate phosphoranes have been reviewed by Burger,[52] Ramirez[175] and Westheimer.[176]

3. The Small-Ring Effect

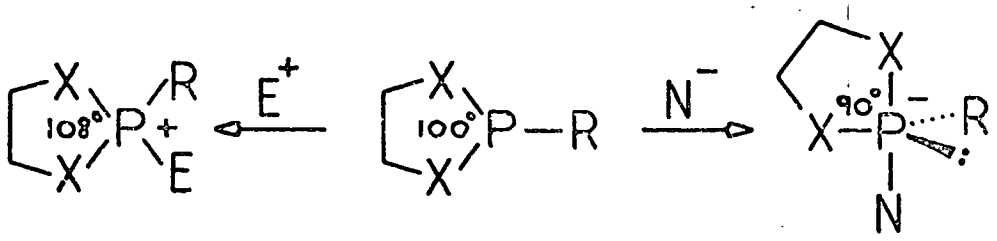
3.1 Origins and manifestations

The small-ring effect was first invoked by Westheimer and Covitz[176,177] to explain the difference in reaction rates for the basic hydrolysis of cyclic and analogous acyclic phosphates. Its origins are not entirely understood, but it is thought that ring strain is a major factor, although entropy and steric factors may also be important.

(i) Ring strain

In an important paper Hudson and Brown[178] attempted to rationalise rate differences between cyclic and analogous acyclic phosphorus compounds upon reaction with electrophiles and nucleophiles using the concept of ring strain. They argued that the natural angle at phosphorus, XPX, in tervalent phosphorus compounds is approximately 100° but upon reaction with an electrophile to give a tetracoordinate product, there is a concomitant increase in bond angle to approximately 108° as shown in Scheme 76. It follows that if phosphorus is enclosed in a small ring this reaction will cause an increase in ring strain and should, therefore, result in a decrease in reactivity relative to an acyclic analogue. Conversely, reaction with a nucleophile should lead to increased reactivity of the cyclic compound relative to its acyclic analogue. As Scheme 76 shows nucleophilic substitution leads to a reduction in the bond angle at phosphorus, XPX, to 90° and hence a relief of ring strain, provided that the ring spans the *ae* sites of the

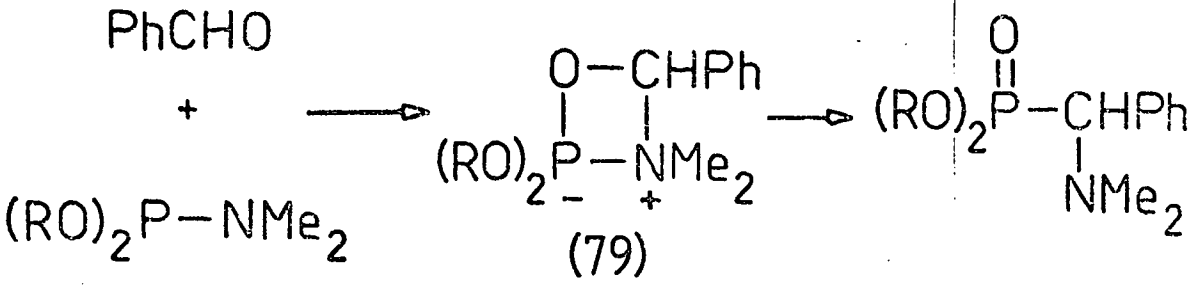
resulting TBP. In this example the phosphorus lone pair of electrons acts as a "phantom" fifth ligand.



Scheme 76

The foregoing effects have been observed in several reactions. For example, Aksnes and Eriksen[179] showed that triethylphosphite reacted approximately seven times faster with the electrophile ethyl iodide than did 3,4-dimethyl-2-ethoxy-1,3,2-dioxaphospholan. Larger rate differences have been observed for other reactions involving electrophilic attack on cyclic and acyclic tervalent phosphorus reagents.[180,181] Hudson and Brown[178] have also noted that the influence of strain appears to increase with the extent of bond formation with the electrophilic reagent.

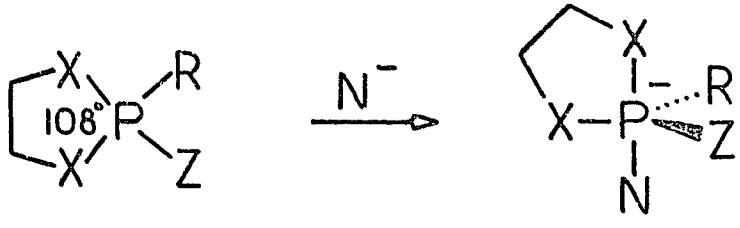
In the reaction of aminophosphites with benzaldehyde, Greenhalgh and Hudson[182] proposed a mechanism involving nucleophilic attack at phosphorus with the formation of a four-membered ring transition state as shown in Scheme 77. They demonstrated that the cyclic reagent (77) reacted *ca.* 1150 times faster than the acyclic analogue (78), an effect which could be attributed to relief of ring strain upon formation of (79).



(77) $(RO)_2 = -OCH_2CH_2O-$ (78) $(RO)_2 = (OCH_3)_2$

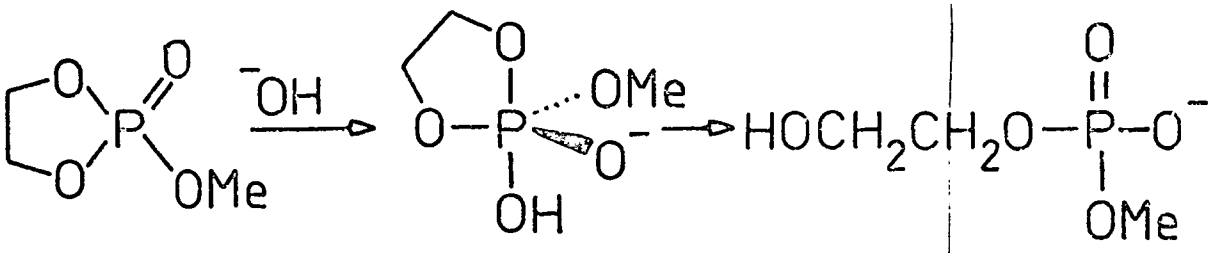
Scheme 77

Release of ring strain, and hence an acceleration of reaction rates, would also be expected to occur upon reaction of nucleophiles with cyclic phosphoryl or phosphonium compounds compared to their acyclic analogues. This follows from the reduction of the XPX angle from *ca.* 108° to *ca.* 90° on going to a TBP structure (Scheme 78).[178]



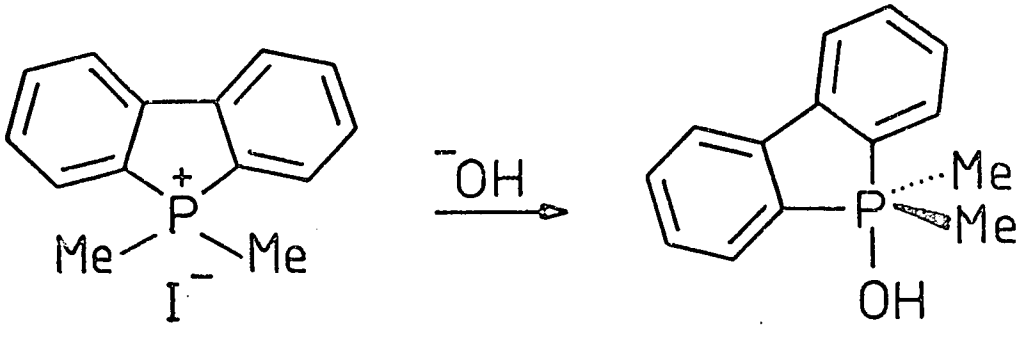
Scheme 78

In this connection, Westheimer and Covitz[176,177] have hydrolysed methyl ethylene phosphate and trimethyl phosphate under base conditions (Scheme 79) and observed large rate differences; the ratio of cyclic rate to acyclic rate was *ca.* 10^6.



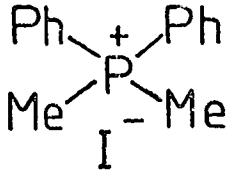
Scheme 79

Allen *et al.*[183] have also observed large differences in the rates of alkaline hydrolysis of cyclic and acyclic phosphonium salts. Thus, the phosphonium salt (80) hydrolysed *ca.* 10^4 times faster than its acyclic analogue (82). The authors attributed the difference in rates to relief of ring strain upon formation of the intermediate phosphorane (81) (Scheme 80). They also noted that the seven-membered ring phosphenium salt (83) was apparently strain free as it hydrolysed at a rate comparable to the acyclic compound (82).

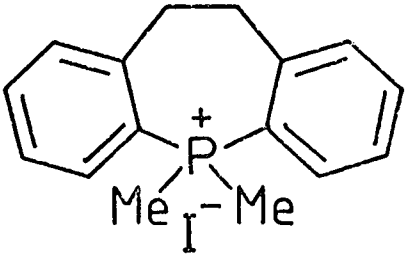


(80) (81)

Scheme 80

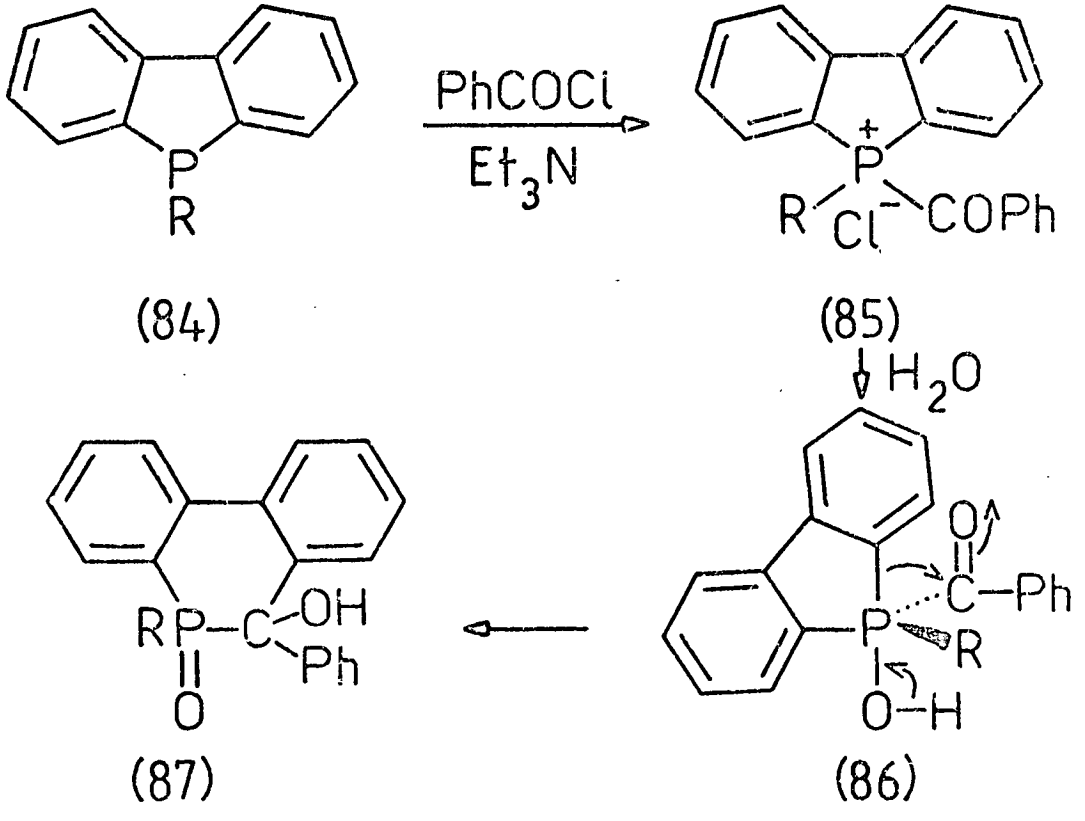


(82)



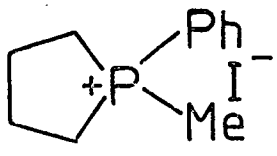
(83)

In a related study, Allen and Oades[184] hydrolysed a series of benzoyldibenzophospholium salts (85), prepared *in situ* by treatment of 5-substituted dibenzophospholes (84) with benzoyl chloride in the presence of triethylamine, and observed ring expansion to dibenzo[b,d]phosphorins (87) as shown in Scheme 81. The driving force of reaction was thought to be the relief of ring strain in both the dibenzophospholium salts (85) and the intermediate phosphorane (86). In this connection, they demonstrated that the ring-angle at phosphorus in the dibenzophospholium salt (85, R = p-bromobenzyl) was 94° as opposed to the accepted tetrahedral angle of 108°.[185]

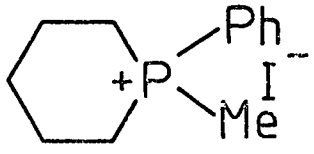


Scheme 81

Whilst ring strain is obviously important, steric factors may also play a part in determining rate differences between cyclic and acyclic analogues. For example, Asknes and Bergesen[186] found that cyclotetramethylene methyl phenyl phosphonium iodide (88) hydrolysed approximately 1300 times faster than the less strained six-membered ring phosphorinan compound (89) under alkaline conditions. The authors suggested that a considerable part of the rate increase was due to the almost planar configuration of the phospholan ring together with the strongly hindered rotation of its substituents (phenyl and methyl) leaving the phosphorus atom, at any time, very exposed to attack from hydroxyl ion; hence leading to an increased frequency factor for this reaction.



(88)



(89)

(ii) Entropy

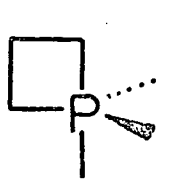
In the above discussion typical examples of the small-ring effect were rationalised in terms of ring strain arguments. However, Aksnes and Bergesen[187] have stated that much of the kinetic acceleration observed in the hydrolyses of five-membered cyclic phosphoryl esters is derived from entropy effects. Greenhalgh and Hudson[182] have also shown that the heats of hydrolysis of the tervalent phosphorus reagents (77) and (78) are similar, indicating the absence of any significant ring

strain in (77). On the basis of this result, these workers concluded that the observed rate difference in the reaction of cyclic and acyclic aminophosphites with benzaldehyde was due, in part, to entropy changes. Similar arguments have been recently applied to nucleophilic substitutions at five- and six-membered ring oxasilacycloalkanes.[188]

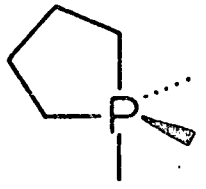
In the case of nucleophilic attack at cyclic tervalent phosphorus compounds or phosphoryl compounds the entropy changes are thought to arise from a "loosening of the permutational motion[189] of the ring on passing to the five-coordinate state", thereby causing an acceleration in reaction rates.[178] Conversely, electrophilic attack on cyclic tervalent phosphorus compounds is expected to cause a restriction of the motions of the ring as it passes from the relatively nonrigid tervalent geometry to the less flexible tetracoordinate form. As a result, a retardation in the rate of reaction is observed.

In addition to having a direct influence upon reaction rates, the small-ring effect also plays an important part in determining the arrangement of ligands around phosphorus in pentacoordinate phosphoranes having a TBP structure. Thus, as mentioned in Section 2.3 (ii), for compounds containing a four-membered ring (90) the natural angle at phosphorus is 90° and the ring prefers to span *ae* because considerable strain will be encountered in the *ee* conformation where the angle at phosphorus is 120°. By comparison, the situation for phosphoranes containing five-membered rings is less definitive since the angle at phosphorus is 108° which is mid-way between the value expected for the structures (91a) and (91b).

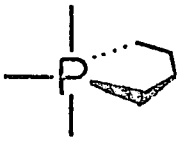
However, molecular orbital calculations of binding energies in pentacoordinate phosphoranes predict[85] that a five-membered ring can accommodate an angle at phosphorus of 90° with minimal ring strain, whereas an angle of 120° leads to considerable strain in the ring.



(90)



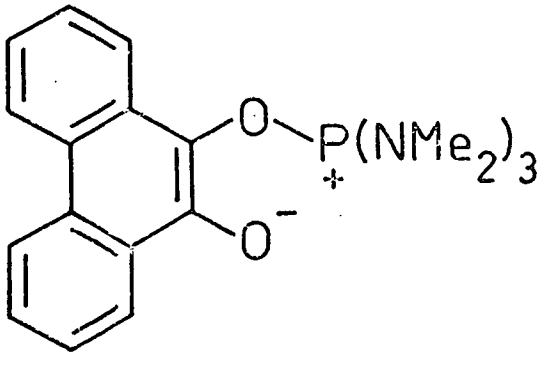
(91a)



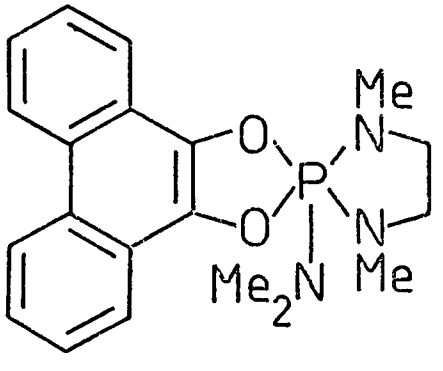
(91b)

Larger, more flexible rings appear to be mostly strain-free and can adopt both *ae* or *ee* conformations depending on the apicophilicity of the atoms attached to phosphorus.[183,190]

Finally, it is to be noted that incorporation of phosphorus into a small ring in a pentacoordinate phosphorane leads to stabilisation *vis-a-vis* its acyclic analogue. This effect can be attributed to a relief of intramolecular crowding by "tying back" the ligands within the ring. For example, ^{31}P n.m.r. studies have shown that compound (92) exists as a zwitterion, δp +38.5, whereas the cyclic analogue, compound (93), is a pentacoordinate phosphorane, δp -29.8.[191]



(92)

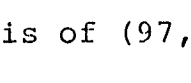


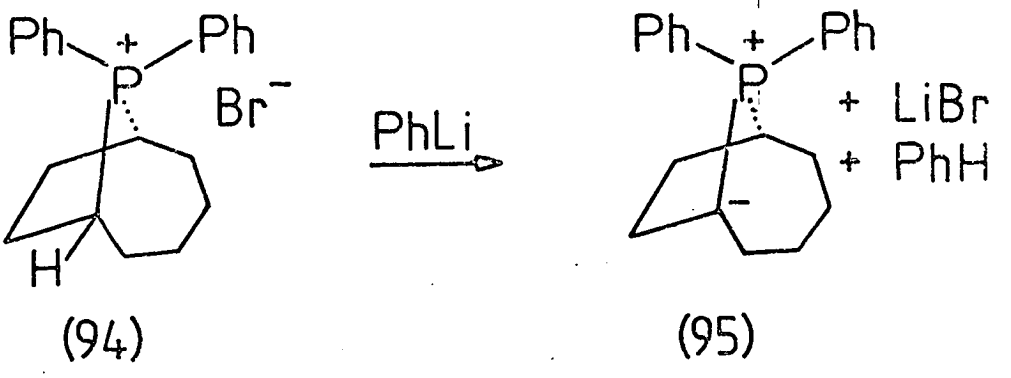
(93)

3.2 The small-ring effect in synthesis; reactions which involve pentacoordinate phosphorus

Over the last decade, several reports have appeared in which the small-ring effect has had a profound influence on the course of reactions and/or the stereochemistry and stability of the products. In the examples to be discussed, the synthetic utility is believed to be derived from the relief of strain on going from a tetracoordinate pentavalent phosphorus species to a pentacoordinate phosphorane, which can break down with formation of a strong P = X bond and elimination of the desired product.

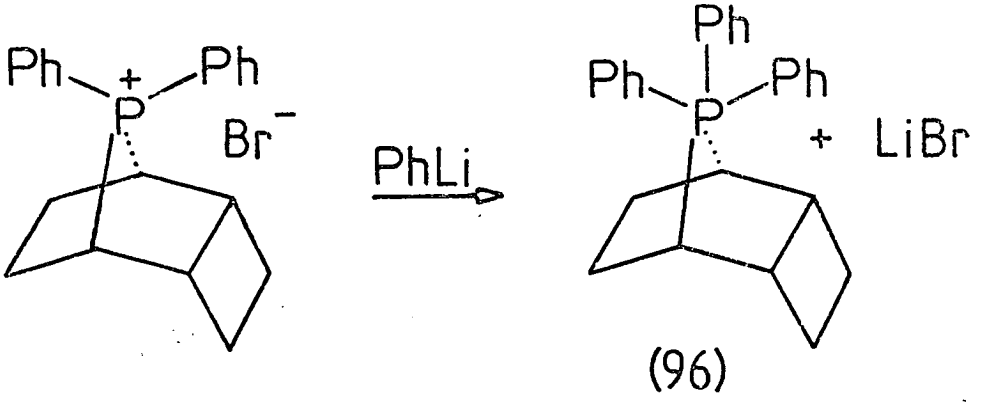
The small-ring effect was first used to synthetic advantage by Turnblom and Katz[172,192] in the preparation of pentacoordinate phosphoranes with five P-C ligands. Thus, for example, reaction of phosphonium salt (94) with phenyl lithium resulted in proton abstraction and the formation of a phosphonium ylide (95) as shown in Scheme 82. However, when the size of the ring which incorporated phosphorus was reduced, nucleophilic attack occurred, in order to relieve ring strain, and the pentacoordinate phosphorane (96) was isolated instead (Scheme 83).

Relief of ring strain has also been associated with the facile formation of benzofurazans (99) from the thermal decomposition of 1-o-nitroarylimino-1,2,5-triphenylphospholes.[64] For example, thermolysis of (97, PR_3=  , X=H) at 150° in mesitylene gave a 65% yield of (99, X=H). Since the corresponding triphenyl (97, R = Ph) and triethoxy (97, R = OEt) analogues did not decompose under similar conditions the authors argued that the reaction proceeded *via* the formation



(94) (95)

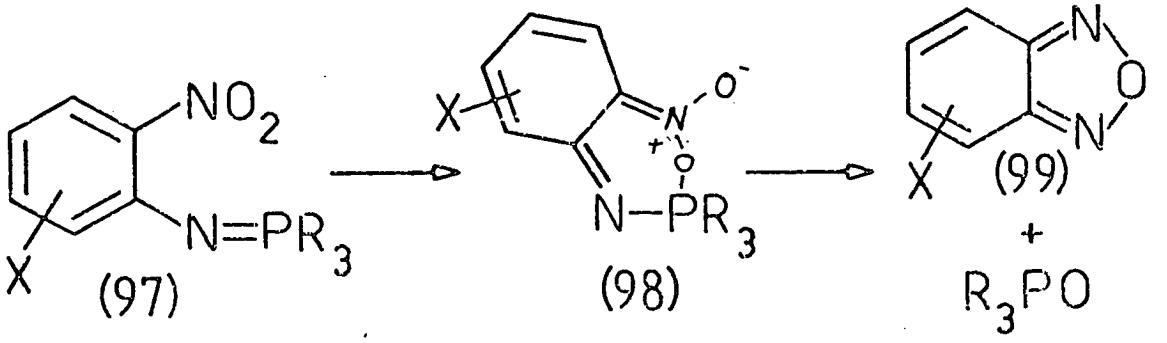
Scheme 82



(96)

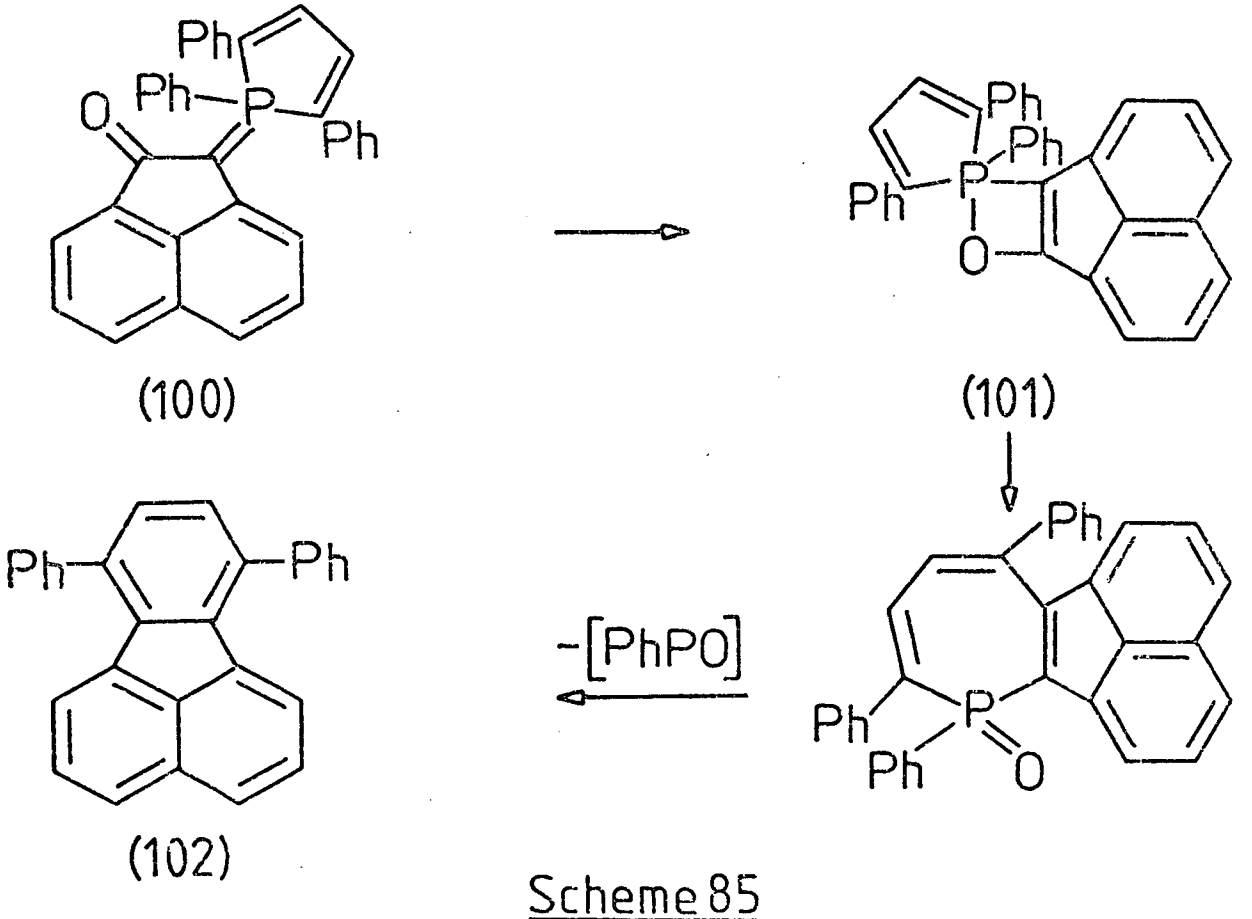
Scheme 83

of the strain-free pentacoordinate phosphorane intermediate (98), which decomposed to benzofurazan and phosphole oxide as shown in Scheme 84.



Scheme 84

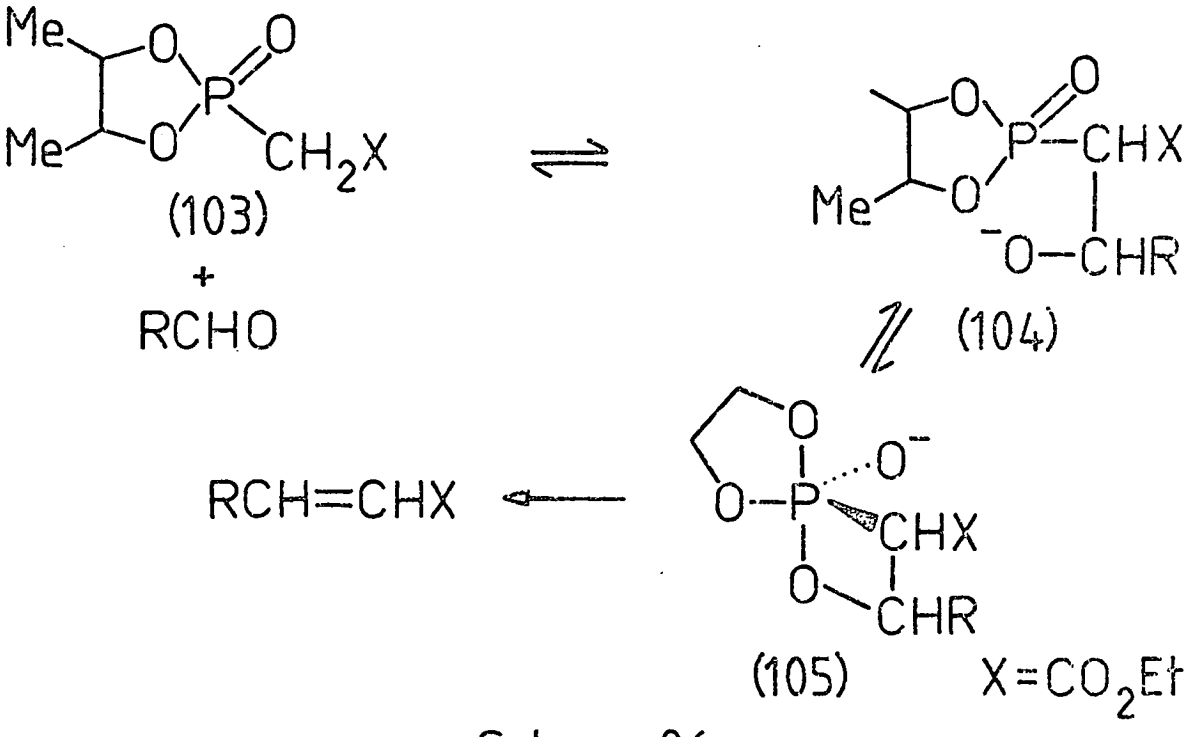
The same workers[193] also showed that 2-(1,2,5-triphenyl-1-λ^5-phosphol-1-ylidene)acenaphthen-1-one (100) underwent smooth decomposition in diphenyl ether at 175°C to give 7,10-diphenylfluoranthene (102), apparently *via* ring enlargement of the strained phosphole ring in (101) (Scheme 85).



Scheme 85

In another instance, relief of ring strain has been used to change the course of the phosphonate modification of the Wittig reaction (i.e. Horner-Emmons reaction) and obtain a higher proportion of *cis*-olefin. Thus, whereas reaction of acyclic phosphonates with carbonyl compounds leads mainly to the formation of *trans*-olefins,[194] the use of the cyclic phosphonate (103) gave rise to the preferential formation of the *cis* isomer (Scheme 86).[195] It was argued that the

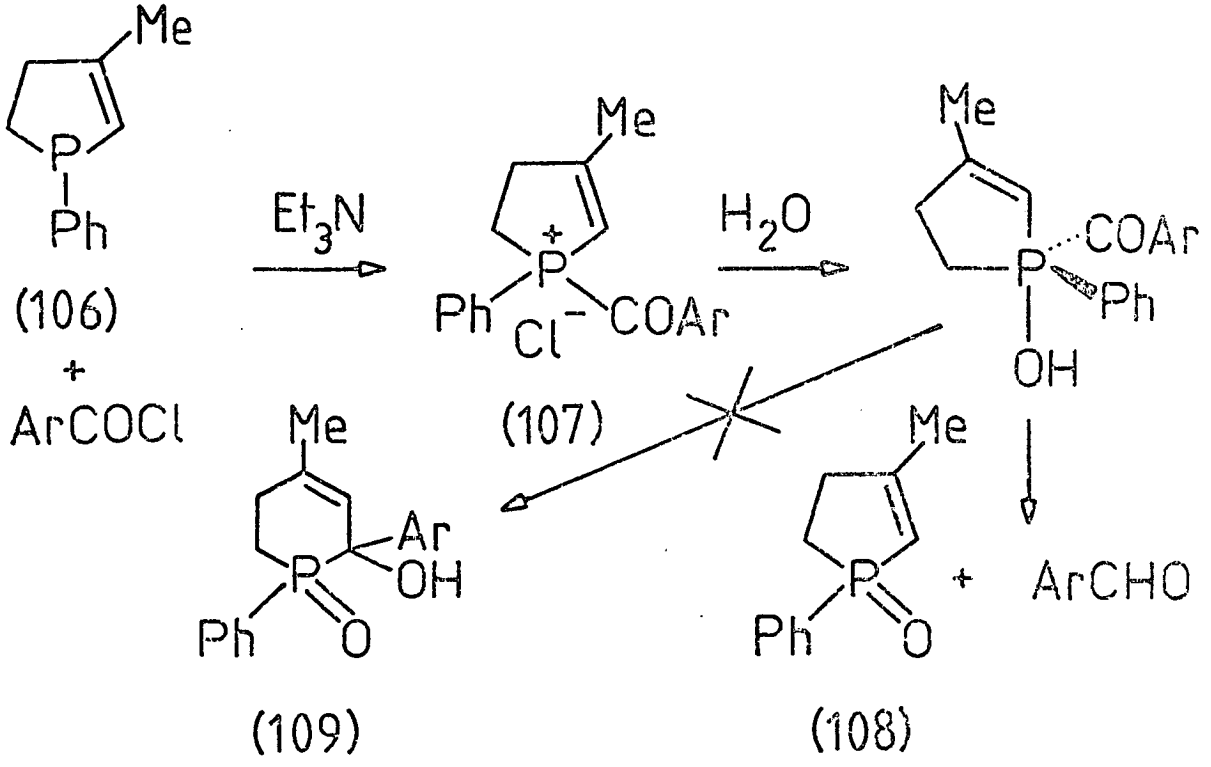
initially formed betaines (104, *threo* and *erythro*) underwent rapid ring closure to the stabilised oxaphosphetan (105) in order to relieve ring strain. As a result, reversible betaine formation was inhibited, and more of the kinetically favoured *erythro* betaine collapsed to cis-olefin.



Scheme 86

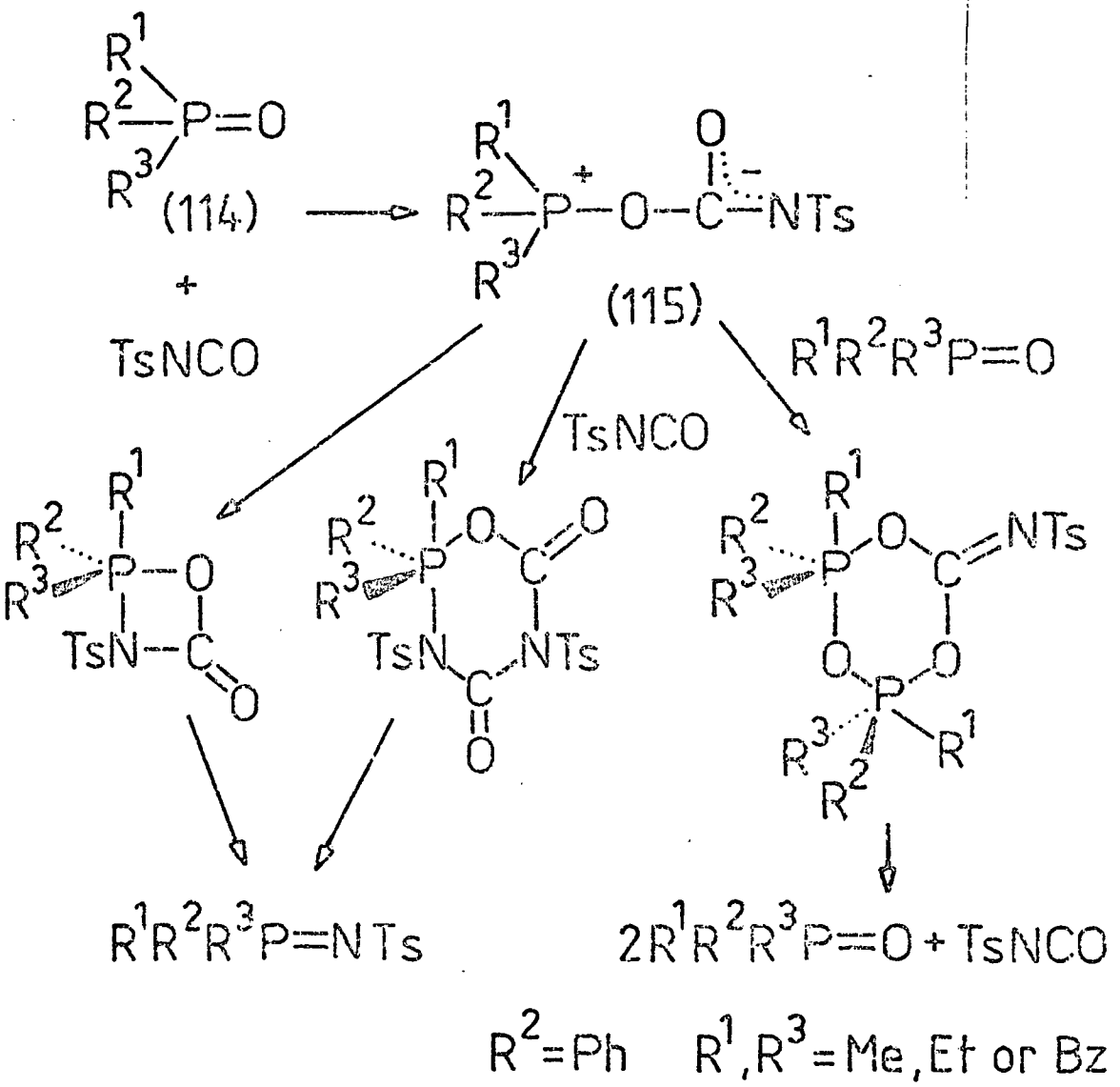
Relief of ring strain in acylphospholenium salts has also provided a simple and mild route to aromatic aldehydes.[196] Thus, reaction of 3-methyl-1-phenyl-2-phospholene (106) with acid chlorides in the presence of triethylamine led to the formation of acyphospholenium salts (107) which on treatment with water gave the corresponding aldehydes and phospholene oxides (108) rather than the expected ring expanded products (109) (Scheme 87).[197] This unusual reaction was thought to

proceed *via* nucleophilic attack at phosphorus and not, as with acyclic phosphonium salts, at the carbonyl carbon.[198] This change in reactivity was ascribed to relief of ring strain in the phospholenium salt (107), leading to an increase in the rate of nucleophilic attack at phosphorus relative to carbon.



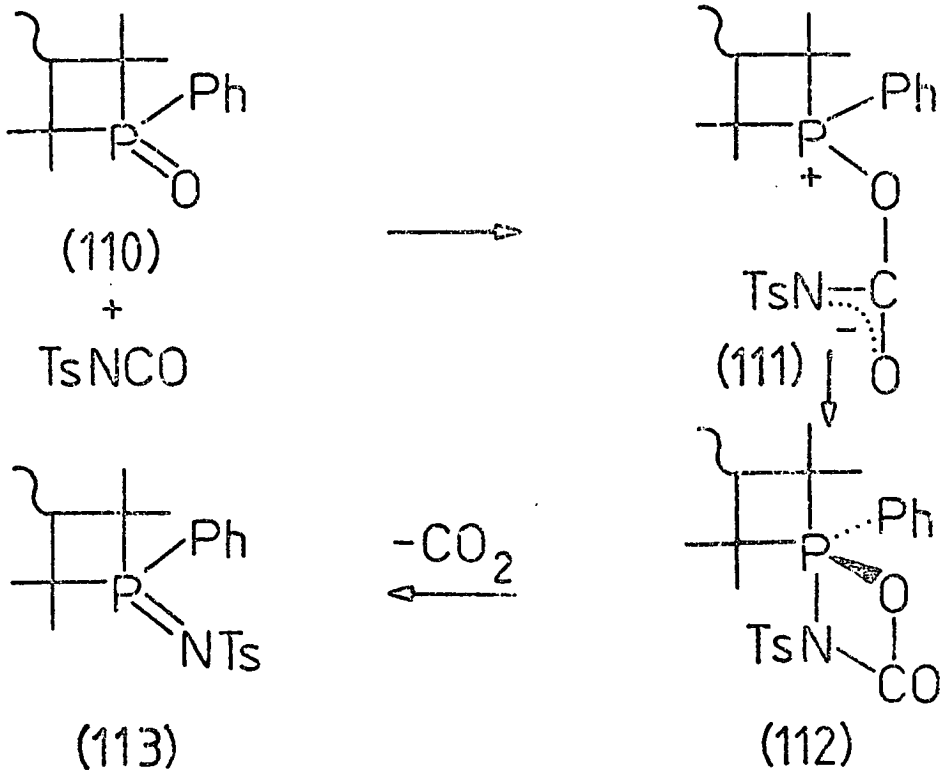
Scheme 87

A kinetic acceleration attributable to the small-ring effect also appears to be the determining factor in the synthesis of the chiral iminophosphorane (113) from the reaction of the phosphetan oxide (110) with tosyl isocyanates.[199] Apparently, the first-formed zwitterion (111) underwent rapid ring closure to the intermediate (112),


(114)
+
TsNCO
(115)
TsNCO
R¹R²R³P=O
R¹R²R³P=NTs
2R¹R²R³P=O + TsNCO
R²=Ph
R¹,R³=Me, Et or Bz

Scheme 89

followed by decomposition to the iminophosphorane (113) with retention of configuration (Scheme 88). By comparison, decomposition of the zwitterion (115) formed from the acyclic phosphine (114), occurred more slowly and other reaction pathways were able to compete, thus causing racemisation at phosphor (Scheme 89).



Scheme 88

SECTION II

EXPERIMENTAL

1. Abbreviations and Symbols

b.p.	boiling point
m.p.	melting point
tlc	thin-layer chromatography
glc	gas liquid chromatography
h.p.l.c.	high pressure liquid chromatograp
n.m.r.	nuclear magnetic resonance
s;d;t;q;m	singlet; doublet; triplet; quartet; multiplet
J	coupling constant
δ	chemical shift
I.R.	infra-red
M^+	mass of molecular ion
m/e	mass to charge ratio
m*	metastable peak
h; min	hours; minutes
p.p.m.	parts per million
mol	moles
mmol	millimoles
ν	wavenumber (cm^{-1})

2. Instrumentation

Infra-red Spectroscopy. I.R. spectra were recorded on a Perkin-Elmer 157G Grating Spectrophotometer. Liquid samples were recorded as thin films, and solid samples (unless otherwise stated) in solution in 'Analar' chloroform using matched cells with sodium chloride windows (path length 0.1 mm) or as nujol mulls. Polystyrene film μ_{max} 1603 cm^{-1} was used as reference for calibration purposes.

Mass Spectroscopy. Mass spectra and exact mass measurements were recorded by Mr. D. Thomas on an A.E.I. MS 902 mass spectrometer.

Nuclear Magnetic Resonance Spectroscopy.

(i) ^{1}H N.m.r. spectra were recorded on a Varian EM 360 spectrometer operating at 60 MHz. The spectra of new compounds were recorded on a Varian HA 100 instrument operating at 100 MHz by Mr. J. Millar or on a Bruker WH 360 spectrometer operating at 360 MHz by Dr. I. Sadler. Samples were examined in solution in deuterochloroform unless otherwise stated. Chemical shifts (δ_H) were measured in parts per million relative to tetramethylsilane as internal standard (δ_H = 0.0).

(ii) ^{13}C N.m.r. spectra were recorded on a Varian CFT 20 spectrometer operating at 20 MHz by Mr. J. Millar. Samples were examined in solution in deuterochloroform, chemical shifts (δ_C) being measured in parts per million relative to tetramethylsilane.

(iii) ^{15}N N.m.r. spectra were recorded either on a Bruker WH360 operating at 36.498 MHz by Dr. I. Sadler or on a Bruker WH180 operating at 18.24 MHz by the Physico-Chemical Measurements Unit, Harwell. Samples were examined in solution in deuterochloroform, chemical shifts (δ_N) being measured in parts per million relative to external nitromethane (δ_N = 0.0).

(iv) ^{31}P N.m.r. spectra were recorded on a Jeol FX60 spectrometer operating at 24.21 MHz. Samples were examined in solution in deuterochloroform (unless otherwise stated), chemical shifts (δ_P) being measured in parts per million relative to 85% external phosphoric acid (δ_P = 0.0). Shifts to high frequency of the standard are positive.

Melting Points. Melting points of new compounds were obtained using a Kofler hot-stage microscope for stable compounds, and on a Gallenkamp melting point apparatus in a 'Parafilm'-sealed capillary tube for atmospherically unstable compounds. Routine melting points were obtained using the Gallenkamp apparatus.

Elemental Analysis. Microanalyses for carbon, hydrogen and nitrogen were carried out using a Perkin-Elmer 204 elemental analyser operated by Mr. J. Grunbaum.

Gas Liquid Chromatography. Gas liquid chromatography was carried out on a Pye 104 Gas Chromatograph fitted with a flame ionisation detector. A 7 foot by $^1/_8$ inch 4% ApL column was used with nitrogen as carrier gas.

High Performance Liquid Chromatography. Chromatograms were obtained using a 15 cm x 0.5 cm polished stainless steel column slurry packed with Hypersil silica. A Cecil CE 212 u.v. detector was used. The solvent used was a 50% methylene chloride/50% n-hexane (25% water saturated) mixture.

Thin Layer Chromatography. Glass plates covered with a 0.3 mm layer of alumina (Merck, Aluminium oxide G, type E), deactivated to Brockman activity 3, or silica (Merck, silica gel G), with added fluorescent indicator (M. Woelm, Eschwege, Germany), were used. Components in the developed chromatogram were detected by their reaction with iodine vapour or their fluorescence in ultraviolet light.

Column Chromatography. Alumina (Laporte Industries, Type H) or silica gel (Fisons Scientific Apparatus, 80-200 mesh) was used.

Optical Rotations. A Perkin-Elmer 141 Polarimeter operating at 589.3 nm (sodium D line) was used to measure optical rotations. Solutions were inserted into a quartz cell, path length 1 dm, for measurement. Angles of rotation are expressed as specific rotations $[\alpha]_D^t$ as defined by Vogel.

3. Solvents

Commercially available solvents were used without further purification unless described as 'dry' or 'super-dry'.

Dry Solvents. Light petroleum (petrol, b.p. 40-60°C) and benzene were redistilled and dried over sodium wire before use. Diethyl ether, cyclohexane and tert-butylbenzene were dried by standing over sodium wire. Methylene chloride, 1,2-dichlorobenzene and chlorobenzene were dried by heating under reflux for several hours with phosphorus pentoxide and distilling on to dry molecular sieve.

Pyridine was dried by heating under reflux for several hours with sodium hydroxide pellets and distilling on to sodium hydroxide pellets. Diethylamine and triethylamine were dried by storing over sodium hydroxide pellets.

1,2-Ethanediol was stored over anhydrous sodium sulphate and distilled on to dry molecular sieve before use.

Super-dry Solvents. Super-dry solvents were prepared by heating the sodium dried solvent under reflux for several hours with lithium aluminium hydride and distilling on to dry molecular sieve. Ether, light petroleum (petrol, b.p. 40-60°C), benzene, and 1,4-dioxan were prepared in this manner.

4. Preparation of Tervalent Phosphorus Compounds

Commercially available samples of hexamethylphosphorus triamide, phosphorus trichloride, dichlorophenylphosphine, chlorodiphenylphosphine and triphenylphosphine were used without further purification.

Trimethyl and triethyl phosphite were allowed to stand over sodium wire for 24 h then redistilled from fresh sodium, under an atmosphere of dry nitrogen, on to dry molecular sieve.

Dimethyl phenylphosphonite was prepared by reaction of dichlorophenylphosphine (35.6 g; 0.2 mol) with methanol (16 g; 0.5 mol) in the presence of triethylamine (51 g; 0.5 mol) and dry ether (250 ml).[200] The product was obtained as a colourless oil (25.3 g; 74%), b.p. 68-70°C/3 mm (lit.[201] 101-102°C/15 mm), δ_P+ 160.5.

Methyl diphenylphosphinite was prepared by the method of Quin and Anderson.[202] The reaction of chlorodiphenylphosphine (44.2 g; 0.2 mol) with methanol (8 g; 0.25 ml) in the presence of triethylamine (26 g; 0.26 mol) and dry ether (200 ml) gave methyl diphenylphosphinite (29.7 g; 69%), b.p. 116-118°C/1 mm (lit.[201] 151-152°C/10 mm) as a colourless oil, δ_P+ 117.0.

2-Phenyl-1,3,2-dioxaphospholan was prepared by the procedure of Mukaiyama, Fujisawa, Tamura and Yokota.[203] Thus, 1,2-ethanediol (15.5 g; 0.25 mol) reacted with dichlorophenylphosphine (45 g; 0.25 mol) in the presence of triethylamine (50.5 g; 0.5 mol) and dry benzene (250 ml) under an atmosphere of dry nitrogen, gave 2-phenyl-1,3,2-dioxaphospholan (23.7 g; 56%), b.p. 75°C/1 mm (lit.[203] 79-80°C/0.8 mm) as a colourless oil, δ_P+ 161.8 . The product was either used immediately or stored at -10°C. The ^{31}P n.m.r. spectrum was scanned prior to each use as the compound polymerised slowly on storage.[203]

2-Phenyl-1,3,2-dioxaphosphorinan. A modification of the method of Mukaiyama et al.[203] was used. Dichlorophenylphosphine (35.8 g; 0.2 mol) in dry benzene (200 ml) was added over 1 h to a mixture of freshly distilled 1,3-propanediol (15.2 g; 0.2 mol) and triethylamine (40.4 g; 0.4 mol) in dry benzene (200 ml) with stirring and cooling in an ice/water bath under dry nitrogen. The mixture was then heated at approximately 45°C for 45 min and then kept at 3°C for 12 h to complete precipitation of triethylamine hydrochloride. The mixture was filtered and the benzene removed in vacuo to leave a pale yellow oil which was distilled under reduced pressure. The product was obtained as a colourless oil (18.2 g; 50%), b.p. 97-101°C/0.1 mm (lit.[203] 72-74°C/0.15 mm) δ_P+152.7.

2-Phenyl-1,3,2-dioxaphosphepan was prepared by the procedure of Mukaiyama and co-workers,[203] used above to make 2-phenyl-1,3,2-dioxaphospholan. Dichlorophenylphosphine (45 g; 0.25 mol) in dry benzene (250 ml) was added dropwise over 1 h with stirring to a mixture of 1,4-butanediol (22.5 g; 0.25 mol) and dry triethylamine (50.5; 0.5 mol) in dry benzene (250 ml) under an atmosphere of dry nitrogen with cooling in an ice/water bath. When the addition was complete, the mixture was heated under reflux for 1 h, cooled, filtered and the benzene removed in vacuo. The resultant pale yellow oil was distilled under reduced pressure to give the product as a colourless oil (10.5 g; 21%), b.p. 97-99°C/0.2 mm (Found: C, 61.3; H, 6.7.

$C_{10}H_{13}O_2P$ requires C, 61.2; H, 6.7%), ν_{max} (neat) 1435 (PPH), 1080, 1050, 930, 890 and 850 cm^{-1}. δ_H 1.58-1.94 (4H, m, $OCH_2\underline{CH_2}\underline{CH_2}CH_2O$), 3.70-4.26 (4H, m, $O\underline{CH_2}CH_2CH_2\underline{CH_2}O$), 7.12-7.76 (5H, m, ArH), δ_P+156.5, m/e 196 (M^+, 100%), 143 (49), 125 (45), 77 (48).

The attempted preparation of 2-phenyl-1,3,2-dioxaphosphocan, by the method used to prepare 2-phenyl-1,3,2-dioxaphospholan,[203] gave a viscous pale yellow oil which decomposed on distillation to give, by ^{31}P n.m.r., a large number of phosphorus containing products, exhibiting resonances in the P = O region of the spectrum. A ^{31}P n.m.r. spectrum taken before distillation showed a major resonance at δ_P+155.9 with minor signals at δ_P+153.8 and δ_P+18.9.

Diethylphenylphosphine was supplied by Miss E. Henry. The purity of the compound was checked prior to use by ^1H and ^{31}P n.m.r., δ_P-15.6.

1-Phenyl-2,2-dimethylphosphetan was prepared from 1-phenyl-2,2-dimethylphosphetan oxide, supplied by Mr. K. Wall, by the procedure of Cremer and Chorvat.[204]

Trichlorosilane (2.09 g,15 mmol) in dry benzene (30 ml) was added dropwise over 20 min under nitrogen to 1-phenyl-2,2-dimethylphosphetan oxide (3.0 g, 15 mmol) in dry benzene (25 ml) and triethylamine (1.56 g, 15 mmol). The solution was heated under reflux for 3 h, cooled in an ice bath and sodium hydroxide solution (25 ml, 20%) added dropwise over 40 min. Benzene (100 ml) was added and the organic layer

separated, washed with saturated sodium chloride solution and dried over anhydrous sodium sulphate. The solvent was removed in vacuo to leave an oil which was distilled under reduced pressure to give the phosphetan (0.81 g; 29%) as a colourless oil b.p. 45-47°C/0.25 mm. The product was used immediately as it has been observed that phosphetans of this type oxidise and polymerise rapidly.[204] δ_P-32.4.

1-Phenylphospholan was prepared by a modification of the procedure of Grüttner and Krause.[205] A diGrignard, prepared by the addition of dry 1,4-dibromobutane (136.5 g; 0.63 mol) in dry ether (150 ml) to magnesium turnings (30.9 g) in dry ether, and dichlorophenylphosphine (56.6 g; 0.32 mol), made up with dry ether to the same volume as the Grignard reagent, were added dropwise and simultaneously to dry ether (1 ℓ.), with stirring and cooling in an ice/water bath under dry nitrogen. The mixture was stirred for 3 h then dry diethylamine (300 ml) was carefully added with stirring and cooling. The reaction mixture was allowed to stand for 12 h at room temperature. The resultant white suspension was passed through a short and wide alumina column to remove the magnesium salts and the ether removed in vacuo to leave a pale yellow oil. On distillation the product was obtained as a clear colourless oil (15.9 g; 31%), b.p. 77-80°C/0.2 mm (lit.,[206] 97°C/3mm), δ_P-15.8.

1-Phenylphosphorinan was supplied by Mr. T. Naisby. The purity of the compound was checked prior to use by ^1H and ^{31}P n.m.r., δ_P-33.3.

Dichloromethylphosphine was prepared by the method of Soroka.[207] Phosphorus trichloride (205.5 g; 1.5 mol) and anhydrous aluminium chloride (226 g; 1.7 mol) were heated for 30 min at 60-70°C under nitrogen. The mixture was cooled in an ice/water bath and methyl iodide (213 g; 1.5 mol) added dropwise, with continuous stirring and cooling, over 30 min. After 1 h the complex solidified and dry potassium chloride (127 g; 1.7 mol) and iron powder (90 g) were added. On heating the mixture to melting point a black viscous liquid distilled out b.p. 80-170°C. The crude product was distilled twice on a Vigreux column to yield the phosphine as a colourless oil (55 g; 31%), b.p. 80-82°C (lit.,[207] 80-82°C), δ_P+190.3.

1-Methylphosphorinan was prepared by the procedure of Featherman and Quin.[208] The diGrignard reagent, prepared from dry 1,5-dibromopentane (115 g, 0.5 mol) and magnesium (25 g), in dry ether (200 ml) was treated with dichloromethylphosphine (29.25 g; 0.25 mol) in ether as described in the preparation of 1-phenylphospholan above. The product was obtained as a colourless oil (3g; 10%), b.p. 34-36°C/0.7 mm (lit.,[208] 144-147°C), δ_P-57.6.

N,N-Diethylaminomethylchlorophosphine was prepared by the procedure of Seidel and Issleib.[209] Dry diethylamine (62 g; 0.85 mol) in dry ether (100 ml) was added dropwise, with stirring and cooling in an ice/water bath under nitrogen, to dichloromethylphosphine (50 g; 0.43 mol) in dry ether (300 ml) over 2 h. The mixture was stirred at room temperature for 1 h, filtered and the ether removed in vacuo to leave a

pale yellow oil. On distillation the product was obtained as a colourless oil (47.2 g; 72%), b.p. 28-29°C/0.5 mm (lit.,[209] 71-72°C/0.17 mm), δ_P+147.6.

Methyl-1-naphthylchlorophosphine was prepared by a variation of the procedure of Horner, Schedlbauer and Beck.[210] 1-Naphthylmagnesium bromide, prepared by the addition of 1-bromonaphthalene (31.0 g; 0.15 mol) in dry ether (50 ml) to magnesium (3.64 g) in dry ether (50 ml) and dry benzene (40 ml), was added dropwise to a stirred solution of N,N-diethylaminomethylchlorophosphine (23 g; 0.15 mol) in dry ether (100 ml) with stirring and cooling in an ice/water bath under nitrogen over 2 h. The mixture was warmed and stirred at room temperature for an hour, diethylamine (16 ml) was then added and stirring was continued for a further hour. The resultant white suspension was passed through a celite pad and added dropwise to a stirred solution of hydrogen chloride (16.4 g; 0.45 mol) in ether (200 ml) with cooling in an ice/water bath. The mixture was stirred at room temperature for 1 h, filtered through a celite pad and the solvent removed in vacuo to leave a yellow oil. The oil was distilled under reduced pressure to yield two fractions. The first, a colourless crystalline solid, was identified by ^{1}H n.m.r. as naphthalene (1.62 g; 9%) and the second, a colourless oil, was methyl-1-naphthylchlorophosphine (17.3 g; 55%), b.p. 125-128°C/0.4 mm (Found: C, 63.6; H, 4.8. $C_{11}H_{10}ClP$ requires C, 63.3; H, 4.8%), ν_{max} (neat) 1505, 795 and 770 cm^{-1}. δ_H 1.93 (3H, d, PMe, J_{PH} 10 Hz), 7.12-8.28 (6H, m, ArH), 8.38-8.64 (1H, m, ArH), δ_P+81.6, m/e M^+ not observed.

Methyl methyl-1-naphthylphosphinite was prepared by the general method described by Quin and Anderson.[202] The reaction of methyl-1-naphthylchlorophosphine (17.3 g; 0.083 mol) with methanol (2.67 g; 0.083 mol) in the presence of triethylamine (9 g; 0.09 mol) and dry ether (130 ml) gave methyl methyl-1-naphthylphosphinite (14.6 g; 86%) as a colourless oil, b.p. 100-110°C/0.05 mm (Found: C, 70.4; H, 6.1. $C_{12}H_{13}OP$ requires C, 70.6; H, 6.4%), ν_{max} (neat) 2810, 1505, 1140, 795 and 770 cm^{-1}. δ_H 1.53 (3H, d, PMe, J_{PH} 6Hz), 3.45 (3H, d, POMe, J_{PH} 14 Hz), 7.00-7.90 (6H, m, ArH), 8.08-8.48 (1H, m, ArH), δ_P+114.5, m/e 204 (M^+, 82%), 189 (100), 159 (29), 127 (27).

Methyl methylphenylphosphinite was supplied by Mr. R.S. Strathdee. The purity of the compound was checked prior to use by ^1H and ^{31}P n.m.r., δ_P+119.0.

N,N-Diethylaminophenylchlorophosphine was prepared by the method of Seidel.[211] Dry diethylamine (51.5 g; 0.71 mol) was added dropwise, with stirring and cooling in an ice/water bath under nitrogen, to dichlorophenylphosphine (60 g; 0.335 mol) in dry ether (150 ml) over 2h. The mixture was stirred at room temperature for 1 h, filtered through a pad of alumina and the ether removed in vacuo to leave a yellow oil. On distillation the product was obtained as a colourless oil (28.8 g; 40%), b.p. 81-85°C/0.1 mm (lit.,[211] 82-84°C/0.05 mm), δ_P+142.2.

Phenyl-m-tolylchlorophosphine was prepared by the general procedure of Horner and co-workers,[210] used above to prepare methyl-1-naphthylchlorophosphine. The mixture obtained from the reaction of m-tolylmagnesium bromide, prepared from m-bromotoluene (23.1 g; 0.135 mol) and magnesium (3.6 g) in dry ether (70 ml), with N,N-diethyl-aminophenylchlorophosphine (28 g; 0.13 mol) in dry ether (150 ml) and diethylamine (14 ml) was added to hydrogen chloride (0.39 mol) in dry ether (150 ml). The resultant white suspension was filtered and the ether removed in vacuo to leave a yellow oil which was distilled under reduced pressure to give the product as a colourless oil (18.3 g; 60%), b.p. 126-132°C/1 mm (Found: C, 66.6; H, 5.2. $C_{13}H_{12}ClP$ requires C, 66.5; H 5.2%), ν_{max} (neat) 1440, 780, 750, 720 and 690 cm^{-1}. δ_H 2.32 (3H, s, m Me), 6.93-8.01 (9H, m, ArH), δ_P+82.3, m/e 236 (M^+, 20%), 234 (M^+, 63), 199 (19), 182 (100), 168 (73).

Methyl phenyl-m-tolylphosphinite was prepared by the general method described by Quin and Anderson.[202] Reaction of phenyl-m-tolylchlorophosphine (6.7 g; 0.029 mol) with methanol (0.93 g; 0.029 mol) in the presence of triethylamine (3 g; 0.03 mol) and dry ether (35 ml) gave methyl phenyl-m-tolylphosphinite (5.03 g; 77%) as a colourless oil, b.p. 120-125°C/0.05 mm. (Found: C, 73.0; H, 6.5. $C_{14}H_{15}OP$ requires C, 73.0; H, 6.6%), ν_{max} (neat) 2820, 1430, 1095 and 780 cm^{-1}. δ_H 2.29 (3H, s, m Me), 3.61 (3H, d, POMe, J_{PH}14Hz), 7.00-7.63 (9H, m, arH), δ_P + 117.2, m/e 230 (M^+, 83%), 215 (100), 109 (13), 91 (17), 77 (12).

sec-Butyl phenyl-m-tolylphosphinite was prepared by the general method described by Quin and Anderson.[202] Reaction of phenyl-m-tolylchlorophosphine (9.38 g; 0.04 mol) with sec-butanol (2.96 g; 0.04 mol) in the presence of triethylamine (4.2 g; 0.042 mol) and dry ether (80 ml) gave sec-butyl phenyl-m-tolylphosphinite (8.31 g; 76%) as a colourless oil, b.p. 155-165°C/0.05 mm (Found: C, 74.8; H, 7.6. $C_{17}H_{21}OP$ requires C, 75.0; H, 7.8%), ν_{max} (neat) 1435, 1375, 1095, 745 and 695 cm^{-1}. δ_H 0.88 (3H, t, $CH_2\underline{CH}_3$, J_{HH} 8Hz), 1.24 (3H, d, $CH\underline{CH}_3$, J_{HH} 6Hz) 1.40-1.88 (2H, m, $\underline{CH}_2CH_3$), 2.28 (3H, s, mMe), 3.74-4.14 (1H, m, POCH), 6.98-7.90 (9H, m, ArH), δ_P (diastereoisomers, 1:1)+ 106.5 and + 106.6, m/e 272 (M^+, 17%), 216 (100), 199 (14), 182 (11), 169 (21), 91 (22), 77 (10).

1-Naphthylphenylchlorophosphine was prepared by the method of Horner, Schedlbauer and Beck.[210] The mixture obtained from reaction of 1-naphthylmagnesium bromide, prepared from 1-bromonaphthalene (14 g; 0.068 mol) and magnesium (1.6 g) in dry ether (50 ml) and dry benzene (15 ml), with N,N-diethylaminophenylchlorophosphine (14 g; 0.065 mol) in dry ether (100 ml) and diethylamine (7 ml) was added to hydrogen chloride (0.195 mol) in dry ether (150 ml). The resultant white suspension was filtered and the ether removed in vacuo to leave a yellow oil which was distilled under reduced pressure to yield two fractions. The first, a colourless oil, was identified by ^{31}P n.m.r. δ_P+160.6 as dichlorophenylphosphine (2.3 g; 20%), b.p. 40-44°C/0.05 mm (lit.,[212] 46.47°C/0.7 mm) and the second, a pale yellow oil, as 1-naphthylphenylchlorophosphine (6.23 g; 35%), b.p.[210]

166-170°C/0.05 mm (lit.,[210] 195°C/0.1 mm), δ_P+79.7.

Methyl 1-naphthylphenylphosphinite was prepared by the general method described by Quin and Anderson.[202] Reaction of 1-naphthylphenylchlorophosphine (18.4 g; 0.068 mol) with methanol (2.18 g; 0.068 mol) in the presence of triethylamine (7 g; 0.069 mol) and dry ether (85 ml) gave methyl 1-naphthylphenylphosphinite (11.84 g; 65%) as a pale yellow oil, b.p. 160-170°C/0.05 mm (Found: C, 76.8; H, 5.7. $C_{17}H_{15}OP$ requires C, 76.7; H, 5.7%), ν_{max} (neat) 2820, 1430, 795, 775 and 695 cm^{-1}. δ_H 3.69 (3H, d, POMe, J_{PH} 14 Hz), 7.10-7.92 (11H, m, ArH), 8.16-8.34 (1H, m, ArH), δ_P+113.3, m/e 266 (M^+, 100%), 251 (85), 233 (15), 173 (33), 127 (19), 109 (13), 77 (13).

Hexaethylphosphorus triamide was supplied by Dr. N.J. Tweddle. The purity of the compound was checked prior to use by ^1H and ^{31}P n.m.r., δ_P+118.0.

5. Preparation of Phosphoryl Compounds

Phosphoryl compounds were prepared by the oxidation of tervalent phosphorus compounds by lead tetraacetate as described by Henry.[213]

2-Phenyl-1,3,2-dioxaphospholan oxide was prepared by the portionwise addition of lead tetraacetate (5.39 g; 0.012 mol) to a stirred solution of 2-phenyl-1,3,2-dioxaphospholan (1.86 g; 0.011 mol) in dry methylene chloride (30 ml). Heat was evolved and a white slurry was deposited as the reaction proceeded. After 1 h of continuous

stirring the mixture was filtered, washed with water, dried over anhydrous magnesium sulphate and the solvent removed in vacuo to leave a yellow oil which on distillation gave 2-phenyl-1,3,2-dioxaphospholan oxide (1.47 g; 72%), b.p. 120°C/0.05 mm (lit.,[213] 210°C/6-7 mm) as a colourless oil, δ_p +36.7. On standing the oil formed a colourless solid, m.p. 55-57°C (lit.,[214] 56-58°C).

2-Phenyl-1,3,2-dioxaphosphepan oxide was prepared by the procedure outlined above. Lead tetraacetate (6.34 g, 0.014 mol) was added to 2-phenyl-1,3,2-dioxaphosphepan (2.55 g; 0.013 mol) in dry methylene chloride (60 ml). After filtration, washing and removal of solvent an oil was obtained which on distillation gave 2-phenyl-1,3,2-dioxaphosphepan oxide (1.99 g; 72%) as a colourless oil which solidified on standing. Recrystallisation from ether gave the oxide as colourless crystals, m.p. 73-74°C (Found: C, 56.7; H, 6.1; $C_{10}H_{13}O_3P$ requires C, 56.6; H, 6.2%), ν_{max} 1445 (P-Ph), 1140, 1030 and 955 cm^{-1}. δ_H 1.68-2.30 (4H, m, $OCH_2\underline{CH_2}\underline{CH_2}CH_2O$), 3.79-4.71 (4H, m, $O\underline{CH_2}CH_2CH_2\underline{CH_2}O$), 7.22-8.04 (5H, m, ArH), δ_p +21.2, m/e 212 (M^+, 48%), 159 (83), 141 (100); m^* 119.3 (212 → 159).

6. Preparation of Azido Compounds

All azido compounds were stored in the absence of light at -10°C. Before use they were warmed to room temperature in a desiccator.

o-Azidophenol was prepared by a modification of the method of Forster and Fierz.[215] To o-aminophenol (10 g, 92 mmol) in concentrated hydrochloric acid (25 ml) and water (75 ml), maintained at between 0-5°C, was added dropwise with stirring sodium nitrite (6 g, 87 mmol) in water (25 ml). Sodium azide (6 g, 92 mmol) in water (15 ml) was then added all at once and the solution stirred for 1 h at room temperature. Ether (500 ml) was added and the organic layer separated and dried over anhydrous sodium sulphate. Filtration, followed by removal of the ether in vacuo at room temperature gave a brown solid which on sublimation at 50°C/0.05 mm gave the product as light sensitive yellow crystals (8.2 g; 66%), m.p. 35-36°C, ν_{max} 2130 cm^{-1} (N_3).

o-Azidophenyl benzoate was prepared by the method of Forster and Fierz.[215] Potassium hydroxide (3.75 g, 67 mmol) in ethanol (54 ml) was added with stirring to o-azidophenol (7.5 g, 56 mmol) in ethanol (15 ml). The solvent was removed in vacuo and dry ether (60 ml) added to the residue. Benzoyl chloride (11.7 g, 83 mmol) in dry ether (20 ml) was then added dropwise with stirring. A precipitate formed during stirring for 20 h. The solution was filtered, washed with water (50 ml) and sodium carbonate solution (2%, 500 ml). The organic layer was separated and dried over anhydrous sodium sulphate. Filtration and evaporation of the solvent left a brown oil which was purified by

repeated recrystallisations from petrol (b.p. 40-60°C) at -78°C. o-Azidophenyl benzoate (4.18; 31%) was obtained as light sensitive pale orange crystals m.p. 40-42°C (lit.,[215] 45°C), ν_{max} 2130 cm^{-1} (N_3).

o-Azidophenyl tosylate was prepared by the method of Forster and Fierz.[215] Potassium hydroxide (2.5 g, 45 mmol) in ethanol (35 ml) was added with stirring to o-azidophenol (5 g, 37 mmol) in ethanol (20 ml). The solvent was removed in vacuo and dry ether (50 ml) added to the residue. p-Toluenesulphonyl chloride (9 g, 47 mmol) in dry ether (50 ml) was then added slowly with stirring. A solid was precipitated from solution and after 20 h stirring the mixture was filtered. On removal of the solvent from the filtrate in vacuo a solid remained which was recrystallised from ethanol to give the product as a colourless crystalline solid (4.9 g, 46%), m.p. 69-71°C (lit.,[215] 72°C), ν_{max} (mull) 2120 cm^{-1} (N_3).

o-Azidobenzyl alcohol was prepared in a two step synthesis by the method of Smolinsky.[216] The initial reduction step was effected by the method of Nystrom and Brown.[217]

Anthranilic acid (15.1 g, 0.11 mol) was contained in a soxhlet over a flask containing lithium aluminium hydride (10 g, 0.26 mol) and ether (600 ml). The solvent was heated under reflux and the acid was gradually washed in. After 1 h the reaction was cooled and excess lithium aluminium hydride destroyed cautiously with water. The

ether layer was decanted off and dried over anhydrous magnesium sulphate. The solution was filtered and the solvent removed in vacuo to leave a colourless solid, o-aminobenzyl alcohol (10.7 g; 79%), m.p. 79-81°C (lit.[217] 82°C), ν_{max} 3620 and 3400 cm^{-1}.

o-Aminobenzyl alcohol (10 g; 0.081 mol) was dissolved in water/hydrochloric acid (1:1; 100 ml), maintained at 0-5°C, and sodium nitrite (5.75 g, 0.083 mol) in water (30 ml) added portionwise. After stirring for ½ h the diazotised solution was added dropwise to a cold solution of sodium azide (6.33 g, 0.097 mol) and sodium acetate (84 g, 1.02 mol) in water (100 ml). A yellow solid precipitated out of solution which was collected, filtered and washed with cold water. The solid was dried and purified by sublimation at 60°C/0.05 mm to give o-azidobenzyl alcohol (8.86 g; 73%) as a colourless crystalline solid m.p. 48-50°C (lit.,[216] m.p. 52-53°C), ν_{max} 2110 cm^{-1} (N_3).

o-Hydroxybenzylazide was prepared in two steps from o-hydroxybenzylalcohol by the method of Hayashi and Oka.[218]

o-Hydroxybenzylalcohol (20 g, 0.16 mol) was dissolved in acetic anhydride (40 g, 0.39 mol) and the mixture heated under reflux for 3 h. On distillation two fractions were obtained. The first, b.p. 20-30°C/1 mm, was identified as a mixture of unreacted anhydride and acetic acid and the second as o-acetoxybenzylacetate (21.5 g; 64%), b.p. 98-99°C/0.8 mm (lit.,[219] 103-104°C/1 mm), ν_{max} (neat) 1740 cm^{-1} (C=O).

A mixture of o-acetoxybenzylacetate (10.4 g, 50 mmol), sodium azide (4.9 g, 75 mmol) and methanol (50 ml) was heated under reflux for 2 h. After cooling, the mixture was added to water (150 ml) and extracted with methylene chloride (100 ml). The extract was dried over anhydrous sodium sulphate, filtered, and the solvent removed in vacuo, at room temperature, to leave a pale yellow oil. On standing at -10°C for 50 h the oil partially crystallised. The crystals were collected and recrystallised from carbon tetrachloride at -10°C to give o-hydroxybenzylazide as a yellow solid (2.64 g; 35%), m.p. 28-30°C (lit.,[218] 31-33.5°C), ν_{max} 2110 cm^{-1} (N_3).

trans-2-azidocyclohexanol was prepared by the method of Vander Werf, Heisler and McEwen.[220] A solution of sodium azide (13.9 g, 0.21 mol) in water (35 ml) was added to a refluxing solution of cyclohexene oxide (16.6 g, 0.17 mol) and 1,4-dioxan (260 ml). The mixture was heated under reflux for 20 h. On cooling two layers formed. The upper organic layer was treated with dilute hydrochloric acid, separated and dried over anhydrous sodium sulphate. Removal of the solvent in vacuo gave a red oil which on distillation under reduced pressure gave a colourless oil identified as trans-2-azidocyclohexanol (5.26 g; 22%), b.p. 69-70°C/0.9 mm (lit.,[220] 70-71°C/1.5 mm), ν_{max} (neat) 2090 cm^{-1} (N_3).

2-Azido-1-phenyl-1-ethanol was prepared by the method of Boyer, Kreuger, and Modler.[221] Attempts to prepare the compound by the method of McEwen, Conrad and VanderWerf[222] or by treatment of 1-bromo-2-hydroxy-1-ethanol[223] with sodium azide resulted in a mixture of isomers.

A solution of α-bromoacetophenone (33.3 g, 0.17 mol) in ethanol (125 ml) and glacial acetic acid (20 ml) was cooled to 0-5°C and sodium azide (22 g, 0.34 mol) in water (100 ml) added portionwise. On standing at 0-5°C for 20 h a crystalline mass formed which was collected, washed twice with water, and dissolved in 1,4-dioxan (50 ml). The solution was added portionwise to sodium borohydride (8.3 g, 0.22 mol) in water (40 ml) and 1,4-dioxan (50 ml). Hydrogen was seen to be evolved. The mixture was stirred at room temperature for 3 h then heated under reflux for 1 h. After cooling dilute hydrochloric acid (50 ml) was added. The solution was extracted with ether (300 ml), dried over anhydrous sodium sulphate, filtered and the solvent removed in vacuo to leave a pale yellow oil. Distillation of the oil under reduced pressure gave 2-azido-1-phenyl-1-ethanol as a colourless oil (17.5 g, 64%), b.p. 88-94°C/0.5 mm (lit.,[221] 111-114°C/0.5 mm) ν_{max} (neat) 2100 cm^{-1} (N_3).

(S)-(+)-2-Azido-1-phenyl-1-ethanol was prepared in three steps by a combination of the methods of Jensen and Kiskis[224] and Nakajima, Kinishi, Oda and Inouye.[225]

Commercially available (S)-(+)- mandelic acid (22 g, 0.14 mol) (Aldrich Chemical Co., 99+% Gold Label) was reduced in dry ether (300 ml) with lithium aluminium hydride (12.2 g, 0.32 mol) to give, after isolation by extraction with methylene chloride and recrystallisation from benzene/ petroleum (b.p. 60-80°), (S)-(+)-phenyl-1,2-ethanediol (7.42 g; 37%), m.p. 66-66.5°C, $[\alpha]_D^{24}$ + 39.9 ± 0.6° (c = 1.33 g, H_2O) (lit.,[226] m.p. 65-66°C, $[\alpha]_D^{24}$ + 40.7 ± 0.5° (c = 3.26 g, H_2O)).

(S)-(+)-phenyl-1,2-ethanediol (7 g, 0.05 mol) in dry pyridine (60 ml) was maintained at 3°C and p-toluenesulphonyl chloride (9.65 g, 0.05 mol) added portionwise with stirring. After stirring for 18 h at 3°C the solution was poured into ice and water (200 ml) and extracted with ether (500 ml). The ether layer was washed with dilute hydrochloric acid (100 ml) and water (100 ml). The organic layer was absorbed on silica and the product obtained from a wet silica column on elution with ether. On removal of the solvent in vacuo a colourless crystalline solid was obtained; identified by ^1H n.m.r. as (S)-(+)-2-phenyl-1,2-ethanediol-1-tosylate (10.3 g; 70%) with no apparent impurities.

To (S)-(+)-2-phenyl-1,2-ethanediol-1-tosylate (7.75 g, 26.5 mmol) in dry benzene (12 ml) was added sodium azide (2.59 g, 40 mmol) and 18-Crown-6 (0.35 g, 1.3 mmol). The mixture was stirred and maintained at 56°C for 90 h then absorbed on silica and the product eluted from a silica column with 1:3, ether:petrol (b.p. 40-60°C). The first fraction eluted was collected and the solvent removed in vacuo to leave a pale yellow oil which on distillation gave a colourless oil identified as (S)-(+)-α-azidomethylbenzyl-

alcohol (2.65 g; 61%), b.p. 100°C/0.05 mm, ν_{max} (neat) 2105 cm^{-1} (N_3). δ_H 2.80 (1H, s, OH), 3.31-3.39 (2H, m, CH_2), 4.50-4.65 (1H, m, CHPh), 7.29 (5H, s, ArH), $[\alpha]_D^{23}$ +124.3 ± 0.6°(c = 2.56 g, Et_2O). No trace of 2-azido-2-phenyl-1-ethanol could be detected in the product by ^1H n.m.r. or by h.p.l.c.

The optical purity of (S)-(+)-α-azidomethylbenzyl alcohol was estimated by reduction of the azide to the corresponding amine and comparison of the measured optical rotation with the literature values.[227,228] To lithium aluminium hydride (0.68 g, 18 mmol) in super-dry tetrahydrofuran (6 ml) was added, dropwise with stirring under nitrogen, (S)-(+)-α-azidomethylbenzyl alcohol (0.58 g, 3.5 mmol) in super-dry tetrahydrofuran (9 ml). The mixture was heated under reflux for 2 h, cooled and water cautiously added. When hydrogen evolution ceased the mixture was extracted with methylene chloride. Removal of the solvent left an oil which was applied to a preparative t.l.c. plate and run with methanol. A band, Rf 0.1, was collected and re-extracted with methanol. Removal of the solvent in vacuo left an oil which on distillation gave a colourless oil which crystallised on standing. The colourless solid was identified as (S)-(+)-α-aminomethylbenzyl alcohol (0.18 g; 36%), b.p. 80-85°C/0.05 mm, m.p. 59.5-61°C (lit.,[227] 61-62°C), ν_{max} (mull) 3330 and 3280 cm^{-1} (NH_2). $[\alpha]_D^{23}$ + 45.3 ± 0.6° (c = 2.20 g, EtOH) (lit.,[228] $[\alpha]_D^{23}$ + 44.8° (c = 2.088 g, EtOH) lit.,[227] $[\alpha]_D^{18}$ + 44.6 ± 2.2° (c = 2.05 g, EtOH)).

N-(o-azidophenyl)phthalimide was prepared in three steps by the method of Smith, Hall and Kan.[229]

o-Nitroaniline (41.2 g, 0.3 mol), phthalic anhydride (66.3 g, 0.45 mol) and triethylamine (8 g; 0.08 mol) were heated under reflux in toluene for 14 h with an attached water separator. On cooling yellow crystals formed which were collected, washed with ether and dried. The product was identified as o-nitrophenylphthalimide (55.3 g, 69%) m.p. 202-203°C (lit.,[230] 200-203°C).

To o-nitrophenylphthalimide (24.2 g, 0.09 mol) in refluxing acetone (1.5 ℓ) was added glacial acetic acid (150 ml), water (150 ml) and powdered iron (59 g). The mixture was stirred rapidly whilst being refluxed for 1 h. The hot solution was filtered and neutralised with sodium carbonate solution. On standing two layers formed. The upper layer was decanted off, added to water (12 ℓ) and cooled in an ice bath. After 2h the solution was filtered and a yellow solid, identified as N-(o-aminophenyl)phthalimide (19.8 g; 92%), obtained. M.p. 190-193°C (lit.,[229] 190-193°C).

To a suspension of N-(o-aminophenyl)phthalimide (18 g, 0.076 mol) in water (1 ℓ) was added concentrated hydrochloric acid (100 ml). The resulting slurry was chilled to 0-5°C and diazotised by the addition of sodium nitrite (6 g, 0.087 mol) in water (25 ml). After stirring for 1 h the solution was filtered and sodium azide (5.7 g, 0.088 mol) in water (25 ml) added dropwise with stirring. A colourless precipitate formed which was collected, washed with water and dried. The product was identified as N-(o-azidophenyl) phthalimide (18.6 g; 93%) m.p. 184°C (lit.,[229] 191°C).

o-Azidoaniline was prepared by the method of Smith, Hall and Kan.[229] A slurry of N-(o-azidophenyl)phthalimide (14.7 g, 0.056 mol) in ethanol (150 ml) was stirred with hydrazine hydrate (2.8 g, 0.056 mol) for 1½h at room temperature then water (100 ml) and sodium hydroxide solution (25 ml; 20%) were added. The solution was filtered and extracted with methylene chloride (500 ml). Separation and drying of the organic layer followed by removal of the solvent in vacuo left yellow-brown crystals. The crude product was recrystallised from methanol/water and finally purified by sublimation, 56°C/0.05 mm, to give o-azidoaniline (4g; 53%) m.p. 60-61°C (lit.,[229] 63-63.5°C) as yellow light sensitive crystals.

N-(o-Azidophenyl)benzamide was prepared by the dropwise addition of benzoyl chloride (5.8 g, 0.04 mol) over ½ h to a suspension of o-azidoaniline (5 g, 0.037 mol) in sodium hydroxide solution (50 ml; 5%) with rapid stirring. Heat was evolved and the reaction mixture stirred for a further 2 h. Ether (200 ml) was added and the organic layer separated and dried. The ether solution was absorbed on alumina and the product obtained from a wet alumina column on elution with ether. On removal of the solvent in vacuo a colourless crystalline solid was obtained which was purified by recrystallisation from ether to give N-(o-azidophenyl)benzamide (5.6 g; 63%), m.p. 87-88°C (Found: C, 65.5; H, 4.2; N, 23.6; $C_{13}H_{10}N_4O$ requires C, 65.5; H, 4.2; N, 23.5%), ν_{max} 3420 (NH), 2120 (N_3) and 1685 cm^{-1} (C=O).

δ_H 7.00-7.30 (3H, m, ArH), 7.32-7.62 (3H, m, ArH), 7.72-7.97 (2H, m, ArH), 8.24 (1H, s, NH), 8.36-8.61 (1H, m, ArH), m/e 238 (M^+, 14%), 210 (28), m^* 185.3 (238 → 210), 105 (100), 77 (37).

N-(o-Azidophenyl)-p-toluene-sulphonamide was prepared by the portionwise addition of toluene-p-sulphonyl chloride (2.13 g, 11 mmol) to o-azidoaniline (1 g, 7.5 mmol) in pyridine (10 ml). Heat was evolved and the mixture was stirred for 1 h. Water (500 ml) was added and a white solid precipitated which was collected and dried. Recrystallisation of the solid from methylene chloride/ether gave N-(o-azidophenyl)-p-toluene-sulphonamide (1 g; 47%) as pale brown crystals, m.p. 137.5-139°C (Found: C, 54.4; H, 4.2; N, 19.4; $C_{13}H_{12}N_4O_2S$ requires C, 54.2; H, 4.2; N, 19.4%), ν_{max} 3340 (NH), 2130 (N_3) and 1165 cm^{-1}. δ_H2.32 (3H, s, pMe), 6.72-7.78 (9H, m, ArH + NH), m/e 288 (M^+, 21%), 260 (14), m^* 234.7 (288 → 260), 156 (36), 105 (100), 92 (84), 91 (80).

o-Azido-N-triphenylmethylaniline was prepared by the dropwise addition of triphenylmethylchloride (1.04 g, 3.7 mmol) in pyridine (4 ml) to a solution of o-azidoaniline (0.5 g, 3.7 mmol) in pyridine (4 ml). The mixture was stirred at room temperature for 70 h. The solvent was removed under high vacuum and the residue absorbed on alumina. The product was obtained from a wet alumina column on elution with ether/petrol (b.p. 40-60°C), 5:95. Removal of the solvent left a purple oil which was dissolved in methylene chloride/petrol

(b.p. 40-60°C). On standing at -10°C purple crystals formed which were collected and dried. The product was identified as o-azido-N-triphenylmethylaniline (0.59 g; 42%), m.p. 124-125°C (Found: C, 79.5; H, 5.5; N, 14.7; $C_{25}H_{20}N_4$ requires C, 79.8; H, 5.4; N, 14.9%), ν_{max} 3420 (NH) and 2115 cm^{-1} (N_3). δ_H 5.52 (1H, s, NH), 5.95-6.19 (1H, m, ArH), 6.33-6.70 (2H, m, ArH), 6.70-7.02 (1H, m, ArH), 7.02-7.60 (15H, m, ArH), m/e 376 (M^+, 7%), 271 (6), 243 (100), 165 (37).

o-Azido-(N-2,4-dinitrophenyl)aniline was prepared by the addition of 1-chloro-2,4-dinitrobenzene (3.83 g, 19 mmol) and anhydrous sodium acetate (1.5 g, 18 mmol) to o-azidoaniline (3 g, 22 mmol) in methanol (22 ml). The mixture was heated under reflux for 4½ h. The solvent was removed under reduced pressure and the mixture absorbed on silica. The product was obtained from a wet silica column on elution with ether/petrol (b.p. 40-60°C), 1:9. Removal of the solvent in vacuo left a red crystalline solid which was recrystallised from ethanol/methylene chloride. The product was recrystallised from ethanol/methylene chloride. The product was identified as o-azido-(N-2,4-dinitrophenyl)aniline (1 g, 18%), m.p. 137.5-140°C (Found: C, 27.8; H, 2.7; N, 27.8; $C_{12}H_8N_6O_4$ requires C, 48.0; H, 2.7; N, 28.0%), ν_{max} 3340 (NH), 2115 (N_3), 1510 and 1340 cm^{-1}. δ_H 7.02 (1H, d, 6'-ArH, J_{HH}9Hz collapses on irradiation at δ8.16), 6.8-7.55 (4H, m, ArH), 8.16 (1H, d of d, 5'-ArH, J_{HH}9Hz, J_{HH}3Hz), 9.12 (1H, d, 3'-ArH, J_{HH}3Hz collapses on irradiation at δ8.16),

9.72 (1H, s, NH), m/e 300(M^+, 46%), 272(26), m^* 246.6 (300 → 272), 225 (35), 179 (46), m^* 142.4 (225 → 179), 106 (100).

Phenylazide was prepared by the method of Lindsay and Allen.[231] To concentrated hydrochloric acid (55.5 ml) and water (100 ml), stirred and cooled in an ice/water bath, was added dropwise phenylhydrazine (35.5 g, 0.33 mol). On cooling to 0°C ether (100 ml) was added all at once followed by the portionwise addition, over ½ h, of sodium nitrite (25 g, 0.36 mol) in water (30 ml). The organic layer was separated and the azide purified by passing down a wet alumina column eluted with ether. The solvent was removed in vacuo to leave an orange oil, stored at -10°C over dry molecular sieve, phenylazide (24.1 g; 62%), ν_{max} (neat) 2100 cm^{-1} (N_3).

7. Preparation of Iminophosphoranes and Pentacoordinate Phosphoranes: Reaction of Azido Compounds with Tervalent Phosphorus Reagents

General Procedure

These reactions were carried out in carefully dried glassware and solvents as iminophosphoranes and pentacoordinate phosphoranes are hydrolytically unstable. Unless otherwise stated all reactions were carried out at room temperature.

A solution of azide (1-10 mmol) in super-dry solvent (5-20 ml) was added, dropwise with stirring under an atmosphere of dry nitrogen, to a tervalent phosphorus reagent (1-10 mmol) in super-dry solvent (5-20 ml). Nitrogen and heat were evolved and the rate of addition of azide solution regulated so as to maintain a steady mild reaction. The reactions were generally complete within 2 h, as shown by ^{31}P n.m.r., and the products were isolated by recrystallisation from super-dry solvents or by distillation. All manipulations involving these labile compounds were carried out in a dry-box under an atmosphere of dry nitrogen.

7.1 Reaction of o-Azidophenol with Tervalent Phosphorus Reagents

(i) 2,2,2-Trimethoxy-1,3,2-benzoxazaphospholine was prepared by the addition of o-azidophenol (1.55 g, 11.5 mmol) in super-dry petrol (b.p. 40-60°C, 20 ml) to trimethylphosphite (1.44 g, 11.6 mmol) in super-dry petrol (b.p. 40-60°C, 10 ml). Nitrogen was evolved and the mixture stirred under an atmosphere of dry nitrogen for 30 h. The solution was blown down to small volume, with a stream of dry nitrogen, and left to stand at -10°C for 100 h. The phospholine (2.60 g; 98%) was obtained as pale orange crystals, m.p. 42-44°C (Found: C,47.0; H,6.0; N,6.1; $C_9H_{14}NO_4P$ requires C,46.8; H,6.1; N,6.1%), ν_{max} 3470 (NH), 2840, 1500, 1390, 1270 and 910 cm^{-1}. δ_H 3.58 (9H, d, POMe, J_{PH} 13Hz), 5.58 (1H, d, NH, J_{PH} 20 Hz), 6.62-6.84 (4H, m, ArH), δ_P-51.5, m/e 231 (M^+, 64%), 200 (90), 199 (100), 185 (32), 184 (28), m^* 171.4 (231 → 199), 169 (26), 109 (34), 93 (78).

(ii) 2,2,2-Triethoxy-1,3,2-benzoxazaphospholine was prepared by the addition of o-azidophenol (1.50 g, 11.1 mmol) in super-dry petrol (b.p. 40-60°C, 12 ml) to triethylphosphite (1.91 g, 11.5 mmol) in super-dry petrol (b.p. 40-60°C, 8 ml). Nitrogen was evolved and the mixture stirred under an atmosphere of dry nitrogen for 20 h. ^{31}P N.m.r. showed complete conversion to the phospholine. The solution was blown down to small volume, with a stream of dry nitrogen, and cooled to -10°C for 20 h. The phospholine (2.92 g; 96%) was obtained as a colourless crystalline solid, m.p. 32-34°C. A satisfactory analysis could not be obtained due to the hydrolytic instability of the compound, however an exact mass measurement was obtained, found, M, 273.112342, $C_{12}H_{20}NO_4P$ requires M, 273.112987. ν_{max} 3470 (NH), 1500, 1390, 1270 and 890 cm^{-1}. δ_H 1.16 (9H, d of t, $OCH_2\underline{CH}_3$, J_{HH} 7 Hz, J_{PH} 1.5 Hz), 3.93 (6H, d of q, $O\underline{CH}_2CH_3$, J_{HH} 7 Hz, J_{PH} 8.5 Hz), 5.50 (1H, d, NH, J_{PH} 20 Hz), 6.46-6.82 (4H, m, ArH), δ_P-53.9, m/e 273 (M^+, 13%), 228 (17), 227 (15), 171 (100), 153 (12), 109 (23), 79 (30).

(iii) 2,2-Dimethoxy-2-phenyl-1,3,2-benzoxazaphospholine was prepared by the addition of o-azidophenol (0.83 g, 6.1 mmol) in super-dry petrol (b.p. 40-60°C, 10 ml) to dimethyl phenyl-phosphonite (1.06 g, 6.2 mmol) in super-dry ether (10 ml). Nitrogen was evolved and the mixture stirred under an atmosphere of dry nitrogen for 80 h. The solvent was blown down to small volume, with a stream of dry nitrogen, super-dry petrol (b.p. 40-60°C, 10 ml) added and the mixture left to stand

at -10°C. The phospholine (1.58 g; 92%) was obtained as a colourless crystalline solid, m.p. 70-72°C (Found: C, 60.8; H, 5.8; N, 5.0; $C_{14}H_{16}NO_3P$ requires C, 60.7; H, 5.8; N, 5.1%), ν_{max} 3460 (NH), 2730, 1495, 1385 and 905 cm^{-1}. δ_H 3.52 (6H, d, POMe, J_{PH} 12 Hz), 5.58 (1H, d, NH, J_{PH} 19 Hz), 6.47-7.90 (9H, m, ArH), δ_P-39.8, m/e 277 (M^+, 29%), 263 (9), 245 (100), 231 (18), 155 (35), 138 (62), 109 (47), 77 (59).

(iv) 2,2-Diphenyl-2-methoxy-1,3,2-benzoxazaphospholine was prepared by the addition of o-azidophenol (0.64 g, 4.7 mmol) in super-dry petrol (b.p. 40-60°C, 10 ml) to methyl diphenylphosphinite (1.04 g, 4.8 mmol) in super-dry petrol (b.p. 40-60°C, 5 ml). On addition the solution instantly turned yellow followed by rapid evolution of nitrogen. When the reaction was complete, the phospholine (1.38 g; 90%), a colourless solid precipitated out of solution and was collected, washed with super-dry petrol (b.p. 40-60°C), and dried. M.P. > 240°C (decomp.) (Found: C, 70.3; H, 5.6; N, 4.4; $C_{19}H_{18}NO_2P$ requires C, 70.6; H, 5.6; N, 4.3%), ν_{max} 3460 (NH), 2830, 1495, 1440, 1385, 1260 and 885 cm^{-1}. δ_H 2.98 (3H, d, POMe, J_{PH} 11 Hz), 4.86 (1H, d, NH, J_{PH} 20 Hz), 6.45-6.80 (4H, m, ArH), 7.20-7.90 (10 H, m, ArH), δ_P-36.0, m/e 323 (M^+, 2%), 309 (68), 291 (9), 201 (100), 185 (7), 183 (6), 77(27).

(v) 2-Phenylspiro-[1,3,2-dioxaphospholan-2,2'-[1,3,2]-benzoxazaphospholine] was prepared by the addition of o-azidophenol (0.46, 3.4 mmol) in super-dry ether (11 ml) to 2-phenyl-1,3,2-dioxaphospholan (0.58 g, 3.5 mmol) in super-dry ether

(6 ml). Nitrogen was evolved and the solution stirred for 18 h. On standing at -10°C the product crystallised as a colourless solid. The phospholine (0.66 g; 70%) was collected and dried, m.p. 141-144°C (Found: C, 61.3; H, 5.1; N, 5.0; $C_{14}H_{14}NO_3P$ requires C, 61.1; H, 5.1; N, 5.1%), ν_{max} 3460 (NH), 1490, 1380, 1260, 1070 and 905 cm^{-1}. δ_H 3.40-4.24 (4H, m, OCH_2CH_2O), 5.73 (1H, d, J_{PH} 18 Hz), 6.40-6.94 (4H, m, ArH), 7.02-7.94 (5H, m, ArH), δ_P-26.4, m/e 275 (M^+, 96%), 231 (100), m^* 194 (275 → 231), 109 (62).

(vi) N-(2-Hydroxyphenyl)iminodiethylphenylphosphine was prepared by the addition of o-azidophenol (1.31 g, 9.8 mmol) in super-dry benzene (10 ml) to a refluxing solution of diethylphenyl-phosphine (1.69 g; 10.2 mmol) in super-dry benzene (10 ml). On addition the solution instantly turned deep red followed by the vigorous evolution of nitrogen. The mixture was heated under reflux for 1 h then the solvent was removed with a stream of dry nitrogen. A red oil was obtained, shown by ^{31}P n.m.r. to be the only phosphorus containing product, which was purified by bulb to bulb distillation at 150-160°C/0.05 mm to give the phosphinimine (2.29 g; 87%) as a pale brown oil (Found: C, 70.3; H, 7.3; N, 5.1; $C_{16}H_{20}NOP$ requires C, 70.3; H, 7.4; N, 5.1%), ν_{max} 3290 (broad band OH), 1495, 1115, 1045, 1020 and 695 cm^{-1}. δ_H 1.04 (6H, d of t, $CH_2\underline{CH}_3$, J_{HH} 8Hz, J_{PH} 17 Hz), 2.11 (4H, d of q, $\underline{CH}_2CH_3$, J_{HH} 8 Hz, J_{PH} 11 Hz), 6.28-6.96 (4H, m, ArH), 7.24-7.85 (6H, m, ArH +OH), δ_P+21.5, m/e 273 (M^+, 100%), 256 (11), 244 (28), 216 (20), 196 (11),

165 (92), 138 (50), 120 (55), 109 (74), 105 (36). No P^V species were observed in the ^{31}P n.m.r. spectrum after standing in solution at room temperature for 120 h.

(vii) 2',2'-Dimethyl-2-phenylspiro-[1,3,2-benzoazaphospholine-2,1'-phosphetan] was prepared by the addition of o-azidophenol (0.51 g, 3.8 mmol) in dry methylene chloride (7 ml) to freshly distilled 2,2-dimethyl-1-phenylphosphetan (0.81 g, 4.6 mmol) in dry methylene chloride (5 ml). Nitrogen was evolved and the solution stirred for 17 h. The solvent was blown down to small volume, with a stream of dry nitrogen, super-dry petrol (b.p. 40-60°C) added and the mixture left to stand at -10°C. The spirophosphorane (0.90 g; 83%) was obtained as a pale orange crystalline solid, m.p. 142-145°C (Found: C, 71.6; H, 7.2; N, 4.7; $C_{17}H_{20}NOP$ requires C, 71.6; H, 7.1; N, 4.9%), ν_{max} 3460 (NH), 1490, 1380, 1100 and 905 cm^{-1}. δ_H 0.85-2.64 (4H, m, ring CH_2), 1.47 (3H, d, Me, J_{PH} 19 Hz), 1.48 (3H, d, Me, J_{PH} 22 Hz), 4.21 (1H, d, NH, J_{PH} 28 Hz), 6.38-6.81 (4H, m, ArH), 7.18-8.03 (5H, m, ArH), δ_P-40.7, m/e 285 (M^+, 71%), 257 (29), 229 (100), 214 (36), 138 (79), 91 (19), 77 (10).

(viii) 2-Phenylspiro-[1,3,2-benzoxazaphospholine-2,1'-phospholan was prepared by the addition of o-azidophenol (0.43 g, 3.2 mmol) in dry methylene chloride (12 ml) to 1-phenylphospholan (0.53 g, 3.2 mmol) in dry methylene chloride (12 ml). Nitrogen was rapidly evolved and a colourless solid precipitated from solution. The spirophosphorane was collected and dried (0.82 g; 95%), m.p. > 210°C (decomp.) (Found: C, 70.7;

H, 6.7; N, 5.1; $C_{16}H_{18}NOP$ requires C, 70.8; H, 6.7; N, 5.2%), ν_{max} (mull) 3140 (NH), 1490, 1370, 1115 and 920 cm^{-1}. δ_H(d^6-DMSO) 1.24-2.20 (8H, m, ring $\underline{CH_2}$), 6.12-6.82 (5H, m, ArH + NH), 7.24-7.76 (5H, m, ArH), δ_P ($CDCl_3$)-20.1, m/e 271 (M^+, 100%), 242(58), 219 (38), 205 (29), 163 (75), 138 (92).

(ix) N-(2-Hydroxyphenyl)imino-1-phenylphosphorinan was prepared by the addition of o-azidophenol (0.94 g, 7 mmol) in dry methylene chloride (7 ml) to a refluxing solution of 1-phenylphosphorinan (1.25 g, 7 mmol) in dry methylene chloride (8 ml). On addition the solution instantly turned dark red followed by the rapid evolution of nitrogen. The mixture was heated under reflux for 2 h, cooled and the solvent removed with a stream of dry nitrogen. A red oil was obtained which was purified by bulb to bulb distillation at 150°C/0.05 mm to give the phosphinimine (1.41 g; 71%) as a viscous red oil which crystallised on standing m.p. 106-108°C (Found: C, 71.7; H, 7.0; N, 4.8; $C_{17}H_{20}NOP$ requires C, 71.6; H, 7.1; N, 4.9%), ν_{max} 3260 (broad OH), 1110, 1040 and 930 cm^{-1}. δ_H 1.20-2.63 (10H, m, ring $\underline{CH_2}$), 6.30-6.92 (4H, m, ArH), 7.26-7.88 (6H,m, ArH + OH), δ_P+7.7, m/e 285 (M^+, 97%), 268 (11), 242 (19), 177 (100), 109 (31), 91 (14).

7.2 Reaction of o-Azidophenylbenzoate with Tervalent Phosphorus Reagents

(i) N-(2-Benzoxyloxyphenyl)iminotriphenylphosphine was prepared by the addition of o-azidophenylbenzoate (0.45g, 1.9 mmol) in super-dry petrol (b.p. 40-60°C, 10 ml) to a solution of triphenylphosphine (0.49 g, 1.9 mmol) in super-dry ether (4 ml). Nitrogen was evolved and an oil deposited which crystallised on stirring to give colourless crystals of the iminophosphorane (0.80 g; 90%), m.p. 108-110°C (Found: C,78.4; H,5.0; N,2.9; $C_{31}H_{24}NO_2P$ requires C,78.6; H,5.1; N,3.0%), ν_{max}(mull) 1720 (C=O), 1360, 1100 and 705 cm^{-1}. δ_H 6.44-6.86 (2H, m, ArH), 7.00-7.84 (19H, m, ArH), 7.98-8.40 (3H, m, ArH), δ_p+ 3.4, m/e 473 ± 3 (M^+, < 1%), 278 (19), 277 (31), 195 (100), 167 (8). This compound was very unstable, decomposing rapidly in solution, and could only be isolated by the precipitation procedure described above.

7.3 Reaction of o-Azidophenyl tosylate with Tervalent Phosphorus Reagents

(i) N-(2-p-Toluenesulphonoxylphenyl)iminotrimethyl phosphite was prepared by the addition of o-azidophenyl tosylate (0.58 g, 2 mmol) in dry ether (5 ml) to trimethylphosphite (0.27 g, 2.2 mmol) in dry ether. Nitrogen was evolved and after stirring for 20 h the iminophosphorane (0.70 g; 91%), a colourless crystalline solid, crystallised out of the solution, m.p. 84-85°C (Found: C,50.0; H,5.2; N,3.7; $C_{16}H_{20}NO_6PS$ requires C,49.9; H,5.2; N,3.6%), ν_{max} (mull)

760, 725, 690 and 660 cm^{-1}. δ_H 2.40 (3H, s, p Me), 3.72 (9H, d, POMe, J_{PH} 11Hz), 6.42-7.32 (6H, m, ArH), 7.70-7.85 (2H, m, ArH), δ_p-0.1, m/e 385 (M^+, 39%), 230 (100), 202 (56), 109 (20), 93 (15), 91(16).

(ii) N-(2-p-Toluenesulphonoxylphenyl)iminotriphenylphosphine was prepared by the addition of o-azidophenyl tosylate (0.47 g, 1.6 mmol) in dry ether (5 ml) to triphenylphosphine (0.42 g, 1.6 mmol) in dry ether (5 ml). Nitrogen was rapidly evolved and after 2½ h the iminophosphorane (0.76 g; 94%), a colourless crystalline solid, crystallised out of solution, m.p. 206-209°C (Found: C,71.1; H,5.0;, N,2.7; $C_{31}H_{26}NO_3PS$ requires C,71.1; H,5.0; N,2.7%), ν_{max} (mull) 1110, 880, 770, 750 and 715 cm^{-1}. δ_H 2.24 (3H, s, p Me), 6.24-7.85 (23H, m, ArH), δ_p+4.4, m/e 523 ± 4(M^+, 13%), 366 ± 2(100), 340 ± 2(29), 262(16), 183(29), 108(18), 91(9).

7.4 Reaction of o-Azidobenzyl alcohol with Tervalent Phosphorus Reagents

(i) N-(2-Hydroxymethylphenyl)iminomethyl diphenylphosphinite was prepared by the addition of o-azidobenzyl alcohol (1.20 g, 8 mmol) in super-dry ether (10 ml) to methyl diphenylphosphinite (1.74 g, 8 mmol) in super-dry ether (8 ml). Nitrogen was evolved and the solution stirred for 1h at room temperature. The reaction mixture was cooled to -10°C and the iminophosphorane (2.37 g; 88%), a colourless crystalline solid, crystallised out of solution, m.p. 65-68°C (Found: C,71.0; H,6.1; N,4.2;

$C_{20}H_{20}NO_2P$ requires C,71.2; H,6.0; N,4.2%), ν_{max} 3340 (broad OH), 1485, 1440, 1125 and 690 cm^{-1}. δ_H 3.67 (3H, d, POMe, J_{PH} 11 Hz), 4.87 (2H, d, $\underline{CH_2}OH$, J_{HH} 6Hz), 5,84 (1H, d of t, $CH_2\underline{OH}$, J_{HH} 6Hz, J_{PH} 2Hz), 6.54-8.06 (14H, m, ArH), δ_p+22.4, m/e 337 (M^+, 3%), 322(1), 305(4), 232(93), 231(100), 202(20), 199(26), 155(33), 77(55). The iminophosphorane reacted rapdily in solution to give after 18 h three major products, δ_p ($CDCl_3$) +33.4, +18.4, +17.7 and a minor peak at δ_p+22.3. The crystalline compound turned yellow on standing at -10°C and ^{31}P n.m.r. showed that it had decomposed to give several phosphoryl products.

(ii) 2-Phenylspiro-[Δ^4-1,3,2-benzoxazaphosphorinan-2,2'-[1,3,2]-dioxaphospholan] was prepared by the addition of o-azidobenzyl alcohol (0.88 g, 5.9 mmol) in super-dry ether (18 ml) and super-dry petrol (b.p. 40-60°C, 6 ml) to 2-phenyl-1,3,2-dioxaphospholan (0.99 g, 5.9 mmol) in super-dry ether (10 ml). Nitrogen was slowly evolved and after 3 h a trace quantity of an oil had deposited. The reaction mixture was cooled to -10°C and the spirophosphorane (1.03 g; 61%), a colourless crystalline solid, crystallised out of solution, m.p. 95-98°C (Found: C, 62.5; H,5.5; N,4.8; $C_{15}H_{16}NO_3P$ requires C,62.3; H,5.6; N,4.8%), ν_{max} 3430 (NH), 1470, 1275, 940 and 695 cm^{-1}. δ_H 3.32-4.28 (4H, m, $O\underline{CH_2}\underline{CH_2}O$), 4.56 (1H, d of d, $\underline{H}CH$, J_{HH} 14Hz, J_{PH} 17Hz), 4.90 (1H, d of d, $HC\underline{H}$, J_{HH} 14Hz, J_{PH} 17Hz), 5.82 (1H, d, NH, J_{PH} 8Hz), 6.45-7.90 (9H, m, ArH), δ_p-44.5, m/e 289 (M^+, 51%), 185 (100), 141 (42), 105 (58), 77(28).

(iii) N-(2-Hydroxymethylphenyl)iminotriphenylphosphine was prepared by the addition of o-azidobenzyl alcohol (0.46 g, 3.1 mmol) in dry ether (8 ml) to triphenylphosphine (0.80 g, 3.1 mmol) in dry ether (8 ml). On addition the solution instantly turned bright yellow followed by the evolution of nitrogen. After stirring for 1½h a pale yellow crystalline solid was isolated by filtration and washed with ether to give the iminophosphorane (0.59 g; 51%), m.p. 148-149°C (Found: C,78.1; H,5.7; N,3.6; $C_{25}H_{22}NOP$ requires C,78.3; H,5.8; N,3.7%), ν_{max} 3340 (OH, broad), 1480, 1110 and 690 cm^{-1}. δ_H 4.85 (2H, d, CH_2, J_{HH} 6Hz), 5.97 (1H, t, OH, J_{HH} 6Hz), 6.39-8.01 (19H, m, ArH), δ_p+6.7, m/e 383 (M^+, 60%), 352(18), 278(53), 277(100), 262(77), 183(48), 108(26), 77(20). The product was stable in solution at room temperature indefinitely.

7.5 Reaction of o-Hydroxybenzylazide with Tervalent Phosphorus Reagents

(i) 2-Phenylspiro-[Δ^5-1,3,2-benzoxazaphosphorinan-2,2'-[1,3,2]-dioxaphospholan] was prepared by the addition of o-hydroxybenzylazide (0.50 g, 3.4 mmol) in dry methylene chloride (8 ml) to 2-phenyl-1,3,2-dioxaphospholan (0.56 g, 3.3 mmol) in dry methylene chloride (5 ml). Nitrogen evolution was very slow therefore the mixture was heated under reflux for 2h. The reaction mixture was concentrated to *ca.* 5 ml and on cooling to -10°C the spirophosphorane (0.58g; 60%), a colourless crystalline solid, crystallised out of solution m.p. 144-147°C (Found: C,62.1; H,5.6; N,4.8; $C_{15}H_{16}NO_3P$ requires C,62.3; H,5.6; N,4.8%), ν_{max} 3460 (NH), 1490, 1080 and

885 cm^{-1}. δ_H 3.26-3.40 (5H, m, $O\underline{CH_2}\underline{CH_2}O$ + NH), 4.10 (2H, d of d, $Ar\underline{CH_2}N$, J_{HH} 4Hz, J_{PH} 18Hz), 6.56-7.90 (9H, m, ArH), δ_p-40.9, m/e 289 (M^+, 100%), 244 (20), 168(17), 140(35), 121(27), 105(12), 91(8), 77(19).

7.6 Reaction of trans-2-Azidocyclohexanol with Tervalent Phosphorus Reagents

(i) 2,2-Diphenyl-2-methoxy-trans-4,5-cyclohexyl-1,3,2-oxazaphospholan was prepared by the addition of trans-2-azidocyclohexanol (0.74 g, 5.2 mmol) in dry methylene chloride (8 ml) to methyl diphenylphosphinite (1.15 g, 5.3 mmol) in dry methylene chloride (3 ml). Nitrogen was evolved and the solution stirred for 3h. The solvent was removed with a stream of dry nitrogen to leave an oil which crystallised from super-dry petrol (b.p. 40-60°C, 3.5 ml) at -10°C to give the phosphorane (1.06 g; 62%) as a colourless crystalline solid, m.p. 71-73°C (Found: C,69.1; H,7.4; N,4.0; $C_{19}H_{24}NO_2P$ requires C,69.3; H,7.3; N,4.3%), ν_{max} 3460 (NH), 2850, 1435 and 690 cm^{-1}. δ_H 1.00-2.10 (10H, m, aliphatic H), 2.79 (3H, d, POMe, J_{PH} 11Hz), 6.92-8.02 (10H, m, ArH), NH not observed, δ_p-44.7, m/e 329 (M^+, 41%), 298(97), 254(46), 216(99), 201(100), 155(20), 96(50), 77(69).

(ii) 2-Phenylspiro-[trans-4,5-cyclohexyl-1,3,2-oxazaphospholan-2,1'-phospholan] was prepared by the addition of trans-2-cyclohexanol (0.42 g, 3 mmol) in super-dry ether (10 ml) to 2-phenylphospholan (0.49 g, 3 mmol) in super-dry

ether (6 ml). Nitrogen was slowly evolved and after stirring for 1h the spirophosphorane (0.49 g; 60%), a white crystalline solid, crystallised slowly out of solution m.p. 37-39°C. A satisfactory analysis could not be obtained due to the hydrolytic instability of the compound, however an exact mass measurement was obtained, found, M, 277.155569, $C_{16}H_{24}NOP$ requires M, 277.159544. ν_{max} 3450 (NH), 1435, 1115 and 690 cm^{-1}. δ_H 0.71-3.20 (18H, m, aliphatic H), 7.10-7.85 (5H, m, ArH), δ_p-40.1, m/e 277(M^+, 8%), 248(6), 219(6), 180 (72), 164(68), 152(54), 77(92), 68(100). It was observed, by ^{31}P n.m.r., that the compound hydrolysed extremely rapidly on addition of water to give 1-phenylphosphorinan oxide.

7.7 Reaction of 2-Azido-1-phenyl-1-ethanol with Tervalent Phosphorus Reagents

(i) 2,2-Dimethoxy-2,5-diphenyl-1,3,2-oxazaphospholan was prepared by the addition of 2-azido-1-phenyl-1-ethanol (0.50 g, 3 mmol) in dry methylene chloride (8 ml) to dimethyl phenylphosphonite (0.52 g, 3 mmol) in dry methylene chloride (5 ml). Nitrogen was evolved and the solution was stirred for 20h. The solvent was removed with a stream of dry nitrogen to leave an oil which crystallised from super-dry ether (4 ml) and petrol (b.p. 40-60°C, 15 ml) at -10°C to give the phosphorane (0.60 g; 65%) as a colourless crystalline solid, m.p. 55-58°C (Found: C,62.7; H,6.5; N,4.7; $C_{16}H_{20}NO_3P$ requires C,62.9; H,6.6; N,4.6%), ν_{max} 3480 (NH), 1325, 1270, 950 and 700 cm^{-1},

δ_H 2.70-2.98 (1H, m, $N\underline{CH}_1H_2$), 3.04-3.50 (1H, m, $NCH_1\underline{H}_2$), 3.40 and 3.61 (6H, 2 x d, 2 x POMe, J_{PH} 11Hz and J_{PH} 11Hz; both collapse on irradiation at the same ^{31}P frequency), 4.54-4.80 (1H, m, O$\underline{CH}$Ph), 6.95-7.90 (10H, m, ArH), NH not observed, δ_p-44.8, m/e 305 (M^+, <1%), 262 (4), 186(13), 118(100), 91(35), 77(19).

(ii) 2-Methoxy-2,2,5-triphenyl-1,3,2-oxazaphospholan was prepared by the addition of 2-azido-1-phenyl-1-ethanol (0.53 g, 3.3 mmol) in dry methylene chloride (10 ml) to methyl diphenylphosphinite (0.71 g, 3.3 mmol) in dry methylene chloride (5 ml). Nitrogen was rapidly evolved and the solution was stirred for 2h. The colourless phosphorane (0.99 g; 85%) crystallised as the solvent was blown off with a stream of dry nitrogen and was washed with super-dry petrol (b.p. 40-60°, 5 ml), m.p. 103-105°C. (Found: C,71.7; H,6.5; N,3.9; $C_{21}H_{22}NO_2P$ requires C,71.8; H,6.3; N,4.0%), ν_{max} 3470 (NH), 1440 and 695 cm^{-1}. δ_H 2.86(3H, d, POMe, J_{PH} 10Hz), 3.00-3.60(2H, m, $N\underline{CH}_2$), 4.38-4.58 (1H, m, O$\underline{CH}$Ph), 6.85-8.13 (10H, m, ArH), NH not observed, δ_p-42.6, m/e M^+ not observed.

(iii) 2,5-Diphenylspiro-[1,3,2-oxazaphospholan-2,1'-phospholan] was prepared by the addition of 2-azido-1-phenyl-1-ethanol (0.54 g, 3.3 mmol) in dry methylene chloride (10 ml) to 2-phenylphospholan (0.54, 3.3 mol) in dry methylene chloride (5 ml) Nitrogen was evolved and the solution stirred for 4h. The solvent was removed with a stream of dry nitrogen to leave an oil which crystallised from super-dry petrol (b.p. 40-60°C, 10 ml) at -10°C to give the spirophosphorane (0.84g; 84%) as a colourless crystalline solid, m.p. 45-47°C. A satisfactory analysis could not be obtained due to the hydrolytic

instability of the compound. However, an exact mass measurement was obtained, found, M, 299.143432, $C_{18}H_{22}NOP$ requires M, 299.143894. ν_{max} 3460 (NH), 1430, 1255, 845 and 690 cm^{-1}. δ_H 0.80-2.51 (9H, m, phospholan ring CH_2 + NH), 2.50-2.78 (1H, m, HCH), 2.92-3.33 (1H, m, HCH) 4.28-4.52 (1H, m, OCHPh), 7.20-7.79 (10H, m, ArH), δ_p-36.9, m/e 299 (M^+, 5%), 270 (7), 193(15), 180(98), 179(78), 164(42), 152(96), 118(100), 77(79).

(iv) 2,5-Diphenyl-2-methoxy-2-α-naphthyl-1,3,2-oxazaphospholan was prepared by the addition of re-distilled 2-azido-1-phenyl-1-ethanol (1.29 g, 7.9 mmol) in dry methylene chloride (12 ml) to methyl 1-naphthylphenylphosphinite (2.09 g, 7.9 mmol) in dry methylene chloride (8 ml). Nitrogen was evolved and the solution stirred for 24 h. ^{31}P N.m.r. showed three pairs of signals δ_p+25.5 and +24.9 (10%), δ_p (diastereoisomers, 1:1) -40.7 and -41.9 (80%), δ_p-47.0 and -47.2 (10%). The solution was concentrated to *ca* 10 ml and super-dry ether (5 ml) added. On cooling to -10°C a colourless crystalline solid formed which was collected and dried. ^{31}P N.m.r. showed this solid to be a single diastereoisomer, δ_p-41.9, containing a trace, approximately 5%, of the other isomer, δ_p-40.7. The solid was recrystallised from methylene chloride/ether to give, as shown by ^{31}P n.m.r., the isomerically pure phosphorane as a colourless crystalline solid (0.90 g; 29%), m.p. 118-120°C (Found: C, 74,6; H, 6.1; N,3.4; $C_{25}H_{24}NO_2P$ requires C,74.8; H,6.0; N,3.5%), ν_{max} 3480 (NH), 1440, 940, 830 and 700 cm^{-1}. δ_H 2.90 (3H, d, POMe, J_{PH} 8.5 Hz), 3.06 (1H, s, NH), 3.08-3.16 (1H, m, HCH), 3.39-3.51 (1H, m, HCH), 4.44-4.49 (1H, m, OCHPh), 7.17 (5H, s, ArH), 7.32-7.75 (7H, m, ArH), 7.81-7.97 (2H, m, ArH), 8.07-8.28 (2H, m, ArH), 8.82-8.92 (1H, m, ArH),

δ_C 142.2-123.9, 71.6 (POMe), 50.7, (d, $\overline{POCCN}$, J_{PC} 7Hz), 46.7 (d, $\overline{POCCN}$, J_{PC} 9Hz), δ_p-41.1, m/e 401 (M^+, 4%), 370 (47), 369(64), 295(36), 251(100), 173(36), 118(45), 91(27), 77(19).

The more soluble diastereoisomer could not be isolated from the reaction mixtures. A ^{13}C n.m.r. spectrum was also taken of a crude reaction mixture immediately after nitrogen evolution $\delta_C(CDCl_3)$ 144.2-123.5, 71.8 and 71.5 (2 x POMe), 50.9 (d, $\overline{POCCN}$, J_{PC} 7Hz), 50.3 (d, $\overline{POCCN}$, J_{PC} 5Hz), 47.1 (d, $\overline{POCCN}$, J_{pc} 9Hz), 46.6 (d, $\overline{POCCN}$, J_{PC} 10Hz).

The stability of the isolated phosphorane towards thermal racemisation was investigated by observing a solution of the pure phosphorane in dry $CDCl_3$ over 50h at room temperature during which time there was no change in the ^{31}P n.m.r. spectrum. On observing the pure phosphorane by ^{31}P n.m.r. at 120°C over 2h in 1,2-dichlorobenzene it was observed that the phosphorane resonance diminished slightly and a new peak appeared, δ_p-54.8.

7.8 Reaction of (s)-(+)-2-Azido-1-phenyl-1-ethanol with Tervalent Phosphorus Reagents

(i) With methyl naphthylphenylphosphinite. This reaction was carried out in precisely the same manner as reaction 7.7.(iv). The same peaks and peak ratios were observed by ^{31}P n.m.r. Attempted crystallisation of the reaction products, from petrol (b.p. 40-60°C), ether, methylene chloride and mixtures of these, failed.

(ii) 2-Phenyl-5-(S)-phenyl-2-methoxy-2-methyl-2-α-naphthyl-1,3,2-oxazaphospholan was prepared by the addition of redistilled (S)-(+)-2-azido-1-phenyl-1-ethanol (1.03 g, 6.3 mmol) in super-dry ether (10 ml) to methyl methylnaphthylphosphinite (1.39 g, 6.8 mmol). Nitrogen was evolved and the solution was stirred for 20 h. ^{31}P N.m.r. showed signals at δ_p+31.7 (10%) and δ_p (diastereoisomers, 1:1) -33.9 and -34.3. The solution was cooled to -10°C and the phosphorane (1.58 g; 73%), a colourless crystalline solid, crystallised out of solution, m.p. 60-62°C. A satisfactory analysis could not be obtained for this compound, however an exact mass measurement was obtained, found, M, 339.137350, $C_{20}H_{22}NO_2P$ requires M, 339.138808. ν_{max} 3480 (NH), 1325, 1300, 990 and 700 cm^{-1}. δ_H(diastereoisomers, 1:1) 2.12 (3H, 2 x d, PMe, J_{PH} 15Hz), 2.50-3.50 (3H, m, CH_2 + NH), 2.82 and 2.88 (3H, 2 x d, POMe, J_{PH} 10Hz), 4.29-4.51 and 4.81-5.01 (1H, 2 x m, OCHPh), 6.87-8.31 (11H, m, ArH), 8.47-8.65 and 8.71-8.87 (1H, 2 x m, ArH), δ_p-32.3 and -33.4, m/e 339 (M^+, 10%), 308(73),233(100), 189(82), 141(27), 118(29), 91(14), 77(13).

(iii) 2-Methoxy-2-methyl-2-phenyl-5-(S)-phenyl-1,3,2-oxazaphospholan was prepared by the addition of redistilled (S)-(+)-2-azido-1-phenyl-1-ethanol (1.01 g, 6.2 mmol) in super-dry ether (8 ml) to methyl methylphenylphosphinite (1.05 g, 6.8 mmol) in super-dry ether (7 ml). Nitrogen was evolved and the solution stirred for 20 h. ^{31}P N.m.r. showed three pairs of signals δ_p+33.1 and +32.9 (10%), δ_p (diastereoisomers, 1:1) -37.5 and -38.2 (80%),

δ_P -42.7 and -43.4 (10%). The solution was concentrated to *ca* 5 ml and on cooling to -10°C the phosphorane (1.06 g; 59%), a colourless crystalline solid, crystallised out of solution, m.p. 58-60°C. A satisfactory analysis could not be obtained for this compound. ν_{max} 3480(NH), 1440, 1320, 1055 and 700 cm^{-1}. δ_H (diastereoisomers, 1:1) 1.92 (3H, 2 x d, PMe, J_{PH} 15Hz), 2.50-3.60 (3H, m, CH_2 + NH), 2.92 and 2.98 (3H, 2 x d, POMe, J_{PH} 10Hz), 4.33-4.54 and 4.78-4.98 (1H, 2 x m, OCHPh), 7.02-7.84 (10H, m, ArH), δ_P -35.5 and -35.7, m/e M^+ not observed.

7.9 Reaction of N-(o-Azidophenyl)phthalimide with Tervalent Phosphorus Reagents

(i) N-(2-N-Phthalimidophenyl)iminotrimethylphosphite was prepared by the addition of a suspension of N-(o-azidophenyl) phthalimide (0.66g, 2.5 mmol) in dry methylene chloride (12 ml) to trimethylphosphite (0.34 g, 2.7 mmol). The azide dissolved immediately, the solution turned yellow and nitrogen was evolved. The reaction mixture was heated under reflux for 4h, cooled and dry ether (20 ml) added. On cooling to -10°C the iminophosphorane (0.76 g; 84%), a pale brown crystalline solid, crystallised out of solution, m.p. 141-143°C. (Found: C,56.9; H,4.8; N,7.8; $C_{17}H_{17}N_2O_5P$ requires C,56.7; H,4.8; N,7.8%), ν_{max} (mull) 1720 (C=O), 1120, 1010, 865, 750 and 730 cm^{-1}. δ_H 3.55 (9H, d, POMe, J_{PH} 11Hz), 6.75-7.30 (4H, m, ArH), 7.60-7.96 (4H, m, ArH),

δ_p+0.1, m/e 360 (M^+, 100%), 329 (10), 301 (4), 251 (10), 236 (40), 220 (22), 109 (16), 93 (16).

(ii) N-(2-N-Phthalimidophenyl)iminotriphenylphosphine was prepared by the addition of a suspension of N-(o-azidophenyl)phthalimide (0.51 g, 1.9 mmol) in dry methylene chloride (5 ml) to triphenylphosphine (0.50 g, 1.9 mmol) in dry methylene chloride (5 ml). The azide slowly dissolved and nitrogen was evolved. After 20 h, petrol (b.p. 40-60°C) was added and the iminophosphorane (0.91 g, 95%), a yellow solid crystallised, m.p. 208-210°C (Found: C, 77.2; H,4.7; N,5.6; $C_{32}H_{23}N_2O_2P$ requires C,77.1; H,4.7; N,5.6%), ν_{max}(mull) 1720 (C=O), 1110, 885, 745, 725 and 690 cm^{-1}. δ_H 6.38-8.00 (23H, m, ArH), δ_p+3.6, m/e 498 (M^+, 100%), 352(21), 278(15), 277(31), 220(37), 201(14), 183(30), 91(17), 77(15).

7.10 Reaction of o-Azidoaniline with Tervalent Phosphorus Reagents

(i) N-(o-Aminophenyl)iminomethyl diphenylphosphinite was prepared by the addition of freshly sublimed o-azidoaniline (0.19 g, 1.4 mmol) in super-dry petrol (b.p. 40-60°C, 12 ml) to methyl diphenylphosphinite (0.31 g, 1.8 mmol) in super-dry petrol (b.p. 40-60°C, 4 ml). Nitrogen was rapidly evolved and an oil was deposited which slowly crystallised. The iminophosphorane (0.39 g; 86%), a colourless crystalline solid, was collected and dried m.p. 54-56°C. Due to the hydrolytic instability of the iminophosphorane a satisfactory analysis could not be obtained. However, an exact mass

measurement was obtained, found, M, 322.123619, $C_{19}H_{19}N_2OP$ requires M, 322.123494. ν_{max} 3440 and 3350 (NH_2), 1440, 1125, 1030 and 695 cm^{-1}. δ_H 3.68 (3H, d, POMe, J_{PH} 12Hz), 4.24 (2H, broad s, NH_2), 6.30-8.06 (14H, m, ArH), δ_p+19.7, m/e 322 (M^+, 100%), 290(20), 213(23), 201(16), 183(13), 161(6), 109(9), 77(13). This compound decomposed rapidly in solution to give several phosphorus containing products.

(ii) 2-Phenylspiro-[1,3,2-dioxaphospholan-2,2'-[1,3,2]-benzdiazaphospholine] was prepared by the addition of freshly sublimed o-azidoaniline (0.42 g, 3.1 mmol) in super-dry ether (12 ml) and super-dry petrol (4 ml) to 2-phenyl-1,3,2-dioxaphospholan (0.56 g, 3.3 mmol) in super-dry ether (6 ml). Nitrogen was slowly evolved and after stirring for 1 h seed crystals had deposited. On cooling to -10°C the phosphorane (0.62 g; 72%), a colourless crystalline solid, crystallised out of solution, m.p. 137-141°C (Found: C,61.1; H,5.5; N,10.3; $C_{14}H_{15}N_2O_2P$ requires C,61.3; H,5.5; N,10.2%), ν_{max} 3470(NH), 1500, 1405, 1285 and 1070 cm^{-1}. δ_H 3.46-4.12 (4H, m, OCH_2CH_2O), 5.30 (2H, 2NH, broad doublet at 25°C, sharpens at -23°C, J_{PH} 12Hz), 6.56 (4H, s, ArH), 7.16-7.72 (5H, m, ArH), δ_p-39.0, m/e 274 (M^+, 100%), 230 (79), m* 193.0(274 → 230), 153 (17), 152(20), 137(25), 105(15), 77(13).

(iii) 2-Phenylspiro-[1,3,2-dioxaphosphorinan-2,2'-[1,3,2]-benzdiazaphospholine] was prepared by the addition of freshly sublimed o-azidoaniline (0.30 g, 2.2 mmol) in dry methylene chloride (6 ml) to 2-phenyl-1,3,2-dioxaphosphorinan (0.41 g, 2.3 mmol) in dry methylene chloride (4 ml). Nitrogen was rapidly evolved and the reaction mixture was

stirred for 17 h. The solvent was concentrated to *ca* 5 ml and super-dry ether (10 ml) added. On standing at -10°C the spirophosphorane (0.33 g; 53%), a colourless crystalline solid, crystallised out of solution, m.p. 140-143°C (Found: C,62.3; H, 6.0; N,9.6; $C_{15}H_{17}N_2O_2P$ requires C,62.5; H,5.9; N,9.7%), ν_{max} 3470 (NH), 1505, 1290 and 1090 cm^{-1}. δ_H 1.22-2.30 (2H, m, $OCH_2\underline{CH_2}CH_2O$), 3.46-4.64 (4H, m, $O\underline{CH_2}CH_2\underline{CH_2}O$), 5.27 (2H, d, 2NH, J_{PH} 12Hz), 6.38-7.04 (4H, m, ArH), 7.12-7.98 (5H, m, ArH), δ_p-57.8, m/e 288 (M^+, 100%), 230 (38), m* 183.7 (288 → 230), 153(9), 152(7), 107(10), 105(8), 77(6).

7.11 Reaction of N-(o-azidophenyl)benzamide with Tervalent Phosphorus Reagents

(i) N-(2-N-Benzamido)phenyliminotrimethylphosphite was prepared by the addition of N-(o-azidophenyl)benzamide (0.72 g, 3 mmol) in dry methylene chloride (15 ml) to trimethylphosphite (0.38 g, 3.1 mmol) in dry methylene chloride (3 ml). Nitrogen was evolved and the reaction mixture was stirred for 20 h. The solvent was removed with a stream of dry nitrogen and dry ether (7 ml) and dry petrol (b.p. 40-60°C, 7 ml) added. On cooling to -10°C the iminophosphorane (0.66 g; 65%), a colourless crystalline solid, crystallised out of solution, m.p. 72-73°C (Found: C,57.3; H, 5.7; N,8.2; $C_{16}H_{19}N_2O_4P$ requires C,57.5; H,5.7; N,8.4%), ν_{max} 3350 (NH), 2860 and 1660 cm^{-1} (C=O). δ_H 3.74 (9H, d, POMe, J_{PH} 12Hz), 6.76-7.00 (3H, m, ArH), 7.28-7.56(3H, m, ArH), 7.80-8.02 (2H, m, ArH), 8.40-8.62 (1H, m, ArH), 9.62 (1H, s, NH), δ_p+4.2, m/e 334 (M^+, 97%), 257 (18), 229 (25), 194(100), m* 112.6 (334 → 194), 109(16), 105(43), 93(22), 77(12).

(ii) N-(2-N-Benzamido)phenyliminotriphenylphosphine was prepared by the addition of N-(o-azidophenyl)benzamide (0.45 g, 1.9 mmol) in dry ether (16 ml) to triphenylphosphine (0.49 g, 1.9 mmol) in dry ether (7 ml). On addition the solution instantly turned a bright yellow followed by the evolution of nitrogen. The reaction mixture was stirred for 1 h and the iminophosphorane (0.72 g; 81%), a colourless crystalline solid, crystallised out of solution, m.p. 191-193°C (Found: C,79.0; H,5.4; N,5.8; $C_{31}H_{25}N_2OP$ requires C,78.8; H,5.3; N,5.9%), ν_{max} 3310 (NH), 1660 (C=O), 1110 and 690 cm^{-1}. δ_H 6.37-6.81 (3H, m, ArH), 7.19-8.08 (20H, m, ArH), 8.47-8.64 (1H, m, ArH), 10.45 (1H, s, NH), δ_p +8.4, m/e 472 ±4 (M^+, 100%), 395 (28), 367 (15), 277 (35), 262 (15), 194 (57), 183 (34), 108 (14), 105 (16), 77 (24).

7.12 Reaction of N-(o-azidophenyl)-p-toluene-sulphonamide with Tervalent Phosphorus Reagents

(i) N-(2-N-p-toluenesulphonamido)phenyliminotrimethylphosphite was prepared by the addition of N-(o-azidophenyl)-p-toluene-sulphonamide (0.51 g, 1.8 mmol) in dry methylene chloride (9 ml) to trimethylphosphite (0.22 g, 1.8 mmol) in dry methylene chloride (5 ml). Nitrogen was evolved and the reaction mixture was stirred for 20 h. The solution was concentrated to *ca* 5 ml and super-dry ether (15 ml) added. On cooling to -10°C the iminophosphorane (0.64 g; 95%), a colourless crystalline solid, crystallised out of solution, m.p. 98-100°C (Found: C, 49.9; H, 5.4;

N, 7.1; $C_{16}H_{21}N_2O_5PS$ requires C,50.0; H,5.5; N,7.3%), ν_{max} 3250 (NH), 1500, 1165 and 1135 cm^{-1}. δ_H 2.29 (3H, s, p Me), 3.62 (9H, d, POMe, J_{PH} 11Hz), 6.56-6.94 (3H, m, ArH), 7.02-7.78 (5H, m, ArH), 7.94 (1H, s, NH), δ_p+5.0, m/e 384 (M^+, 30%), 230 (100), 197(7), 167(6), 109(7), 93(14). No pentacoordinate phosphoranes were observed in the ^{31}P n.m.r. spectrum after standing in solution at room temperature for 240 h.

(ii) N-(2-N-p-toluenesulphonamido)phenyliminodimethyl phenylphosphonite was prepared by the addition of N-(o-azidophenyl)-p-toluene-sulphonamide (0.89 g, 3.1 mmol) in dry methylene chloride (8 ml) to dimethyl phenylphosphonite (0.54 g, 3.2 mmol) in dry methylene chloride (6 ml). On addition the solution instantly turned bright yellow followed by the rapid evolution of nitrogen. After stirring for 2 h the solvent was blown off with a stream of dry nitrogen to leave an oil which was recrystallised from super-dry ether/ petrol (b.p. 40-60°C) to give colourless crystals of the iminophosphorane (1.17 g; 87%), m.p. 102-103°C (Found: C,58.6; H, 5.4; N,6.5; $C_{21}H_{23}N_2O_4PS$ requires C,58.6; H,5.4; N,6.5%), ν_{max} 3250(NH), 2850, 1595 and 935 cm^{-1}. δ_H 2.26 (3H, s, p Me), 3.49 (6H, d, POMe, J_{PH} 11Hz), 6.58-6.90 (3H, m, ArH), 6.97-7.85 (10H, m, ArH), 8.12 (1H, s, NH), δ_p+21.4, m/e 430 (M^+, 31%), 398 (2), 275(100), 260(9), 243(17), m* 175.9(430 → 275), 155(14), 93(10), 91(12), 77(14). No peaks corresponding to pentacoordinate phosphoranes were observed in the ^{31}P n.m.r. spectrum after heating at 120°C for 2h in chlorobenzene or at 120°C in the presence of a trace amount of pyridine for ½ h.

(iii) 2-Phenyl-1'-(p-toluenesulphonyl)-[1,3,2-dioxaphospholan-2,2'-[1,3,2]-benzdiazaphospholine] was prepared by the addition of N-(o-azidophenyl)-p-toluene-sulphonamide (0.69 g, 2.4 mmol) in dry methylene chloride (5 ml) to 2-phenyl-1,3,2-dioxaphospholan (0.41 g, 2.4 mmol) in dry methylene chloride (1 ml) and super-dry ether (4 ml). Nitrogen was evolved and the reaction mixture was stirred for 2 h. ^{31}P N.m.r. showed quantitative conversion of the tervalent phosphorus reagent into the spirophosphorane. On cooling to -10°C the spirophosphorane (0.30 g; 29%), a colourless crystalline solid, crystallised out of solution and was collected and dried, m.p. 118-120°C (Found: C,58.6; H,4.9; N,6.3; $C_{21}H_{21}N_2O_4PS$ requires C,58.9; H,4.9; N,6.5%), ν_{max} 3450 (NH), 1595, 1390 and 1160 cm^{-1} $\delta_H(CDCl_3)$ 2.24 (3H, s, pMe), 3.78-4.52 (4H, m, OCH_2CH_2O), 5.85 (1H, d, NH, J_{PH} 18Hz), 6.42-7.86 (13H, m, ArH), δ_P (d_6-DMSO) -28.9, m/e 428 (M^+, 97%), 273(100), 245(32), 229(64), 181(31), 107(67), 91(35), 77(31).

(iv) N-(2-N-p-toluenesulphonamido)phenylimino-2-phenyl-1,3,2-dioxaphosphepan was prepared by the addition of N-(o-azidophenyl)-p-toluene-sulphonamide (0.47 g, 1.6 mmol) in dry methylene chloride (7 ml) to 2-phenyl-1,3,2-dioxaphosphepan (0.32 g, 1.6 mmol) in dry methylene chloride (4 ml). On addition nitrogen was evolved and the reaction mixture was stirred for 2 h. The solvent was removed with a stream of dry nitrogen to leave an oil which crystallised from super-dry ether (10 ml) at -10°C to give pale brown crystals of the

iminophosphorane (0.48 g; 64%), m.p. 131-132°C (Found: C,60.3; H,5.7; N,6.0; $C_{23}H_{25}N_2O_4PS$ requires C,60.5; H,5.5; N;6.1%), ν_{max} 3240 (NH), 1500, 1165 and 1020 cm^{-1}. δ_H 1.78-2.10 (4H, m, $OCH_2\underline{CH_2}\underline{CH_2}CH_2O$), 2.27 (3H, s, p Me), 3.80-4.44 (4H, m, $O\underline{CH_2}CH_2CH_2\underline{CH_2}O$), 6.50-6.88 (3H, m, ArH), 6.98-7.86 (10H, m, ArH), 8.16 (1H, s, NH), δ_p+19.7, m/e 456 (M^+, 41%), 384 (4), 301(100), 229(21), m*198.6 (456 → 301), 181(9), 141(9), 107(40), 91(19). No peaks corresponding to pentacoordinate phosphoranes were observed in the ^{31}P n.m.r. spectrum after standing in solution at room temperature for 180 h.

(v) N-(2-N-p-toluenesulphonamido)-phenylimino-1-phenylphospholan was prepared by the addition of N-(o-azidophenyl)-p-toluene-sulphonamide (0.67 g, 2.3 mmol) in dry methylene chloride (10 ml) to 1-phenylphospholan (0.38, 2.3 mmol) in dry methylene chloride (6 ml). On addition the solution instantly turned bright yellow followed by the rapid evolution of nitrogen. The reaction mixture was stirred for 2 h then cooled to -10°C. The iminophosphorane (0.74 g; 75%), a pale yellow crystalline solid, crystallised out of solution and was collected and dried, m.p. 175-177°C (Found: C,64.9; H,5.9; N,6.6; $C_{23}H_{25}N_2O_2PS$ requires C, 65.1; H,5.9; N,6.6%), ν_{max} (mull) 3180 (NH), 1120, 1080, 740, 690 and 650 cm^{-1}. δ_H 1.84-2.59 (8H, m, aliphatic ring), 2.31 (3H, s, p Me), 6.07-6.26 (1H, m, ArH), 6.44-6.72 (2H, m, ArH), 7.03-7.94 (11H, m, ArH + NH), δ_p+37.5, m/e 424 (M^+, 19%), 269(100), 213(6), m*170.6 (424 → 269), 137 (10), 91(11). No peaks corresponding to pentacoordinate phosphoranes were observed in the ^{31}P n.m.r. spectrum after standing in solution at room temperature for 24 h.

7.13 Reaction of azidobenzene with Tervalent Phosphorus Reagents

(i) N-Phenylimino-2-phenyl-1,3,2-dioxaphosphepan was prepared by the addition of azidobenzene (0.55 g, 4.6 mmol) in dry methylene chloride (11 ml) to 2-phenyl-1,3,2-dioxaphosphepan (0.91 g, 4.6 mmol) in dry methylene chloride (6 ml). On addition nitrogen was evolved and the reaction mixture was stirred for 20 h. The solution was concentrated to *ca* 5 ml and super-dry petrol (b.p. 40-60°C, 20 ml) added. On cooling to -10°C the iminophosphorane (0.97 g; 73%), a colourless crystalline solid, crystallised out of solution and was collected and dried, m.p. 103-105°C (Found: C,66.7; H,6.5; N,4.7; $C_{16}H_{18}NO_2P$ requires C,66.9; H,6.3; N,4.9%), ν_{max} 1500, 1140, 1080, 1020 and 795 cm^{-1}. δ_H 1.66-2.30 (4H, m, $OCH_2\underline{CH}_2\underline{CH}_2CH_2O$), 3.81-4.60 (4H, m, $O\underline{CH}_2CH_2CH_2\underline{CH}_2O$), 6.54-8.01 (10H, m, ArH), δ_p+14.8, m/e 287 (M^+, 100%), 233 (30), 216 (23), 215(20), 141(18), 93(83), 77(38).

8. ^{31}P N.m.r. Studies of the Reaction of Azido Compounds with Tervalent Phosphorus Reagents

These reactions were carried out, first of all, on a preparative scale but the products were either too unstable to isolate or gave an inseparable multi-component mixture.

General Method

The azide (approximately 50 mg) dissolved in dry deuterochloroform (0.3 ml) was added to a solution of the tervalent phosphorus reagent (1.0-1.2 molar equivalents)

in dry deuterochloroform (0.3 ml). After nitrogen evolution had ceased (5-10 min) the reaction was monitored by ^{31}P n.m.r. at room temperature. N.B. The supposed nature of the products are given in brackets following the observed chemical shift.

8.1.(i) Reaction of o-Azidophenol with sec-Butyl phenyl-m-tolylphosphinite

The solution turned bright yellow and no nitrogen was evolved. Only one major peak was observed at δ_p+40.0 (phosphatriazene) with six very minor peaks between δ_p+18.8 and +32.0. The spectrum did not change significantly after 24 h.

8.2 Reaction of o-Azidobenzyl alcohol with Tervalent Phosphorus Reagents

(i) With dimethyl phenylphosphonite. Nitrogen was rapidly evolved and initially only one peak at δ_p+20.2 (iminophosphorane) was observed. However, after standing for 24 h seven major peaks were observed between δ_p+18.1 and +21.7.

(ii) With 1-phenylphospholan. Nitrogen was rapidly evolved and initially only one peak at δ_p+36.4 (iminophosphorane) was observed, which decreased in intensity and disappeared over 6 h. Simultaneously another peak at δ_p+60.4 (1-phenylphospholan oxide) appeared.

8.3.(i) Reaction of o-Hydroxybenzylazide with Dimethyl phenylphosphinite

Nitrogen evolution was complete after 2 h and three major peaks were observed, δ_p+24.4 (oxide), +21.7 (iminophosphorane) and -62.9 (diazadiphosphetidine). The mixture was essentially unchanged after 24 h.

8.4.(i) Reaction of 2-Azido-1-phenyl-1-ethanol with Methyl phenyl-m-tolylphosphinite

Nitrogen was rapidly evolved and two major peaks were observed, δ_p-42.10 and -42.26 (diastereomeric phosphoranes, 1:1).

8.5 Reaction of o-Azidoaniline with Tervalent Phosphorus Reagents

(i) With dimethyl phenylphosphonite. Nitrogen was rapidly evolved and initially only one peak was observed, δ_p+17.7 (iminophosphorane), but after 1 h four major peaks were present in the spectrum between δ_p+17.7 and +27.4.

(ii) With 2-phenyl-1,3,2-dioxaphosphepan. Nitrogen was rapidly evolved and initially only one major peak was observed, δ_p+15.0 (iminophosphorane), but this disappeared after 70 h to be replaced by 5 peaks between δ_p+15.0 and +25.6.

(iii) With 1-phenylphospholan. Nitrogen was rapidly evolved and initially only one major peak at δ_p+34.9 (iminophosphorane) was observed which decreased in intensity and disappeared over 150 h. Simultaneously another peak at δ_p+60.3 (1-phenylphospholan oxide) appeared.

8.6 Reaction of o-Azido-N-triphenylmethylaniline with Tervalent Phosphorus Reagents

(i) With dimethyl phenylphosphonite. Nitrogen was rapidly evolved and a single peak was observed at δ_p+17.6 (iminophosphorane). The spectrum was unchanged after 24 h.

(ii) With 2-phenyl-1,3,2-dioxaphospholan. Nitrogen evolution was complete after 1 h. Initially only one major peak was observed, δ_p+25.1 (iminophosphorane), but after 3h three further minor peaks had appeared at δ_p+18.9, +14.3 and δ_p-35.8 (spirophosphorane). After 24 h the spectrum was still composed of these four peaks.

(iii) With 1-phenylphospholan. Nitrogen was rapidly evolved and only one peak was observed δ_p+33.6 (iminophosphorane). The spectrum was unchanged after 24 h.

8.7 Reaction of o-Azido-(N-2,4-dinitrophenyl)aniline with Tervalent Phosphorus Reagents

(i) With dimethyl phenylphosphonite. Nitrogen was rapidly evolved and a single peak was observed at δ_p+19.5 (iminophosphorane). The spectrum was unchanged after 24 h.

(ii) With 2-phenyl-1,3,2-dioxaphospholan. Nitrogen was rapidly evolved and four major peaks were observed, δ_p+26.3 (iminophosphorane), +16.0, -38.3(phosphorane) and -52.3 (diazadiphosphetidine). After 24 h the spectrum was still predominantly composed of these four peaks but several additional minor peaks had appeared between δ_p+17.7 and +36.7.

(iii) With 1-phenylphospholan. Nitrogen was rapidly evolved and a single peak was observed at δ_p+38.7 (iminophosphorane). The spectrum was unchanged after 24 h.

9. Preparation of Pentaccordinate Phosphoranes: Reaction of Iminophosphoranes with Alcohols

General Procedure

The iminophosphorane was usually prepared *in situ* by addition of azidobenzene (5-10 mmol) in dry methylene chloride (10-20 ml) to the tervalent phosphorus reagent (5-10 mmol) in dry methylene chloride (10-20 ml). Once nitrogen evolution had subsided the alcohol (5-10 mmol) was added to the reaction mixture and stirred rapidly at room temperature for several hours. The solvent was blown off with a stream of dry nitrogen and aniline distilled from the reaction mixture by bulb to bulb distillation until at least 95% had been removed. The phosphorane remaining in the reaction flask was then purified by distillation or by recrystallisation from dry solvents.

9.1 Reaction of N-Phenylimino-2-phenyl-1,3,2-dioxaphospholan with Alcohols

The iminophosphorane was prepared and used *in situ* due to low solubility in common organic solvents.[232] Its presence in the reaction mixtures was detected by ^{31}P n.m.r., $\delta_p(CH_2Cl_2)$ + 9.5.

(i) 2,2-Dimethoxy-2-phenyl-1,3,2-dioxaphospholan

Azidobenzene (1.06 g, 8.9 mmol) in dry methylene chloride (10 ml) was added to 2-phenyl-1,3,2-dioxaphospholan (1.45 g, 8.6 mmol) in dry methylene chloride. After 10 min nitrogen evolution had subsided and dry methanol (0.68 g, 21 mmol) was added and the reaction mixture stirred for 2 h.

^{31}P N.m.r. showed complete conversion of the reactants into the phosphorane. The solvent was blown off with a stream of dry nitrogen and aniline (0.63 g; 78%) removed by distillation, b.p. 60°C/0.05 mm, to leave an oil which was purified by bulb to bulb distillation. The phosphorane was obtained as a light orange oil (1.48 g; 74%), b.p. 120°C/0.05 mm (Found: C,52.5; H,6.4; $C_{10}H_{15}O_4P$ requires C,52.2; H,6.6%), ν_{max} (neat) 1440, 1180, 950 and 900 cm^{-1}. δ_H 3.52 (6H, d, POMe, J_{PH} 12Hz), 3.79 (4H, d, OCH_2CH_2O, J_{PH} 14Hz), 7.14-7.76 (5H, m, ArH), δ_p-34.2, m/e 230 (M^+, 4%), 199 (100), 186 (27), 155(56), 141(22), 91(42), 77(51).

(ii) 2-Phenylspiro-[1,3,2-dioxaphospholan-2,2'-[1,3,2]-dioxaphospholan]

Azidobenzene (0.90 g, 7.6 mmol) in dry methylene chloride (16 ml) was added to 2-phenyl-1,3,2-dioxaphospholan (1.25 g, 7.4 mmol) in dry methylene chloride (6 ml). After 10 min nitrogen evolution had subsided and 1,2-ethanediol (0.47 g, 7.6 mmol) was added in super-dry ether (8 ml) and the reaction mixture stirred for 72 h. ^{31}P N.m.r. showed complete conversion of the reactants into the spirophosphorane. The solvent was blown off with a stream of dry nitrogen and aniline (0.50 g; 72%) removed by distillation, b.p. 60°C/0.05 mm, to leave a solid which was recrystallised from methylene chloride/ether to give the spirophosphorane (1.44 g; 85%) as a colourless crystalline solid m.p. 124-126°C (lit.[233] 123°C), (Found: C,52.6; H,5.7; $C_{10}H_{13}O_4P$ requires C,52.6; H,5.7%), δ_c134.6 (d, PC, J_{PC} 211Hz), 131.5-127.5, 59.1 (d, POC, J_{PC} 5Hz), δ_p-19.2.

(iii) 2-Phenylspiro-[1,3,2-dioxaphosphorinan-2,2'-[1,3,2]-dioxaphospholan]

Azidobenzene (1.20 g, 10 mmol) in dry methylene chloride (14 ml) was added to 2-phenyl-1,3,2-dioxaphospholan (1.68 g, 10 mmol) in dry methylene chloride (6 ml). After 10 min nitrogen evolution had subsided and 1,3-propanediol (0.77 g, 10.1 mmol) was added with dry methylene chloride (10 ml) and the reaction mixture stirred for 17 h. ^{31}P N.m.r. showed almost complete conversion of the reactants into the spirophosphorane. The solvent was blown off with a stream of dry nitrogen and aniline (0.93 g; 86%) removed by distillation, b.p. 60°C/0.05 mm, to leave a solid which was recrystallised from methylene chloride/ether to give the spirophosphorane (1.90 g, 79%) as a colourless crystalline solid m.p. 92-94°C (Found: C,54.5; H,6.2; $C_{11}H_{15}O_4P$ requires C,54.6; H,6.2%), ν_{max} 2890, 1435, 940 and 690 cm^{-1} δ_H 1.59-2.24 (2H, m, $OCH_2\underline{CH_2}CH_2O$), 3.77 (4H, d, $O\underline{CH_2}\underline{CH_2}O$, J_{PH} 14Hz), 3.68-4.40 (4H, m, $O\underline{CH_2}CH_2\underline{CH_2}O$, simplifies on irradiation at δ1.90), 7.19-7.85 (5H, m, ArH). δ_C 137.4 (d, PC, J_{PC} 230Hz), 129.2-127.1, 62.9 (d, $\overline{POC\underline{C}\underline{C}O}$, J_{PC} 7Hz), 60.1($\overline{POC\underline{C}O}$), 25.8 (d, $\overline{POC\underline{C}CO}$, J_{PC} 8Hz), δ_P-34.1, m/e 242 (M^+, 15%), 212(81), 199(48), 185(40), 141(100), 91(46), 77(85).

(iv) 2-Phenylspiro-[1,3,2-dioxaphosphepan-2,2'-[1,3,2]-dioxaphospholan]

Azidobenzene (0.87 g, 7.3 mmol) in dry methylene chloride (24 ml) was added to 2-phenyl-1,3,2-dioxaphospholan (1.20 g, 7.1 mmol) in dry methylene chloride (6 ml). After 10 min nitrogen evolution had subsided and 1,4-butanediol

(0.65 g, 7.2 mmol) was added and the mixture stirred for 20 h. ^{31}P N.m.r. showed almost complete conversion of the reactants into the spirophosphorane. The solvent was blown off with a stream of dry nitrogen and aniline (0.66 g; 67%) removed by distillation, b.p. 60°C/0.05 mm, to leave an oil which crystallised from super-dry ether on standing at -10°C for 20 h to give the spirophosphorane (1.49 g; 82%) as a colourless crystalline solid, m.p. 70-72°C (Found: C,56.1; H,6.6; $C_{12}H_{17}O_4P$ requires C,56.3; H,6.7%), ν_{max} 2890, 1435, 1130, 940,890 and 850 cm^{-1}. δ_H 1.55-1.91 (4H, m, $OCH_2\underline{CH_2}\underline{CH_2}CH_2O$), 3.72 (4H, d, $O\underline{CH_2}\underline{CH_2}O$, J_{PH} 14Hz), 3.60-4.39 (4H, m, $O\underline{CH_2}CH_2CH_2\underline{CH_2}O$, simplifies on irradiation at δ 1.76), 7.17-7.93 (5H, m, ArH). δ_c 137.0 (d, PC, J_{PC} 239Hz), 131.8-127.1, 65.6 (d,$\overline{PO\underline{C}C\underline{C}\underline{C}O}$, J_{PC} 9Hz), 59.9 (d, $\overline{PO\underline{C}\underline{C}O}$, J_{PC} 1Hz), 28.9 ($\overline{POCCCCO}$), δ_p-30.2, m/e 256 (M^+, 17%), 226(48), 213(47), 185(100), 173(43), 155(40), 141(97), 108(53), 91(30), 77(73).

(v) Attempted preparations of 2-phenylspiro-[1,3,2-dioxaphosphocan-2,2'-[1,3,2]-dioxaphospholan

(a) Azidobenzene (0.98 g, 8.2 mmol) in dry methylene chloride (20 ml) was added to 2-phenyl-1,3,2-dioxaphospholan (1.36 g, 8.1 mmol) in dry methylene chloride (10 ml). After 10 min nitrogen evolution had subsided and 1,5-pentanediol (0.84 g, 8.1 mmol) was added and the reaction mixture stirred for 2 h. ^{31}P N.m.r. showed complete conversion of the reactants into spirophosphorane compounds, δ_p-35.8 and -36.2. The solvent was removed and aniline (0.47 g, 62%)

distilled from the reaction mixture, b.p. 60°C/0.05 mm, to leave an orange gum (2.19 g, 100%) which failed to crystallise. Attempts to purify the gum by distillation led to decomposition and the formation of several phosphoryl compounds. However, a satisfactory analysis was obtained for the crude material (Found: C,57.6; H,7.2; empirical formula $C_{13}H_{19}O_4P$ requires C,57.8; H,7.1%), ν_{max} 2760, 1435, 945 and 790 cm^{-1}. δ_H 1.12-1.90 (6H, m, $OCH_2\underline{CH_2}\underline{CH_2}\underline{CH_2}CH_2O$), 3.36-4.28 (8H, m, 4 x O $\underline{CH_2}$), 7.18-7.95 (5H, m, ArH). δ_C 138.4 (d, PC, J_{PC} 230Hz), 131.6-126.6, 65.5 (d, $\overline{POC\underline{C}CCC\underline{C}O}$, J_{PC} 10Hz), 59.8 ($\overline{POC\underline{C}O}$), 30.3 (d, $\overline{POC\underline{C}C\underline{C}CO}$, J_{PC} 8Hz), 22.0 ($\overline{POCC\underline{C}CCO}$). Expansion of the ^{13}C n.m.r. spectrum in the region δ_C25-80 showed two sets of minor doublets at δ_C 66.9(J_{PC} 10Hz) and 30.1(J_{PC} 9Hz) in the ratio of 1:10 to the peaks at δ_C66.5(J_{PC} 10Hz) and 30.3 (J_{PC} 8Hz). δ_P-36.1 (3034%) and -36.5 (9799%), m/e 270 (M^+, 7%), 185(71), 141(100). M, 270.101305, $C_{13}H_{19}O_4P$ requires M, 270.102089. The molecular weight of the gum was determined in benzene on a Perkin Elmer Vapour Pressure Osmometer (Model 115), calibrated with benzil, and found to be MW = 300 ± 15.

The ^{31}P n.m.r. spectrum of the gum in 1,2-dichlorobenzene showed an apparent coalescence of peaks (28°C, δ_P-36.3, -36.5 and -36.9) at approximately 120°C (δ_P-36.3).

Solutions of the gum 0.6 M, 0.3 M and 0.15 M in 1,2-dichlorobenzene were monitored by ^{31}P n.m.r. over 120 h at room temperature and it was observed that the peak ratios remained constant.

(b) Reaction of 1,5-butanediol (0.88 g, 9.8 mmol) and 2-phenyl-1,3,2-dioxaphospholan (1.42 g, 8.5 mmol) with N-chlorodi-iso-propylamine (1.33 g, 9.8 mmol) in super-dry ether (25 ml) according to the method of Trippett[145] gave a colourless gum (70%), δ_p-36.1 (1259%) and -36.5 (8211%).

(vi) 2-Phenylspiro-[trans-4,5-cyclohexyl-1,3,2-dioxaphospholan-2,2'-[1,3,2]-dioxaphospholan]

Azidobenzene (1.13 g, 9.5 mmol) in dry methylene chloride (14 ml) was added to 2-phenyl-1,3,2-dioxaphospholan (1.57 g, 9.3 mmol) in dry methylene chloride (6 ml). After 10 min nitrogen evolution had subsided and trans-1,2-cyclohexanediol (1.09 g, 9.4 mmol) was added with dry methylene chloride (10 ml) and the reaction mixture was stirred for 20 h. ^{31}P N.m.r. showed almost complete conversion of the reactants into the spirophosphorane. The solvent was blown off with a stream of dry nitrogen and aniline (0.87 g; 77%) removed by distillation, b.p. 60°C/0.05 mm, to leave a solid which was recrystallised from super-dry ether to give the spirophosphorane (1.80 g; 68%) as a colourless crystalline solid m.p. 93-96°C (Found: C,59.6; H,6.8; $C_{14}H_{19}O_4P$ requires C,59.6; H, 6.8%), ν_{max} 2860, 1435, 940 and 885 cm^{-1}. δ_H 1.04-2.25 (8H, m, cyclohexyl ring), 2.84-3.14 (1H, m, cyclohexyl ring H), 3.23-4.11 (5H, m, OCH_2CH_2O + cyclohexyl ring H), 7.20-7.50 (3H, m, ArH), 7.59-8.00 (2H, m, ArH), δ_p-22.5, m/e 282 (M^+, 36%), 185 (100), 141(38), 91(24), 77(30).

(vii) 2-Phenylspiro-[1,3,2-dioxaphospholan-2,2'-[1,3,2]-benzodioxaphospholine]

Azidobenzene (0.53 g, 4.5 mmol) in dry methylene chloride (12 ml) was added to 2-phenyl-1,3,2-dioxaphospholan (0.76 g, 4.5 mmol) in dry methylene chloride (5 ml). After 10 min nitrogen evolution had subsided and 1,2-dihydroxybenzene (0.49, 4.5 mmol) in dry methylene chloride (15 ml) was added and the reaction mixture stirred for 20 h. ^{31}P N.m.r. showed complete conversion of the reactants into the spirophosphorane. The solvent was removed and aniline (1.11 g; 70%) distilled from the reaction mixture, b.p. 60°/0.05 mm, to leave a solid which was recrystallised from super-dry ether to give the spirophosphorane (0.26 g; 21%) as a colourless crystalline solid m.p. 113-115°C (Found: C,61.0; H,4.8; $C_{14}H_{13}O_4P$ requires C,60.9; H,4.7%), ν_{max} 2900, 1480, 1435, 1350, 1125, 1005 and 945 cm^{-1}. δ_H 3.63-4.30 (4H, m, $O\underline{CH}_2\underline{CH}_2O$), 6.62-7.00 (4H, m, ArH), 7.18-7.48 (3H, m, ArH), 7.62-8.01 (2H, m, ArH), δ_p-14.3, m/e 276 (M^+, 100%), 233 (40), 232 (26), 141 (26), 110 (26), 77 (23).

This spirophosphorane was also prepared by the method of Trippett.[145] 1,2-Dihydroxybenzene (0.62 g, 5.6 mmol) in super-dry ether (10 ml) was added slowly to 2-phenyl-1,3,2-dioxaphospholan (0.92 g, 5.5 mmol) in super-dry ether (25 ml) maintained at -78°C. N-Chlorodiiso-propylamine (0.75 g, 5.5 mmol) in super-dry ether (10 ml) was then added slowly and the mixture stirred at -78°C for ½ h. The reaction mixture was warmed to room temperature and stirred for a further 120 h. The amine salt crystallised out of solution and was filtered off. The filtrate was blown down to half

its original volume and left to stand at -10°C for 20 h. The spirophosphorane (1.12 g; 74%), a colourless crystalline solid, crystallised out of solution and was collected and dried m.p. 113-115°C, δ_p-14.3.

(viii) 2-Phenylspiro-[1,3,2-dioxaphospholan-2,2'-[1,3,2]-m-tert-butylbenzodioxaphospholine]

Azidobenzene (0.86 g, 7.2 mmol) in dry methylene chloride (6 ml) was added to 2-phenyl-1,3,2-dioxaphospholan (1.20 g, 7.1 mmol) in dry methylene chloride. After 10 min nitrogen evolution had subsided and 4-tert-butylcatechol (1.19 g, 7.2 mmol) in dry methylene chloride (12 ml) was added and the reaction mixture stirred for 17 h. ^{31}P N.m.r. showed complete conversion of the reactants into the spirophosphorane. The solvent was removed and aniline (0.66 g; 50%) distilled from the reaction mixture, b.p. 60°C/0.05 mm, to leave a solid which was purified by distillation, b.p. 180°C/ 0.05 mm, and recrystallisation from super-dry ether to give the spirophosphorane (1.68 g; 71%) as a colourless crystalline solid m.p. 110-113°C (Found: C,65.2; H,6.4; $C_{18}H_{21}O_4P$ requires C, 65.1; H, 6.4%), ν_{max} 2890, 1495, 1260, 1070, 930 and 865 cm^{-1}. δ_H 1.20 (9H, s, $C(CH_3)_3$), 3.68-4.21 (4H, m, OCH_2CH_2O), 6.79 (2H, s, ArH), 6.96 (1H, s, ArH), 7.26-7.58 (3H, m, ArH), 7.68-8.03 (2H, m, ArH), δ_p-14.2, m/e 332 (M^+, 78%), 317 (100), 151 (62), 141 (24), 93 (70), 77 (24).

(ix) 2-Phenylspiro-[1,3,2-dioxaphospholan-2,2'-[naphtho[c]-1,3,2-dioxaphospholine]]

Azidobenzene (0.95 g, 8 mmol), in dry methylene chloride (10 ml) was added to 2-phenyl-1,3,2-dioxaphospholan (1.32 g, 7.9 mmol) in dry methylene chloride (6 ml). After 10 min nitrogen evolution had subsided and 2,3-dihydroxynaphthalene (1.26 g, 7.9 mmol) was added in super-dry ether (14 ml) and the reaction mixture stirred for 20 h. ^{31}P N.m.r. showed complete conversion of the reactants into the spirophosphorane. The solvent was removed and aniline (0.46 g; 63%) distilled from the mixture, b.p. 60°C/0.05 mm, to leave a solid which was recrystallised from dry methylene chloride to give the spirophosphorane (1.89 g; 69%) as a colourless crystalline solid m.p. > 270°C (decomp.) (Found: C,66.3; H,4.7; $C_{18}H_{15}O_4P$ requires C, 66.3; H,4.6%), ν_{max} (mull) 1155, 1130, 865 and 745 cm^{-1}. δ_H 3.70-4.42 (4H, m, OCH_2CH_2O), 7.12-8.00 (11H, m, ArH), δ_p-14.1, m/e 326 (M^+, 100%), 282(80), 160(83), 141(29), 114(36), 77(22).

(x) 2-Phenylspiro-[di-O-methyl-α-D-glucanopyranosyl-1,3,2-dioxaphosphorinan-2,2'-[1,3,2]-dioxaphospholan

Azidobenzene (0.57 g, 4.8 mmol) in super-dry ether (7 ml) and dry methylene chloride (3 ml) was added to 2-phenyl-1,3,2-dioxaphospholan (0.78 g, 4.64 mmol) in dry methylene chloride (7 ml). After 10 min nitrogen evolution had subsided and methyl-2,3-di-O-methyl-α-D-glucanopyranoside[234] (1.03 g, 4.64 mmol) was added and the reaction mixture stirred for 18 h. ^{31}P N.m.r. showed complete conversion

of the reactants into the spirophosphorane. The solvent was removed and aniline (0.43 g; 66%) distilled from the reaction mixture, b.p. 70°C/0.05 mm, to leave the spirophosphorane (1.80 g; 100%) as an orange gum which would not crystallise. Attempts to distill the product led to decomposition. However, satisfactory analytical data was obtained for the crude product (Found: C,52.8; H,6.6; $C_{17}H_{25}O_8P$ requires C,52.6; H,6.5%), ν_{max} 1130, 1100, 960 and 845 cm^{-1}. δ_H 2.86-4.88 (11H, m, aliphatic H), 3.38 (3H, s, OMe), 3.46 (3H, s OMe), 3.66 (3H, s, OMe), 7.17-7.86 (5H, m, ArH), δ_p-33.8, m/e 388 (M^+, 2%), 357 (3), 285(3), 185(22), 142(17), 129(9), 101(26), 88(100). M, 388.126757, $C_{17}H_{25}O_8P$ requires M, 388.128693.

(xi) 3'-Methyl-2-phenylspiro-[1,3,2-dioxaphospholan-2,2'-[1,3,2]-oxazaphospholan]

Azidobenzene (0.68 g, 5.7 mmol) in dry methylene chloride (6 ml) was added to 2-phenyl-1,3,2-dioxaphospholan (0.91 g, 5.4 mmol) in dry methylene chloride (6 ml). After 10 min nitrogen evolution had subsided and 2-(methylamino)-ethanol (0.43 g, 5.7 mmol) was added and the reaction mixture stirred for 20 h. ^{31}P N.m.r. showed complete conversion of the reactants into the spirophosphorane. The solvent was removed and aniline (0.46 g; 91%) distilled from the reaction mixture, b.p. 60°C/0.05 mm, to leave a solid which was recrystallised from super-dry ether to give the spirophosphorane (0.98 g; 75%) as a colourless crystalline solid m.p. 68-71°C (Found: C, 55.0; H,6.7; N,5.7; $C_{11}H_{16}NO_3P$ requires C,54.8;

H,6.7; N,5.8%), ν_{max} 2870, 1185, 965 and 950 cm^{-1}. δ_H 2.64-4.16 (8H, m, aliphatic ring H), 3.00 (3H, d, NMe, J_{PH} 8Hz), 6.92-7.86 (5H, m, ArH), δ_p-34.9, m/e 241 (M^+, 100%), 185 (44), 141 (73), 77 (47).

(xii) 2-Phenylspiro-[1,3,2-dioxaphospholan-2,2'-1,3,2-benzothiazaphospholine]

Azidobenzene (0.71 g, 6 mmol) in dry methylene chloride (13 ml) was added to 2-phenyl-1,3,2-dioxaphospholan (0.99 g, 5.9 mmol) in dry methylene chloride (10 ml). After 10 min nitrogen evolution had subsided and monothiocatechol (0.75 g, 6 mmol) in dry methylene chloride (5 ml) was added and the reaction mixture stirred for 20 h. ^{31}P N.m.r. showed one major resonance at δ_p+4.6 plus several minor peaks at between δ_p+15 and +20. The solvent was removed and aniline (0.29 g, 52%) distilled from the reaction mixture, b.p. 60°C/0.05 mm, to leave an oil which on crystallisation from super-dry ether/petrol (b.p. 40-60°C) gave the spirophosphorane (1.27 g; 74%) as a colourless crystalline solid m.p. 96-97°C (Found: C, 57.6; H,4.6; $C_{14}H_{13}O_3PS$ requires C,57.5; H,4.5%), ν_{max} 1470, 940 and 650 cm^{-1}. δ_H 3.40-4.36 (4H, m, OCH_2CH_2O), 6.62-8.06 (9H, m, ArH), δ_p+4.7, m/e 292 (M^+, 100%), 249(18), 233(14), 215(11), 184(15), 171(13), 155(22), 137(17), 108(18), 91(22), 77(16).

9.2 Reaction of N-Phenylimino-2-phenyl-1,3,2-dioxaphosphepan with Alcohols

(i) To the iminophosphorane (1.15 g, 4 mmol) in dry methylene chloride (20 ml) was added 1,2-ethanediol (0.25 g,

4 mmol) and the reaction monitored by ^{31}P n.m.r. After 20 h two major products were present in the reaction mixture at δ_p-19.0 (1282%) and -30.2 (6970%), these were identified by peak enhancement as 2-phenylspiro-[1,3,2-dioxaphospholan-2,2'-[1,3,2]-dioxaphospholan] and 2-phenylspiro-[1,3,2-dioxaphosphepan-2,2'-[1,3,2]-dioxaphospholan] respectively, together with unreacted iminophosphorane δ_p+12.7 (661%). Removal of solvent and aniline (0.20 g; 55%) *in vacuo* yielded a pale orange oil which on crystallisation from ether gave 2-phenylspiro-[1,3,2-dioxaphosphepan-2,2'-[1,3,2]-dioxaphospholan] (0.39 g; 38%), m.p. 70-72°C.

10. ^{31}P N.m.r. Studies of the Reaction of Iminophosphoranes and Pentacoordinate Phosphoranes with Alcohols

(i) Reaction of N-phenylimino-2-phenyl-1,3,2-dioxaphospholan, prepared *in situ*, with 2-mercaptoethanol in dry methylene chloride at room temperature gave after 17 h an inseparable multi-component mixture of phosphorus-containing products. ^{31}P N.m.r. (CH_2Cl_2) showed five major peaks at δ_p+35.7, +20.4, +18.8, +18.0 and +4.5.

(ii) Reaction of N-phenyliminotriethylphosphite, δ_p(CH_2Cl_2) -0.7, with a five fold excess of ethanol in dry methylene chloride gave no detectable reaction after 300 h at room temperature.

(iii) To a 0.2 M solution of 2-phenylspiro-[1,3,2-dioxaphosphepan-2,2-[1,3,2]-dioxaphospholan], δ_p-30.3, in dry methylene chloride was added 1,2-ethanediol (1.1 molar equivalents) with stirring at room temperature. After 50 h ^{31}P n.m.r. showed complete conversion of the reactants into 2-phenylspiro-[1,3,2-dioxaphospholan-2,2'-[1,3,2]-dioxaphospholan],

δ_p -19.1, by comparison with an authentic sample.

(iv) Addition of 1,4-butanediol (4 molar equivalents) to a 0.2 M solution of 2-phenylspiro-[1,3,2-dioxaphospholan 2,2''-[1,3,2]-dioxaphospholan] dissolved in dry methylene chloride gave no new pentacoordinate phosphoranes after 48 h at room temperature.

11. Variable Temperature N.m.r. Studies on 1,3,2-Oxazaphosphoranes

General Method. The oxazaphosphorane (*ca.* 50 mg) was dissolved in dry methylene chloride or deuterochloroform, in a 5 mm n.m.r. tube. The temperature of the sample was adjusted in the spectrometer probe and allowed to stabilise before spectra were recorded on either a Varian HA 100 instrument (^{1}H n.m.r.) or a Jeol FX60 (^{31}P n.m.r.). The coalescence temperature was determined to be the temperature at which separate peaks merged to become indistinguishable.

The free energy of activation (ΔG^*) for two-site exchange processes was calculated by a combination of a simplified Gutowsky-Holm equation[235] for the situation at coalescence temperature ($2\pi\tau\Delta\nu = \sqrt{2}$, where τ is half the lifetime of either site and $\Delta\nu$ is the frequency difference between the separated resonances at slow exchange) and the Eyring equation[236] ($k^1 = \sigma kT/h)\exp(-\Delta G^*/RT)$, where σ is the transmission coefficient, k^1 is the rate constant for the exchange process, T is the coalescence temperature (^oK),

and other symbols are conventional. Thus $k^1 = \pi\Delta\nu/\sqrt{2}$ and hence $\Delta G^* = RT \ln(\frac{\sigma kT\sqrt{2}}{\pi\Delta\nu h})$. The transmission coefficient was taken as unity. The above relation for ΔG^* applies only to the coalescence of equally populated peaks and will suffice for the examples here quoted.

In each of the examples studied below the spectrum at room temperature was identical before and after the experiment.

11.1 Variable temperature ^1H n.m.r. studies on 2,2-dimethoxy-2-phenyl-1,3,2-benzoxazaphospholine

At 28°C the spectrum exhibited a sharp doublet, δ_H (CH_2Cl_2) 3.56 (6H, d, POMe, J_{PH} 12Hz) which on cooling to -18°C was replaced by a broad convex shaped mound. Further cooling to -26°C caused the sides of the mound to become concave; T_c was judged to have occurred at -24 ± 2°C when the mound was of an intermediate shape. At -66°C the mound was replaced by two sharp sets of doublets. The coupling constants of the high field set was 10 Hz whilst that of the low field set was 14 Hz. Thus, with $\Delta\nu$ = 66Hz, ΔG^* = 50 ± 1 kJ mol^{-1}.

11.2 Variable temperature ^1H n.m.r. and ^{31}P n.m.r. studies on 2,2-dimethoxy-2,5-diphenyl-1,3,2-oxazaphospholan

The ^1H n.m.r. signals studied were at δ_H($CDCl_3$, 24°C) 3.40 and 3.61 (6H, 2 x d, 2 x POMe, J_{PH} 11Hz and J_{PH} 11Hz;

both doublets collapse on irradiation at the same ^{31}P frequency) and δ_H 4.54-4.80 (1H, m, OCHPh).

At -12°C, the sp^3 proton (OCHPh) appeared as a broad mound which on further cooling to -32°C started to separate into two signals. At -75°C, two distinct sp^3 signals of equal area were present between δ_H 4.58-4.85 and 5.00-5.26 T_c was judged to have been at -29 ± 3°C. Thus, with $\Delta\nu$ = 42Hz, ΔG^* = 50 ± 1 kJ mol^{-1}.

At -12°C the methoxyl signals formed a broad mound. On further cooling to -75°C four doublets separated from this mound, δ_H 3.28 and 4.32 (6H, 2 x d, 2 x POMe, J_{PH} 10Hz and J_{PH} 12Hz), 3.39 and 4.02 (6H, 2 x d, 2 x POMe, J_{PH} 11Hz and J_{PH} 13Hz). These signals were attributed to two different oxazaphosphoranes as each set of doublets collapsed to a set of singlets on irradiation at different phosphorus frequencies. A coalescence temperature could not be determined from these signals due to the confused overlap with the ring methylene signals.

At temperatures up to 135°C in diphenyl ether the methoxy signals, $\Delta\nu$ = 21Hz, did not coalesce, thereby giving a minimum ΔG^* = 88 kJ mol^{-1} for coalescence.

At 28°C the ^{31}P n.m.r. spectrum showed a single peak, δ_p ($CDCl_3$)-44.8. On cooling this peak broadened and at -62°C two sharp signals, of approximately equal intensity, were observed at δ_p-43.4 and -46.5. T_c was judged to be at -25 ± 2°C. Thus, with $\Delta\nu$ = 74Hz, ΔG^* = 50 ± 1 kJ mol^{-1}.

12. The Acidic Hydrolysis of Pentacoordinate Oxazaphosphoranes

General Procedure

To the pure oxazaphosphorane (0.34-10 mmol) in super-dry ether (10-20 ml) was added a solution of p-toluenesulphonic acid (1.1 molar equivalents of a 0.225 M solution) with stirring at room temperature. The reactions were very rapid with the product usually being precipitated from solution within minutes. The loss of methanol or ethanol upon hydrolysis was detected by glc analysis of the crude reaction mixture or by ^{1}H n.m.r.

(i) Dimethyl N-(2-hydroxyphenyl)phosphoramidate was prepared by the addition of standard acid solution (180 µl, 10% excess) to 2,2,2-trimethoxy-1,3,2-benzoxazaphospholine (2.10 g; 9.1 mmol) dissolved in super-dry ether (20 ml). After stirring for 2 min a colourless solid (1.97 g; 100%) precipitated out of solution and was isolated by removal of the solvent *in vacuo*. Recrystallisation from methylene chloride/ether gave the pure phosphoramidate as a colourless crystalline solid, m.p. 78.5-79°C (Found: C,44.4; H,5.7; N,6.4; $C_8H_{12}NO_4P$ requires C,44.3; H,5.6; N,6.5%), ν_{max} 3360 (NH), 3140 (broad OH), 1520, 840 and 750 cm^{-1}. δ_H 3.72 (6H, d, POMe, J_{PH} 12Hz), 6.08(1H, d, NH, J_{PH} 10Hz), 6.62-7.25(4H, m, ArH), 7.94 (1H, s, OH), δ_p+6.3, m/e 217 (M^+, 16%), 185 (100), 170(24), 155 (22), 109 (58).

(ii) Diethyl N-(2-hydroxyphenyl)phosphoramidate was prepared by the addition of standard acid solution (83 µl, 10% excess) to 2,2,2-triethoxy-1,3,2-benzoxazaphospholine (1.15 g, 4.2 mmol) dissolved in super-dry ether (20 ml). After stirring for 5 min a colourless solid (1.03 g; 100%) precipitated out of solution and was isolated by removal of the solvent *in vacuo*. Recrystallisation from ether gave the pure phosphoramidate as a colourless crystalline solid, m.p. 61-62°C (Found: C,49.0; H,6.5; N,5.7; $C_{10}H_{16}NO_4P$ requires C, 49.0; H,6.6; N,5.7%), ν_{max} 3360 (NH), 3240 (broad OH), 1510, 1025 and 980 cm^{-1}. δ_H 1.27 (6H, t, $CH_2\underline{CH}_3$, J_{HH} 7Hz), 3.84-4.36 (4H, m, $\underline{CH}_2CH_3$, prochiral), 6.08 (1H, d, NH, J_{PH} 10Hz), 6.60-7.28 (4H, m, ArH), 8.90 (1H, s, OH), δ_p+3.1, m/e 245 (M^+, 16%), 217 (4), 199 (28), m* 192.2 (245 → 217), 189 (7), 171 (100), m*164.6 (217 → 189), 153 (13), m* 146.9 (199 → 171), 109 (29), 77 (21).

(iii) Diphenyl N-(2-hydroxyphenyl)phosphinamidate was prepared by the addition of standard acid solution (24 µl, 10% excess) to 2,2-diphenyl-2-methoxy-1,3,2-benzoxazaphospholine (0.39 g, 1.2 mmol) in super-dry ether (20 ml). After stirring for 1 min a colourless solid precipitated out of solution, the phosphinamidate (0.36 g; 95%) isolated by filtration, m.p. > 200°C (decomp.) (Found: C, 69.8; H,5.2; N,4.3; $C_{18}N_{16}NO_2P$ requires C,69.9; H,5.2; N,4.5%), ν_{max} (mull) 3360 (NH), 3060 (OH, broad), 1170, 940, 740 and 700 cm^{-1}. $\delta_H(d_6$-DMSO) 6.40-8.00 (14H, m, ArH), 6.90 (1H, d, NH, J_{PH} 11Hz), 9.88 (1H, s, OH), $\delta_p(d_6$-DMSO) + 18.6, m/e 309 (M^+, 76%), 291 (10), 201 (100), 185 (12), m* 130.7 (309 → 201), 77 (24).

(iv) Diphenyl N-(trans-2-hydroxycyclohexyl)phosphinamidate was prepared by the addition of standard acid solution (40 µl, 10% excess) to 2,2-diphenyl-2-methoxy-trans-4,5-cyclohexyl -1,3,2-oxazaphospholan (0.67 g, 2 mmol) in super-dry ether (10 ml). After stirring for 5 min a colourless solid precipitated out of solution, the phosphinamidate (0.62 g; 97%) isolated by filtration m.p. 152-154°C (Found: C,68.3; H,7.1; N,4.4; $C_{18}H_{22}NO_2P$ requires C,68.6; H,7.0; N,4.4%), ν_{max} 3360 (NH), 3300 (OH, broad), 2850, 1440 and 690 cm^{-1}. δ_H 0.80-3.45 (10H, m, aliphatic H), 4.00-6.00 (1H, broad peak, NH or OH), 7.24-8.08 (10H, m, ArH), δ_p+26.1, m/e 315 (M^+, 36%), 297 (4), 201(38), 114(100), 77(20).

(v) Diphenyl N-(β-hydroxy-α-phenethyl)phosphinamidate was prepared by the addition of standard acid solution (7 µl, 10% excess) to 2-methoxy-2,2,5-triphenyl-1,3,2-oxazaphospholan (0.123 g, 0.34 mmol) in super-dry ether (10 ml). After stirring for 10 min a colourless solid precipitated out of solution, m.p. 167-169°C, the phosphinamidate (0.114g; 97%) isolated by filtration, (Found: C,71.2; H,6.0; N,4.1; $C_{20}H_{20}NO_2P$ requires C,71.2; H,6.0; N,4.2%), ν_{max} (mull) 3260 (NH), 3160 (OH, broad), 1170, 720 and 695 cm^{-1}. δ_H 2.86-3.88 (3H, m, CH_2 + NH or OH), 4.78-4.96 (1H, m, HOCHPh), 7.02-7.96 (16H, m, ArH + NH or OH), δ_p+26.7, m/e 377(M^+, <1%), 308 (3), 231 (85), 202 (100), 201 (71), 118 (13), 77 (25).

13. Thermal Reactions of some Iminophosphoranes

(i) N-(2-Benzoxyloxyphenyl)iminotriphenylphosphine

The iminophosphorane was prepared *in situ* by the reaction of o-azidophenylbenzoate (1.26 g, 5.3 mmol) with triphenylphosphine (1.39 g, 5.3 mmol) in dry methylene chloride (18 ml). The reaction was monitored by ^{31}P n.m.r. over a period of 100 h at room temperature. Initially, only one peak was observed, δ+2.9 (iminophosphorane), but after 14 h another peak, δ+27.4 (triphenylphosphine oxide), had appeared in approximately the same intensity. After 100 h the iminophosphorane resonance had disappeared and the only peak present was that due to triphenylphosphine oxide. Chromatography of the reaction mixture on alumina with petrol (b.p. 40-60°C) as eluant gave two fractions; 2-phenylbenzoxazole (0.70 g; 68%), m.p. 98-100°C (lit.[237] 103°C) and triphenylphosphine oxide (0.68 g; 46%), m.p. 153-155°C (lit.[238] 153.5°C), δ_p+29.0.

The reaction was also monitored by ^{31}P n.m.r. in chloroform. In this case a transient intermediate, δ_p-58.0, was detected.

(ii) N-(2-N-Phthalimidophenyl)iminotriphenylphosphine

The iminophosphorane (1.45 g, 2.9 mmol) in super-dry tert-butylbenzene (10 ml) was heated under reflux under nitrogen for 18 h and the reaction mixture examined by ^{31}P n.m.r. Only one peak was observed, δ_p+28.6 (triphenylphosphine oxide). The reaction mixture was cooled and a yellow solid crystallised out of the solution which was recrystallised from ethanol to give 11H-isoindolo[2,1-α]benzimidazol-11-one (0.42 g; 65%) as bright yellow crystals, m.p. 213-214°C (lit.[239]

211-212°C), ν_{max} 1765, 1740 cm^{-1} (C=O). Chromatography of the mother liquors on alumina with ether as eluant gave triphenylphosphine oxide (0.65 g; 80%), m.p. 155-156°C (lit.[238] 153.5°C), δ_p+ 28.9.

(iii) N-(2-N-Phthalimido)iminotrimethylphosphite

The iminophosphorane (1.84 g, 5.1 mmol) in dry chlorobenzene (16 ml) was heated under reflux under nitrogen for 7 h and the reaction monitored by ^{31}P n.m.r. It was observed that during this time the iminophosphorane resonance disappeared and another peak, δ_p+2.2 (trimethylphosphate) appeared. Removal of solvent and phosphate *in vacuo* gave a brown solid which was recrystallised from ethanol to give bright yellow crystals of 11H-isoindolo[2,1-α]benzimidazol-11-one (0.74 g; 66%), m.p. 210-212°C (lit.[239] 211-212°C).

(iv) N-(2-N-Benzamido)phenyliminotriphenylphosphine

The iminophosphorane (0.53 g; 1.1 mmol) in super-dry tert-butylbenzene (7 ml) was heated under reflux under nitrogen for 15 h and the reaction was monitored by ^{31}P n.m.r. It was observed that during this time the iminophosphorane resonance disappeared and another peak, δ_p+25.1 (triphenylphosphine oxide) appeared. Chromatography of the reaction mixture on alumina with methylene chloride gave two fractions; 2-phenylbenzimidazole (0.14 g; 63%), m.p. 272-282°C (lit.[240] 294°C), ν_{max} (mull) 2680 (NH), 1315, 1275 and 970 cm^{-1}, m/e 194 (M^+, 100%) and triphenylphosphine oxide (0.27 g; 87%) m.p. 146-149°C (lit.[238] 153.5°C), δ_p+28.9.

(v) N-(2-N-Benzamido)phenyliminotrimethylphosphite

The iminophosphorane (1.20 g, 3.6 mmol) in dry chlorobenzene (8 ml) was heated under reflux under nitrogen for 5 h and the reaction monitored by ^{31}P n.m.r. It was observed that during this time the iminophosphorane resonance disappeared and another peak appeared, δ_p+8.7. Significantly no peak due to trimethylphosphate was observed. The reaction mixture was cooled to -10°C and a black crystalline mass was deposited. Chromatography of the solid on alumina with ether gave dimethyl N-methyl-N-benzamidophenylphosphoramidate (0.23 g; 19%), pale brown crystals m.p. 113-114°C (Found: C, 57.2; H,5.8; N,8.2; $C_{16}H_{19}N_2O_4P$ requires C,57.5; H,5.7; N,8.4%), ν_{max} 3410(NH), 1675(C=O), 925 and 835 cm^{-1}. δ_H 3.01(3H, d, $PNCH_3$, J_{PH} 10Hz), 3.69 (6H, d, $POCH_3$, J_{PH} 11Hz), 7.00-7.58 (6H, m, ArH), 7.90-8.34 (3H, m, ArH), 9.44 (1H, s, NH), δ_p+9.1, m/e 334 (M^+, 34%), 317 (4), 257(14), 229(41), 212(75), 208(39), 197(14), 167(7), 119(18), 105(100), 77(49).

(vi) N-(2-p-Toluenesulphonoxylphenyl)iminotrimethylphosphite

The iminophosphorane (2.00 g, 5.2 mmol) in super-dry tert-butylbenzene (10 ml) was heated under reflux under nitrogen for 16 h and the reaction monitored by ^{31}P n.m.r. It was observed that during this time the iminophosphorane resonance disappeared and another peak, δ_p+7.4, appeared. Removal of the solvent and chromatography of the residue on alumina with methylene chloride/ether 1:9 gave a colourless oil which on crystallisation from ether (3 ml) gave colourless crystals of dimethyl N-2-p-toluenesulphonyloxyphenylphosphoramidate (1.16 g; 58%), m.p. 65.5-66.5°C, (Found: C,49.8; H,5.2; N,3.6; $C_{16}H_{20}NO_6PS$ requires C,49.9; H,5.2; N,3.6%),

ν_{max} 1495, 1095, 930, 815 and 660 cm^{-1}. δ_H 2.42 (3H, s, p Me), 2.89 (3H, d, $PNCH_3$, J_{PH} 9Hz), 3.72 (6H, d, $POCH_3$, J_{PH} 11Hz), 6.91-7.47 (6H, m, ArH), 7.72-7.89 (2H, m, ArH), δ_p+7.9, m/e 385(M^+,27%), 230(100), 214(9) 198(20), 168(12), 120(14), 109(17), 91(14), 77(9).

(vii) N-(2-p-Toluenesulphonoxylphenyl)iminotriphenylphosphine (2.00 g, 3.8 mmol) was heated under reflux in tert-butylbenzene (10 ml) for 18 h. After this time ^{31}P n.m.r. showed that no reaction had occurred and the iminophosphorane was recovered in 96% yield.

14. Preparation of Phosphatriazenes: Reaction of Tervalent Phosphorus Compound with Azido Compounds

(i) N-(2-Hydroxyphenyl)-P,P,P-triphenylphosphatriazene was prepared by the addition of o-azidophenol (0.52 g, 3.85 mmol) in super-dry petrol (b.p. 40-60°C, 8 ml) to triphenylphosphine (0.99 g, 3.8 mmol) in super-dry petrol (b.p. 40-60°C, 5 ml) and super-dry ether (5 ml) with stirring under nitrogen at room temperature. A pale yellow solid gradually crystallised out of the reaction mixture. Care was taken to exclude light since on exposure the product discoloured rapidly. Removal of solvent by decantation gave the phosphatriazene (1.41 g; 94%) as a pale orange crystalline solid m.p. > 150°C (decomp.) (Found: C,72.4; H,5.0; N, 10.4; $C_{24}H_{20}N_3OP$ requires C,72.5; H,5.1; N,10.6%), ν_{max} 1440, 990 and 685 cm^{-1}.

δ_H 6.65-7.05 (3H, m, ArH), 7.20-7.92 (16H, m, ArH), OH not observed, δ_p+23.6, m/e 397 (M^+,not observed), 369 (M^+-N_2, 100%), 292 (17), 262 (70), 183 (68), 108 (39).

(ii) N-(2-Hydroxyphenyl)-P,P,P-tris(diethylamino)phosphatriazene was prepared by the addition of o-azidophenol (0.58 g, 4.3 mmol) in super-dry petrol (b.p. 40-60°C, 10 ml) to hexaethylphosphorus triamide (1.09 g, 4.4 mmol) in super-dry ether (4 ml) with stirring under nitrogen at room temperature. After 1 h a yellow oil had deposited which crystallised on cooling to -10°C to give yellow crystals of the phosphatriazene (1.28 g; 78%), m.p. 43-45°C (Found: C,56.6; H,9.2; N,21.8; $C_{18}H_{35}N_6OP$ requires C,56.5; H,9.2; N,22.0%), ν_{max} 1105, 950 and 660 cm^{-1}. δ_H 1.13 (18, t, $CH_2\underline{CH_3}$, J_{HH} 7Hz), 3.17 (12H, d of q, $\underline{CH_2}CH_3$, J_{HH} 7Hz, J_{PH} 10Hz), 6.70-7.08 (3H, m, ArH), 7.40-7.58 (1H, m, ArH), OH not observed, δ_N+94.6 (1N, d, J_{PN} 18Hz), +14.8 (1N, d, J_{PN} 24Hz), -139.1 (1N, d, 34Hz), -332.6 (3N, d, 18Hz), δ_p+40.6, m/e 382 (M^+, not observed), 354 (M^+-N_2, < 1%), 262(6), 233(12), 191(19), 119(100), 72(47).

(iii) N-(2-Benzoyloxyphenyl)-P,P,P-tris(dimethylamino) phosphatriazene was prepared by the method of Cadogan, Stewart and Tweddle.[38] o-Azidophenyl benzoate (3.41 g, 14 mmol) in dry cyclohexane (100 ml) was added to hexamethylphosphorus triamide (2.34 g, 14 mmol) in dry cyclohexane (180 ml) under nitrogen. The reaction mixture was stirred for 30 h at room temperature and the phosphatriazene (5.29 g; 92%), a yellow solid, crystallised out of

solution, m.p. > 95°C (decomp), ν_{max} 1730 cm^{-1} (C=O). δ_N + 134.7 (1N, d, J_{PN} 21Hz), +1.7 (1N, d, J_{PN} 27Hz), -132.9 (1N, d, J_{PN} 36Hz), -358.0 (3N, d, J_{PN} 24Hz), δ_p+42.4.

(iv) N-(2-p-Toluenesulphonoxylphenyl)-P,P,P-tris(diethylamino)phosphatriazene was prepared by the addition of o-azidophenyl tosylate (0.35 g, 1.2 mmol) in dry cyclohexane to hexaethylphosphorus triamide (0.30 g, 1.2 mmol) in dry cyclohexane (5 ml). On addition the solution instantly turned bright yellow and the reaction mixture was stirred for 22 h at room temperature. A yellow oil was deposited which was recrystallised from dry methylene chloride to give the phosphatriazene (0.56 g; 86%) as a yellow crystalline solid, m.p. 79-81°C (Found: C,56.0; H,7.7; N,15.7; $C_{25}H_{41}N_6O_3PS$ requires C,56.0; H,7.7; N,15.7%), ν_{max} (mull) 1300, 1090, 875 and 665 cm^{-1}. δ_H 1.06 (18H, t, $CH_2\underline{CH}_3$, J_{HH} 7Hz), 2.32 (3H, s, pMe), 3.12 (12H, d of q, J_{HH} 7Hz, J_{PH} 10Hz), 6.86-7.37 (6H, m, ArH), 7.80-7.97 (2H, m, ArH), δ_p+42.5, m/e 536 (M^+, 0.7%), 508 (2), 479(0.7), 365 (3), 353 (6), 247(22), 175(100), 106(45), 104(69).

15. Miscellaneous Reactions

(i) N-(2-p-Toluenesulphonoxylphenyl)iminohexaethylphosphorus triamide was prepared by heating under reflux for 8 h a solution of N-(2-p-toluenesulphonoxylphenyl)-P,P,P-tris(diethylamino)phosphatriazene (1.45 g, 2.7 mmol) in dry chlorobenzene (20 ml). The reaction was monitored by ^{31}P n.m.r. and it was observed that during this time the phosphatriazene resonance disappeared and another peak appeared,

δ_p+18.6. The solvent was removed *in vacuo* to leave a brown oil which on crystallisation from dry methylene chloride/ether at -10°C gave the iminophosphorane (0.24 g; 17%) as yellow-brown crystals, m.p. 76-77°C (Found: C,58.9; H,8.2; N,10.8; $C_{25}H_{41}N_4O_3PS$ requires C,59.0; H,8.1; N,11.0%), ν_{max} 1495, 1090 and 1015 cm^{-1}. δ_H 1.03 (18H, t, $CH_2\underline{CH}_3$, J_{HH} 6Hz), 2.36 (3H, s, p-Me), 3.07 (12H, d of q, $\underline{CH}_2CH_3$, J_{HH} 6Hz, J_{PH} 10Hz), 6.23-6.60 (2H, m, ArH), 6.72-6.94 (2H, m,ArH), 7.12-7.28 (2H, m,ArH), 7.64-7.84 (2H, m, ArH), δ_p+19.9, m/e 508 (M^+, 49%), 479(11), 365(48), 353(89), 282(21), 209(31), 175(100), 104(46).

The phosphatriazene showed no decomposition, by ^{31}P n.m.r., on heating under reflux in dry cyclohexane for 19 h.

(ii) Thermal decomposition of 2-phenylspiro-[1,3,2-dioxaphosphepan-2,2'-[1,3,2]-dioxaphospholan]. The phosphorane (0.64 g, 2.5 mmol) was heated under reflux in super-dry tert-butylbenzene (11 ml) for 48 h under nitrogen. The reaction was monitored by ^{31}P n.m.r. and it was observed that initially a single peak, δ_p-31.1 (phosphorane) was gradually replaced by peaks at δ_p+33.4 (10286%) and +18.3(3183%). Tetrahydrofuran was detected by glc analysis and the yield estimated to be 34%, by calibration against standard solutions in tert-butylbenzene. Removal of solvent *in vacuo* gave a dark brown oil from which the phosphorus containing products could not be separated but which were identified by peak enhancement as 2-phenyl-1,3,2-dioxaphospholan oxide (19%), δ_p+33.4, and 2-phenyl-1,3,2-dioxaphosphepan (81%), δ_p+18.3. The yields of these two compounds were estimated from the ^1H n.m.r. spectrum by integration of the methylene signals.

(iii) 2,2-Di(dimethylamino)-1,3,2-benzoxazaphosphole was prepared by the method of Cadogan, Stewart and Tweddle.[38] A suspension of N-(2-benzoyloxyphenyl)-P,P,P-tris(dimethylamino)phosphatriazene (6.83 g, 17 mmol) in dry cyclohexane (100 ml) was heated with rapid stirring at 75°C for 20 h, during which time nitrogen was slowly evolved. The light brown solid which deposited was filtered off and repeatedly recrystallised from dry methylene chloride/ether to give the phosphole (1.16 g; 30%) as colourless crystals, m.p. 174-177°C, δ_p +68.0.

(iv) 2,2-Di(dimethylamino)-3,4-biscarbomethoxy-Δ^6-1,5,2-benzoxazaphosphepine was prepared by the addition of 2,2-di(dimethylamino)-1,3,2-benzoxazaphosphole (0.43 g, 1.9 mmol) in dry methylene chloride (8 ml) to a stirred solution of dimethyl acetylene dicarboxylate (0.28 g, 2 mmol) in dry methylene chloride (6 ml) under nitrogen at room temperature. The reaction was monitored by ^{31}P n.m.r. which showed that the phosphole was completely converted over 2 h into a single product, δ_p +71.6. Removal of solvent *in vacuo* gave a pale orange solid which was recrystallised from dry ether to give the phosphepine as pale brown crystals (0.64 g; 90%), m.p. 164-166°C (Found: C,52.5; H,6.1; N,11.1; $C_{16}H_{32}N_3O_5P$ requires C,52.3; H,6.0; N,11.4%), ν_{max} 1730 (C=O), 1640 (C=O), 1430, 1095 and 1000 cm^{-1}. δ_H 2.73 (12H, d, NMe_2, J_{PH} 10Hz), 3.59 (3H, s, CO_2Me), 3.87 (3H, s, CO_2Me), 6.82-7.38 (4H, m, ArH), δ_C 37.1 (d, $N(CH_3)_2$, J_{PC} 4Hz), 49.9 (s, $CO_2\underline{CH}_3$), 51.9 (s, $CO_2\underline{CH}_3$), 61.4 (d, P=C, J_{PC} 178Hz), 120.5-141.1, 159.6

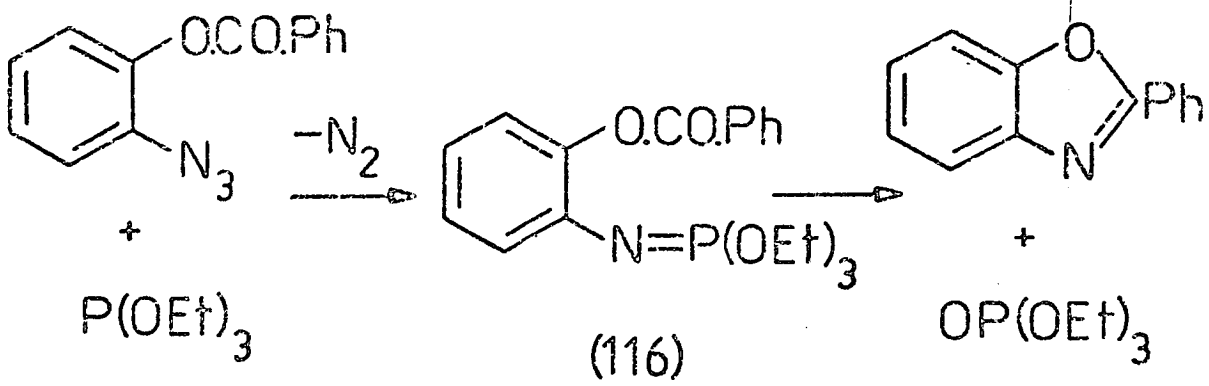
(d, C=N, J_{PC} 4Hz), 167.1 168.0 168.8 (2, $\underline{C}O_2Me$), δ_p+72.2, m/e 367 (M^+, 100%), 336 (7), 323 (8), 309 (48), 308 (59), 280 (69), 135 (83), 106 (43), 76 (26).

2,2-Di(dimethylamino)-3,4-biscarbomethoxy-Δ^6-1,5,2-benzoxazaphosphine.hydrochloride was prepared by the addition of concentrated hydrochloric acid (0.4 ml, 4 mmol) to a stirred solution of 2,2-di(dimethylamino)-3,4-biscarbomethoxy-Δ^6-1,5,2-benzoxazaphosphine (0.73 g, 2 mmol) in methylene chloride (8 ml) at room temperature. The reaction was monitored by ^{31}P n.m.r. and it was observed that after 1 h the starting material had been completely converted into a single product. Removal of the solvent *in vacuo* left a foam which was crystallised from methanol/ether at -10°C to give the hydrochloride as colourless crystals (0.56 g; 70%), m.p. 162°C (decomposes with gas evolution) (Found: C,47.3; H,5.9; N,10.7; $C_{16}H_{23}ClN_3O_5P$ requires C,47.6; H, 5.7; N,10.4%), ν_{max} 2650 (very broad peak 2100-3000 cm^{-1}), 1755 (C=O), 1720 (C=O), 1440, 1090 and 1010 cm^{-1}. δ_H 2.79 (12H, d, NMe_2, J_{PH} 10Hz), 3.78 (3H, s, CO_2Me), 4.04 (3H, s, CO_2Me), 7.04-7.58 (3H, m, ArH), 7.86-8.10 (1H, m, ArH), 13.62 (1H, broad s sharpens on cooling to -55°C), δ_C37.1 (d, $N(CH_3)_2$, J_{PC} 5Hz), 51.9 (s,$CO_2\underline{C}H_3$), 53.1 (s, $CO_2\underline{C}H_3$), 75.0 (d, P-C, J_{PC} 174 Hz), 121.3-139.8, 158.9 (d, C=N, J_{PC} 3Hz), 161.8 (d, $\underline{C}O_2Me$, J_{PC} 17Hz), 163.9 (d, $\underline{C}O_2Me$, J_{PC} 13Hz), δ_p+55.9, m/e 405, 403 (M^+, not observed), 367 (M^+-HCl, 100%).

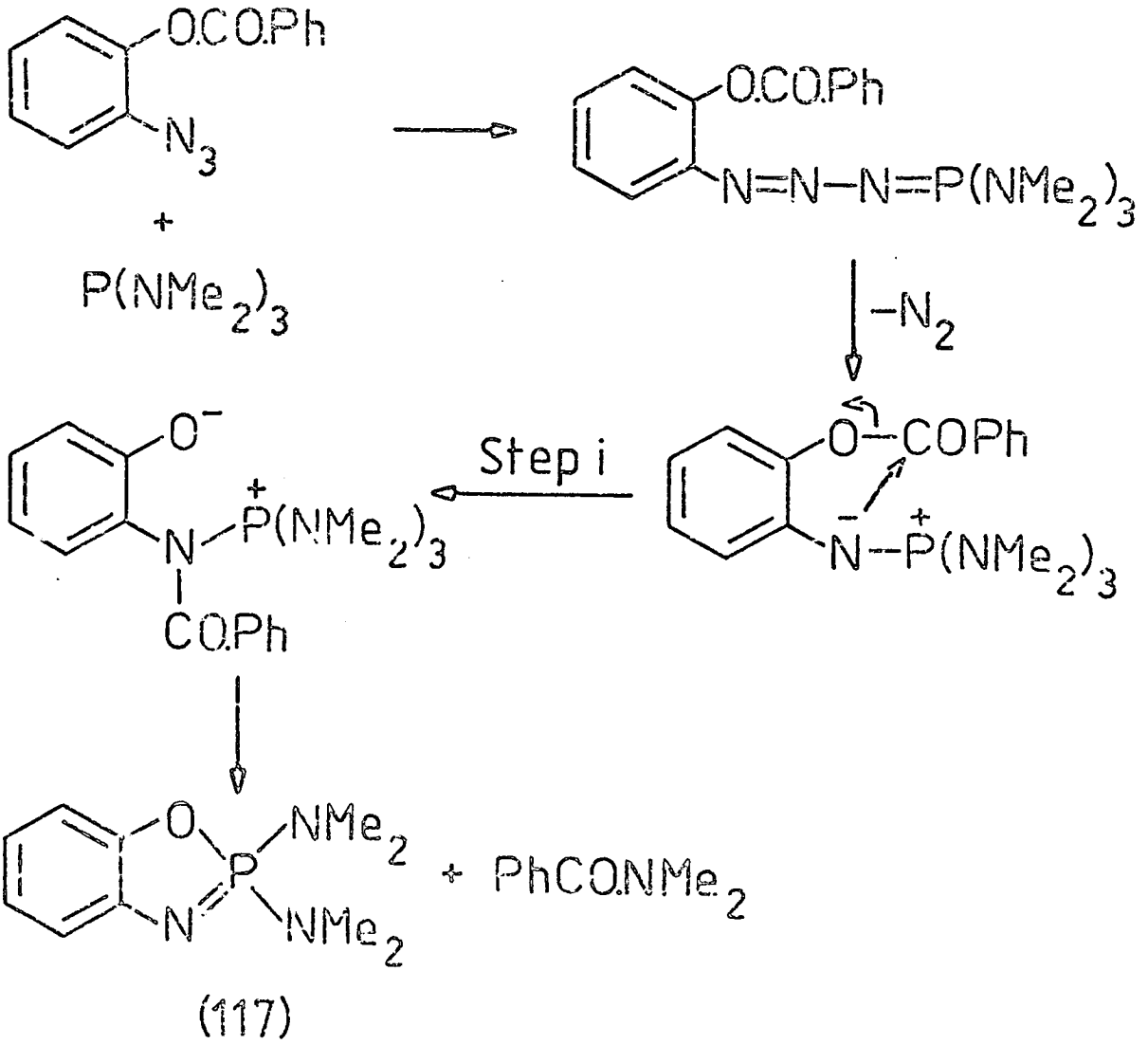
On addition of excess triethylamine to the salt in deuterochloroform at room temperature, it was observed by ^{31}P n.m.r. that the ylide was regenerated within seconds.

SECTION III

DISCUSSION



Scheme 90



Scheme 91

Discussion

Preamble

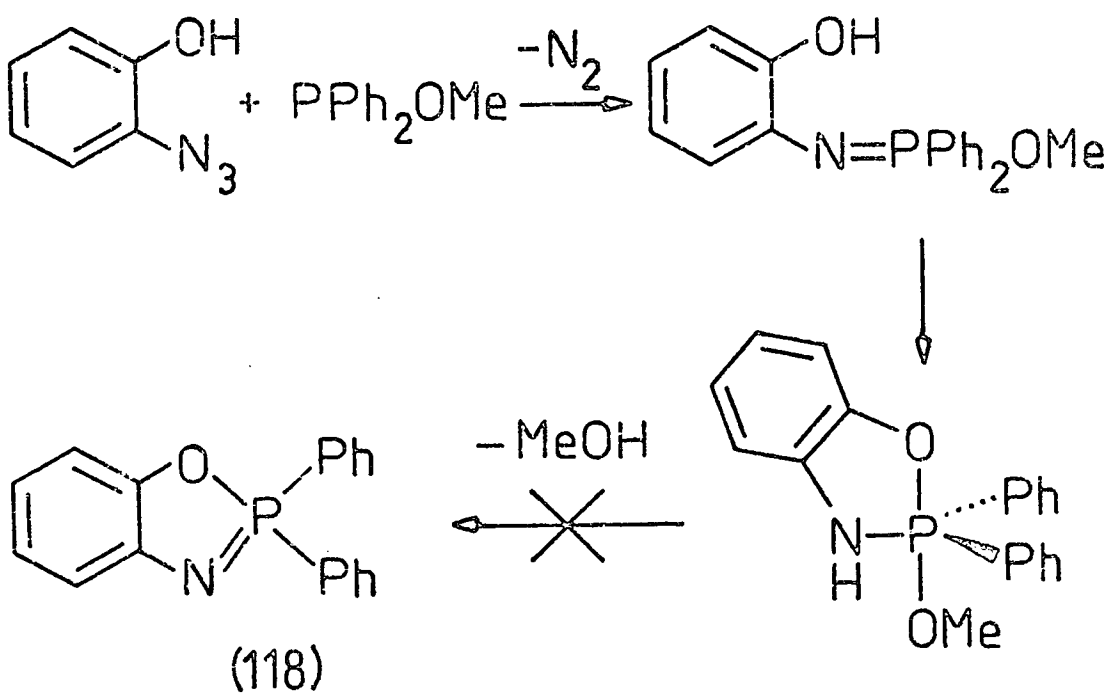
Leyshon and Saunders[62] have shown that reaction of o-azidophenyl benzoate with triethylphosphite leads to the formation of an intermediate iminophosphorane (116) which undergoes intramolecular ring closure to give 2-phenyl-1,3,2-benzoxazole and triethylphosphate (Scheme 90). In a preliminary study, as part of an Honours Degree programme, the author found that reaction of o-azidophenyl benzoate with hexamethylphosphorus triamide at 80°C in cyclohexane followed a different course to give a novel cyclic iminophosphorane (117) and N,N-dimethylbenzamide (Scheme 91). It was thought that the key step in the formation of 2,2-di(dimethylamino)-1,3,2-benzoxazaphosphole (117, δp +68.0) involved migration of the benzoyl group from oxygen to nitrogen as shown in Step 1.

The reaction in Scheme 91 was of particular interest because past work in this laboratory had been concerned with intramolecular reactions of iminophosphoranes[64] and the preparation and study of benzoxaza- and benzthiaza-phospholines[147-151] in particular. Inspection of Scheme 91 shows that if the migration in Step 1 is general; i.e. occurs for groups other than benzoyl, the reaction might provide a simple route to other novel phosphorus heterocycles. For this reason, a detailed study was undertaken of the reactions of bifunctional azides with tervalent phosphorus reagents, beginning with o-azido phenol.

1. Reaction of bifunctional azides with tervalent phosphorus reagents; formation of pentacoordinate phosphoranes

1.1 o-Azidophenol with methyl diphenylphosphinite

When o-azidophenol was added to methyl diphenylphosphinite in super-dry ether at room temperature, the colourless solution instantly turned bright yellow and nitrogen was rapidly evolved. After a few minutes the reaction had subsided and a colourless solid was deposited. Examination of this compound by ^{31}P n.m.r. revealed a large negative phosphorus chemical shift, δp -36.0, which pointed towards a pentacoordinate structure rather than the expected iminophosphorane structure (118), formed by intramolecular hydrogen migration and loss of methanol (Scheme 92).



(118)

Scheme 92

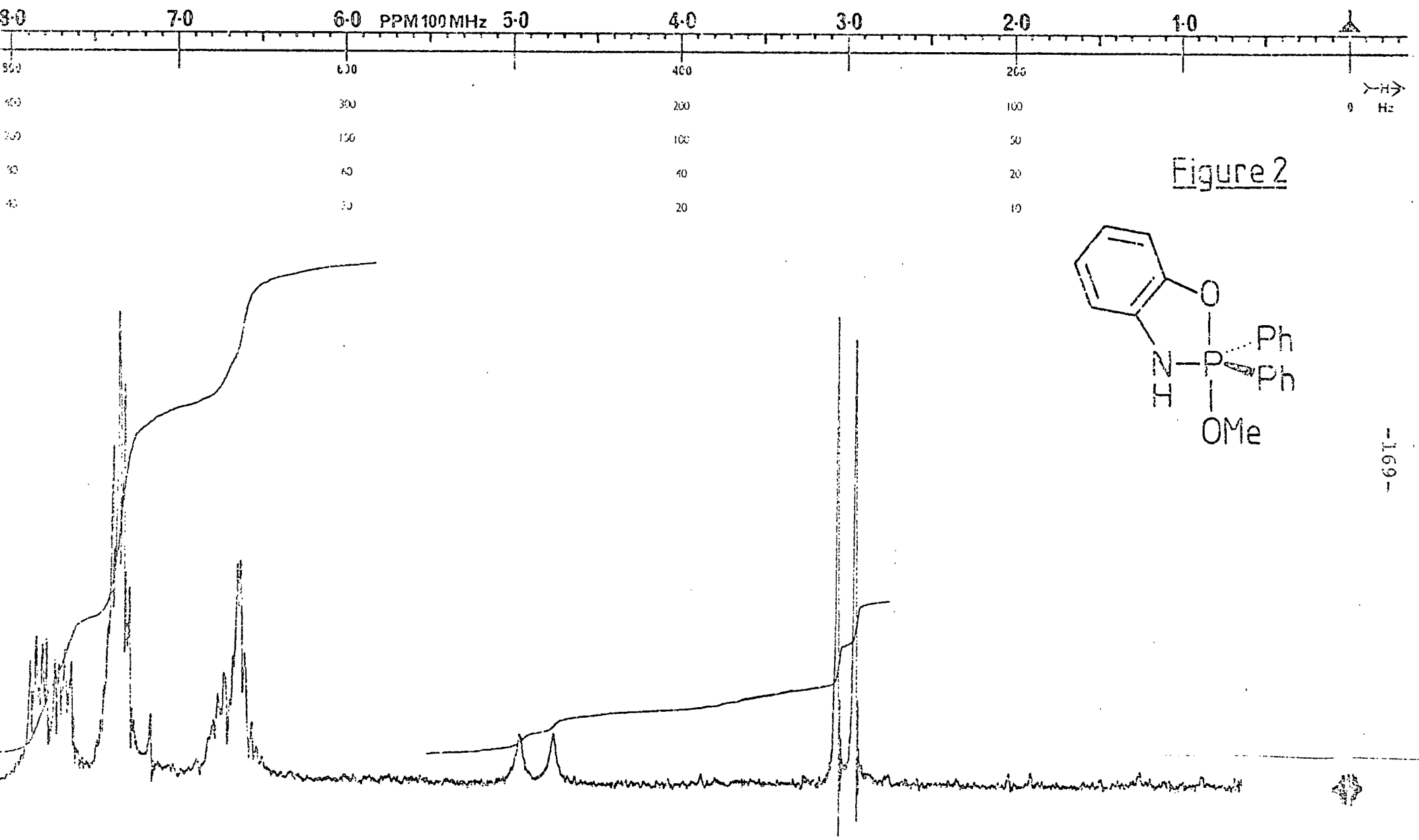
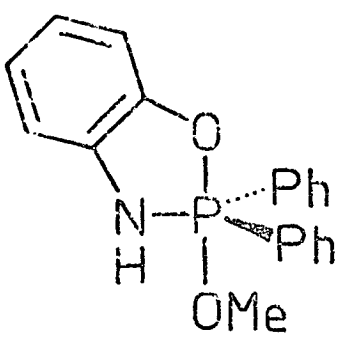


Figure 2

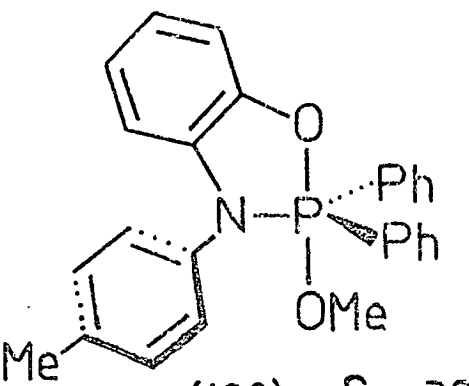
On the basis of the analytical, spectral and chemical evidence the structure of the colourless product was established as 2,2-diphenyl-2-methoxy-1,3,2-benzoxazaphospholine (119). Elemental analysis gave percentage compositions for carbon, hydrogen and nitrogen consistent with an empirical formula $C_{19}H_{18}NO_2P$. This was verified by observation in the mass spectrum of a molecular ion peak at m/e 323.

The ^1H n.m.r. spectrum of the product is shown in Figure 2. The structurally significant peaks are located at δ_H 2.98, a three proton doublet (J_{PH} 11Hz) assigned to a POMe group, and δ 4.86, a single proton doublet with a large coupling constant (J_{PH} 20Hz) typical of a two bond coupling through nitrogen.[241] This absorption was assigned to a PNH grouping. Evidence in support of the latter was obtained from the I.R. spectrum which showed a strong sharp NH stretch at 3460 cm^{-1}.

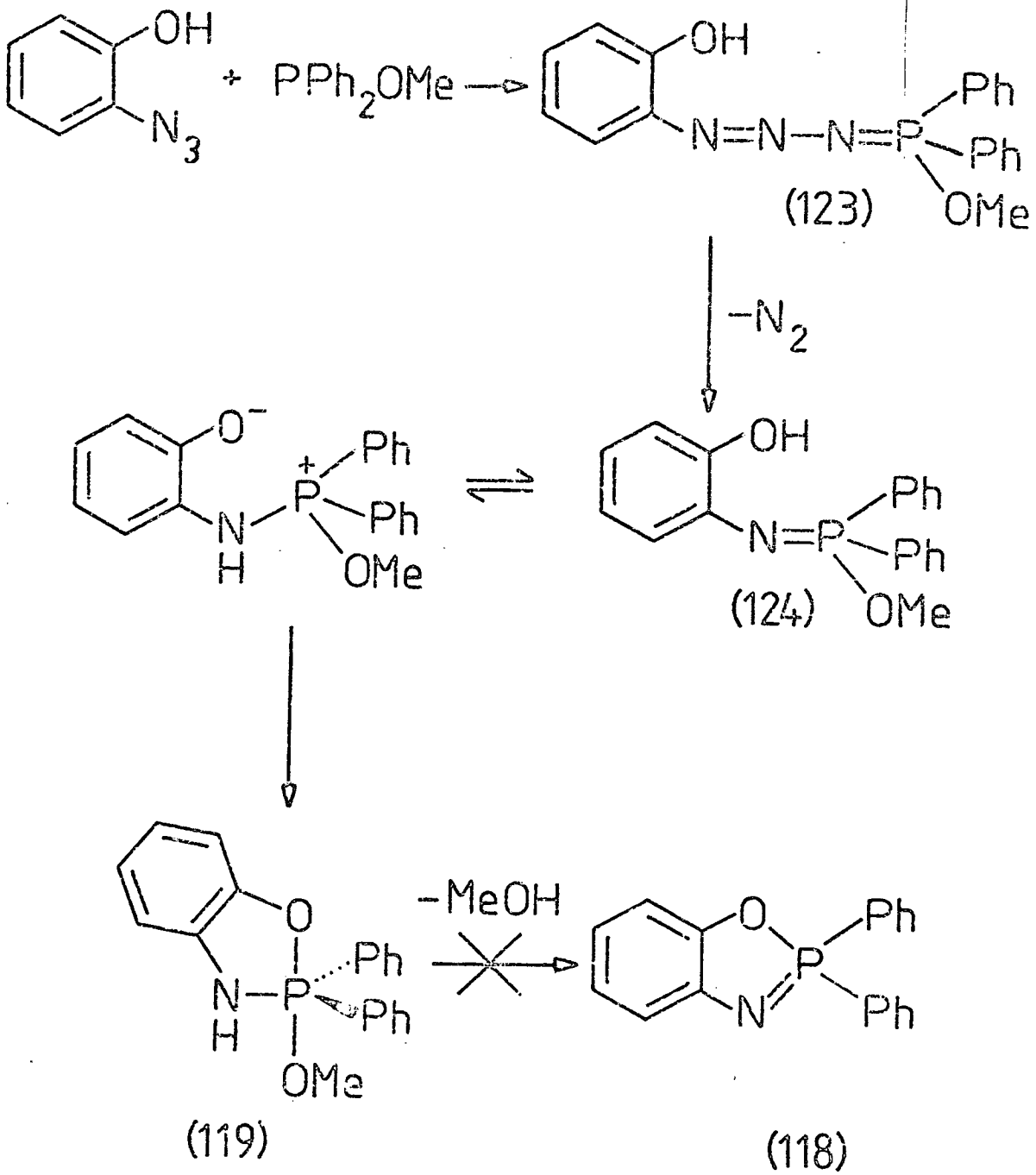
As already mentioned, the sign and magnitude of the ^{31}P chemical shift, δ_p -36.0, indicated a pentacoordinate environment for the phosphorus nucleus (see Experimental page 85). In addition, the magnitude of the shift was comparable to that previously observed for N-substituted benzoxazaphospholines of the type (120, δ_p -39.9).[151]



(119) δ_P-36·0

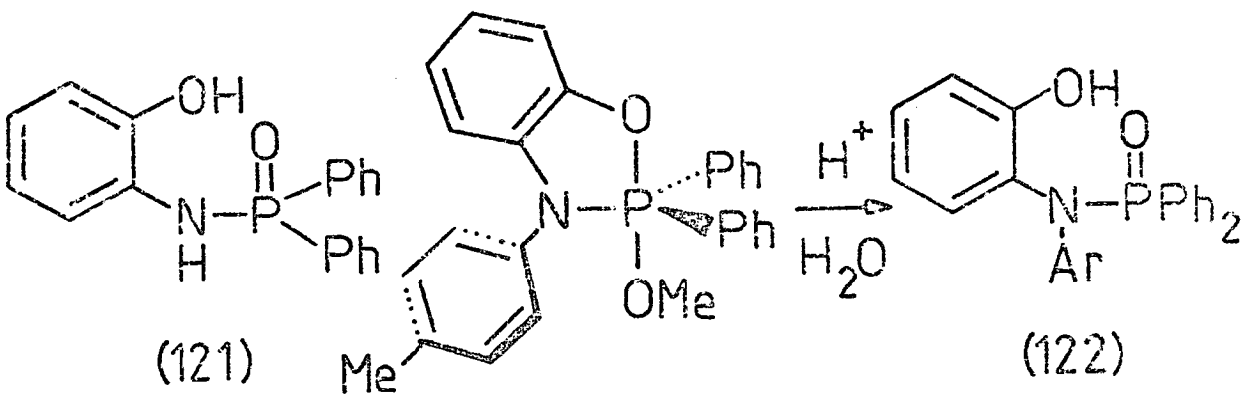


(120) δ_P-39·9


OH
N3
+ PPh2OMe
OH
N=N–N=P
Ph
Ph
OMe
(123)
–N2
O⁻
N
H
P⁺
Ph
Ph
OMe
OH
N=P
Ph
Ph
OMe
(124)
O
N
H
P
Ph
Ph
OMe
(119)
–MeOH
O
N
P
Ph
Ph
(118)

Scheme 94

Chemical evidence in support of the proposed structure (119) was obtained by acid hydrolysis in ether, which gave a 95% yield of a single phosphorus containing product; the phosphinamidate (121). This result accords with the formation of (122), previously observed by Cadogan *et al.*[242] from the acid hydrolysis of 2,3-dihydro-2,2-diphenyl-2-methoxy-3-p-tolyl-1,3,2-benzoxazaphosph(V)ole (Scheme 93).



Scheme 93

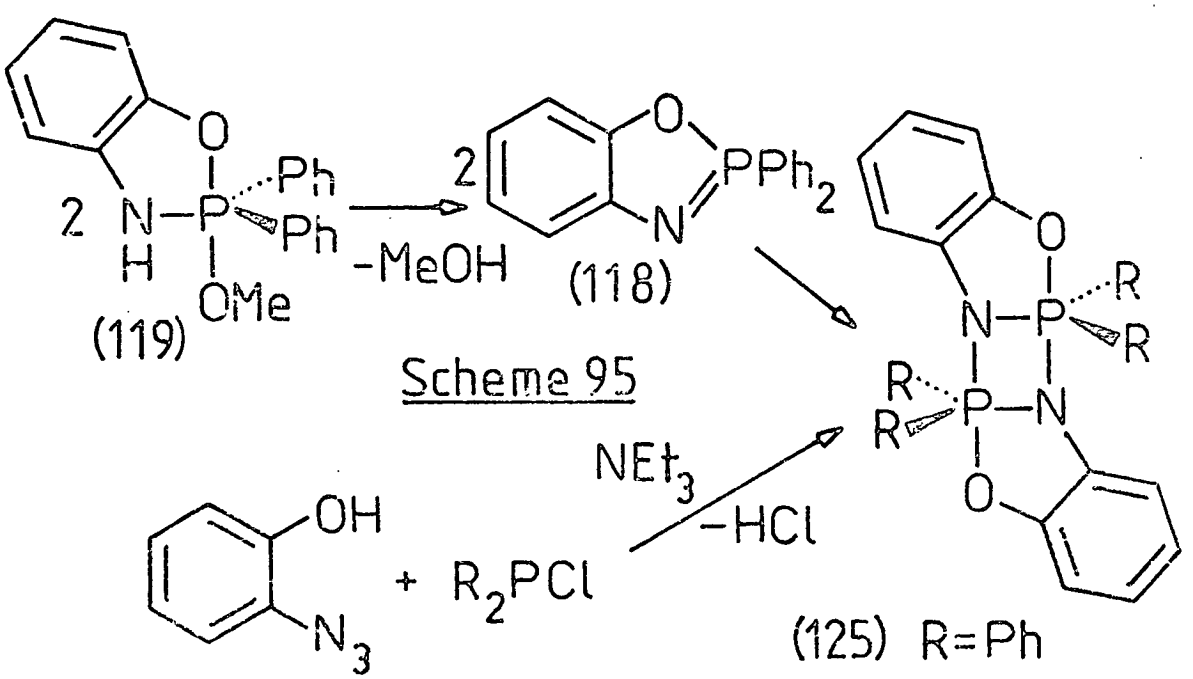
Final proof of the structure (119) was obtained by an alternative synthesis[243] from o-aminophenol, methyl diphenylphosphinite, and N-chlorodi-isopropylamine according to the method of Trippett.[145]

1.2 Mechanism

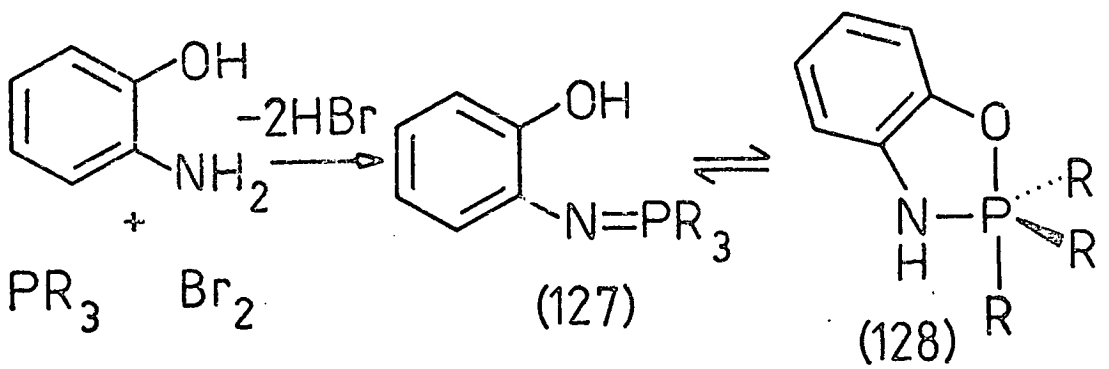
The proposed mechanism is shown in Scheme 94 and involves nucleophilic attack by phosphorus at the terminal azide nitrogen,[14] leading to the formation of a coloured phosphatriazene (123), which decomposes with loss of nitrogen to give an intermediate iminophosphophosphorane (124). Subsequent proton transfer to nitrogen, followed by attack of the oxyanion at electropositive phosphorus then gives rise to the benzoxazaphospholine (119). Interestingly, loss of

methanol from this product is not observed. This would be equivalent to the elimination of N,N-dimethylbenzamide which occurs upon formation of 2,2-di(dimethylamino)-1,3,2-benzoxazaphosphole (see Scheme 91). That methanol is not lost from (119) could be a consequence of different reaction conditions since during the course of this study a co-worker[244] has observed the formation of the diazadiphosphetidine (125) in 71% yield from the thermolysis of (119) in boiling toluene for 1½ h. This product is thought to arise by loss of methanol from (119), and subsequent dimerisation[37] of the derived benzoxazaphosphole (118) (Scheme 95).

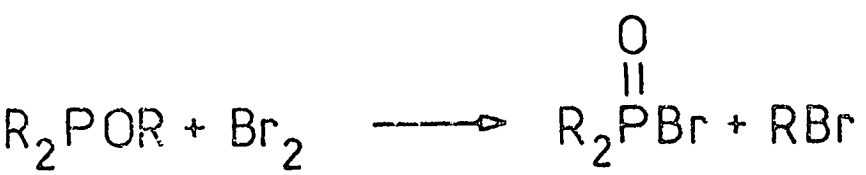
In connection with the latter observation it is worth noting that Kabachnik *et al.*[35] have observed the analogous elimination of hydrogen chloride in the formation of (126) from the reaction of dialkyl- or diaryl-phosphinous chlorides with o-azidophenol (Scheme 96).



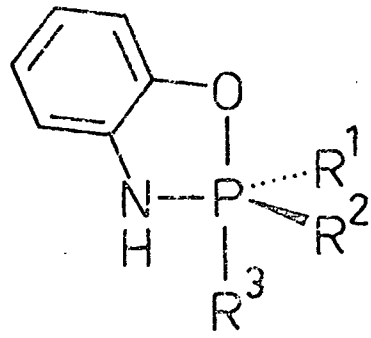
Finally, attention is drawn to studies by Stegmann *et al.*[164] who found that iminophosphoranes of the type (127) existed in equilibrium with a pentacoordinate phosphorane form (128) as shown in Scheme 97. The former compounds were prepared by the procedure of Kirsanov, a method that is largely restricted to tervalent phosphorus reagents containing phosphorus-carbon bonded ligands. Introduction of alkoxy groups, for example, would be expected to lead to rearrangement of the phosphorus reagent, by a variation of the Arbuzov reaction (Scheme 98).[245] By comparison, the reaction of bifunctional azides with tervalent phosphorus reagents does not suffer this drawback and offers a potentially simple, and mild route to pentacoordinate phosphoranes, a class of compounds which are generally thermally and hydrolytically unstable. The utility of this approach is discussed in the following section.



Scheme 97



Scheme 98



(129)

	R^1	R^2	R^3	δ_p ($CDCl_3$)	Yield (%)	M.Pt. (°C)	Analysis[a] C	H	N	M.I.[a,b]
130	OMe	OMe	OMe	-51.5	98	42-44°C	47.0 46.8	6.0 6.1	6.1 6.1	231
131	OEt	OEt	OEt	-53.9	96	32-34°C	-	-	-	273.112342 273.112987
132	Ph	OMe	OMe	-39.8	92	70-72°C	60.8 60.7	5.8 5.8	5.0 5.1	277
133	Ph	Ph	OMe	-36.0	90	>240°C (decomp.)	70.3 70.6	5.6 5.6	4.4 4.3	323
134	Ph	$-OCH_2CH_2O-$		-26.4	70	141-144°C	61.3 61.1	5.1 5.1	5.0 5.1	275
135	Ph	$-CMe_2CH_2CH_2-$		-40.7	83	142-145°C	71.6 71.6	7.2 7.1	4.7 4.9	285

Table 1

[a] Top row found, bottom row requires.

[b] M.I., molecular ion.

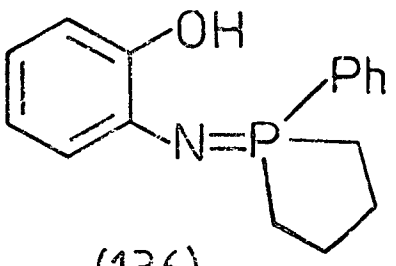
1.3 General reaction of o-azidophenol with tervalent phosphorus reagents

Following the successful isolation of 2,2-diphenyl-2-methoxy-1,3,2-benzoxazaphospholine from the reaction of o-azidophenol with methyl diphenylphosphinite, the scope of the reaction was investigated with tervalent phosphorus reagents of different nucleophilicity; including a phosphite, phosphonite, phosphinite, dioxaphospholan, and a phosphetan.

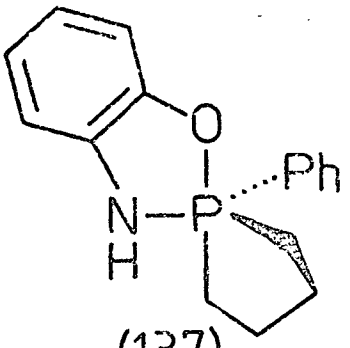
The general procedure adopted was to add o-azidophenol to the tervalent phosphorus reagent in super-dry petrol or ether at room temperature. After the evolution of nitrogen had ceased the products were isolated as colourless solids by crystallisation and identified as pentacoordinate phosphoranes of the type (129), principally on the basis of their large negative phosphorus chemical shifts. Additional support for this assignment was obtained by the observation, in most cases, of a NH doublet (J_{PH} 18-28 Hz) in the ^{1}H n.m.r. spectrum and a strong NH stretch in the I.R. spectrum at *ca.* 3450 cm^{-1}.

Table 1 lists the benzoxazaphospholines prepared in this manner together with their ^{31}P n.m.r. chemical shifts, yields, melting points, elemental analyses and molecular ion masses.

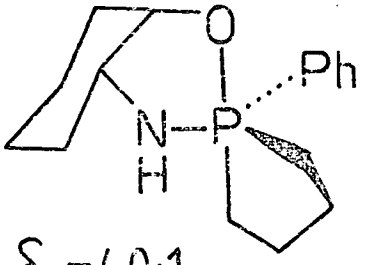
The benzoxazaphospholines (130-135) were hygroscopic solids which hydrolysed rapidly on exposure to the atmosphere. The triethylphosphite derivative (131) could not be obtained analytically pure for this reason, despite rigorous attempts to exclude water. Otherwise, the compounds were stable and could be stored indefinitely under dry nitrogen at -10°C.



(136)

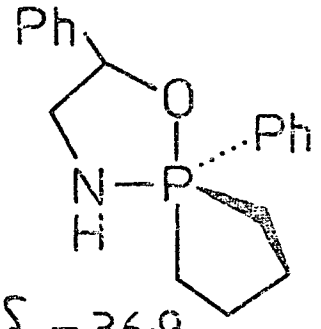


(137)



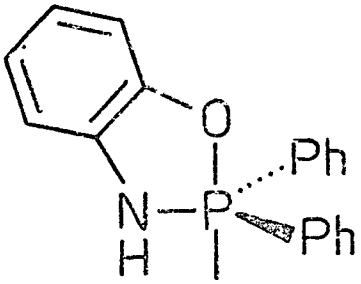
δ_P -40·1

(146)



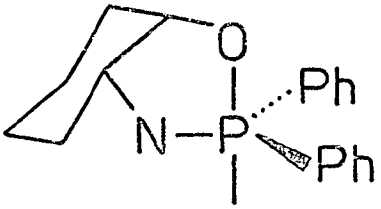
δ_P -36·9

(149)



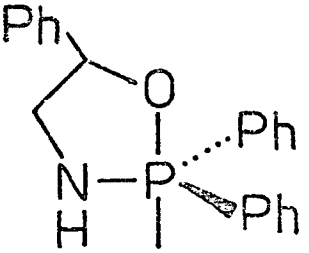
δ_P -36·0

(133)



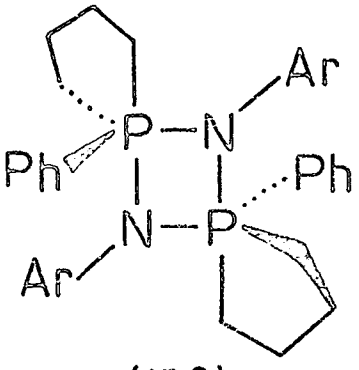
δ_P -44·7

(145)

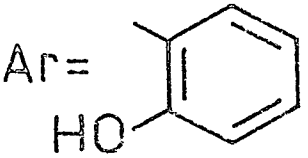


δ_P -42·6

(148)



(138)

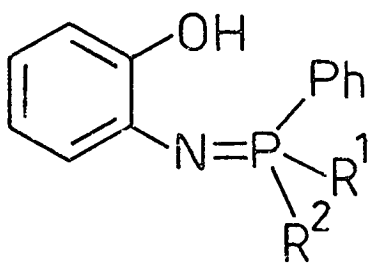


The majority of the benzoxazaphospholines were sparingly soluble in ether but dissolved readily in chloroform. In marked contrast to this observation, the colourless product obtained from the reaction of o-azidophenol with 1-phenylphospholan was found to be sparingly soluble in both chloroform and methylene chloride, but could be dissolved in more polar dimethyl sulphoxide. That this compound might be structurally different from (130-135) was indicated by the observation of an atypical broad absorption at 3140 cm^{-1} in its I.R. spectrum, indicative of an hydroxyl group. An initial proposal that the compound was an iminophosphorane of the type (136) was discounted on the basis of the observed ^{31}P chemical shift at δ_p -20.1, which indicated a pentacoordinate phosphorus environment. This shift differs from that of the oxazaphosphoranes (146; -40.1) and (149; -36.9) by 17 and 20 ppm respectively, whereas the shifts for the corresponding methyl diphenylphosphinite derivatives (145; -44.7) and 148; -42.6) differ by only 6 and 8 ppm from the benzoxazaphospholine (133; -36.0). This argues strongly against the benzoxazaphospholine structure (137) for the compound obtained from the reaction of o-azidophenol with 1-phenylphospholan.

A structure that could account for these observations is the diazadiphosphetidine (138), formed by intermolecular dimerisation of the intermediate iminophosphorane (136). Although no parent ion peak was observed at 542 it is well known that diazadiphosphetidines cleave to the monomer upon thermolysis in the mass spectrometer.[164,244]

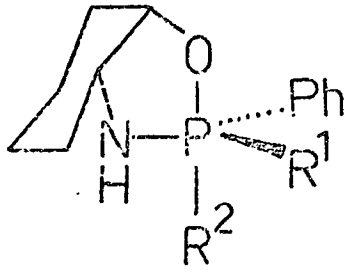
Whilst the available evidence points to the diaza-diphosphetidine (138) as the most likely structure, any final assignment must await the results of molecular weight and/or X-ray crystal structure determinations.

In some instances, the reaction of o-azidophenol with tervalent phosphorus reagents resulted in the formation of iminophosphoranes. Thus, addition of the azido compound to diethylphenylphosphine and 1-phenylphosphorinan at room temperature led to the initial formation of unstable deeply coloured phosphatriazenes which decomposed at higher temperatures with loss of nitrogen to give, in each case, a single phosphorus-containing product. These compounds were identified as iminophosphoranes by their characteristic positive ^{31}P chemical shifts, and a broad OH stretch at *ca.* 3270 cm^{-1}. Physical and analytical data for these compounds are listed in Table 2.



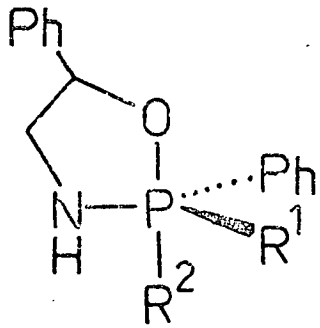
	R^1	R^2	$\delta_p(CDCl_3)$	Yield (%)	M.Pt. (°C)	Analysis[a] C	H	N	Molecular ion
139	Et	Et	+21.5	87	liquid	70.3 70.3	7.3 7.4	5.1 5.1	273
140	$-(CH_2)_5-$		+7.7	71	106-108°C	71.7 71.6	7.0 7.1	4.8 4.9	285

Table 2



(143)

	R^1	R^2	$\delta_p(CDCl_3)$	Yield (%)	M.Pt. (^oC)	Analysis[a] C	H	N	M.I.[a,b]
145	Ph	OMe	-44.7	62	71-73	69.1 69.3	7.4 7.3	4.0 4.3	329
146	$-(CH_2)_4-$		-40.1	60	37-39	-	-	-	277.155569 277.159544

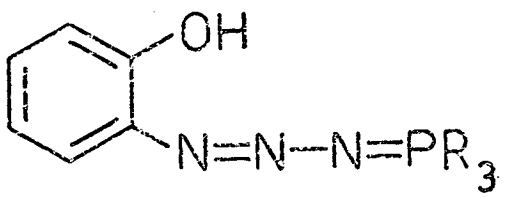


(144)

	R^1	R^2	$\delta_p(CDCl_3)$	Yield (%)	M.Pt. (^oC)	Analysis[a] C	H	N	M.I.[a,b]
147	OMe	OMe	-44.8	65	55-58	62.7 62.9	6.5 6.6	4.7 4.6	305
148	Ph	OMe	-42.6	85	103-105	71.7 71.8	6.5 6.3	3.9 4.0	not observed
149	$-(CH_2)_4-$		-36.9	84	45-47	-	-	-	299.143432 299.143894

Table 3

In the case of triphenylphosphine and hexaethylphosphorus triamide it was possible to isolate and characterise the intermediate phosphatriazenes (141) and (142) which on thermolysis yielded a plethora of phosphorus containing products rather than the expected iminophosphorane.[246]

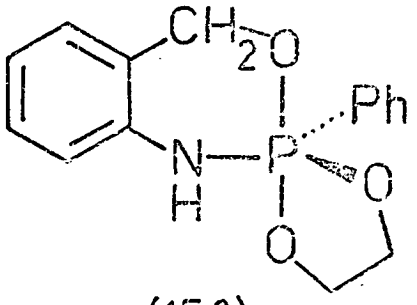


(141) R=Ph (142) R=NEt_2

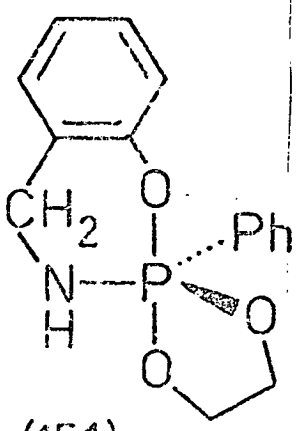
1.4 Reaction of other azido alcohols with tervalent phosphorus reagents

1.4.1 trans-2-Azidocyclohexanol; 2-azido-1-phenyl-1-ethanol

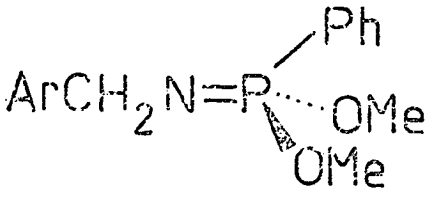
In view of the facile formation of pentacoordinate benzoxazaphospholines from o-azidophenol and tervalent phosphorus reagents it was decided to examine the corresponding reactions with aliphatic azido alcohols such as trans-2-azidocyclohexanol and 2-azido-1-phenyl-1-ethanol. Since such azides are known to be less reactive than aromatic azides,[61] it was necessary to use more nucleophilic phosphorus reagents to promote reaction. The products obtained are listed in Table 3 together with their physical and analytical data which are consistent with the pentacoordinate structures 143 and 146. Qualitatively, the oxazaphospholes (145-149) were hydrolytically more unstable than the corresponding benzoxazaphospholines. This is reflected in the number of derivatives which could not be isolated in an analytically pure form (see also Table 8 and page 227).



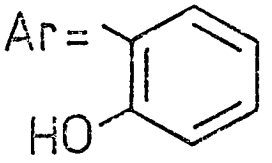
(150)

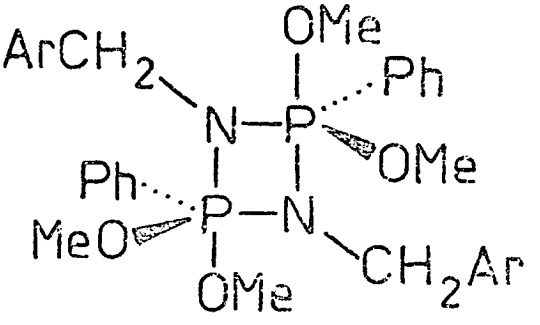


(151)

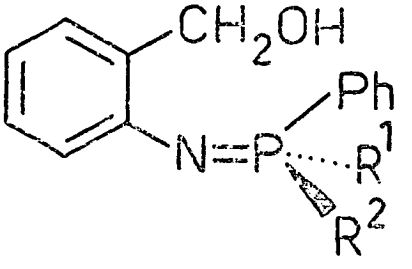


(152)





(153)



(154) R^1 = OMe R^2 = OMe (155) R^1 = Ph R^2 = OMe

(156) R^1 = Ph R^2 = Ph

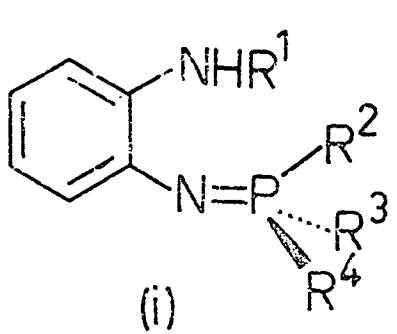
	δ_p ($CDCl_3$)	Yield (%)	M.Pt. (°C)	Analysis[a] C	H	N	Molecular ion
150	-40.9	60	144-147	62.1 62.3	5.6 5.6	4.8 4.8	289
151	-44.5	61	95-98	62.5 62.3	5.5 5.6	4.8 4.8	289
155	+22.4	88	65-68	71.0 71.2	6.1 6.0	4.2 4.2	337
156	+6.7	51	148-149	78.1 78.3	5.7 5.8	3.6 3.7	383

Table 4

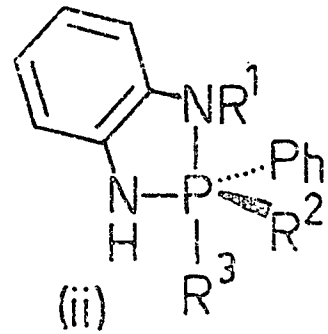
1.4.2 o-Hydroxybenzyl azide; o-azidobenzyl alcohol

Generally speaking, the vast majority of pentacoordinate phosphoranes isolated to date contain at least one five-membered ring, whereas those compounds which contain a six-membered ring are seldom encountered in the literature.[201] Accordingly, an attempt was made to provide a general route to this class of compound by exploring the reactions of o-hydroxybenzyl azide and o-azidobenzyl alcohol with various tervalent phosphorus reagents.

Initial investigations proved successful and in the case of 2-phenyl-1,3,2-dioxaphospholan led to the ready formation of the isomeric pentacoordinate phosphoranes (150) and (151). However, further reactions with other tervalent phosphorus reagents gave unstable products, tentatively identified by their ^{31}P chemical shifts as iminophosphoranes. Thus, addition of o-hydroxybenzyl azide to dimethyl phenylphosphonite gave three products; an iminophosphorane (152; δ_p+ 21.7), dimethyl phenylphosphonate, presumably formed by hydrolysis of (152), and the diazadiphosphetidine (153; δ_p- 62.9). That the iminophosphorane (152) is hydrolytically unstable is not unexpected since the ease of hydrolysis can be correlated with the basicity of nitrogen.[70] In the case of (152), for example, there is no possibility for the delocalisation of the negative charge on nitrogen into the aromatic ring, since conjugation is precluded by the intervening methylene group. As a result hydrolysis is facile.



(i)



(ii)

Table 5

	Isomer	R^1	R^2	R^3	R^4	$\delta_p(CDCl_3)$	Yield (%)	M.Pt. (°C)	Analysis[a] C	H	N	M.I.[a,b]
158	i	H	Ph	$-OCH_2CH_2O-$		-39.0	72	137-141	61.1 61.3	5.5 5.5	10.3 10.2	274
159	i	H	Ph	$-OCH_2CH_2CH_2O-$		-57.8	53	140-143	62.3 62.5	6.0 5.9	9.6 9.7	288
160	ii	H	Ph	Ph	OMe	+19.7	86	54-56	-	-	-	322.123619 322.123494
161	i	Ts	Ph	$-OCH_2CH_2O-$		-28.9	29	118-120	58.6 58.9	4.9 4.9	6.3 6.5	428
162	ii	Ts	OMe	OMe	OMe	+5.0	95	98-100	49.9 50.0	5.4 5.5	7.1 7.3	384
163	ii	Ts	Ph	OMe	OMe	+21.4	87	102-103	58.6 58.6	5.4 5.4	6.5 6.5	430
164	ii	Ts	Ph	$-O(CH_2)_4O-$		+19.7	64	131-132	60.3 60.5	5.7 5.5	6.0 6.1	456
165	ii	Ts	Ph	$-(CH_2)_4-$		+37.5	75	175-177	64.9 65.1	5.9 5.9	6.6 6.6	424

Other unstable iminophosphoranes were also obtained upon reaction of o-azidobenzyl alcohol with methyl diphenylphosphinite (155, δ_p +22.4), and dimethyl phenylphosphonite (154, δ_p +36.4). However, it is unclear why these compounds should decompose on standing at room temperature in solution since the corresponding triphenylphosphine derivative (156, δ_p +6.7) is stable indefinitely under the same conditions.

The physical and analytical data obtained for compounds (150), (151), (155) and (156) are listed in Table 4 together with their yields.

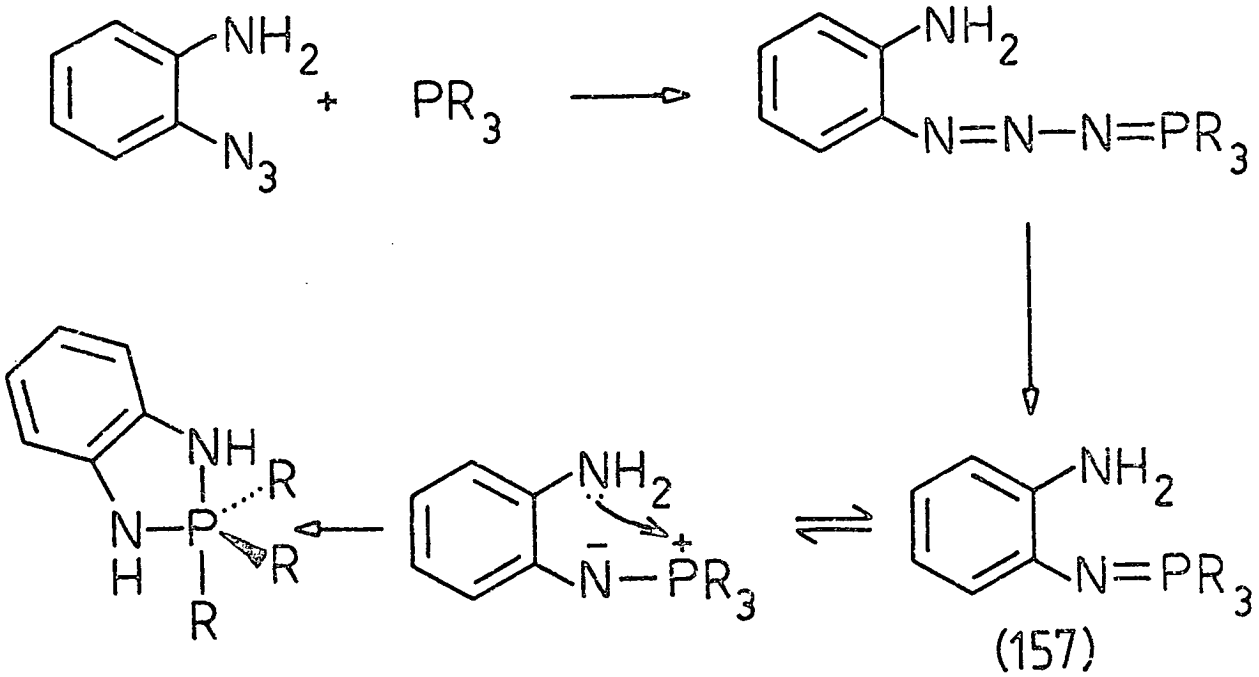
1.5 Reaction of o-azidoanilines with tervalent phosphorus reagents; formation of benzdiazaphospholines

Few examples of benzdiazaphospholines are known,[166] and recent attempts at their synthesis *via* reaction of o-phenylenediamine with tervalent phosphorus reagents in the presence of N-chlorodi-isopropylamine have failed.[146] It was therefore considered desirable to investigate the synthetic potential of the reaction of o-azidoaniline with tervalent phosphorus reagents as a route to this class of compounds.

1.5.1 o-Azidoaniline

As in the case of the corresponding reaction with o-azidophenol condensation of 2-phenyl-1,3,2-dioxaphospholan and 2-phenyl-1,3,2-dioxaphosphepan with o-azidoaniline led to the immediate generation of pentacoordinate phosphoranes, characterised as (158) and (159) respectively on the basis of their large negative ^{31}P n.m.r. shifts (see Table 5).

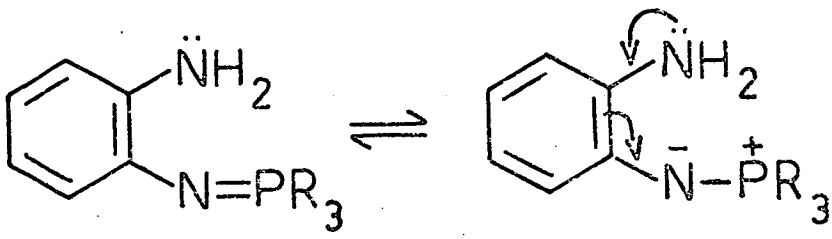
A plausible mechanism for the formation of (158) and (159) is shown in Scheme 99 and involves the intermediacy of an iminophosphorane (157) which rearranges by nucleophilic attack of the amino nitrogen at electropositive phosphorus followed by a proton shift to the ylide nitrogen.



Scheme 99

This reaction however, whilst providing a useful route to the benzdiazaphospholines (158) and (159) was found not to be general and the corresponding reaction with other tervalent phosphorus reagents led to the formation of an unstable iminophosphorane rather than a pentacoordinate phosphorane. Thus, iminophosphoranes were observed transiently with methyl diphenylphosphinite (160, δ_p+19.7), dimethyl phenylphosphonite (δ_p+17.7), 2-phenyl-1,3,2-dioxaphosphepan (δ_p+15.0), and 1-phenylphospholan (δ_p+34.9). In all cases, instability

could be ascribed to increased basicity, leading to facile hydrolysis, due to delocalisation of the lone pair of electrons on nitrogen into the ylide system as shown in Scheme 100 (see also compound (152) on page 183). Significantly, the related N-phenyl-iminophosphoranes which have no such electron donation to the ylide nitrogen are relatively stable and consequently isolable.[232]



Scheme 100

The physical and analytical data for the compounds obtained from the reaction with o-azidoaniline with tervalent phosphorus reagents are listed in Table 5.

1.5.2 o-Azidoaniline derivatives

In an attempt to overcome the problem of instability observed with o-azidoaniline, the latter was converted into derivatives in which an amine hydrogen was replaced by an electron withdrawing group (e.g. p-toluenesulphonyl). It can be argued that the presence of such groups would stabilise iminophosphorane derivatives with respect to hydrolysis and other reactions by reducing the nucleophilicity of the ylide nitrogen atom. In practice stable and isolable iminophosphoranes were obtained from the reaction of N-(o-azidophenyl)-p-toluene-sulphonamide with trimethylphosphite (162, δ_p+5.0),

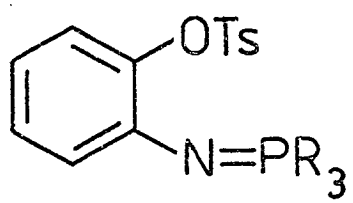
dimethyl phenylphosphonite (163, δ_p+21.4), 2-phenyl-1,3,2-dioxaphosphepan (164, δ_p+19.7) and 1-phenylphospholan (165, δ_p+37.5). As before, reaction with 2-phenyl-1,3,2-dioxaphospholan resulted in the formation of a pentacoordinate phosphorane (161), typified by its ^{31}P chemical shift at δ_p-28.9. The physical and analytical data obtained for these compounds are listed in Table 5.

Two other amino derivatives, o-azido-N-triphenylmethyl-aniline and o-azido-(N-2,4-dinitrophenyl)aniline, were also prepared with the intention of investigating the steric effect of bulky nitrogen substituents upon pentacoordinate phosphorane formation. Unfortunately, no such compounds were formed with either dimethyl phenylphosphonite, or the cyclic reagents, 2-phenyl-1,3,2-dioxaphospholan and 1-phenylphospholan and this line of research was not pursued any further (see Experimental p.138).

1.6 Reaction of o-azidophenyl tosylate with tervalent phosphorus reagents

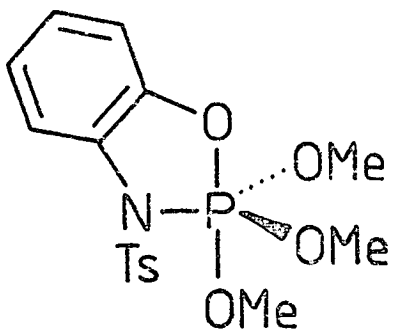
As Schemes 94 and 99 show the formation of pentacoordinate phosphoranes in sections1.1 to 1.5 requires the transfer of a proton from a hetero-atom to the nitrogen atom of the ylide. To test if groups other than hydrogen would similarly migrate, o-azidophenyl tosylate was prepared and reacted with triphenyl-phosphine and trimethylphosphite. Stable iminophosphoranes (166) and (167) were obtained which showed no propensity to rearrange to pentacoordinate phosphoranes *via* tosyl group

migration at room temperature. In an attempt to induce isomerisation, the iminophosphorane (166) was heated under reflux in tert-butylbenzene, but even after 18 h was recovered unchanged. By way of contrast thermolysis of the trimethylphosphite derivative (167) in chlorobenzene for 5 h led to a rearrangement, but not to the desired pentacoordinate phosphorane (168). Instead, the phosphoramidate (169) was formed in 58% yield, presumably by the precedented migration of a methyl group from oxygen to nitrogen.[247]

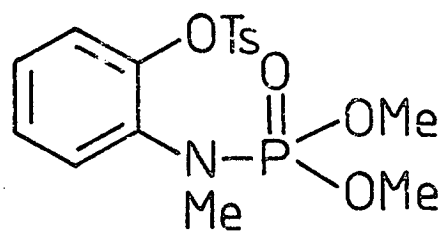


(166) R=Ph

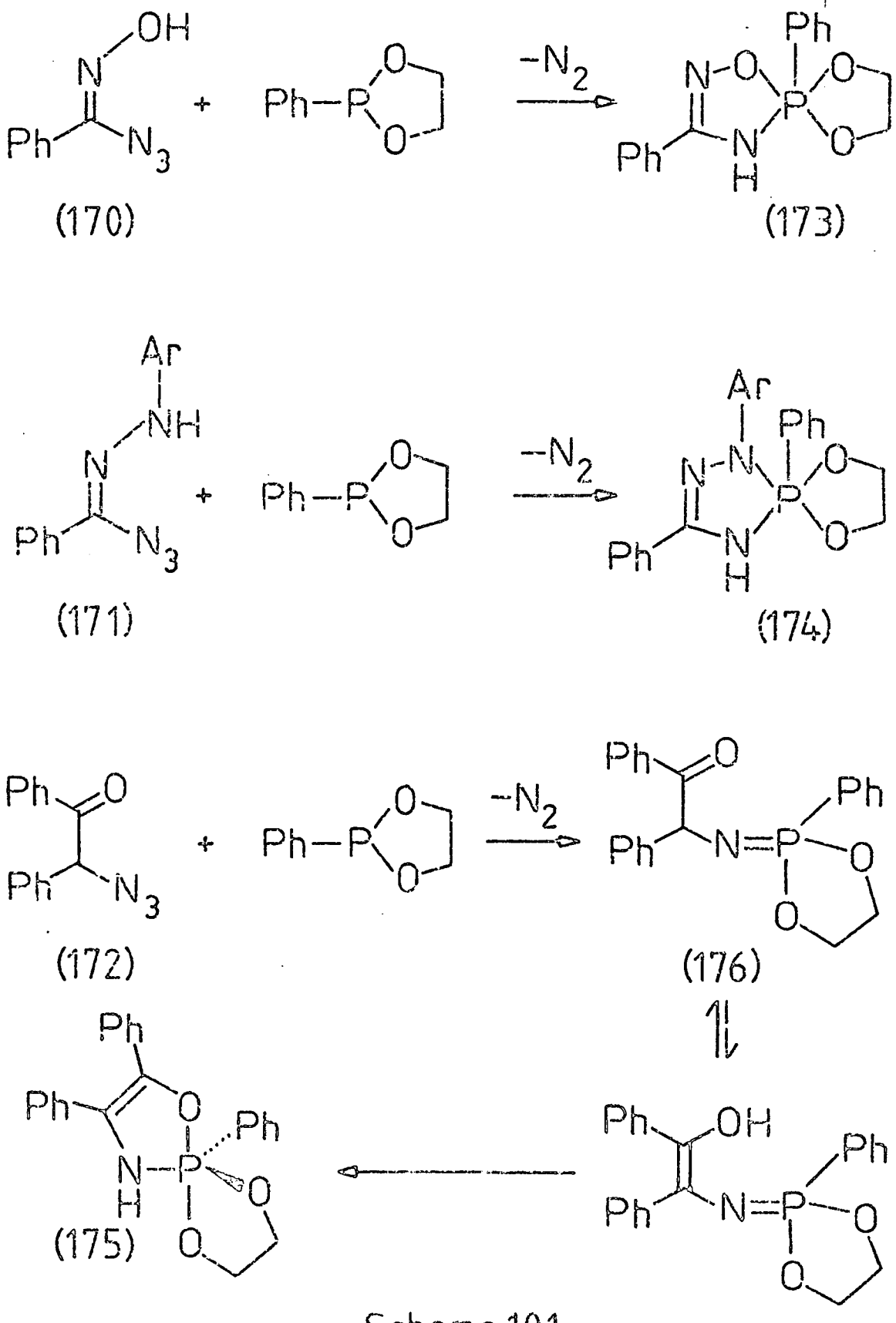
(167) R=OMe



(168)



(169)


OH
N
Ph
N3
Ph
P
O
O
-N2
Ph
N
O
P
O
Ph
N
H
(170)
(173)
Ar
NH
N
Ph
N3
Ar
Ph
N
N
P
O
O
Ph
N
H
(171)
(174)
Ph
O
Ph
N3
Ph
O
Ph
N
P
O
O
(172)
(176)
Ph
Ph
O
N
H
P
Ph
O
O
(175)
Ph
OH
Ph
N
P
O
O

Scheme 101

1.7 Conclusions

The foregoing investigations demonstrate that a variety of pentacoordinate phosphoranes, including cyclic oxaza- and diaza-phosphoranes, can be prepared in high yield and under mild conditions by the reaction of bifunctional azides with tervalent phosphorus reagents. In addition to the described results, co-workers[248] concurrently extended the scope of the reaction by isolating pentacoordinate phosphoranes from the reaction of benzohydroximic azide (170), α-azidobenzaldehyde 2,4-dibromophenylhydrazone (171) and α-azidoacetophenones (172) with tervalent phosphorus reagents. Representative examples of these reactions are shown in Scheme 101. For derivatives (173) and (174), reaction presumably proceeds by a mechanism analogous to that described earlier in Schemes 94 and 99 in which a proton is shifted from the ω-hetero-atom to the ylide nitrogen atom with ring closure. In the case of (175) a hydrogen shift can be envisaged as occurring *via* the enol form of ketone (176).

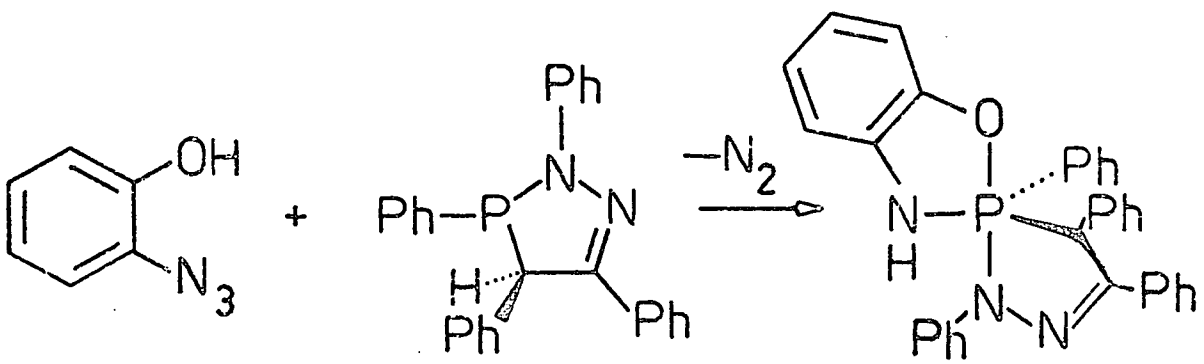
It should be noted that the proposed mechanisms for pentacoordinate phosphorane formation involve the intermediacy of an iminophosphorane. Although this may seem a reasonable assumption, considering such compounds are the usual products of the Staudinger reaction, in no case was an iminophosphorane detected as an intermediate, which subsequently cyclised to a pentacoordinate phosphorane.

The reaction of bifunctional azides with tervalent phosphorus reagents is complementary to the previously described reaction of ω-amino-substituted phosphites with phenyl azide leading to pentacoordinate cyclic oxazaphosphoranes (Scheme 69).[165] Furthermore, the reaction is one of a growing number of syntheses by which pentacoordinate phosphoranes are formed by interaction of phosphorus ylides with alcohols and amines (see Introduction p.59).

As a synthetic method for the preparation of pentacoordinate phosphoranes the reaction is comparable to that developed by Trippett and co-workers,[145] whereby an aminoalcohol, for example, is condensed with a tervalent phosphorus reagent in the presence of N-chlorodiisopropylamine. In some respects Trippett's procedure offers distinct advantages. Thus, it obviates the need to convert the amine precursor into an azido compound and significantly it is possible to use tervalent phosphorus reagents which are of sufficiently low nucleophilicity that they normally would not react with an azido compound below its decomposition temperature. Nonetheless, under certain circumstances the 'azide route' will be the method of choice. For example when preparing unstable pentacoordinate phosphoranes since any handling of the product (and consequently exposure to moisture and nucleophiles) is minimal. Moreover, the leaving group is nitrogen as opposed to an insoluble ammonium salt and the need for filtration and transfer of product from the reaction flask is removed. In addition the azido compound/tervalent phosphorus reagent reaction is fast in comparison to the Trippett reaction which often takes several days to reach completion. Therefore, any

decomposition of the product dependent on time is reduced to a minimum. These latter factors may account for the successful isolation of pentacoordinate benzdiazaphospholines, (159) and (160), by the 'azide route' and the failure of the Trippett method.

In summary, the reaction of bifunctional azides with tervalent phosphorus reagents provides a simple, mild and efficient synthesis of pentacoordinate phosphoranes which should prove to be a useful alternative to the method of Trippett and co-workers. Indeed, these reaction features have been recently utilised to advantage by Baccolini *et al.*[249] to effect the facile synthesis of the first pentacoordinate phosphorane incorporating the 2H-1,2,3-diazaphosphole ring system (Scheme 102).



Scheme 102

Many other possibilities can be envisaged, and in this respect it would be worthwhile to investigate the interaction of S-H and C-H bonds with the phosphorus-nitrogen double bond in the hope of further extending the scope and synthetic utility of the 'azide route'.

2. Factors influencing pentacoordinate phosphorane formation vs. iminophosphorane formation

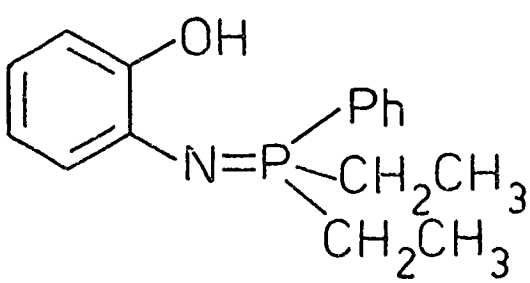
An important feature of the reactions described in sections 1.1 to 1.5 is that in some instances a pentacoordinate phosphorane is formed whereas in others the product is an iminophosphorane. From the results obtained it is possible to identify and study in isolation some of the factors which determine the coordination state of the product obtained since series of examples can be found in which only one parameter is varied.

Before entering into a detailed discussion of these factors it is necessary to make a basic assumption concerning the nature of these products. Namely, that the compounds isolated from the reaction of bifunctional azides with tervalent phosphorus reagents are thermodynamic not kinetic products. In the case of pentacoordinate products this is not an unreasonable assumption since their formation most probably involves the intermediacy of the isomeric iminophosphorane form. When the final product of reaction, however, is an iminophosphorane the assumption is more difficult to justify although the following observations do give some support to this argument. Thus, if it is accepted that an iminophosphorane is an intermediate then its isomerisation to the pentacoordinate phosphorane must be rapid on the n.m.r. time scale since the former cannot be detected by ^{31}P n.m.r. in any of the

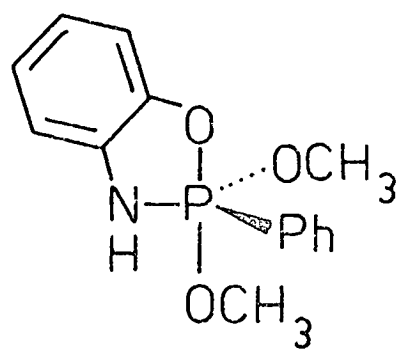
examples studied. Moreover, in systems where an observable equilibrium does exist between tetra- and penta-coordinate forms[164] it has been noted that the equilibrium is rapidly re-established upon perturbation of the system. Therefore, it seems likely that if an iminophosphorane is formed as a kinetic product it would, upon standing in solution, isomerise to the thermodynamically more stable pentacoordinate form. To test this possibility several of the iminophosphoranes isolated were observed in solution by n.m.r. spectroscopy for up to 120 h and in no instance did conversion into a pentacoordinate phosphorane occur.

2.1 Electronic effects at phosphorus

From a comparison of the reactions of o-azidophenol with diethylphenylphosphine and dimethyl phenylphosphonite it is apparent that electronic effects at phosphorus play an important role in determining the nature of the products obtained. Thus, the former reagent gives rise to an iminophosphorane (139) whereas the latter in which the electropositivity of phosphorus is increased by the presence of two oxygen atoms, affords a pentacoordinate phosphorane (132).

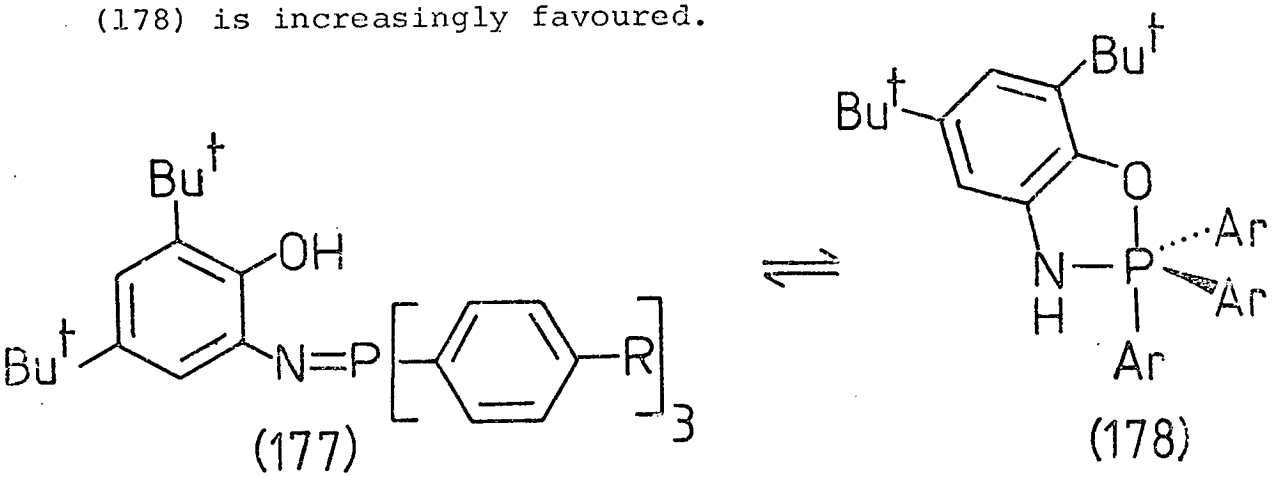


(139)



(132)

This result accords with those of Stegmann *et al.*[164] who found that for a series of N-(2-hydroxy-3,5-di-tert-butylphenyl)-iminophosphoranes (177) the position of the iminophosphorane-pentacoordinate phosphorane equilibrium depended upon the electronic environment at phosphorus. The data in Table 6 shows that as phosphorus became progressively more electropositive the pentacoordinate form (178) is increasingly favoured.



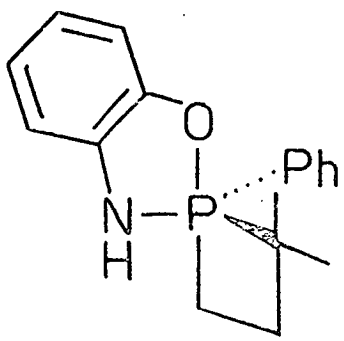
R	%(177)	%(178)
CH_3O-	89	11
CH_3-	60	40
H-	33	67
CH_3CO-	-	100

Table 6

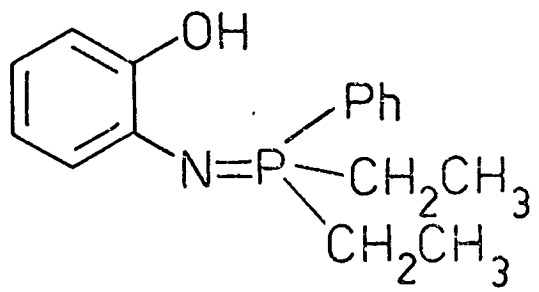
A further example of this electronic effect may be found by comparing compounds (161) and (165).

2.2 Small-ring effect

Another significant point to emerge from the study of the reactions of bifunctional azides with tervalent phosphorus reagents is that the incorporation of phosphorus into a small-ring appears to favour the formation of a pentacoordinate rather than a tetracoordinate product. This effect is manifest, for example, in the reactions of o-azidophenol with 1-phenyl-2,2-dimethylphosphetan and diethylphenylphosphine leading to (135) and (139) respectively. Whilst the degree of electropositivity at each phosphorus atom is expected to be similar the phosphetan derivative is found to exist in the penta-coordinate form. Apparently, in this case the small-ring effect acts to overcome an otherwise unfavourable electronic environment at phosphorus thus promoting pentacoordinate phosphorane formation. Further examples of this manifestation of the small-ring effect can be identified by comparing compounds (155) and (150), and (163) and (161).

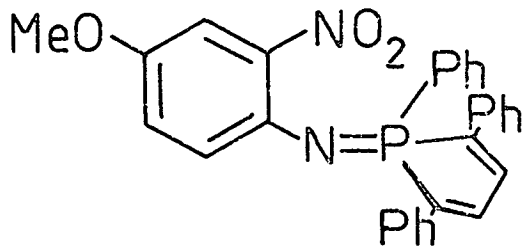


(135)



(139)

The source of this effect may be best visualised in terms of relief of ring strain but as already noted entropy factors and relief of molecular crowding are probably also involved (see Introduction pages 68-75). It can therefore be argued that in compounds containing a four-membered ring, the natural angle at phosphorus should be approximately 90°. Hence on going from four (CPC, 108°) to five (CPC, *ae*, 90°) coordination a relief of ring strain can be achieved which will act as a driving force for pentacoordinate phosphorane formation. Support for the view that "small-ring" iminophosphoranes are strained has come from X-ray data of N-(4-methoxy-2-nitrophenyl)-imino-1,2,5-triphenylphosphole (179).[250]

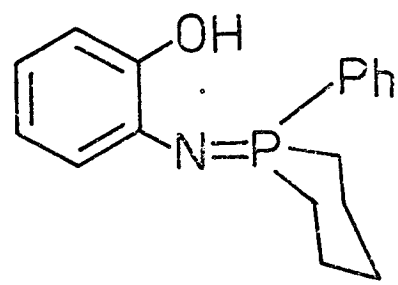


(179)

The observed bond angle $C_4P_1C_1$ of the phosphole ring is 94° which is much closer to the 90° *ae* angle of a TBP than the tetrahedral value of 109°. The exocyclic bond angle $N_1P_1C_{17}$ is fairly close to 109.5° and indicates that phosphorus is tetrahedrally coordinated. There must therefore be a considerable degree of strain present in the phosphole ring.

Strong support for the importance of the small-ring effect in determining the coordination state comes from an inspection of the nature of products obtained as the

ring size increases. Thus, the six-membered ring compound (140) exists as an iminophosphorane unlike the isomeric four-membered ring pentacoordinate phosphorane (135). This difference in behaviour presumably arises because there is no significant small-ring effect in (140) therefore the electronic effects, as discussed earlier in relation to the acyclic analogue (139), dominate. An additional example of this competition between effects may be found by comparing (161) and (164).



(140)

2.3 Other factors

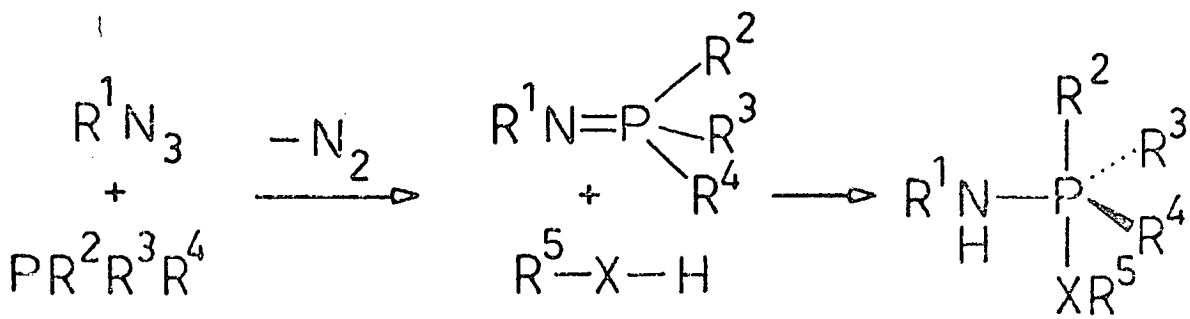
In addition to small-ring and electronic effects other factors can be envisaged which could influence pentacoordinate phosphorane formation. For example, a comparison of the series of derivatives of o-azidophenol (130-135) with o-azidoanilines (158-165) leads to the conclusion that the NH group shows less propensity to undergo intramolecular cyclisations to give pentacoordinate phosphoranes than does OH. The source of this phenomenon is probably electronic in nature and may be associated with the different apicophilicities of oxygen and nitrogen.[103]

Amongst other possible factors which may also exert an influence on pentacoordinate phosphorane formation are steric effects of ligands at phosphorus, p_π-p_π donation from ylidic nitrogen, the phospholan effect,[186,187] and the size of the new ring formed in the intramolecular cyclisation. However, insufficient information is available from this study to allow an evaluation of these factors in isolation.

In conclusion, two distinct factors have been identified as having a profound influence on the coordination state of the product derived from the reactions of bifunctional azides with tervalent phosphorus reagents. These are the small-ring effect and the electronic nature of substituents at phosphorus.

3. Formation of pentacoordinate phosphoranes by reaction of iminophosphoranes with alcohols.

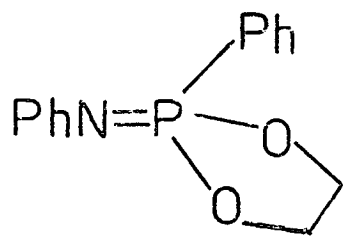
The successful outcome of the reaction of bifunctional azides with tervalent phosphorus reagents as a route to pentacoordinate phosphoranes prompted an investigation of the related intermolecular reaction as depicted in Scheme 103.



(180)

Scheme 103

Assessment of the factors involved in the intramolecular reaction suggested that the above intermolecular reaction would most likely be achieved if an iminophosphorane was selected with an electropositive phosphorus atom enclosed within a small-ring (R^2-R^3). Other considerations also led to the constraint that the third substituent at phosphorus (R^4) should be firmly bound, in order to minimise the possibility of ligand exchange by nucleophilic attack. Both these requirements are met by the iminophosphorane (181). In view of the anticipated lability of the -NHR^1 group (180) it was decided to employ a bifunctional alcohol or else a monofunctional alcohol in two molar excess in order to displace this group and hence avoid a mixture of products.

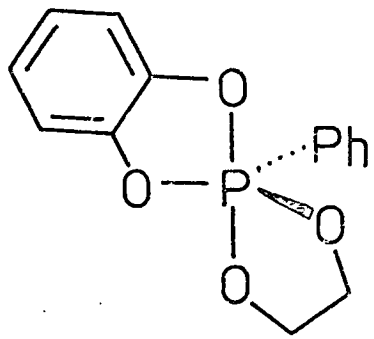


(181)

3.1 Reaction of N-phenylimino-2-phenyl-1,3,2-dioxaphospholan with 1,2-dihydroxybenzene

Reaction of 2-phenyl-1,3,2-dioxaphospholan, azidobenzene with the bifunctional reagent 1,2-dihydroxybenzene in methylene chloride at room temperature led to the

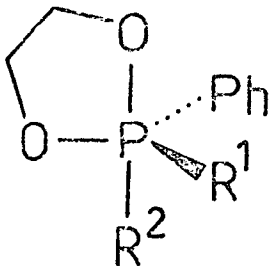
successful, and by ^{31}P n.m.r., quantitative formation of a pentacoordinate phosphorane. On the basis of the analytical and spectral data the compound was identified as 2-phenylspiro-[1,3,2-dioxaphospholan-2,2'-[1,3,2]-benzodioxaphospholine] (187) and its structure confirmed by an alternative synthesis after the method of Trippett *et al.*[145]



(187)

3.2 General reaction of N-phenylimino-2-phenyl-1,3,2-dioxaphospholan with alcohols

The generality of the foregoing reaction as a route to pentacoordinate phosphoranes was examined by reacting the iminophosphorane (181) with a range of alcohols. The pentacoordinate products obtained are listed in Table 7 together with their ^{31}P n.m.r. shifts, yields, melting points, elemental analyses and molecular ion masses. Particular points of interest which arise from this data are discussed below.



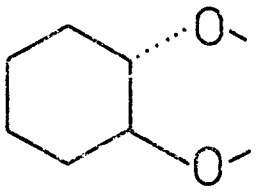
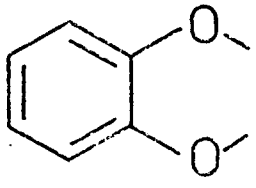
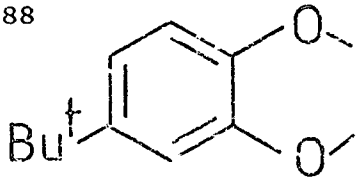
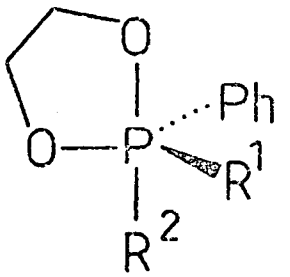
	R^1	R^2	$\delta_p(CDCl_3)$	Yield (%)	M.Pt. (°C)	Analysis[a] C	H	N	M.I.[b]
182	OME	OMe	-34.2	74	liquid	52.5 52.2	6.4 6.6	-	230
183	$-OCH_2CH_2O-$		-19.2	85	124-126*	52.6 52.6	5.7 5.7	-	-
184	$-O(CH_2)_3O-$		-34.1	79	92-94	54.5 54.6	6.2 6.2	-	242
185	$-O(CH_2)_4O-$		-30.2	82	70-72	56.1 56.3	6.6 6.7	-	256
186			-22.5	68	93-96	59.6 59.6	6.8 6.8	-	282
187			-14.3	21	113-115	61.0 60.9	4.8 4.7	-	276
188			-14.2	71	110-113	65.2 65.1	6.4 6.4	-	332

Table 7

*Lit.[233] = 123°C



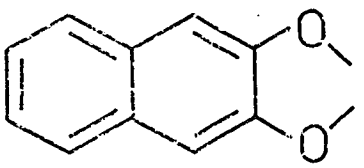
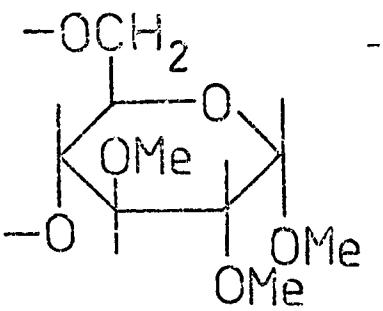
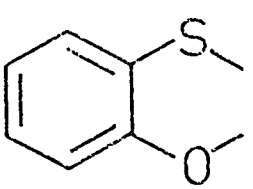
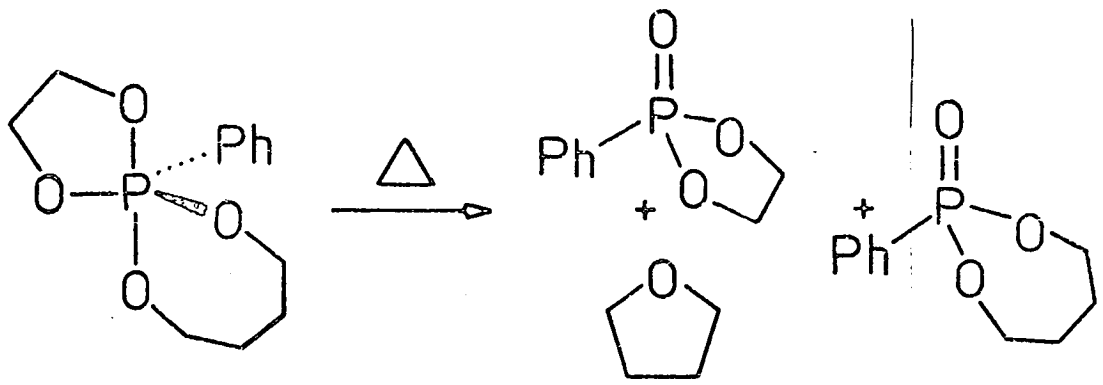
	R^1	R^2	$\delta_p(CDCl_3)$	Yield (%)	M.Pt. (°C)	Analysis[a] C	H	N	M.I.[b]
189			-14.1	69	>270	66.3 66.3	4.7 4.6	-- -	326
190			-33.8	100	-	52.8 52.6	6.6 6.5	- -	388
191	$-NMeCH_2CH_2O-$		-34.9	75	68-71	55.0 54.8	6.7 6.7	5.7 5.8	241
192			+4.7	74	96-97	57.6 57.5	4.6 4.5	- -	292

Table 7 (contd.)

Thus, the reaction worked equally well for both aliphatic and aromatic alcohols even though these functional groups differ in acidity by a factor of approximately 10^{8}.[251] Moreover, the method was not restricted to diols only, but also worked with methanol, 2-(methylamino)ethanol (191) and monothiocatechol (192). In contrast to these successes no pentacoordinate product was obtained with 2-mercaptoethanol. However, this result may be due to an inherent instability in pentacoordinate phosphoranes which contain a 1,3,2-thiaoxaphospholan ring rather than a failure of the method since Trippett *et al.*[146] were also unable to prepare pentacoordinate derivatives from this material.

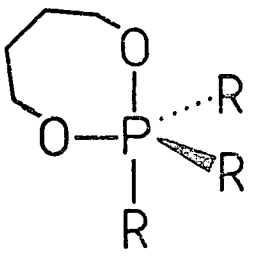
Generally, compounds (182-192) were stable crystalline materials which were easier to handle than the pentacoordinate products described in sections 1.1 to 1.5. This was particularly true of the tetraoxyphosphoranes (183-190) and can be attributed to the spirobicyclic structure of these compounds[252] combined with the stabilising electronic effect of the electronegative oxygen atoms attached to phosphorus.[253]

The considerable thermal stability demonstrated by (185) is particularly noteworthy. Decomposition occurred only after heating under reflux in tert-butylbenzene for 48h whereupon 2-phenyl-1,3,2-dioxaphospholan oxide, 2-phenyl-1,3,2-dioxaphosphepan oxide and tetrahydrofuran were formed in 81, 19 and 34% yield respectively (Scheme 104).

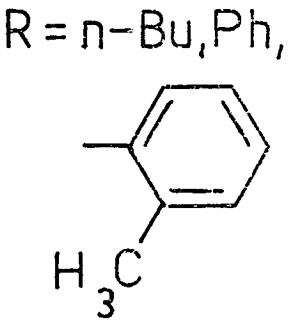


Scheme104

By comparison, De'ath and Denney[254] were unable to isolate the pentacoordinate 1,3,2-dioxaphosphephans (193) at room temperature because of the ready formation of phosphine oxides and tetrahydrofuran.



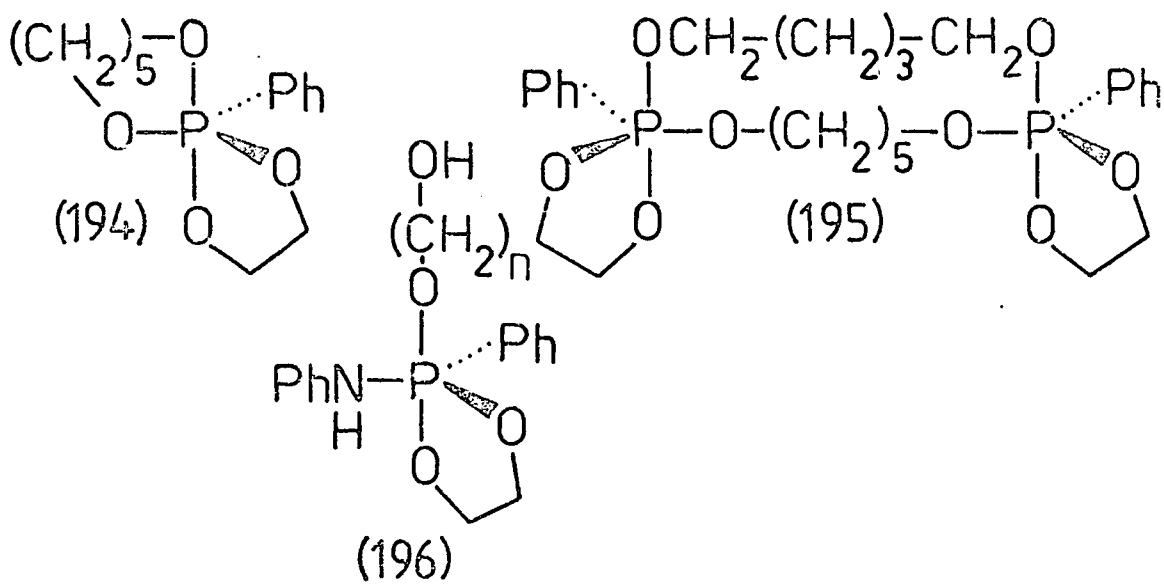
(193)



The scope of the intermolecular reaction, with respect to the size of the new ring formed, was investigated by the preparation of the series of compounds (183-185). These were isolated as colourless crystalline solids each of which exhibited a single phosphorus resonance and the expected pattern of peaks in the ^{13}C spectrum. By contrast, when iminophosphorane (181) was reacted with 1,5-pentanediol a gum was obtained which exhibited one major (δ_p-36.9, o-dichlorobenzene) and two minor (δ_p-36.3 and -36.5) phosphorus resonances as well as the corresponding pattern of peaks in the

^{13}C spectrum ($CDCl_3$, see page 143). Attempts to purify the gum by bulb-to-bulb distillation were unsuccessful but a satisfactory analysis was obtained consistent with the empirical formula $C_{13}H_{19}O_4P$. In addition, a peak corresponding to this formula was observed in the mass spectrum.

It was considered that there were three possible explanations that would account for the analytical and spectral data. (i), that the extra peaks arose in the n.m.r. spectra because of a molecular property peculiar to the eight-membered ring pentacoordinate phosphorane (194), for example, the presence of different rotamers; (ii) that the gum consisted of several different pentacoordinate phosphoranes including (194) but also the dimer (195), trimer, etc., which could be formed by intermolecular attack on an intermediate such as (196); this reaction would become statistically favoured as the size of the chain ($HO-(CH_2)_n-$) increased; and (iii) that there existed in solution an equilibrium between monomeric (194), dimeric (195) and other higher forms.



Resolution of this problem by the alternative synthesis of (194) from 2-phenyl-1,3,2-dioxaphosphocan was thwarted by the failure to obtain this reagent from the reaction of dichlorophenylphosphine with 1,5-pentanediol. Various other experiments were therefore devised in an attempt to resolve the problem.

Firstly, an examination of 0.6 M, 0.3 M and 0.15 M solutions of the gum in 1,2-dichlorobenzene over a period of 120 h at room temperature by ^{31}P n.m.r. revealed that there was no significant change in peak areas either within or between samples. On the basis of these observations the third proposal was discounted.

Secondly, a variable temperature ^{31}P n.m.r. study of the gum in 1,2-dichlorobenzene showed that an apparent coalescence of peaks occurred as the temperature was raised to 120°C. This suggested the presence of several equilibrating rotamers. However, it is difficult to identify a high energy pseudorotational process within compound (194) which would account for this result especially since conformational processes within eight-membered rings are of low energy.[255] An alternative explanation of this observation is that it is caused by changes in peak chemical shifts with temperature which results in a fortuitous overlap of peaks.

In a third experiment, to test the second proposed explanation, the preparation of (194) was attempted under conditions of high dilution which might be expected to favour monomer formation. Unfortunately, these experiments were frustrated by the insolubility of the iminophosphorane (181, see page 139, 9.1) and no significant results were obtained.

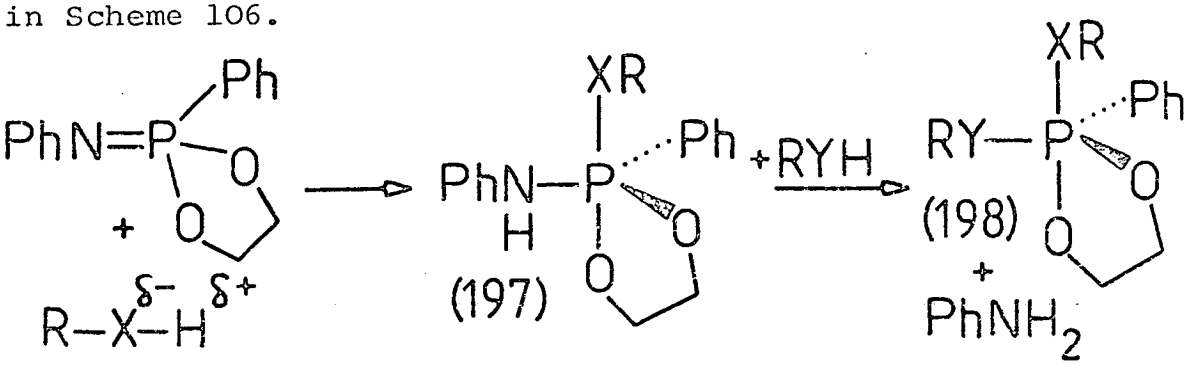
In a final attempt to find an explanation for the phenomena, (194) was prepared by the method of Trippett *et al.*[145] An examination of the pentacoordinate phosphorane obtained under these conditions by ^{31}P n.m.r. revealed that the peak positions remained unaltered but that the ratio of peaks was significantly changed (formerly 3044: 9799, by this reaction 1259:8211). This result is at variance with the first explanation but supports the second; that the gum consisted of several different pentacoordinate phosphoranes including (194) but also the dimer (195), trimer, etc. Corroboration of the second explanation was therefore sought by determining the molecular weight of the gum, which due to the presence of polymeric forms ought to be higher than 270. A single measurement gave the slightly high figure of 300, but given the limited accuracy of this technique no great significance can be attached to this result.

In conclusion, the problem remains unresolved and awaits further work which should be directed towards the purification of the crude reaction product since ^{13}C n.m.r. spectroscopy indicated contamination by 1,5-pentanediol. Molecular weight determinations may then give decisive results.

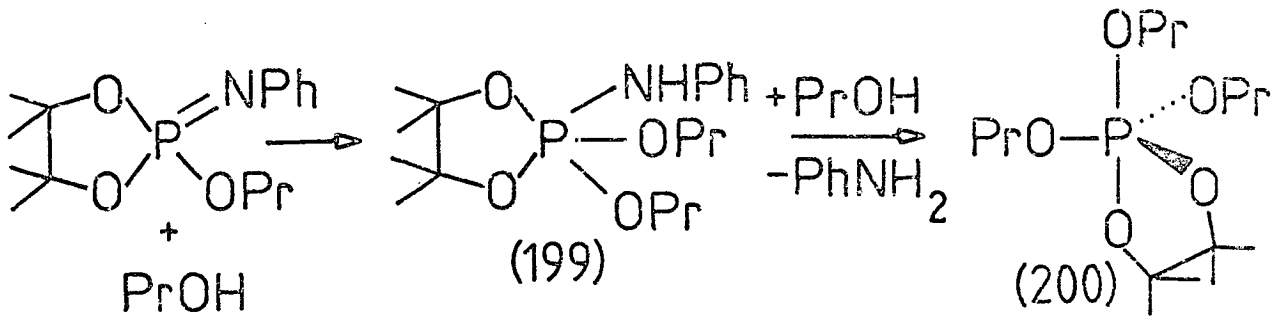
3.3 Mechanism

The proposed mechanism of the intermolecular iminophosphorane/alcohol reaction is shown in Scheme 105 and involves addition of the $RX^{\delta-}H^{\delta+}$ unit across the P = N bond with formation of the intermediate (197). Attack from a second $RY^{\delta-}H^{\delta+}$ unit results in displacement of aniline and formation of the pentacoordinate phosphorane (198).

No experimental evidence was obtained to support the intermediacy of (197) but Sanchez *et al.*[256] have recently demonstrated, in an analogous system, that compound (200) is formed by displacement of aniline from (199) as shown in Scheme 106.

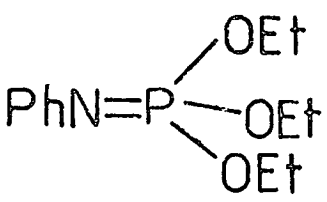


Scheme 105

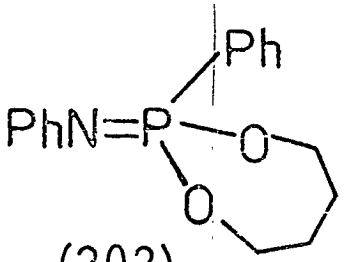


Scheme 106

The driving force for the intermolecular reaction is presumably derived from the small-ring effect since the acyclic iminophosphorane (201) failed to react with ethanol under the same conditions that led to the formation of (182) from (181) with methanol. However, the influence of the small-ring effect does not account for the fact that the unstrained cyclic iminophosphorane (202) reacted with 1,2-ethanediol to form (185) and (183) but failed to react with 1,4-butanediol. Further studies are obviously required to identify the role which other factors play in the intermolecular iminophosphorane/alcohol reaction.



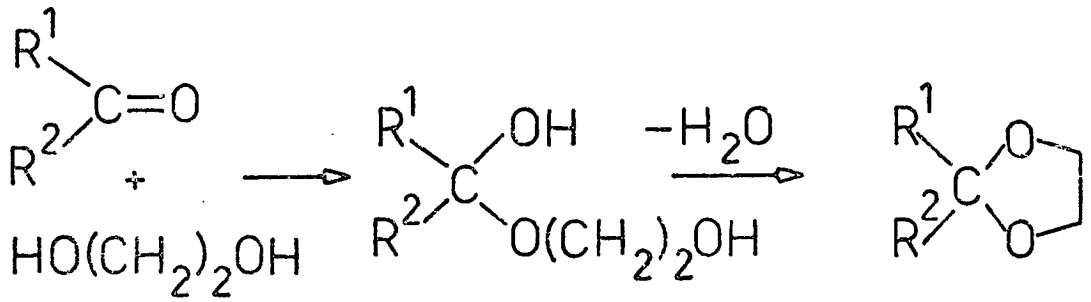
(201)



(202)

3.4 Conclusions

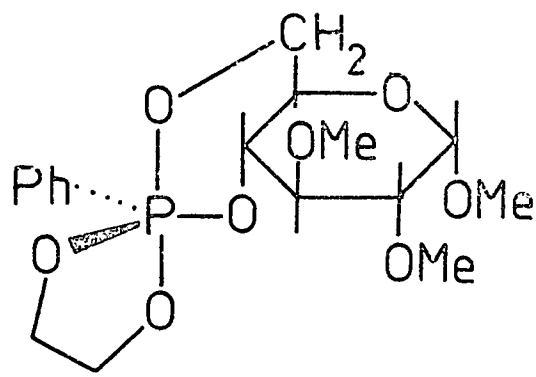
It has been demonstrated that iminophosphoranes will react with alcohols to form pentacoordinate phosphoranes and that these reactions are facilitated by enclosure of the phosphorus atom of the iminophosphorane precursor within a small-ring. An interesting parallel can be drawn between this reaction and the formation of acetals from carbonyl compounds and diols (Scheme 107). The net effect of both these reactions is to bind the electron deficient atoms of the $^{\delta+}P = N^{\delta-}$ and $^{\delta+}C = O^{\delta-}$ double bonds to two oxygen atoms within a ring, leading to the expulsion of water and aniline, respectively.



Scheme 107

As with the intermolecular reaction discussed in sections 1.1 to 1.5 this synthetic method is complementary to the Trippett reaction. The same advantages and disadvantages which were previously outlined on page 192 also apply and therefore need not be re-stated.

These initial studies have also shown that the intermolecular reaction provides a useful method for phosphoranylating alcohols as exemplified by formation of the sugar derivative (190). However, due to limitations of time only a limited variety of the many possible combinations of functional groups which would potentially react with iminophosphoranes have been used in this reaction. Consequently, further detailed studies are required to elucidate the synthetic utility of, and the factors controlling, this route to pentacoordinate phosphoranes.

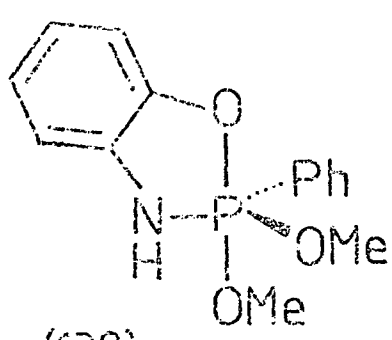


(190)

4. Variable temperature n.m.r. studies of oxazaphosphoranes

The occurrence of pseudorotational processes in molecules (132) and (147) was demonstrated by variable temperature ^{1}H- and ^{31}P- n.m.r. spectroscopy. The oxazaphosphoranes derived from dimethyl phenylphosphonite were chosen for study because the two-site exchange process involving equilibration of apical and equatorial methoxyl ligands can be followed easily by ^{1}H n.m.r., thereby allowing measurement of coalescence temperatures and calculation of ΔG^{*}.

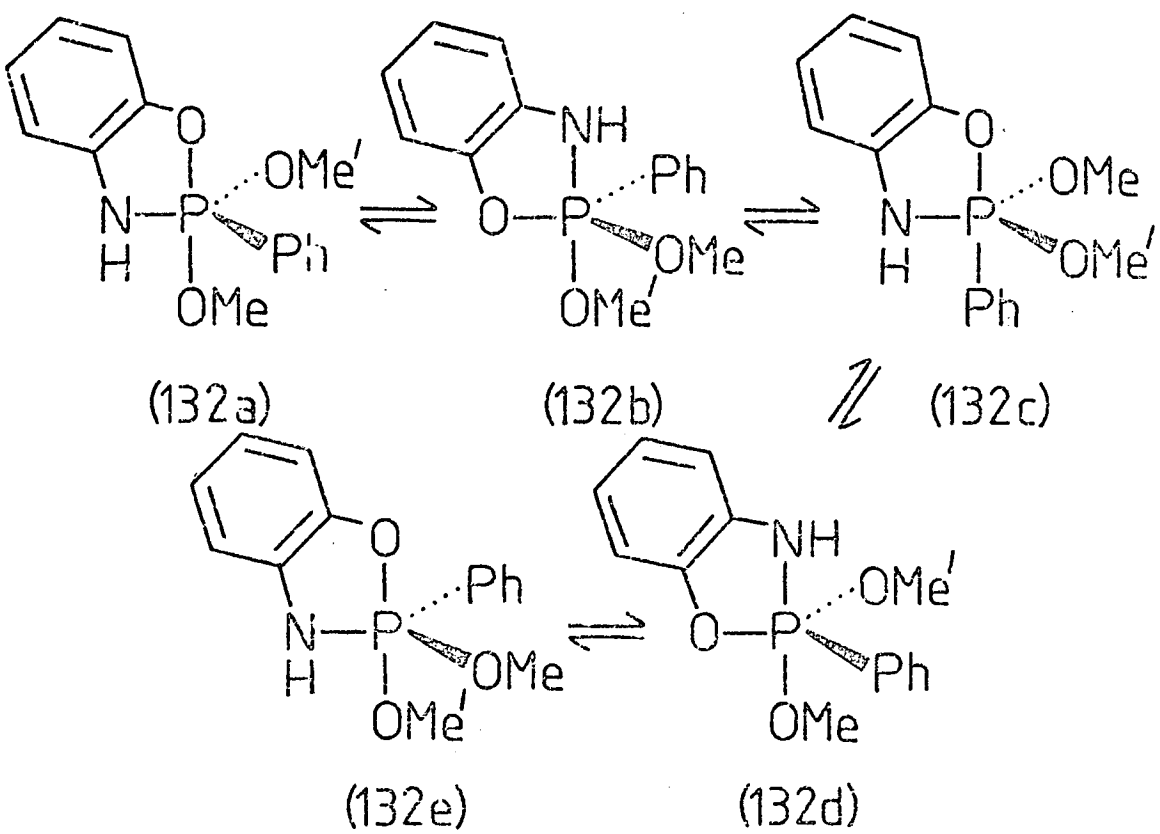
Figure 3



(132)

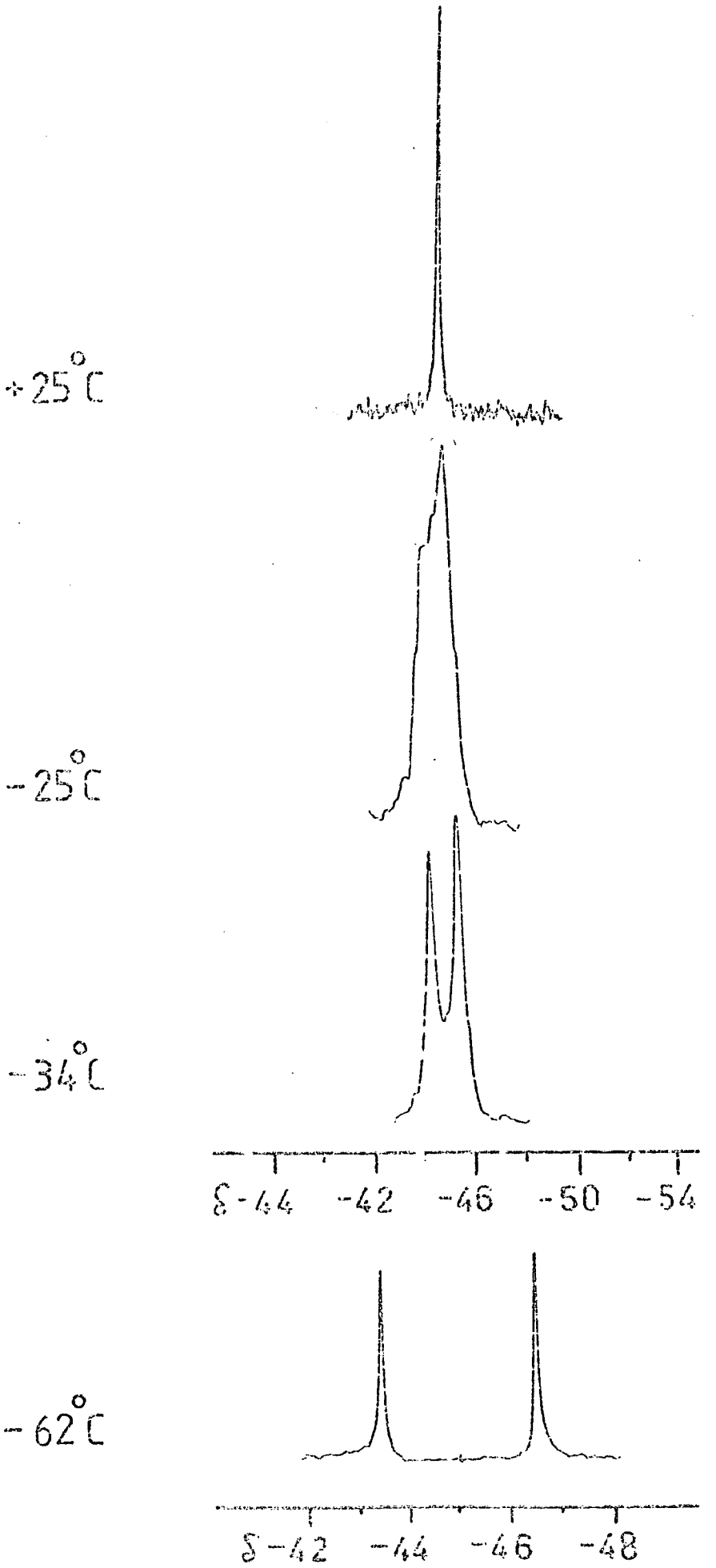
4.1 2,2-Dimethoxy-2-phenyl-1,3,2-benzoxazaphospholine

The ^{1}H n.m.r. spectrum of this compound at 28°C indicated that pseudorotation was unhindered since the methoxyl protons appeared as a single phosphorus coupled doublet (Figure 3). As the temperature was lowered the equivalence of these groups was lost and at the coalescence temperature, -24°C, they appeared as a broad mound. On lowering the temperature still further, pseudorotation became slow on the n.m.r. time scale and the methoxyl signals appeared as two distinct doublets. The lower field doublet was considered to be due to the equatorial methoxyl group, J_{PH} = 14 Hz, whilst the higher field doublet, with the reduced coupling constant of 10 Hz, was ascribed to the apical methoxyl group since it is further from and hence interacts less strongly with the phosphorus atom.[200]



Scheme 108

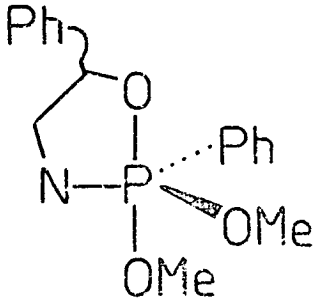
Figure 4



There are several pathways which could account for the equilibration of the two methoxyl groups between apical and equatorial positions in molecule (132). However, the restrictions imposed by ring strain and relative apicophilicities (see Introduction pages 41-47) suggest that only one pathway between isomers (132a) and (132e) need be considered and this is outlined in Scheme 103.

The high energy points of the above process correspond to isomers b, c and d which possess either a nitrogen atom or phenyl group in an apical position. The free energy of activation for this process was calculated to be 50 $\pm$ 1 kJ mol^{-1} by a combination of a simplified Gutowsky-Holm equation[235] and the Eyring equation.[236]

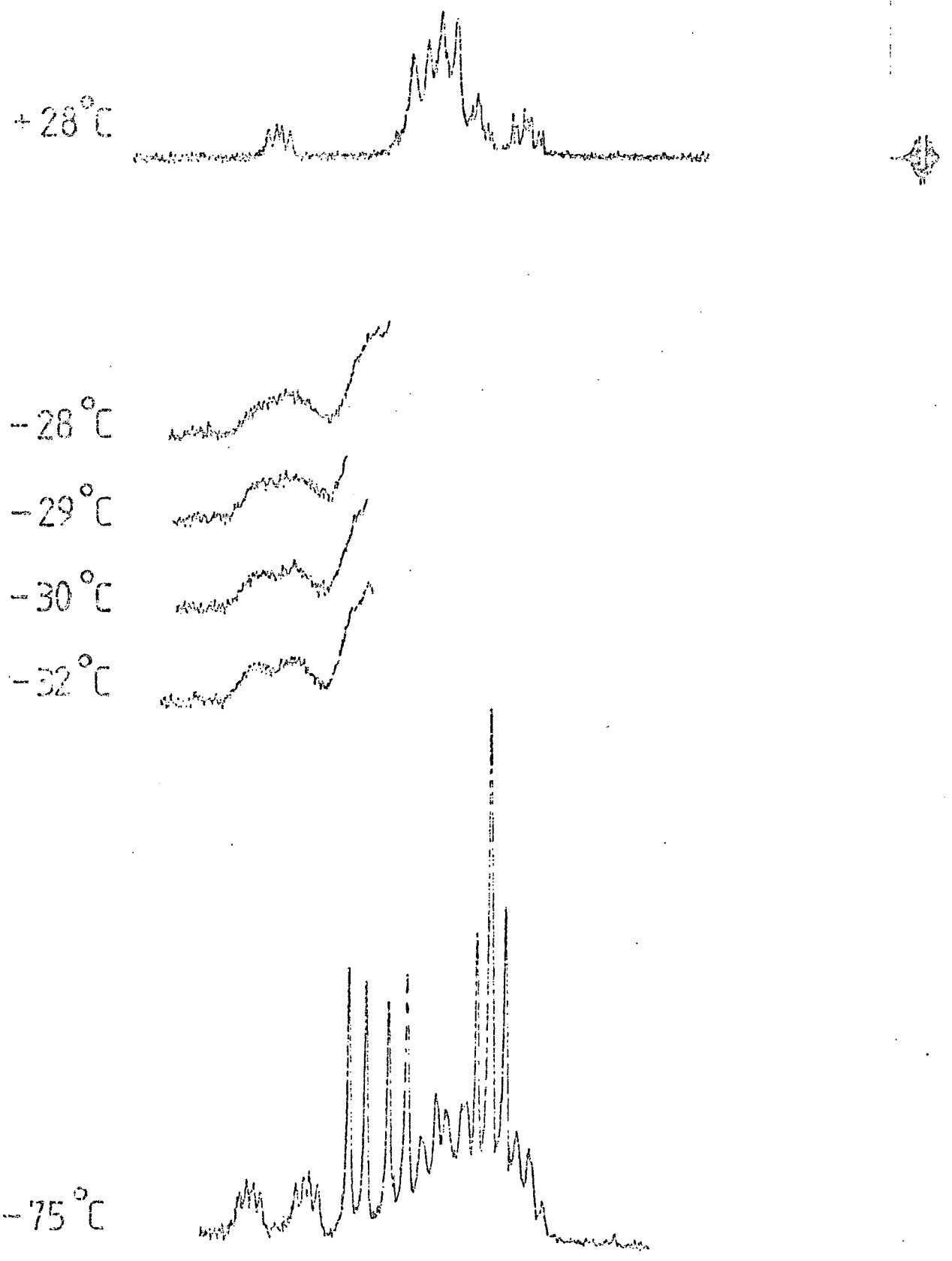
4.2 2,2-Dimethoxy-2,5-diphenyl-1,3,2-oxazaphospholan



(147)

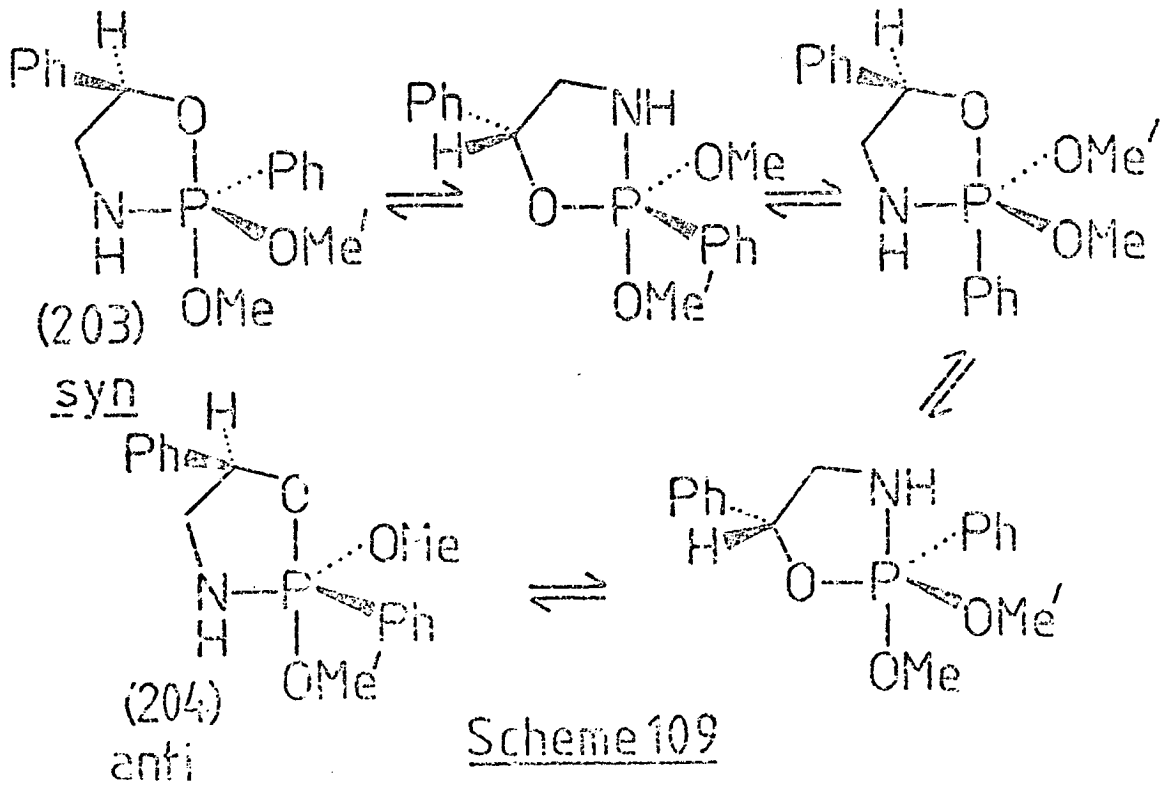
The variable temperature n.m.r. spectra of this molecule proved more complex than the foregoing example. Thus, ^{31}P n.m.r. spectrum at -62°C showed two peaks of approximately equal intensity at δ_p -43.4 and -46.5 (Figure 4). Likewise, the ^{1}H n.m.r. spectrum showed two distinct sp^3 (OCHPh) signals and two sets of *a* and *e* methoxyl signals at -75°C (Figure 5). This data is consistent with the presence of approximately equally populated diastereoisomeric forms (203) and (204)

Figure 5



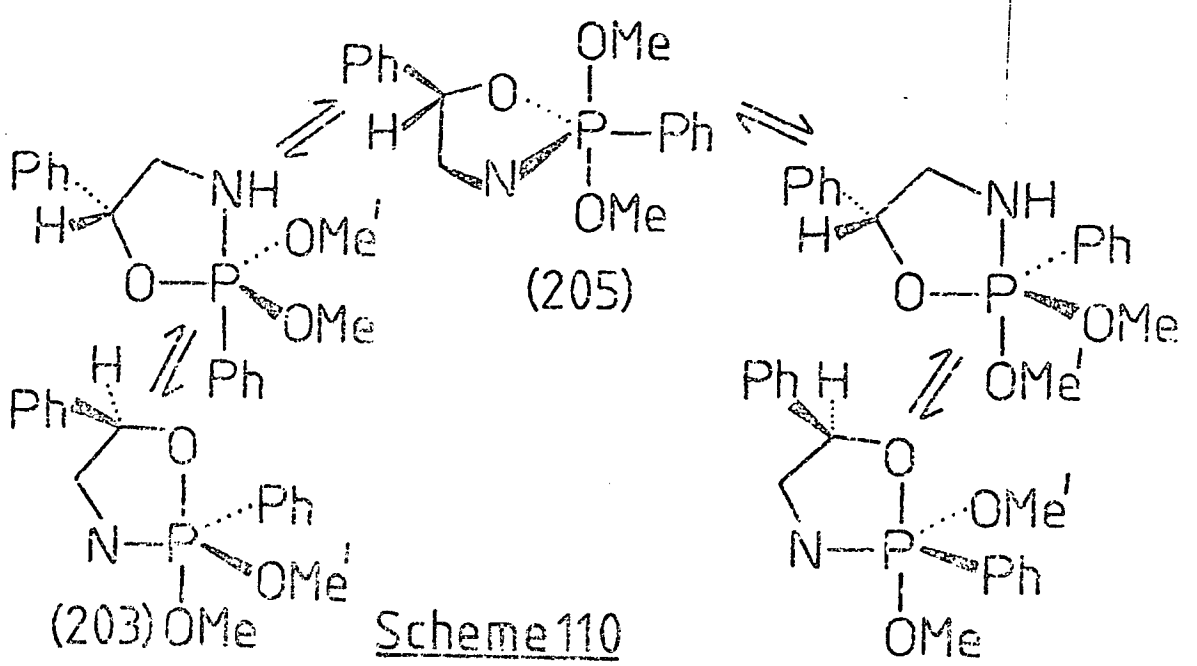
in which the 5-phenyl and 2-phenyl groups adopt either *syn* or *anti* geometry. As a result the phosphorus nucleus experiences two different magnetic environments and two peaks are observed in the ^{31}P n.m.r. spectrum. The same argument also applies to the ^{1}H signals described above.

As the temperature was raised the phosphorus signals coalesced (Figure 4) and at +25°C a single peak was observed at δ_P -44.8. T_c was judged to occur at -25°C from which ΔG^* was calculated to be 50 ± 1 kJ mol^{-1}. An analogous pathway to that described in section 4.1, which effectively allows interconversion of the diastereoisomers (203) and (204) resulting in magnetic equivalence of the phosphorus nuclei at +25°C, is shown in Scheme 109.

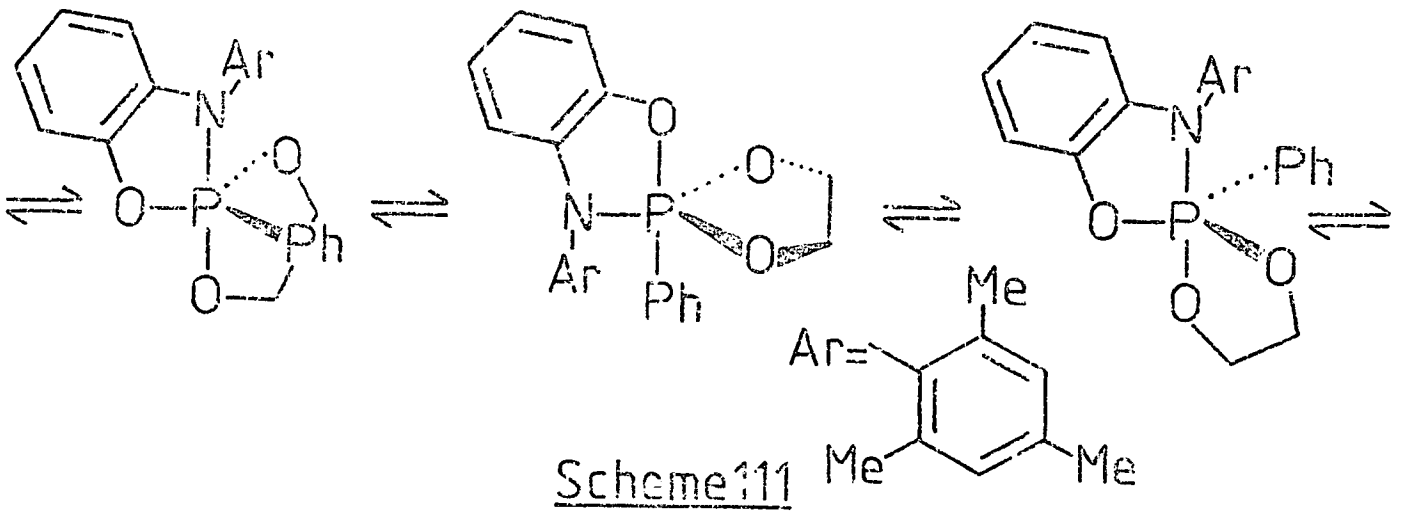


Scheme 109

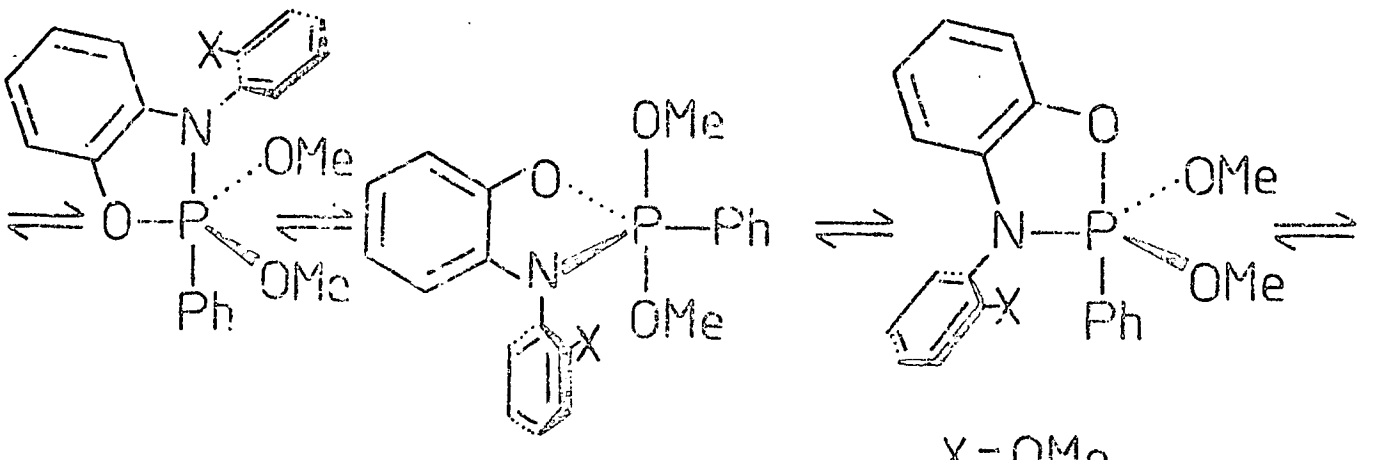
An examination of the ^{1}H n.m.r. spectrum showed that the methoxyl signals coalesced as the temperature was raised, but T_c could not be accurately determined due to overlap with the ring methylene signals. However, coalescence of the sp^3(OCHPh) protons, which can occur by the same process (Scheme 109), is clearly observed as shown in Figure 5.



Scheme 110



Scheme 111



Scheme 112

Calculation of the free energy of activation gave a value of 50 ± 1 kJ mol^{-1} which is in good agreement with that derived from the ^{31}P n.m.r. spectra.

In contrast to that of (132), the ^{1}H n.m.r. spectrum of (147) at +28°C revealed that the methoxyl groups did not equilibrate completely by interchange between the *a* and *e* positions. Instead two distinct doublets of approximately equal intensity were observed, which collapsed to singlets upon irradiation at a single frequency. It was apparent from the positions of these two signals that they were located in the averaged positions of the pairs of *a* and *e* signals observed at -75°C (Figure 5). An explanation of the origin of this phenomenon is provided by reference to Scheme 109. Thus, OMe' which is syn to the 5-phenyl group in (203) cannot be placed anti to this group by this exchange process. The only means by which complete equilibration of these groups can be achieved is *via* an intermediate such as (205) in which the five-membered ring assumes diequatorial placement (Scheme 110), but this process is unlikely owing to ring strain imposed by the 120° angle at phosphorus. Experimentally, no coalescence of the methoxyl signals was observed by ^{1}H n.m.r. up to 135°C in diphenyl ether thereby giving a calculated minimum ΔG^{*} of 88 kJmol^{-1} for this process. It is worth noting that calculations of free energy values for pseudorotation processes involving diequatorial placement of a five-membered ring in related structures have typically yielded values of 93.6 ± 0.5 kJ mol^{-1} (Scheme 111)[257] and 97.4 ± 2.7 kJ mol^{-1} (Scheme 112).[258]

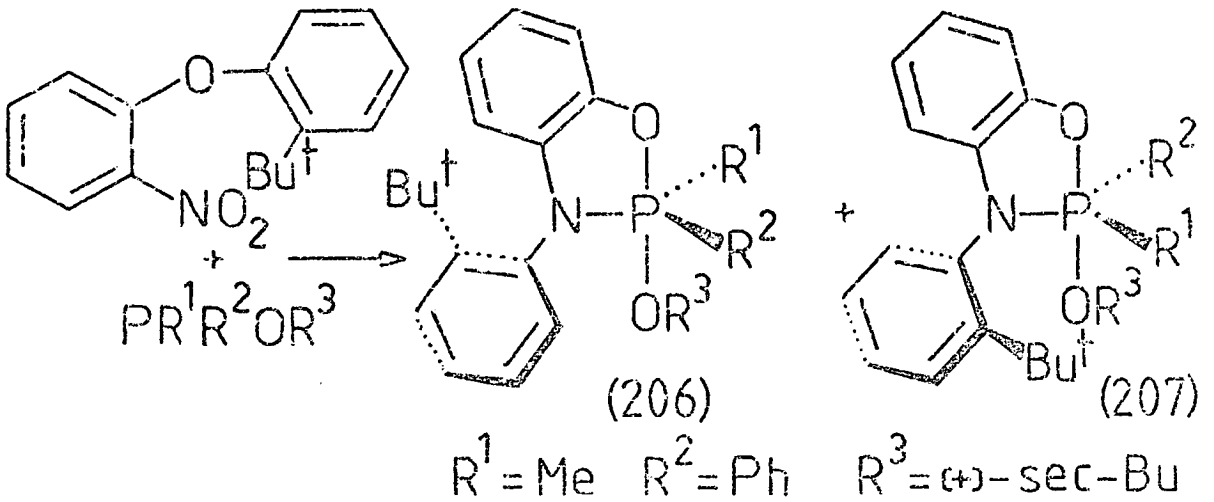
5. Attempted synthesis and isolation of a chiral monocyclic pentacoordinate phosphorane

Preamble

The study of the stereochemical course of reactions of a monocyclic pentacoordinate phosphorane of specific configuration at phosphorus could lead to significant advances in the elucidation of reaction mechanisms at penta- and possibly hexacoordinate phosphorus. To date there has been no report of the isolation of such a compound, which is not surprising given the ease with which most pentacoordinate phosphoranes can undergo racemisation by ligand reorganisation. The preceding variable temperature n.m.r. studies of compound (147) serve to illustrate such a situation.

Although the diastereoisomeric compounds (203) and (204) are both chiral at low temperature they undergo racemisation at higher temperatures, probably *via* a pseudorotation process as shown in Scheme 109. Nonetheless, it was apparent from these studies that a pentacoordinate phosphorane of this type might be devised in which pseudorotational processes could be restricted so as to allow chirality at phosphorus to prevail at room temperature. The key observation which led to this conclusion was that although the methoxyl groups interchanged between *a* and *e* sites at room temperature they did not, on the n.m.r. time scale, alter their geometry relative to the 5-phenyl group. This phenomenon was attributed to the high energy barrier involved in the unfavourable diequatorial placement of the five-membered ring which effectively restricts interchange of the equatorial groups. It followed that if a further restriction was imposed on the exchange of *a* and *e* groups, by

replacement of a single methoxyl group with a group of relatively lower apicophilicity, for example alkyl or aryl (see Figure 1 page 45), then an essentially 'frozen' pentacoordinate phosphorane would be obtained. Support for this proposal is proved by the observation of a $POCH_3$ phosphorus-hydrogen coupling constant of J_{PH} = 10 Hz in the ^1H n.m.r. spectrum of (148) at 28°C, indicating that the methoxyl group is located in an apical position. Moreover, previous work in this laboratory has culminated in the preparation, by reaction of (+)-sec-butyl methylphenylphosphinite with 2-tert-butylphenyl 2-nitrophenyl ether in boiling cumene (Scheme 113), of the non-interconvertible chiral diastereoisomers (206) and (207).[259] Unfortunately, separation of these compounds could not be achieved by fractional crystallisation and attempts to separate them by chromatography were frustrated by hydrolysis. In view of the ease and flexibility offered by the 'azide route' to pentacoordinate phosphoranes it was decided to firstly, establish the validity of the above propositions, and secondly, to attempt the synthesis and isolation of a chiral monocyclic pentacoordinate phosphorane.

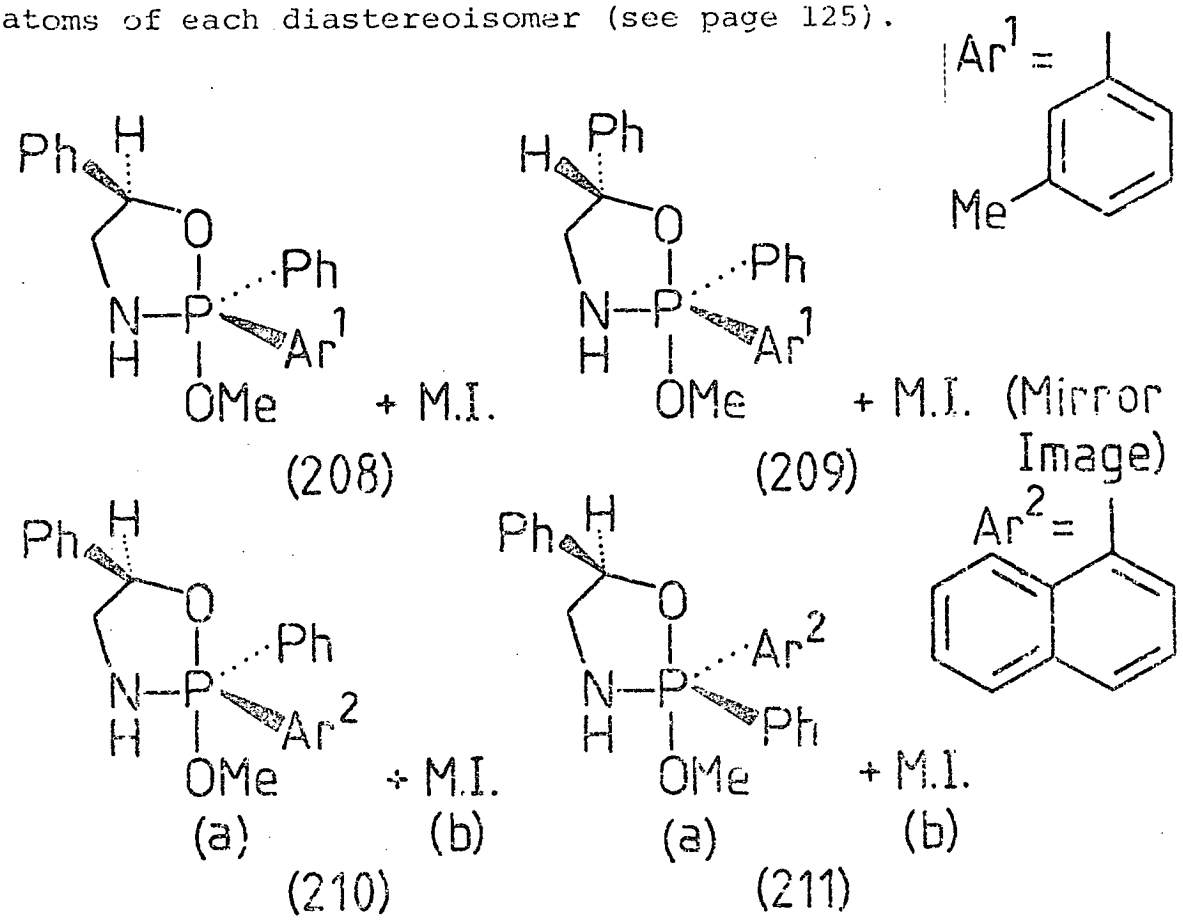


Scheme 113

5.1 Reaction of racemic 2-azido-1-phenyl-1-ethanol with racemic phosphinites

Encouragement for the aforementioned approach was obtained from initial ^{31}P n.m.r. studies of the reaction of 2-azido-1-phenyl-1-ethanol with methyl phenyl-m-tolyl-phosphinite which showed the formation of two pentacoordinate phosphoranes in approximately equal amounts at δ_p -42.10 and -42.26. These signals were assigned to the racemic diastereoisomers (208) and (209), the observation of which implied that their interconversion was slow on the n.m.r. time scale. Even so, it was considered that these compounds were structurally too similar, as reflected by the very small difference in ^{31}P chemical shifts, to facilitate diastereo-isomer separation. The phosphinite precursor was therefore modified such that when methyl 1-naphthylphenylphosphinite was reacted with 2-azido-1-phenyl-1-ethanol two racemic penta-coordinate phosphoranes (210) and (211) were again observed in approximately equal amounts, but in this instance the difference in chemical shift was much larger, δ_p -40.7 and -41.9. On cooling the reaction mixture to -10°C, the latter product crystallised from solution completely free of the other isomer. The more soluble diastereoisomer could not be isolated but ^{13}C n.m.r. spectra of the isolated isomer and of the crude reaction mixture provided supporting evidence that the major products of reaction of the azido compound with methyl 1-naphthylphenylphosphinite were compounds (210) and (211).

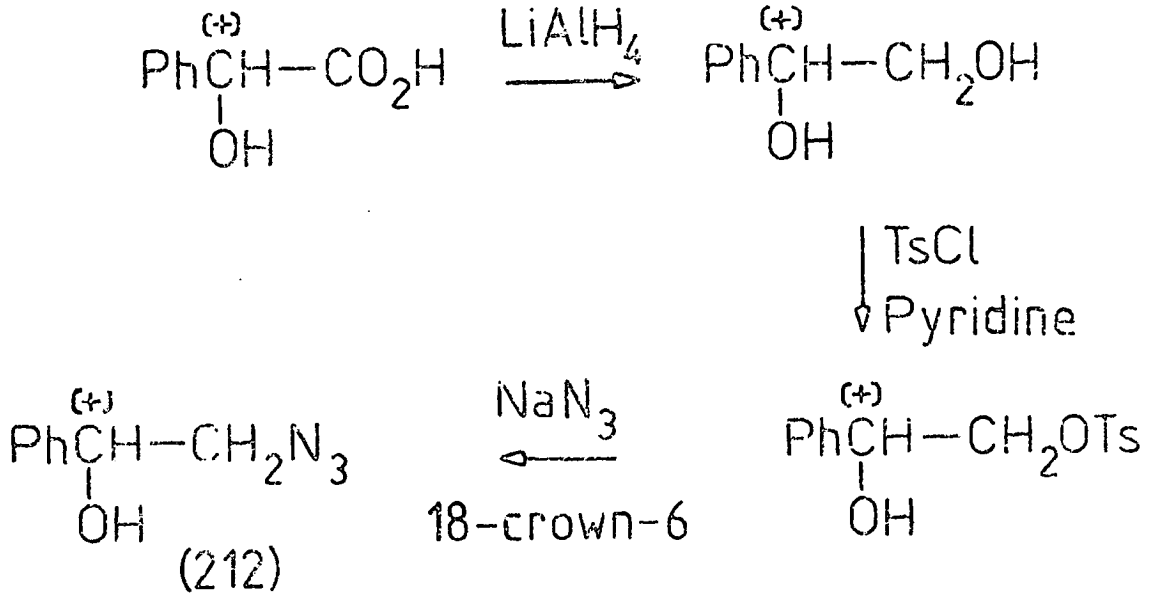
Thus, phosphorus coupled ^{13}C resonances were observed corresponding to the $POCH_3$ group and the two ring carbon atoms of each diastereoisomer (see page 125).



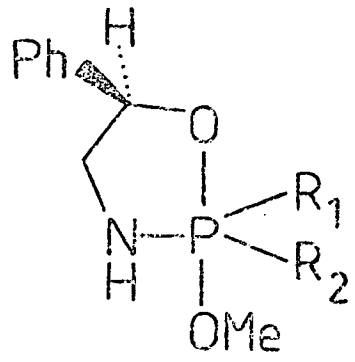
Examination of the isolated diastereoisomer by ^{31}P n.m.r. in deuterochloroform over 50 h at 28°C showed that no detectable stereomutation to the other isomer occurred. Unfortunately, attempts to observe interconversion at 120°C in dichlorobenzene were frustrated by decomposition. Nonetheless, the stability of the compound towards stereomutation at 28°C and its ease of isolation provided sufficient encouragement to justify the synthesis of a single enantiomer of the azido compound and to react it with a racemic phosphinite in order to obtain a single monocyclic chiral pentacoordinate phosphorane.

5.2 Reaction of (S)-(+)-2-azido-1-phenyl-1-ethanol with racemic phosphinites

(S)-(+)-2-Azido-1-phenyl-1-ethanol (212) was prepared in three steps from (S)-(+)-mandelic acid as shown in Scheme 114. As before reaction with racemic methyl 1-naphthylphenylphosphinite gave two pentacoordinate phosphoranes (210a) and (211a) as indicated by ^{31}P n.m.r. In this case, however, neither of the diastereoisomers could be induced to crystallise from the reaction mixture or from a range of pure and mixed solvents. This failure to obtain a single diastereoisomer indicated that a mixed crystal had been isolated from the racemic reaction mixture which could not be formed when only a single enantiomer was present.

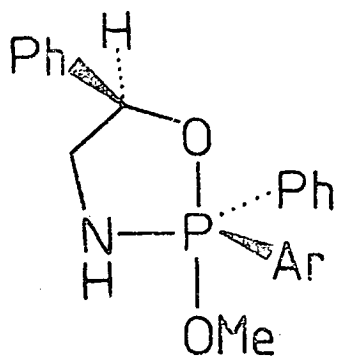


Scheme 114

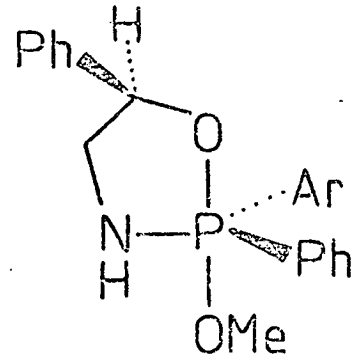


R_1	R_2	δ_p	MPt	M.I.[a,b]
Me	1-Naphthyl	-33.9	60-62°C	339.137350
		-34.3		339.138808
Me	Ph	-42.7	58-60°C	not observed
		-43.4		

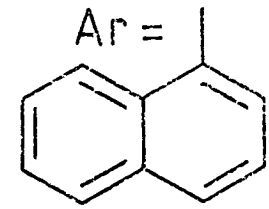
Table 8



(210a)



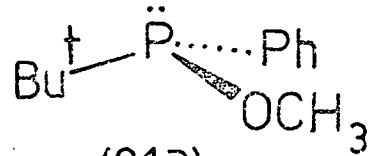
(211a)



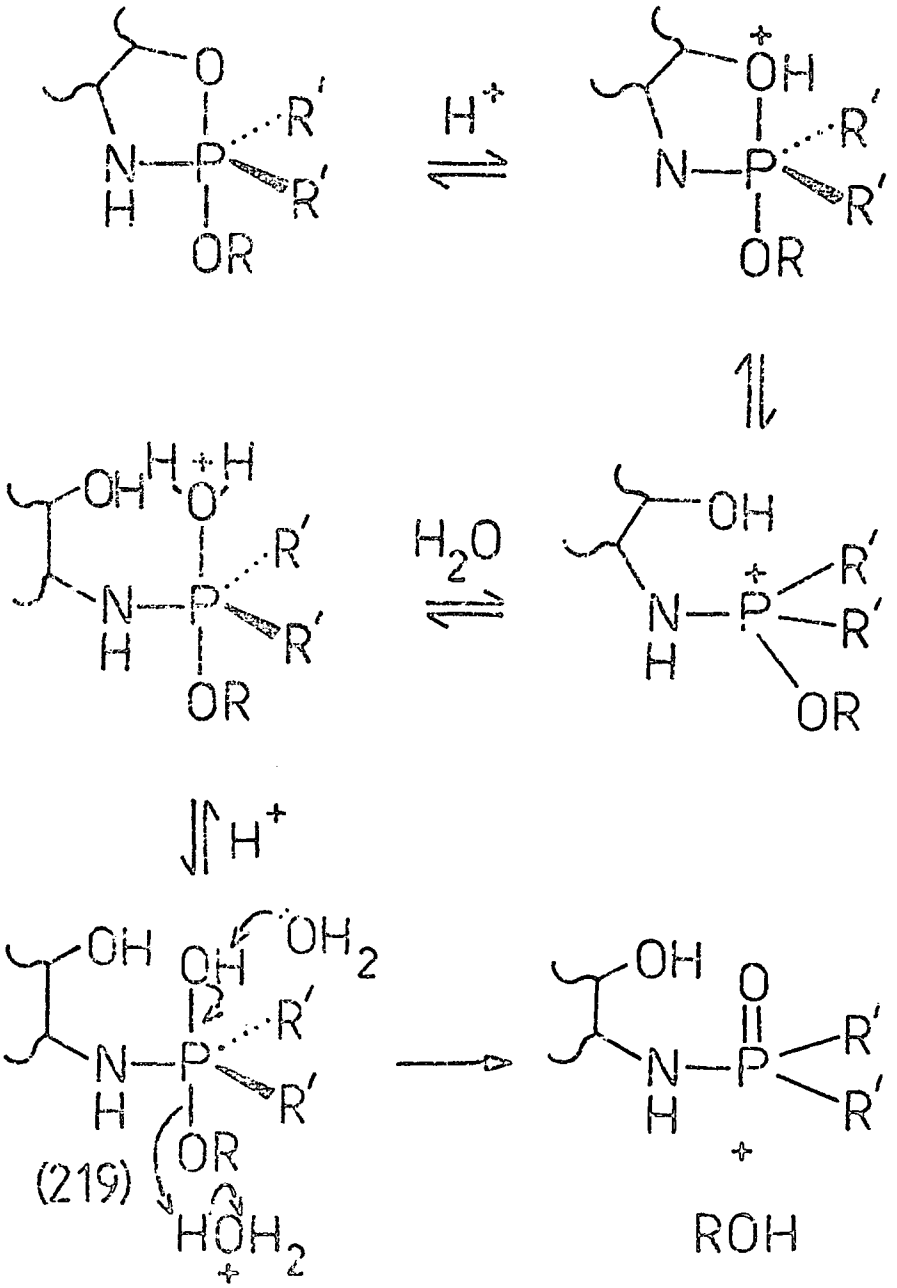
As a consequence of this failure to isolate a chiral monocyclic pentacoordinate phosphorane from the mixture of diastereoisomers (210a) and (211a), two other racemic phosphinites were reacted with the chiral azido compound as recorded in Table 8. In each case a crystalline product was obtained but these proved to be too hydrolytically unstable to be isolated in a pure form. Moreover, no diastereoisomer enrichment could be detected by ^{31}P n.m.r. upon crystallisation of the crude mixture.

In summary, this attempt to prepare and isolate a chiral monocyclic pentacoordinate phosphorane by the reaction of (S)-(+)-2-azido-1-phenyl-1-ethanol with racemic phosphinites resulted in failure. One notable result of this study, however, is the observation that the isolated racemic diastereoisomer (210) or (211) was stable towards stereomutation at 28°C.[260] This confirms that, in molecules of this type, the original proposals concerning the restriction of pseudorotational processes are correct.

As in earlier studies aimed at preparing a chiral monocyclic pentacoordinate phosphorane[259] the strategy failed in the final step, involving separation of the diastereoisomers. A possible solution to this problem is to use a chiral phosphinite in the synthesis and hence obtain a single diastereoisomer only. In this connection Omelanczuk and Mikolajczyk[261] have recently reported the first stereospecific synthesis of the chiral phosphinite (213) with an estimated optical purity of 85%. It seems likely that the isolation of a chiral monocyclic pentacoordinate phosphorane might be facilitated by reacting this compound with (S)-(+)-2-azido-1-phenyl-1-ethanol since a single diastereoisomer would be formed in large excess.



(213)



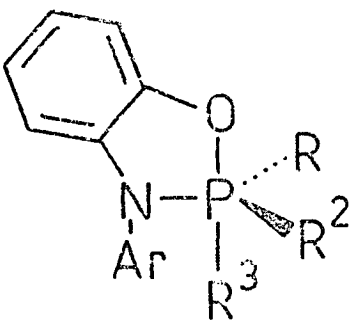
Scheme 115

Appendix

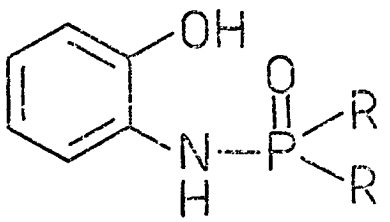
Miscellaneous Studies

1. Hydrolysis of selected pentacoordinate oxazaphosphoranes

As part of a continuing study by Cadogan *et al.*[242,262] involving the hydrolysis of 3-aryl-1,3,2-benzoxazaphospholines (214) selected examples of the related 3-unsubstituted compounds (133),(145), (147), (130) and (131) were hydrolysed under acid catalysed conditions. It was found that in each case the reaction proceeded rapidly at room temperature with the loss of methanol or ethanol to give very high yields (>95%) of the corresponding phosphinamidates (121), (215) and (216) and phosphoramidates (217) and (218). The former results accord with both the observations in the 3-aryl series[242] and with those of Stegmann *et al.*[263]



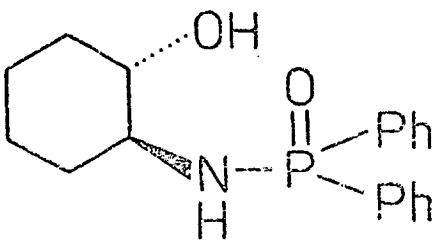
(214)



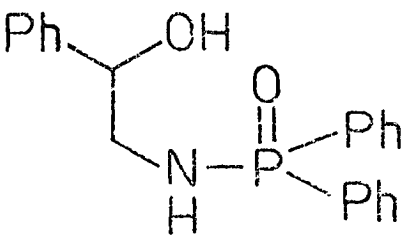
(121) R = Ph

(217) R = OMe

(218) R = OEt



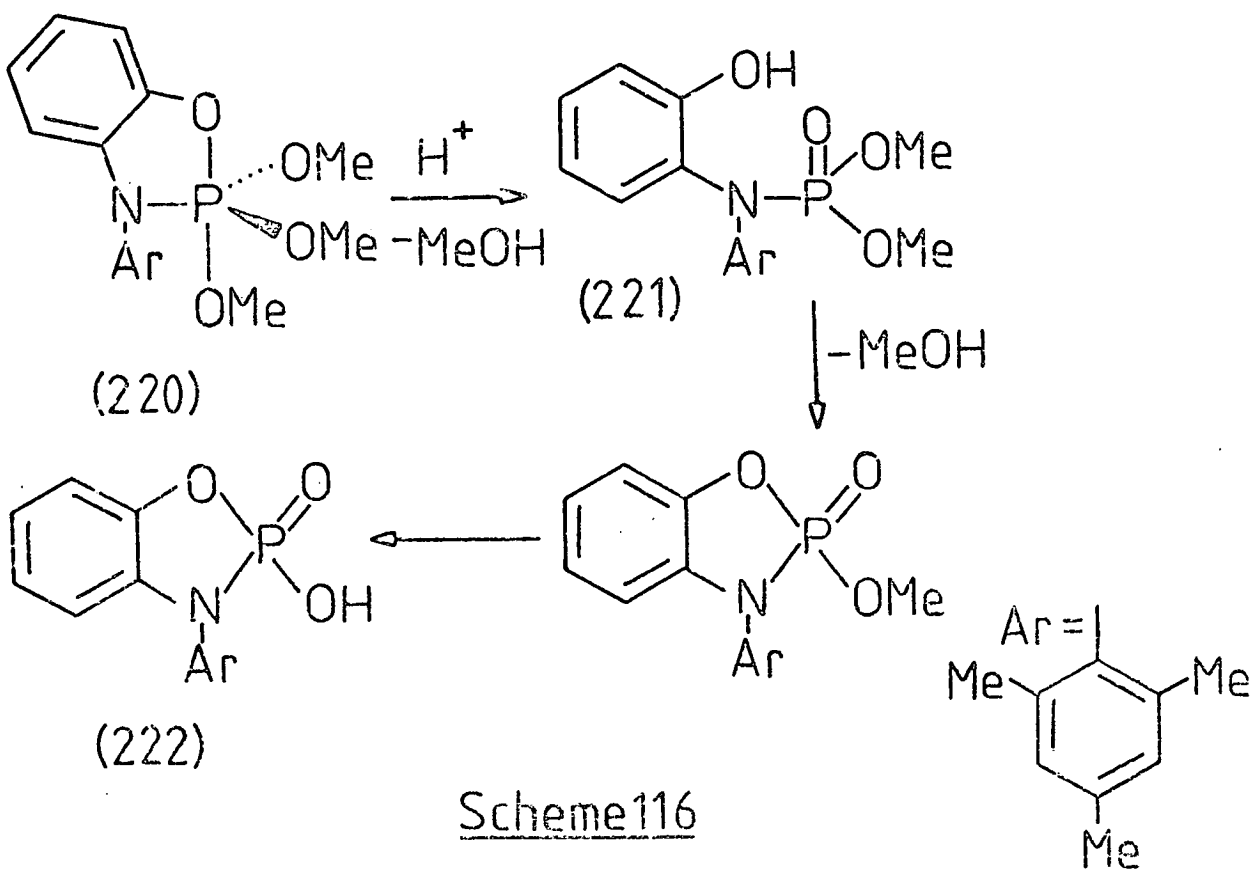
(215)



(216)

A satisfactory account for the above results is provided by the hydrolysis mechanism proposed by Cadogan *et al.*[242] which is shown in Scheme 115. This involves endocyclic cleavage of the phosphorus oxygen bond followed by attack of water at the phosphonium centre to give the intermediate (219) which, upon elimination of an alcohol, yields the phosphinic or phosphoric amides (121, 215-218).

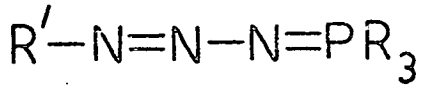
Interestingly, Cadogan *et al.*[242] postulated the intermediacy of phosphoramidate (221) in the hydrolysis of the 3-mesityl derivative (220) but only isolated the cyclic monoester (222) as the final product of the reaction (Scheme 116). This result contrasts with the isolation of phosphoramidates (217) and (218) from the acidic hydrolysis of (130) and (131). This difference in behaviour may be a consequence of employing different reaction conditions in the hydrolyses.



Scheme 116

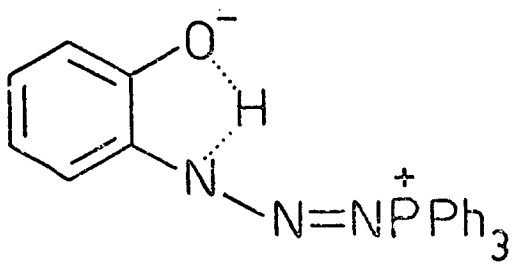
2. Phosphatriazene studies

Mosby and Silva[9] have noted that the general conditions for stabilising a phosphatriazene (3) are that R' should be electron withdrawing, whilst R should be an electron donor.

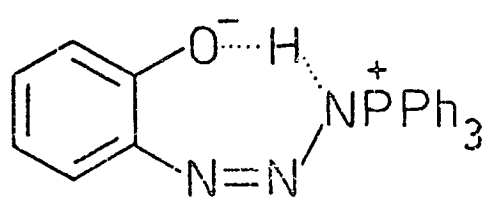


(3)

On this basis it might be expected that the adducts formed from o-azidophenyl benzoate, o-azidophenyl tosylate and N-(o-azidophenyl)-phthalimide with triphenyl phosphine would be more stable relative to that from o-azidophenol due to the electron withdrawing effect of the o-substituents. Surprisingly this proved not to be the case and all the former adducts were found to decompose spontaneously at room temperature to give iminophosphoranes and nitrogen whereas the latter adduct from o-azidophenol could be isolated as a pale yellow crystalline solid. A plausible explanation for this anomalous behaviour may be in the additional stabilisation provided by intramolecular hydrogen-bonding, for example (223) and (224). A similar effect has been proposed to account for the unusual stability of the adduct (10) (see Introduction page 5).



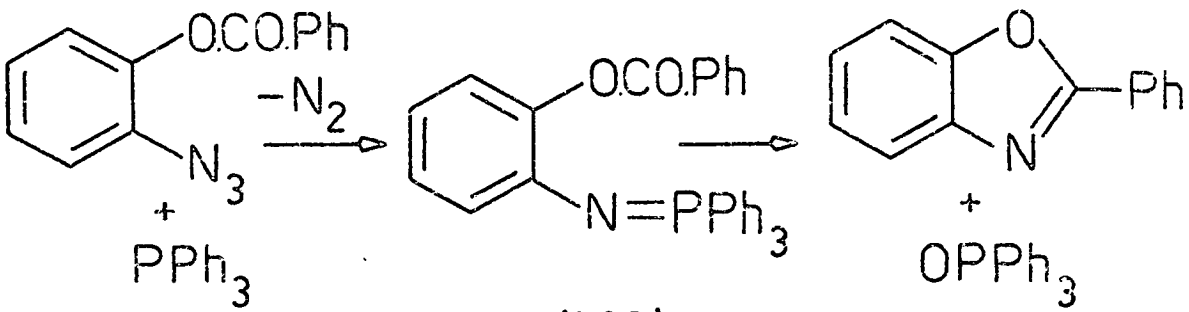
(223)



(224)

3. Intramolecular carbonyl-iminophosphorane reactions

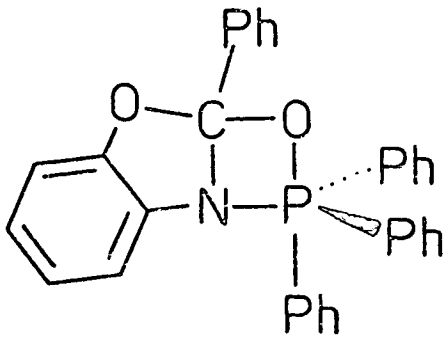
As noted in the Introduction (page 25) Leyshon and Saunders[62] have demonstrated that 2-substituted benzoxazoles can be prepared by the reaction of o-azidophenyl benzoate with phosphites. They proposed that the reaction proceeded *via* the intermediacy of an iminophosphorane. In this study, an iminophosphorane was isolated from the reaction of o-azidophenyl benzoate with triphenylphosphine and characterised as (225), which in solution reacted further to give 2-phenylbenzoxazole and triphenylphosphine oxide in 68 and 46% yield, respectively. Thus, the path of this reaction has now been clearly demonstrated and is shown in Scheme 117.



(225)

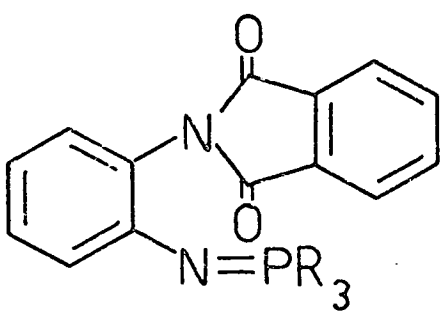
Scheme 117

It was further observed, by ^{31}P n.m.r. that during the course of the reaction an intermediate appeared at δ_p-58.0. An interesting but speculative assignment for this resonance is the pentacoordinate phosphorane (226) which would result from a 2+2 cycloaddition of the C=O and P=N bonds.



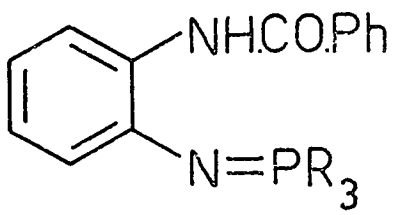
(226)

Although there are several reports in the literature concerning intramolecular reactions of an aldehyde, ketone or ester carbonyl group with iminophosphoranes (see Introduction pages 25-28) there has been no report of an analogous reaction with an amide.[264] Therefore, a short study was made of the thermal reactions of iminophosphoranes (227), (228) and (229), (230).



(227) R=Ph

(228) R=OMe

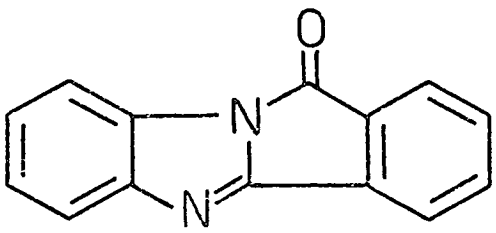


(229) R=Ph

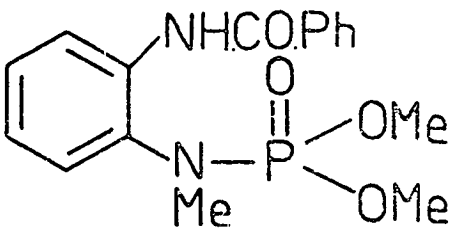
(230) R=OMe

It was found that (227) and (228) slowly decomposed when heated under reflux in tert-butylbenzene to give 11H-isoindolo[2,1-α]benzimidazol-11-one (231) in 65 and 66% yield, respectively, and the corresponding phosphine oxide and phosphate. A similar thermolysis of (229) in tert-butylbenzene gave 2-phenyl-benzimidazole in 63% yield together with triphenylphosphine oxide. However, thermolysis of

(230) in boiling chlorobenzene gave only the phosphoramidate (232), presumably *via* migration of a methyl group from oxygen to nitrogen.[247]



(231)



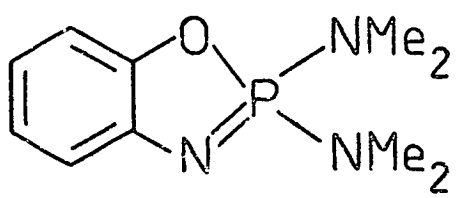
(232)

From these results it is clear that the intermolecular amide-carbonyl/iminophosphorane reaction is feasible and moreover that it is preferable to employ phosphine rather than phosphite derivatives in order to avoid alternative reactions.

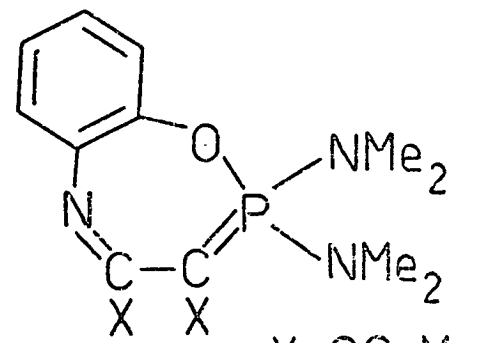
4. Reaction of 2,2-di(dimethylamino)-benzoxazaphosphole with dimethyl acetylene dicarboxylate

There have been several reports recently of the reaction of cyclic iminophosphoranes with ketones,[45] diphenylketene,[46] isocyanates,[47] and isothiocyanates,[48] leading to the formation of pentacoordinate adducts. These reactions are significant because they lend support to the conclusion by Frøyen[44] that the C=O or C=S/P=N reaction proceeds *via* the intermediacy of a pentacoordinate phosphorane.

To test the hypothesis that a pentacoordinate intermediate is involved in the iminophosphorane/acetylene reaction[49] the cyclic iminophosphorane (117) was reacted with dimethyl acetylene dicarboxylate at room temperature and the reaction monitored by ^{31}P n.m.r. No pentacoordinate intermediate was detected but the reaction proceeded smoothly to give the novel stabilised ylide (233).

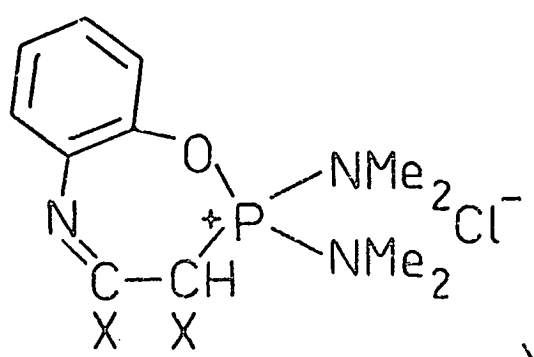


(117)



(233)

The structure of (233) was established principally on the basis of ^{13}C n.m.r. data. Thus, distinctive resonances were observed at δ_C 37.1 (d, $N(CH_3)_2$, J_{PC}4Hz), 49.9(s,$CO_2\underline{C}H_3$), 51.9(s,$CO_2\underline{C}H_3$), 61.4(d,P=C,J_{PC}178Hz), 159.5(d,C=N,J_{PC}4Hz), and 167.1 168.0 168.8 (2 x $\underline{C}O_2Me$). Chemical evidence in support of this structure was provided by the ready formation of the phosphonium salt (234) upon treatment of (233) with hydrogen chloride. In addition the ylide could be regenerated by the addition of triethylamine to a solution of (234).



(234)

Publications

Included in the appendix are copies of publications which are in part based on the work described in this thesis. These are as follows, J.I.G. Cadogan, N.J. Stewart, and N.J. Tweddle, J.Chem.Soc.,Chem.Commun., 1978, 182; J.I.G. Cadogan, I. Gosney, E. Henry, T. Naisby, B. Nay, N.J. Stewart, and N.J. Tweddle, J.Chem.Soc.,Chem.Commun., 1979, 189; and J.I.G. Cadogan, N.J. Stewart, and N.J. Tweddle, J.Chem.Soc., Chem.Commun., 1979, 191.

Phosphorus-containing Heterocycles from Phosphorus(III) Reagents and *ortho*-Azidoaromatic Compounds: Synthesis of 2,2-Di(dimethylamino)-1,3,2-benzoxazaphosphole and Various 2,3-Dihydro-1,3,2-benzoxazaphosph(v)oles

By J. I. G. Cadogan,* Nevin J. Stewart, and Neil J. Tweddle
(Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ)

Reprinted from

Journal of The Chemical Society
Chemical Communications
1978

The Chemical Society, Burlington House, London W1V 0BN

Phosphorus-containing Heterocycles from Phosphorus(III) Reagents and *ortho*-Azidoaromatic Compounds: Synthesis of 2,2-Di(dimethylamino)-1,3,2-benzoxazaphosphole and Various 2,3-Dihydro-1,3,2-benzoxazaphosph(v)oles

By J. I. G. CADOGAN,* NEVIN J. STEWART, and NEIL J. TWEDDLE
(*Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh* EH9 3JJ)

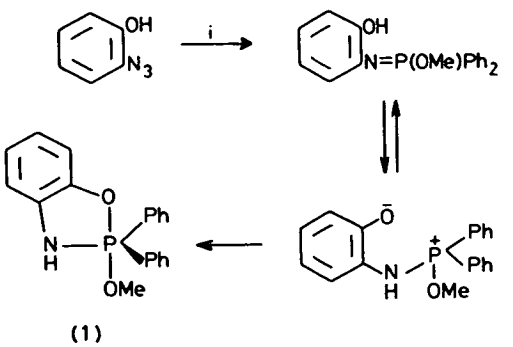
Summary *o*-Azidophenol reacts with methyl diphenylphosphinite to give the amino(oxy)phosphorane, 2-methoxy-2,2-diphenyl-2,3-dihydro-1,3,2-benzoxazaphosph(v)ole (**1**; 90%), which is also produced (55%) from *o*-aminophenol, the phosphinite, and *N*-chlorodi-isopropylamine; *o*-azidophenyl benzoate reacts with hexamethylphosphorous triamide to give 2,2-di(dimethylamino)-1,3,2-benzoxazaphosphole (**2**; 76%) and *NN*-dimethylbenzamide.

ORGANIC azides react readily with organophosphorus(III) reagents to give the corresponding imines[1] [*e.g.*, equation (1)]. We now report the adaptation of this reaction to

$$(EtO)_3P + PhN_3 \rightarrow (EtO)_3P{=}NPh \quad (1)$$

provide a simple, and mild, route to the amino(oxy)phosphorane system (1). Thus, addition under nitrogen of *o*-azidophenol (4·75 mmol) in dry light petroleum (13 ml, b.p. 40—60 °C) to methyl diphenylphosphinite (4·8 mmol) in the same solvent (5 ml) at 0 °C led to evolution of nitrogen with precipitation of 2-methoxy-2,2-diphenyl-2,3-dihydro-1,3,2-benzoxazaphosph(v)ole (1) as a colourless solid [90%, m.p. > 240 °C (decomp.)]. The material had correct elemental analysis and the expected n.m.r. spectra: ^{31}P ($CDCl_3$) δ (positive to high frequency) −36·0 p.p.m.; ^1H ($CDCl_3$) δ, 2·98 [d, 3H, $J(^{31}P–H)$ 11 Hz, POMe], 4·86 [d, 1H, $J(^{31}P–H)$ 20 Hz, NH], 6·45—6·80 (m, 4H, ArH), 7·20—7·45 (m, 6H, ArH), and 7·60—7·90 (m, 4H, Ar-*o*-H of $-PPh_2$). The structure was confirmed by an alternative synthesis (55% yield) from *o*-aminophenol, methyl diphenylphosphinite, and *N*-chlorodi-isopropylamine in an analogue of a synthesis of oxaphosph(v)oles.[2] Trimethyl and triethyl phosphites and dimethyl phenylphosphonite similarly reacted with *o*-azidophenol, to give the corresponding oxazaphosph(v)oles, ^{31}P n.m.r. measurements indicating almost quantitative conversions (^{31}P δ, −52·3, −53·9, and −39·8 p.p.m. respectively). Reaction as in Scheme 1 is suggested.

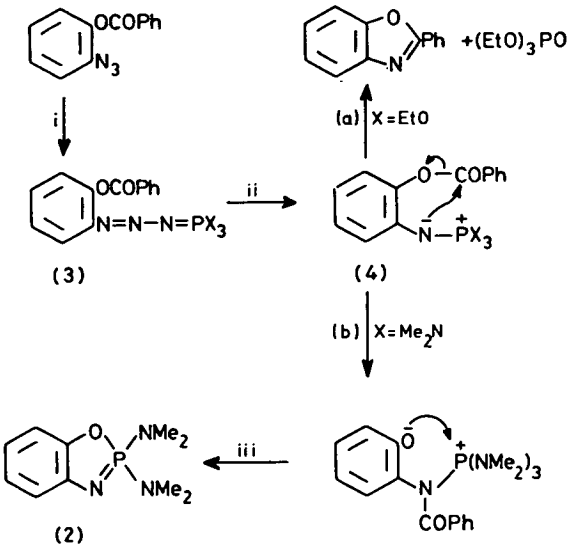
We also report a related novel synthesis of the 1,3,2-benzoxazaphosphole system (2). Addition under dry nitrogen of hexamethylphosphorous triamide (2·15 mmol) in super-dry cyclohexane (5 ml) to *o*-azidophenyl benzoate (1·99 mmol) in dry cyclohexane at 20 °C led to the precipitation of the triazene [(3; X = NMe_2); 94%; m.p. > 95 °C



SCHEME 1. i, Ph_2POMe, $-N_2$.

(decomp.), correct elemental analysis and expected ^1H n.m.r. data; ^{31}P n.m.r., δ +42·4 p.p.m.]. In a replicate experiment the triazene was not isolated but the mixture was boiled under reflux (80 °C) for 24 h when crystalline 2,2-di-(dimethylamino)-1,3,2-benzoxazaphosphole (**2**; m.p. 174—177 °C) was collected (75%). Chromatography of the mother liquors gave *NN*-dimethylbenzamide (86%). Compound (**2**) had the correct analysis and expected n.m.r. spectra: ^{31}P, δ +68·0; ^1H ($CDCl_3$), δ 2·71 [d, 12H, $PNMe_2$, $J(^{31}P–H)$ 11 Hz], and 6·38—6·60 (m, 1H, ArH) and 6·72—6·96 (m, 3H, ArH).

This reaction is noteworthy because the corresponding reaction of *o*-azidophenyl benzoate with triethyl phosphite



SCHEME 2. i, X_3P; ii, $-N_2$; iii, $-PhCONMe_2$.

gives 2-phenyl-1,3-benzoxazole in good yield [Scheme 2, step (a)].[3] One possible explanation of the formation of the oxazaphosphole (**2**) is that it could be due to the high nucleophilicity of the nitrogen end of the P–N dipole (**4**) [step (b)] leading to reaction as in Scheme 2.

(*Received, 29th November* 1977; *Com.* 1225.)

[1] H. Staudinger and E. Hauser, *Helv. Chim. Acta*, 1921, **4**, 861; M. I. Kabachnik and V. A. Gilyarov, *Izvest. Akad. Nauk. S.S.S.R., Otdel. khim. Nauk*, 1956, 790 (*Chem. Abs.*, 1957, 1823).
[2] S. Antczak, S. A. Bone, J. Brierley, and S. Trippett, *J.C.S. Perkin I*, 1977, 278.
[3] L. J. Leyshon and D. G. Saunders, *Chem. Comm.*, 1971, 1608.

A General Route to Pentaco-ordinate Amino(oxy)- and Diamino(oxy)-phosphoranes from Azido-compounds and Phosphorus(III) Reagents

By J. I. G. Cadogan,* Ian Gosney, Elizabeth Henry, Thomas Naisby, Barry Nay, Nevin J. Stewart, and Neil J. Tweddle

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1979

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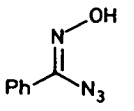
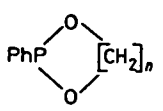
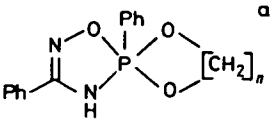
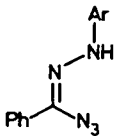
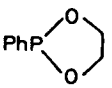
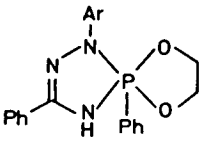
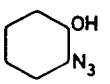
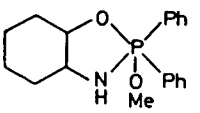
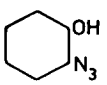
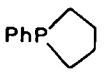
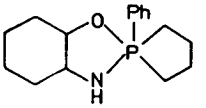
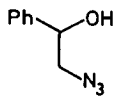
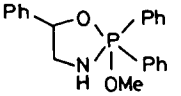
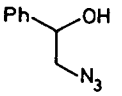
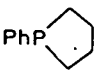
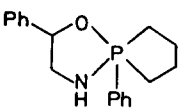
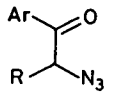
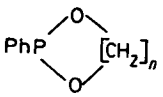
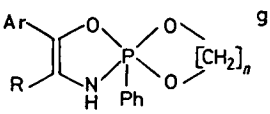
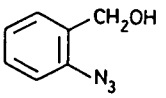
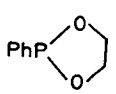
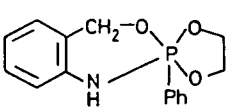
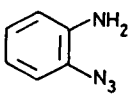
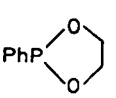
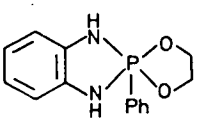
A General Route to Pentaco-ordinate Amino(oxy)- and Diamino(oxy)-phosphoranes from Azido-compounds and Phosphorus(III) Reagents

By J. I. G. CADOGAN,* IAN GOSNEY, ELIZABETH HENRY, THOMAS NAISBY, BARRY NAY, NEVIN J. STEWART, and NEIL J. TWEDDLE

(*Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh* EH9 3JJ)

Summary Bifunctional azido-compounds such as benzohydroximic azide, α-azidobenzaldehyde 2,4-dibromophenylhydrazone, *trans*-1-azido-2-hydroxycyclohexane, 2-azido-1-phenylethanol, 2-azidobenzyl alcohol, *o*-azido-

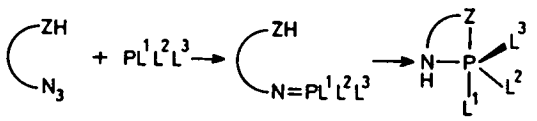
TABLE

Starting azide	P^{III} Reagent	Product	
			a
			b
	Ph_2POMe		c
			d
	Ph_2POMe		e
			f
			g
			h
			i

[a] (1); $n = 2$, 91%, m.p. 123—124 °C, δ − 19·26 [all δ refer to ^{31}P ($CDCl_3$) p.p.m.]; $n = 3$, 97%, m.p. 109 °C, δ − 34·99. [b] Ar = 2,4-$Br_2C_6H_3$; 96%, m.p. 164—166 °C, δ − 40·33. [c] 61%, m.p. 71—73 °C, δ − 44·67. [d] 60%, m.p. 37—39 °C, δ − 40·14. [e] 85%, m.p. 103—105 °C, δ − 42·56. [f] 84%, m.p. 45—47 °C, δ − 36·91. [g] (2); Ar = R = Ph, $n = 2$, 89%, m.p. 88 °C (decomp.), δ − 29·7; Ar = R = Ph; $n = 3$, 96%, m.p. 94 °C (decomp.), δ − 45·6; Ar = Ph, R = H, $n = 2$, 61%, m.p. 84—86 °C (decomp.), δ − 25·4; Ar = Ph, R = H, $n = 3$, 82%, m.p. 87 °C (decomp.), δ − 41·1; Ar = *p*-BrC_6H_4, R = H, $n = 2$, 71%, m.p. 85 °C (decomp.), δ − 25·3; Ar = *p*-BrC_6H_4, R = H, $n = 3$, 85%, m.p. 105 °C (decomp.), δ − 40·8; Ar = *p*-$MeOC_6H_4$, R = H, $n = 2$, 73%, m.p. 99 °C (decomp.), δ − 25·6; Ar = *p*-$MeOC_6H_4$, R = H, n = 3, 74%, m.p. 102 °C (decomp.), δ − 41·2; Ar = *p*-PhC_6H_4, R = H, $n = 2$, 85%, m.p. 105 °C (decomp)., δ − 25·5. [h] 61%, m.p. 95—98 °C, δ − 44·46. [i] 72%, m.p. 137—141 °C, δ − 39·03.

aniline, and α-azidoacetophenones react with a variety of phosphorus(III) reagents to give pentaco-ordinate amino-(oxy)- and diamino(oxy)-phosphoranes.

We report a synthesis of some new pentaco-ordinate phosphoranes by reaction of aliphatic bifunctional azides with organophosphorus(III) reagents. The general reaction, which proceeds *via* the formation of the iminophosphorane function followed by intramolecular cyclisation *via* addition to the P=N group (Scheme), is exemplified as follows: addition of benzohydroximic azide (3·08 mmol) in ether to 2-phenyl-1,3,2-dioxaphospholan (3·27 mmol) in ether at room temperature under nitrogen, followed by removal of



SCHEME

solvent after 24 h gave 2,2-ethylenedioxy-2-phenyl-2,3-dihydro-4-phenyl-1,3,5,2-oxadiazaphosph(v)ole (1; $n = 2$; 91%; Table, footnote a).† Further phosphoranes similarly produced are listed in the Table. That the reaction is capable of extension follows from our preliminary observation of ^{31}P resonances characteristic of phosphoranes (large negative shifts) in reactions of α-azidoacetic acid, α-azidoacetamide, and α-azidophenylacetic acid, with a wide series of cyclic and acyclic phosphorus(III) reagents. The general reaction is thus complementary to the reaction of ω-amino-substituted phosphites with phenyl azide to give amino(oxy)phosphoranes.[1]

The isolation of phosphoranes such as the 2,2-ethylenedioxy-2-phenyl-2,3-dihydro-4-phenyl-1,3,2-oxazaphosph(v)-oles (2; $n = 2$; Table, footnote g) from 2-azido-ketones and 2-phenyl-1,3,2-dioxaphospholan is of interest because reaction[2] of triphenylphosphine with the related azido-ketones, *e.g.* α-azidoacetophenone, does not give an isolable phosphorane; reaction at high temperature gives instead 1,4-diphenylpyrazine.

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† All isolated phosphoranes had the expected elemental analyses and mass spectra.

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A Simple, One-flask Synthesis of Pentaco-ordinate Phosphoranes

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A Simple, One-flask Synthesis of Pentaco-ordinate Phosphoranes

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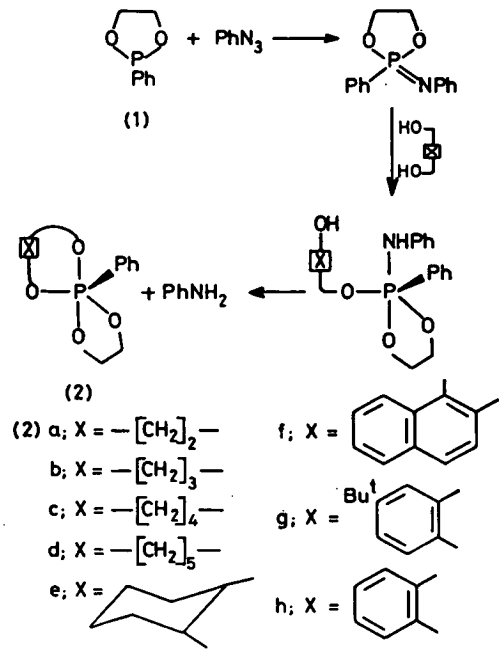
Summary In a synthesis capable of extension, 2-phenyl-1,3,2-dioxaphospholan reacts at room temperature with phenyl azide followed by diols, *o*-dihydroxyarenes, or *o*-hydroxythiophenol to give phosphoranes (68—100%) including the first isolated phosphoranes containing 7- and 8-membered alicyclic rings, *i.e.* 2,2-ethylenedioxy-2-phenyl-1,3,2-dioxaphosph(v)epan and 2,2-ethylenedioxy-2-phenyl-1,3,2-dioxaphosph(v)ocan.

WE here report a simple and convenient one-flask synthesis of pentaco-ordinate phosphoranes, *e.g.* (**2**), from tervalent phosphorus reagents, hydroxy-compounds, and azidobenzene.

We have observed[1,2] that vicinal- or *o*-azidohydroxy compounds, and related bifunctional azides react with phosphorus(III) reagents to give phosphoranes (*e.g.* Scheme in the preceding Communication[2]) *via* intramolecular addition of the $XO^{\delta-} \cdots H^{\delta+}$ unit across the iminophosphorane (P=N) bond. We argued therefore that analogous intermolecular addition should also occur [$R_3^3P{=}NR^1 + R^2OH \rightarrow R_3^3P(OR^2)NHR^1$], and that further reaction *via* displacement of the amino group (R^1NH) by R^2OH should then lead to a new route to phosphoranes [$R_3^3P(OR^2)NHR^1 + R^2OH \rightarrow R_3^3P(OR^2)_2$].

We now report the realisation of this expectation. Thus, reaction under nitrogen of 2-phenyl-1,3,2-dioxaphospholan (**1**) in dry dichloromethane with phenyl azide (1 mol equiv.) over 10 min at room temperature followed by rapid addition of catechol (1 mol equiv.) in ether gave a quantitative conversion (by ^{31}P n.m.r.) into the phosphorane (**2h**). Reaction as in the Scheme is assumed. Removal of the solvent and aniline (78% recovery) at 0·05 mmHg, followed by crystallisation from ether afforded the pure phosphorane (71%), m.p. and mixed m.p. 113—115 °C (^{31}P δ — 14·32 p.p.m.; $CDCl_3$).† The seven phosphoranes (**2a—g**) were produced (68—100%) similarly. Of particular interest are the phosphoranes (**2c**) and (**2d**); the former (m.p. 70—72 °C; ^{31}P δ —30·15 p.p.m.; $CDCl_3$) is the first isolated alicyclic phosphorane containing a seven-membered ring[3] while the latter is the first isolated phosphorane containing an eight-membered ring. Compound (**2d**), an oil with the expected ^{13}C n.m.r. spectrum and exact mass spectrum,† exhibits two ^{31}P resonances in $CDCl_3$ (δ —36·14 and —36·46 p.p.m.)



SCHEME

which we attribute to the presence of two equilibrating conformers. In accordance with this a variable temperature n.m.r. experiment in *o*-dichlorobenzene led to coalescence to a single ^{31}P resonance at δ —36·29 p.p.m. at *ca.* 120 °C.

Also produced in this way is the monothio analogue of (**2h**) [74%; m.p. 96—97 °C; ^{31}P δ +4·73 p.p.m.; $CDCl_3$] from *o*-hydroxythiophenol.

Preliminary experiments using ^{31}P reveal that the reaction is capable of extension to produce less stable phosphoranes, *e.g.* by the use of ethanol, phenol, or *o*-aminophenol in place of the above diols or dihydroxybenzenes.

(*Received, 27th October* 1978; *Com.* 1153.)

† All isolated phosphoranes had the expected elemental analysis and mass spectra.

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