The Synthesis and Reactions of Some Pentacoordinate Phosphorus Compounds.

by

STEPHEN ANTCZAK

A Thesis

presented for the degree of

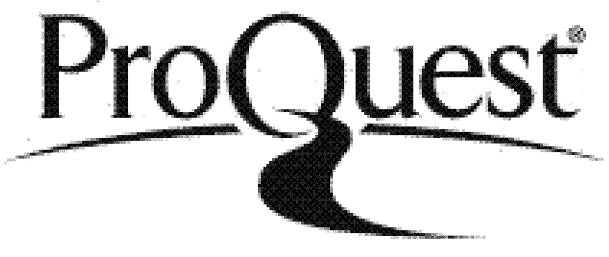
Doctor of Philosophy

in the Faculty of Science

of the

University of Leicester

1977.



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I should also like to thank Maurice Galton and other members of the Leicester University School of Education who are involved with the Ph.D./P.G.C.E. course.

Finally I should like to thank my parents for their constant support and encouragement, and the Science Research Council for a maintenance grant.

TO MY PARENTS.

STATEMENT.

The accompanying thesis submitted for the degree of Doctor of Philosophy entitled "The Synthesis and Reactions of some Pentacoordinate Phosphorus Compounds", is based on work conducted by the author in the Department of Chemistry of the University of Leicester, mainly during the period between September 1974 and August 1977.

All the work recorded in this thesis is original unless otherwise acknowledged in the text or by references. None of the work has been submitted for another degree in this or any other university.

Signed

S Antczak.

25th August 1977.

S. Antczak

August, 1977.

CONTENTS.

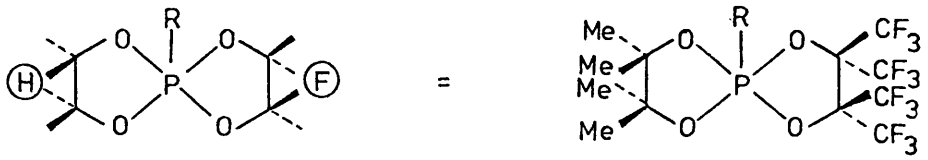
Part of this work has been published in the following paper:

"Synthesis of phosphoranes by using N-Chlorodi-isopropylamine"

by S. Antczak, S.A. Bone, J. Brierley and S. Trippett, J. Chem. Soc. Perkin I, 1977, 278.

Abbreviations

T.B.P.	Trigonal bipyramid
B.P.R.	Berry pseudorotation
T.R.	Turnstile rotation
N.C.D.	N-Chlorodi-isopropylamine
H.F.A.	Hexafluoroacetone
P.F.P.	Perfluoropinacol
D.A.D.	Diethyl azodicarboxylate
Py.	Pyridine
d.n.m.r.	Dynamic n.m.r.



TF– = $CF_3-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-$

ABSTRACT.

The synthesis and reactions of phosphoranes are reviewed, and the mechanisms of ligand permutational isomerisms of phosphoranes are discussed in terms of Berry pseudorotations (B.P.Rs.) and Turnstile rotations (T.Rs.). The factors effecting the activation energies for these pseudorotations are discussed.

The synthesis and thermal reactions of phosphoranes prepared from acyclic trivalent phosphorus compounds and from 3,4-dimethylphosphol-3-enes by using N-chlorodi-isopropylamine is described. A short investigation into the preparation of phosphoranes that contain seven-membered rings suggested that these compounds are inherently unstable.

The synthesis of phosphoranes from cyclic and acyclic phosphine oxides and from phosphetan oxides by using trifluoromethanesulphonic anhydride, is described. Cis-trans isomerisations in 2,2,3,4,4-pentamethylphenylphosphetan ditriflate are discussed in terms of pseudorotations of intermediate phosphoranes.

The dynamic n.m.r. spectra of certain phosphoranes were recorded and, in some cases, the difference in relative apicophilicities of phenyl, methyl and methoxyl groups were determined.

The preparation of phosphoranes from alkoxyphosphetanium salts resulted in Arbuzov reactions whereas the preparation of phosphoranes from alkylthiophosphetanium salts is described and the stereospecific nature of this reaction is discussed in terms of the mechanisms of substitutions in pentacoordinate phosphorus compounds. The preparation and thermal rearrangement of 2,2,3,3-tetrakistrifluoromethyl-5-phenyl-1,4,6-trioxa-5-phospha($5P^{V}$)spiro[4,4]nonane, i.e. the first example of a spirophosphorane containing a 1,2-oxaphospholan ring, is described. Pseudorotations of this phosphorane are discussed.

The preparation of cyclic phosphoranes, containing 1,2--oxaphospholan rings, from epoxides and ylids is discussed and attempts to adapt this reaction to spirophosphorane synthesis is described. The preparation of chlorophosphoranes by the halogenation of allenylphosphonic dichlorides is discussed and attempts to adapt this reaction to allylphosphonates are described. In some cases this reaction lead to carbon-phosphorus bond fission.

Condensation reactions using diethyl azodicarboxylate (D.A.D.) and triphenylphosphine are discussed and the use of these reagents to prepare heterocyclic compounds from diols and related compounds is described.

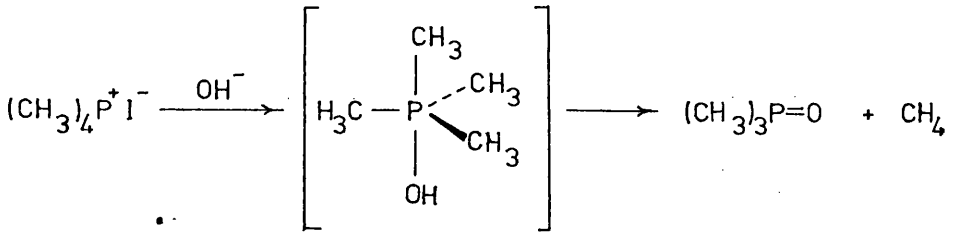
CHAPTER 1. ASPECTS OF PHOSPHORANE CHEMISTRY

1. Synthesis and Reactions of Phosphoranes.

a) Adducts from 1,3-diunsaturated compounds.

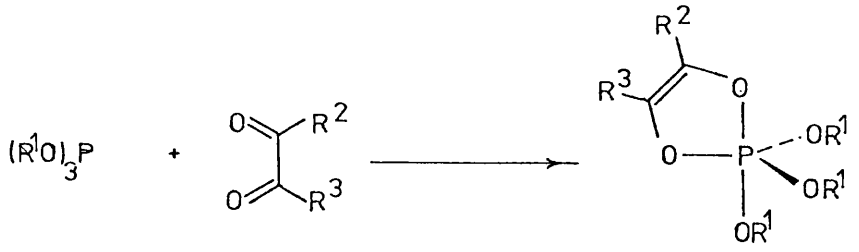
Phosphoranes are compounds which have five covalent bonds between phosphorus and five ligands. They can exist as stable compounds or be present as unstable intermediates, e.g. in the reactions of tetracoordinate phosphorus compounds with nucleophiles.

The first phosphorane intermediate was proposed by Ingold[1] in 1929. He observed the liberation of methane during the alkaline hydrolysis of tetramethylphosphonium iodide which did not occur in the ammonium analogue, and concluded that the intermediate was not a phosphonium hydroxide but a pentacoordinate compound, i.e.



Since then there have been many reports of phosphorane intermediates in both nucleophilic displacement and hydrolytic reactions at tetracoordinate phosphorus.[2-13]

Early work on stable phosphoranes was carried out by Ramirez and his co-workers[16] but a few stable phosphoranes had already been prepared.[17,18] These phosphoranes were 1:1-adducts of phosphites and 1,2-dicarbonyl compounds (1).



1

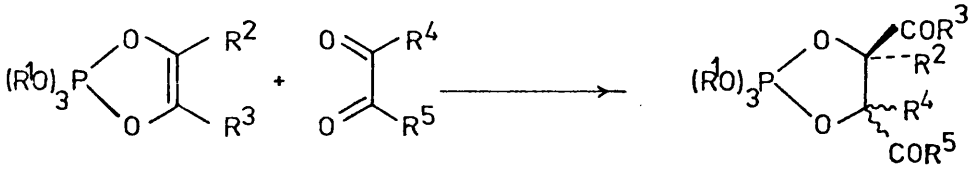
R^1 = Me, Ph.

R^2 = R^3 = Me, Ph, H.

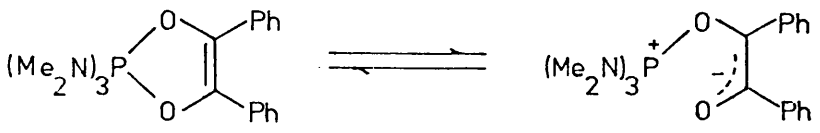
R^2 = Ph, R^3 = H

R^2 = Ph, R^3 = Me

2:1-Adducts can be prepared by reacting the 1:1-adducts with an excess of 1,2-dicarbonyl compound.[16]

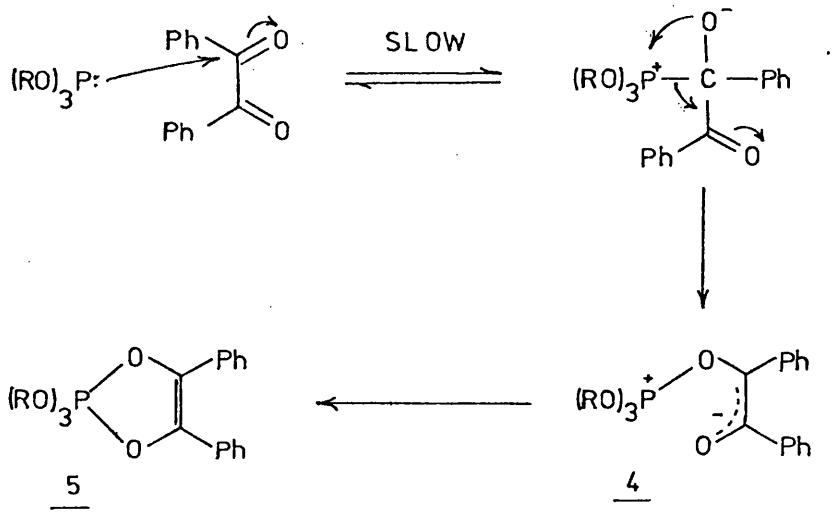


Both the 1:1- and the 2:1-adducts are known to be pentacovalent by their positive ^{31}Pn.m.r. chemical shifts which are typically +50 to +55 ppm. relative to 85% H_3PO_4. When the 1:1-adduct of trisdimethylaminophosphine and benzil is made, the ^{31}Pn.m.r. chemical shift is solvent dependent[19] and varies from +13.1 ppm. in dichloromethane to +32.2 ppm. in hexane showing that the adduct, in solution, is an equilibrium mixture of the pentacoordinate adduct(2) and a phosphonium dipolar ion(3). This demonstrates the ability of amino groups to stabilise positive charges on phosphorus.



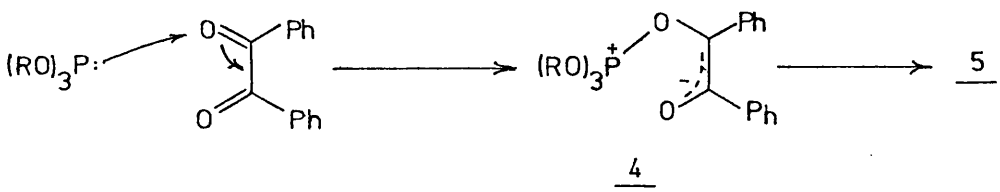
2 3

Ogata and Yamashita[20] have studied the rate of addition of trialkyl phosphites to benzil and they concluded that the first step of the mechanism for this reaction is a rate determining nucleophilic attack of the phosphite on the carbonyl carbon of benzil followed by a rearrangement and cyclisation as shown in scheme 1.



Scheme 1.

Ramirez[21,22] proposed a mechanism involving nucleophilic attack at the carbonyl oxygen atom forming intermediate 4 which subsequently cyclises (scheme 2). This is similar to a Diels-

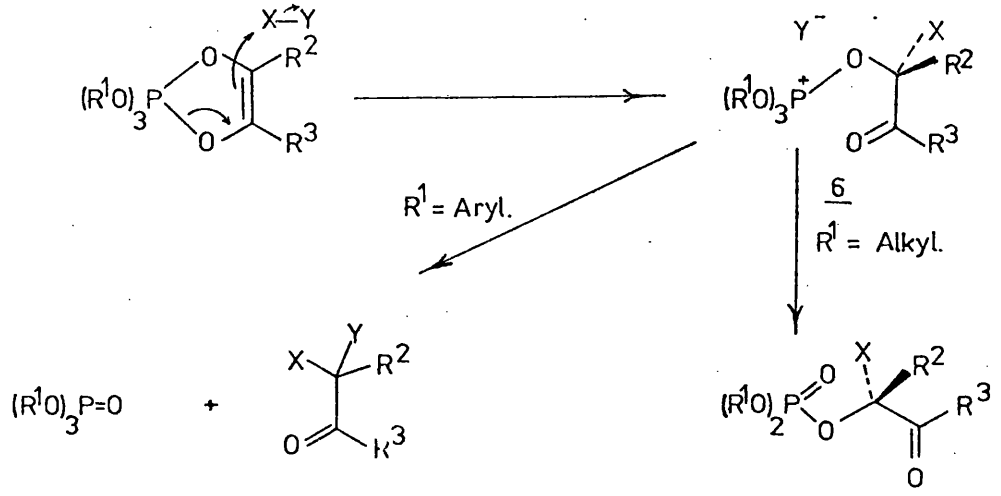


Scheme 2.

Alder reaction but the rate of this reaction shows a solvent dependence and the entropy of activation is too high for an

electrocyclic reaction. There is some e.s.r. spectroscopic evidence that radicals are involved in this type of reaction.[23]

The intermediate 4 is proposed in both mechanisms and it is via this intermediate that the reactions of these adducts are thought to go. In general the reactions occur by the routes outlined in schemes 3, 4 and 5.

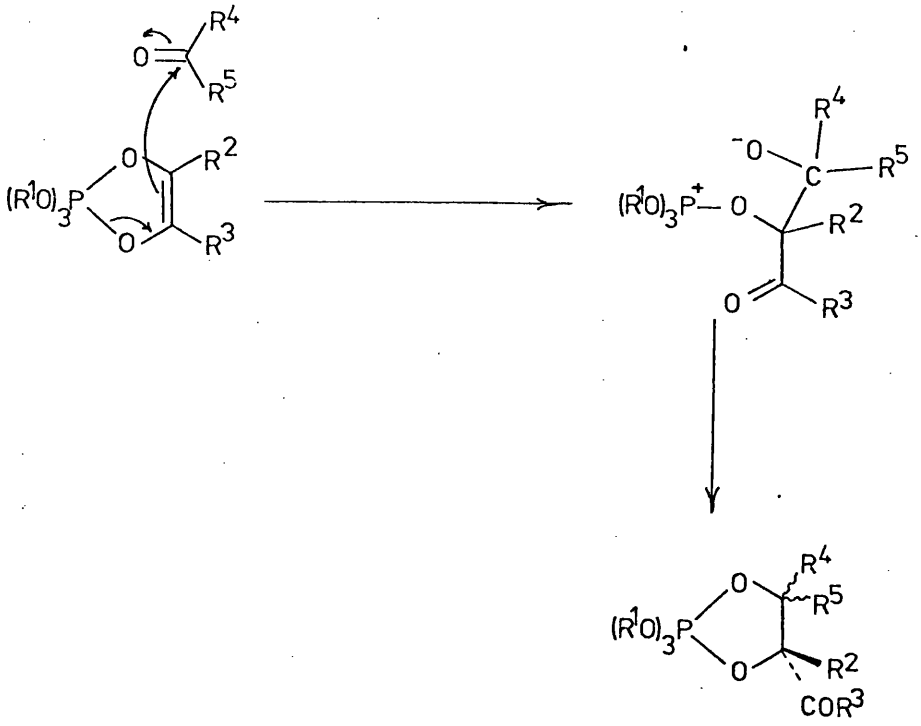


X—Y = Br_2, HCl, H_2O or RCOCl.

Scheme 3.

For the reactions outlined in scheme 3, the first step is electrophilic attack by XY at the 4-position of the 1,3,2-dioxaphosphol-4-ene ring forming a phosphonium intermediate (6). The anion, Y^-, can now attack a carbon atom resulting in an Arbuzov reaction. If R^1= Ph or Aryl, the only carbon available is the carbon bearing the X group but if R^1 is an alkyl group, the anion attacks this preferentially because it is usually the least sterically hindered carbon atom.

These adducts also react with aldehydes, ketones and 1,2-diketones[16,24] as shown in scheme 4. This reaction has

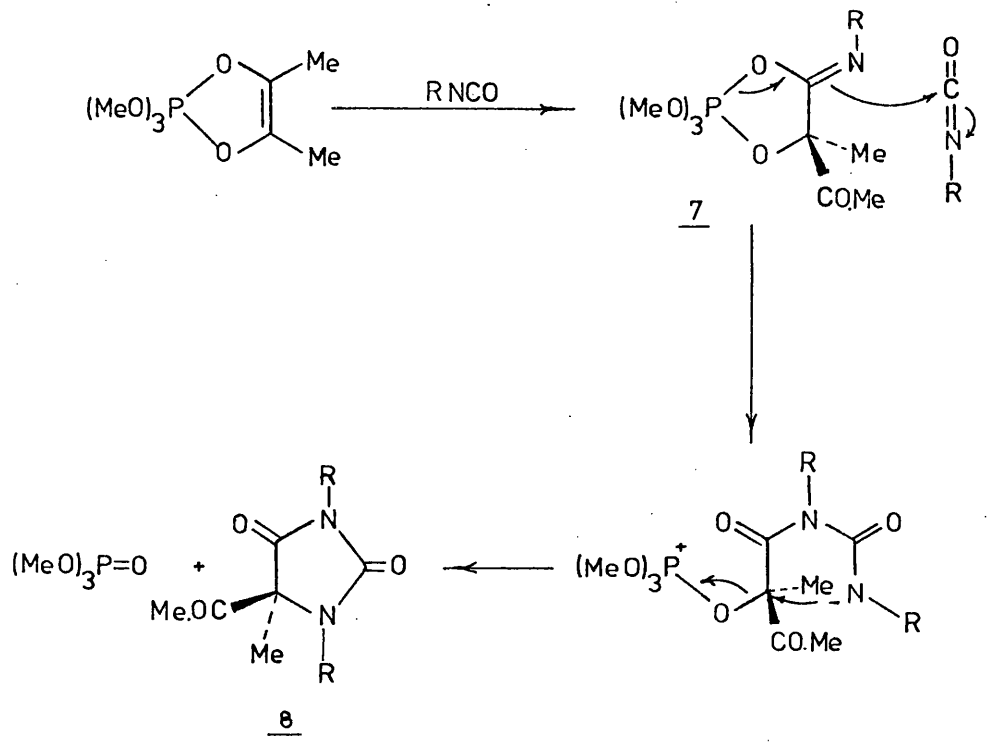


Scheme 4.

been carried out with cyclohexanone, butanone, hexan-3-one, methyl cyclopropyl ketone, hexafluoroacetone, acetophenone, benzophenone, acetaldehyde, benzaldehyde, biacetyl and benzil.

With two moles of isocyanates biacetyl adducts give 5-acetylhydantoins[25] (8) by the route outlined in scheme 5. If only one mole of the isocyanate is used a phosphorane is produced which has a positive ^{31}P.n.m.r. chemical shift showing it to exist as the ring closed form (7) rather than a dipolar species.

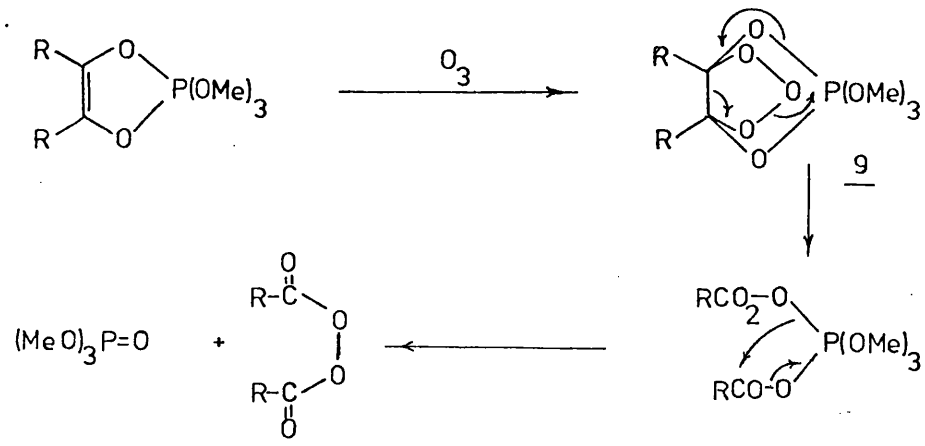
Phenanthraquinone adducts react with carbonyl compounds in a similar way to benzil adducts.[16,26]



R = Ph or p-NC·C_6H_4.

Scheme 5.

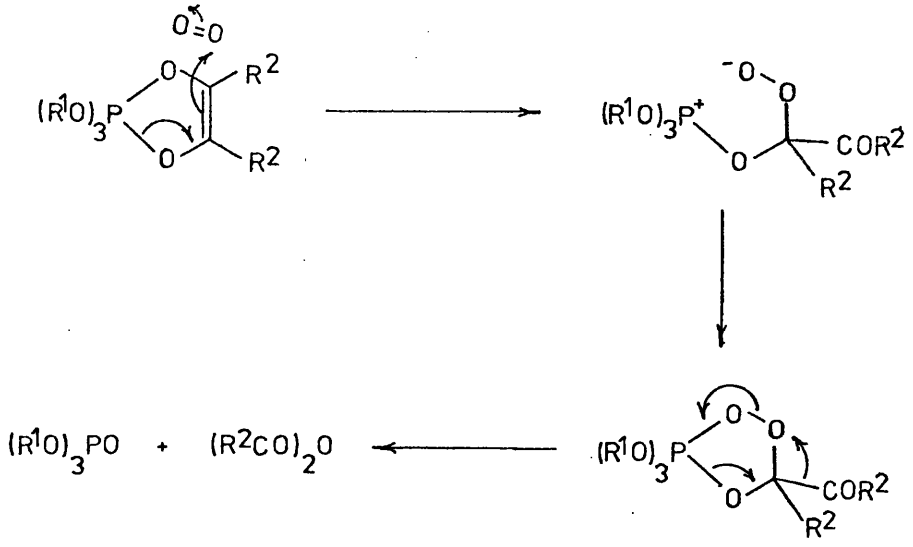
Ozonolysis of these adducts results in the formation of diacyl peroxides[27] which are formed by a rearrangement of a



R = Me, Ph or Phenanthraquinone.

primary ozonide (9) formed by the reaction of ozone with the double bond.

An unusual reaction occurs with molecular oxygen forming carboxylic acid anhydrides.[28] This is thought to occur by the route outlined in scheme 6 where the intermediate



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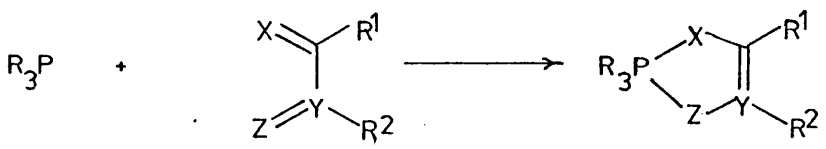
Scheme 6.

1,3,4,2-trioxaphospholan (10) can be considered as a secondary ozonide of a ylid.

It was soon discovered that many other 1,3-diunsaturated compounds form stable 1:1-adducts with trivalent phosphorus compounds.



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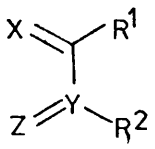
R_3P generalises many different trivalent phosphorus compounds. The various diunsaturated compounds (11) which have

been used are summarised in table 1.

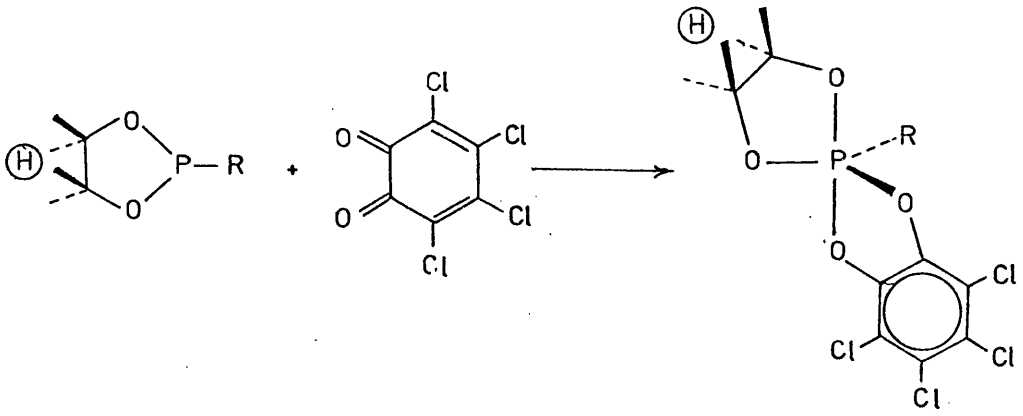
Table 1.

Diunsaturated Compounds



X	Y	Z	R^1	R^2	REFS.
O	N	NPh	Ph	-	29,30,31.
O	N	NCO_2R	OMe	-	29.
O	N	NCO_2R	OEt	-	32.
O	N	$C(CF_3)_2$	Ph	-	33.
O	C	CHPh	Me	CO.Me	34,35,36.
O	C	CHPh	Me	CO.Et	37,38.
O	C	CHMe	Me	CO.Me	39.
O	C	CHMe	Me	CO.Et	37,38,39.
O	C	CMe_2	Me	CO.Me	37.
O	C	CH_2	Me	CO.Me	40.
O	C	CH_2	OH	H	41,42.
O	C	CH_2	NH_2	H	41,42.
O	C	O	CF_3	CF_3	43,44.
O	C	CH_2	H	H	45.
O	C	CH_2	Me	H	45,46.
O	C	CH_2	Ph	Ph	47.
S	C	O	Ph	Ph	48.
CH_2	C	CH_2	H	H	49,50,51,52.
CH_2	C	CH_2	Me	H	51,52.
CH_2	C	CH_2	Me	Me	53.
CH_2	C	CH_2	H	OEt	53.
CHMe	C	CH_2	H	H	51.

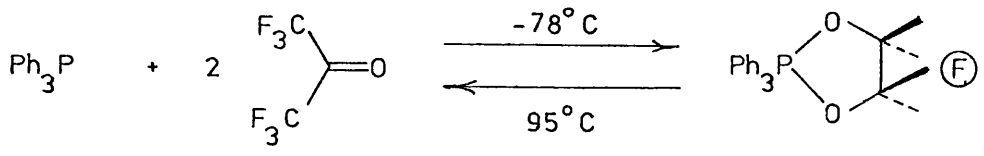
Ortho-benzoquinones,[53,54,55] phenanthraquinones,[26,54,56] 4,5-pyrenequinones[54] and 1,2-naphthoquinones[54] also form stable adducts with trivalent phosphorus compounds, e.g.



R = PhO-, PhS- or Me_2N-.

b) Adducts from Reactive Carbonyl Compounds

Certain reactive carbonyl compounds can form 2:1 adducts with trivalent phosphorus compounds. The best known examples of these are the hexafluoroacetone (H.F.A.) adducts which were first investigated by Ramirez.[22] He found that triphenylphosphine forms a 2:1 adduct (12) with H.F.A. at low temperatures which decomposed to the starting materials at its melting point.



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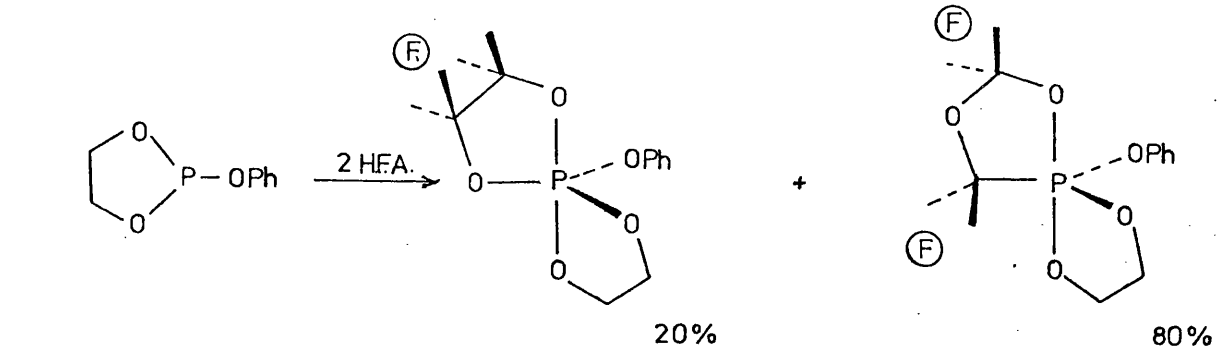
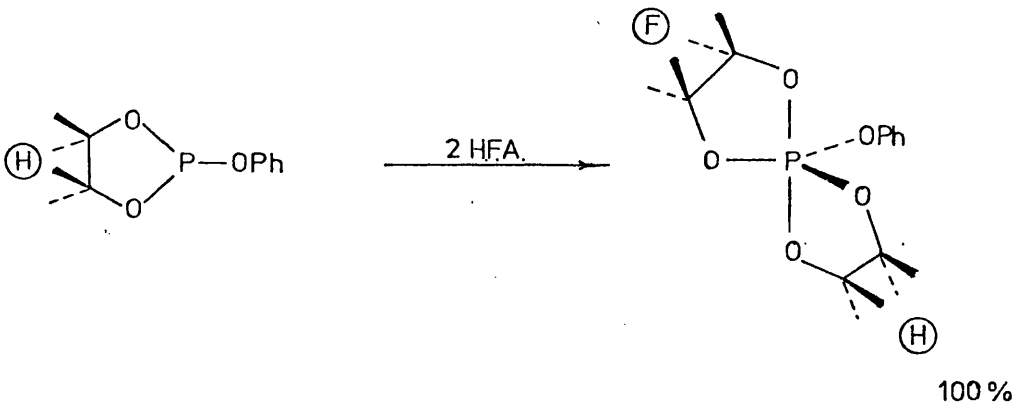
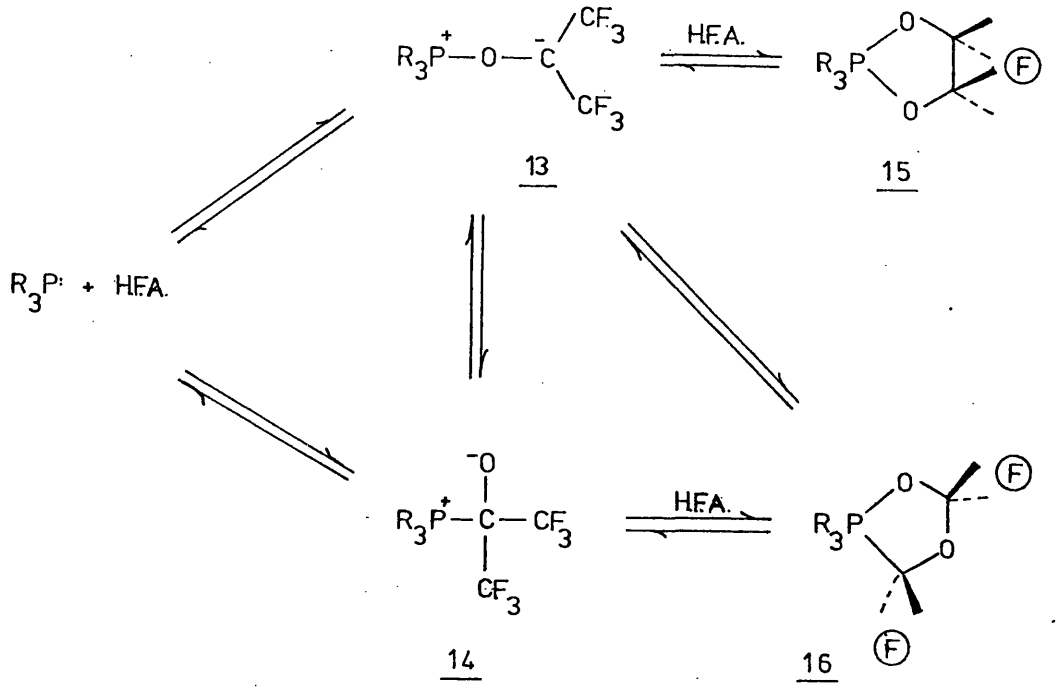
A 1,3,2-dioxaphospholan is usually formed in this reaction but in some cases a 1,4,2-dioxaphospholan is produced[48] (Scheme 7). This suggests that there are two





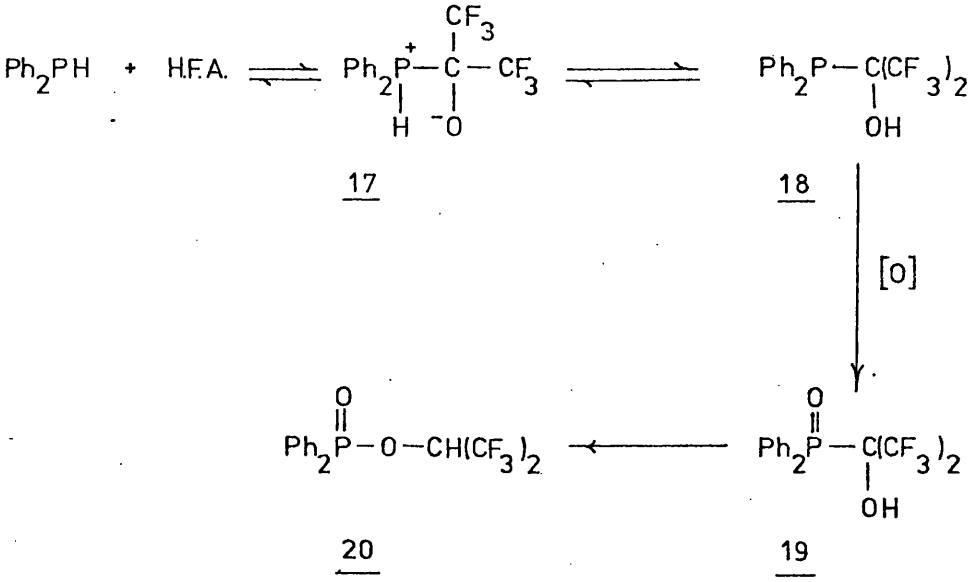
Scheme 7.

possible mechanisms for the formation of these adducts. The initial nucleophilic attack of phosphorus can be on either the carbonyl oxygen or the carbonyl carbon giving zwitterions 13 or 14 respectively (scheme 8). A second mole of H.F.A. can now add to 13 giving either 15 or 16 or it can add onto 14 giving 16.

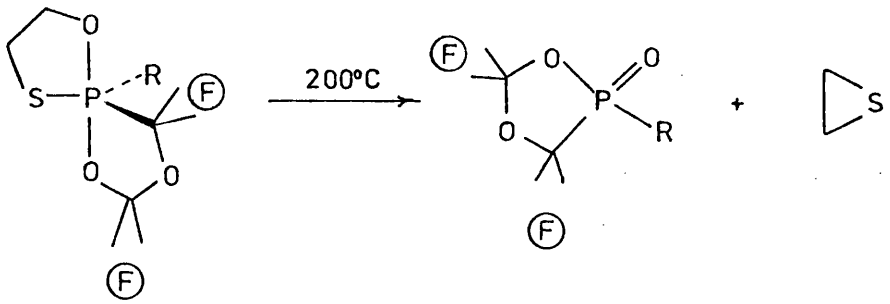


Scheme 8.

Janzen and Vaidya[57] have studied the reaction between H.F.A. and diphenylphosphine and have concluded that the initial attack by phosphorus is at the carbonyl carbon to give 14. This can either rearrange to 13 or it can form a 1,4,2-dioxaphospholan with a further mole of H.F.A. The evidence for this is that phosphine 18 can be identified by spectroscopic techniques in the reaction of H.F.A. with diphenylphosphine, and it is stable under the reaction conditions. This phosphine is easily oxidised to 19 which then readily rearranged to 20. It may well be that zwitterions similar to 14 or 17 can rearrange to zwitterions similar to 13 more easily than the non polar molecule 18.



It is unlikely that 1,3,2-dioxaphospholan adducts are formed by a rearrangement of an initially formed 1,4,2-dioxaphospholan because adducts 21 and 22 are thermally stable up to 200°C when ethylene sulphide is lost.[48]

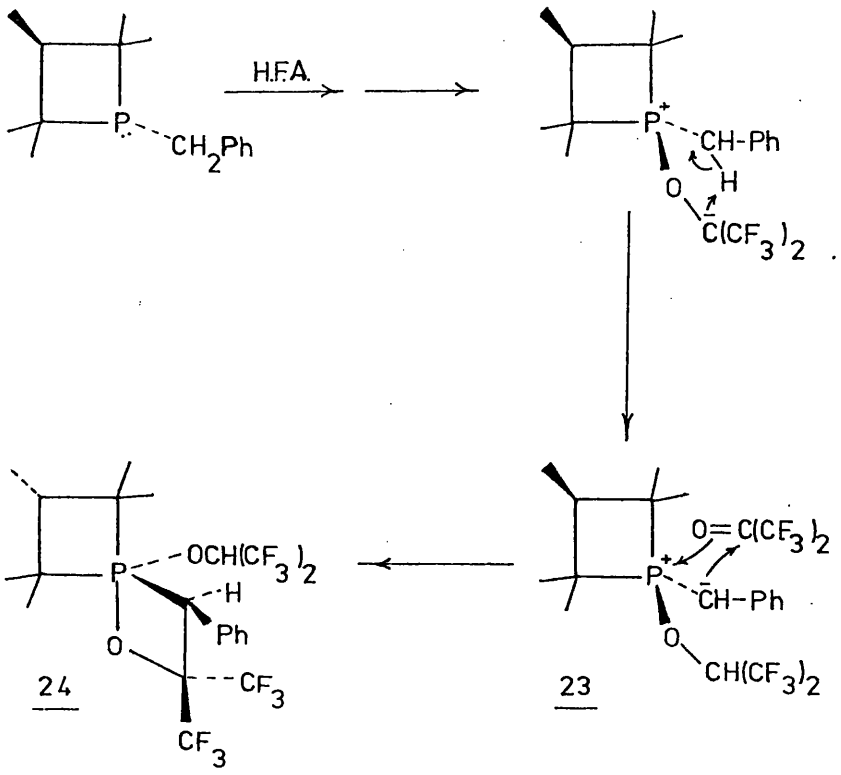


21. R = OPh

22. R = Ph

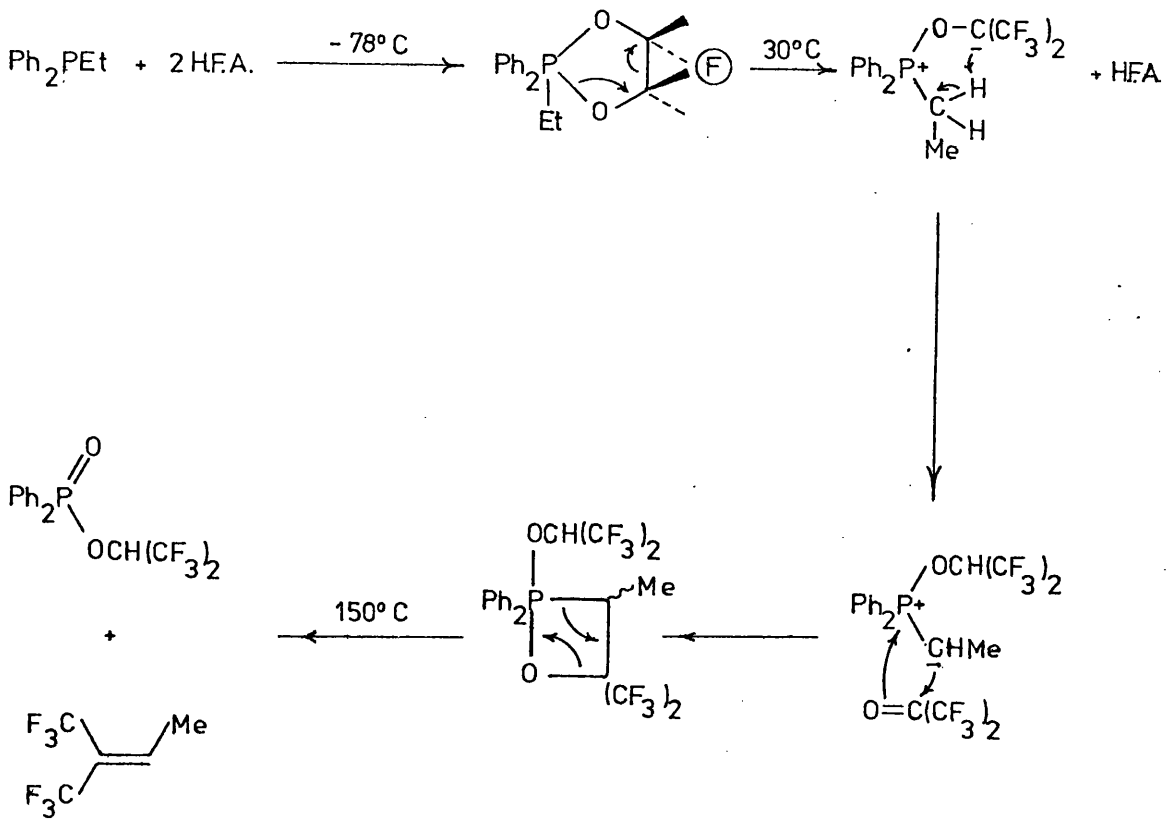
In some cases where there is a methylene group next to phosphorus a 1,2-oxaphosphetan is formed, e.g. 24.[58] This occurs because a proton on the methylene group is transferred to the hexafluoroisopropyl group forming an intermediate ylid (23)

which reacts with a further mole of H.F.A. to produce phosphorane 24. Other examples are known where



1,3,2-dioxaphospholans are formed and then undergo thermal rearrangments to 1,2-oxaphosphetans by a similar mechanism.[59,60] These 1,2-oxaphosphetans can be regarded as stable Wittig intermediates and can be made to eliminate alkenes at elevated temperatures (scheme 9).

Other reactive carbonyl compounds which form 1,3,2-dioxaphospholans with P(III) compounds are _o_- and _p_-nitrobenzaldehyde,[61] fluorenone,[62,63] phthaldehydes,[64] glyoxylic and pyruvate esters,[65] ninhydrin,[66] pentafluorobenzaldehyde,[67] ethyl-2-oxo-2-phenyl propionate[68] and benzoyl cyanide.[69] Non-activated aldehydes also form adducts but the



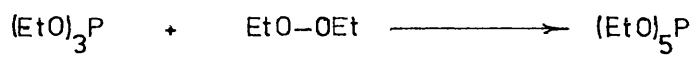
Scheme 9.

1,4,2-dioxaphospholan is usually formed, e.g. 25.[70]

When triethyl phosphite reacts with pentafluorobenzaldehyde the initial product at low temperatures is the 1,4,2-dioxaphospholan which slowly isomerises to the 1,3,2-dioxaphospholan at room temperature.[67]

c) Adducts from Peroxides and Related Compounds.

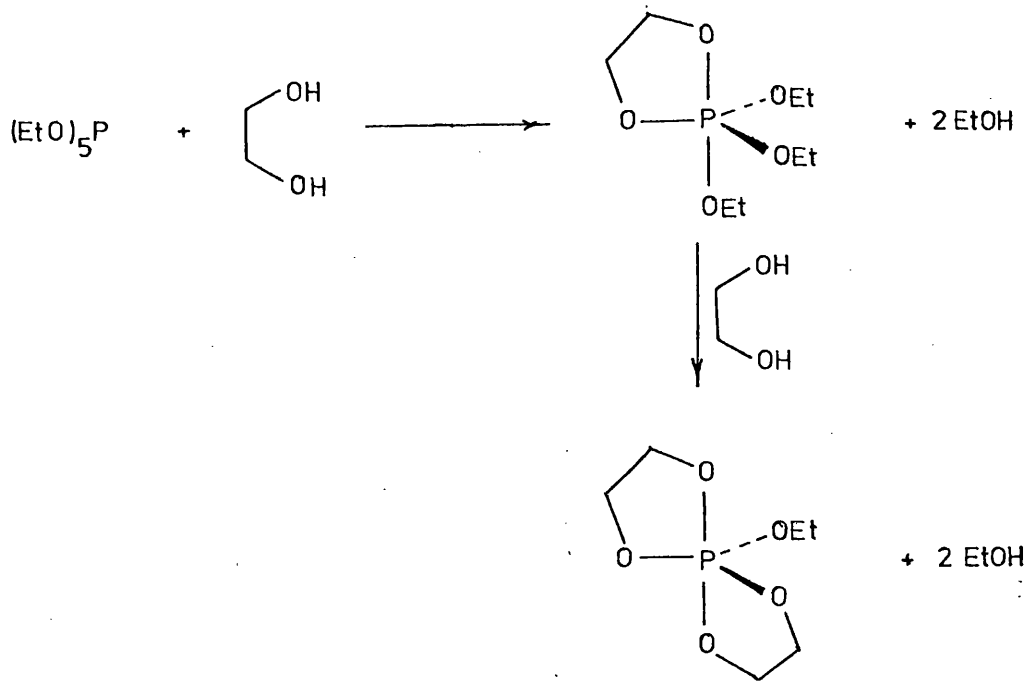
In 1964 Denney and Relles[71] reported the preparation of pentaethoxyphosphorane (26) from triethyl phosphite and diethyl peroxide. Before this, acyclic pentaoxyphosphoranes



26

were unknown. Even pentaphenoxyphosphorane, reported in 1927[72] and 1959,[73] was not successfully made until 1968.[67,74]

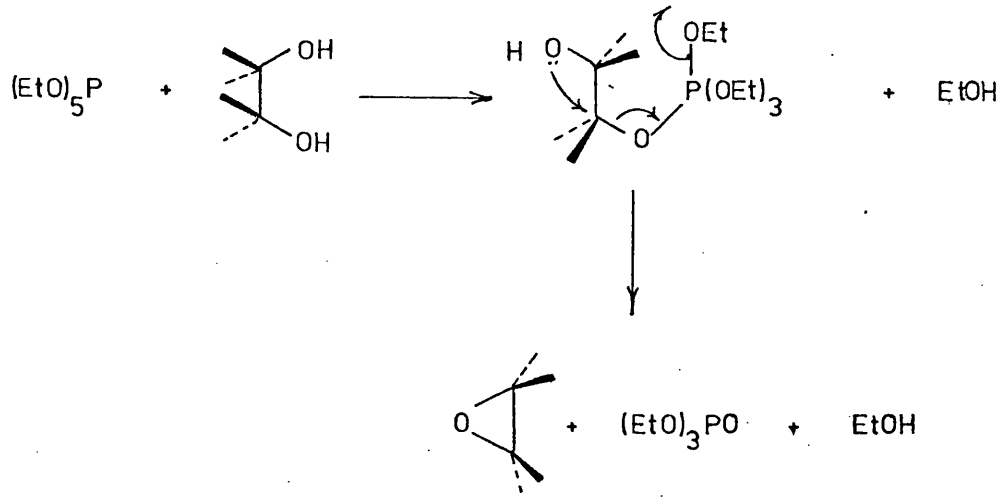
The ethoxy groups of pentaethoxyphosphorane can be displaced by either 1,2- or 1,3-diols forming cyclic or spirophosphoranes and ethanol[75] (scheme 10).



Scheme 10.

This works well for 2,2-dimethylpropane-1,3-diol, propane-1,2-diol, butane-2,3-diol, ethane-1,2-diol and

1-phenylethane-1,2-diol. With pinacol, butane-1,4-diol and pentane-1,5-diol, mono-substitution occurs followed by heterocycle formation (scheme 11).

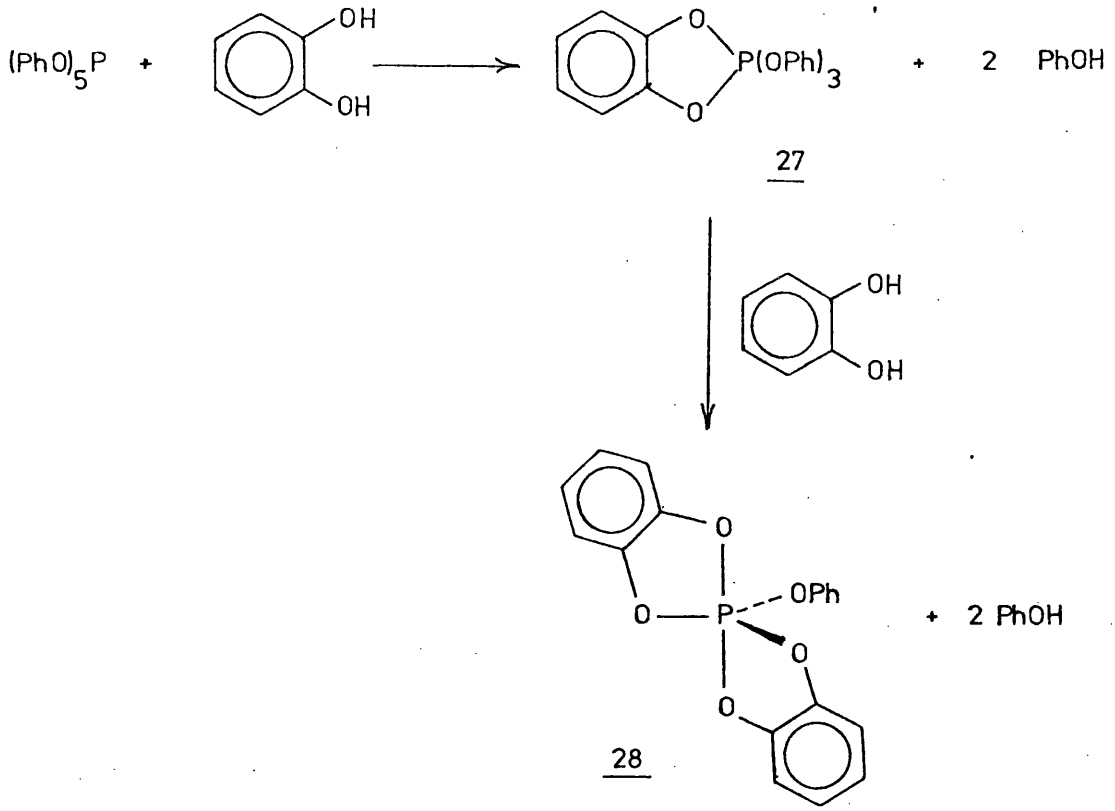


Scheme 11.

When diethoxytriphenylphosphorane is treated with diols, heterocyclic compounds and triphenylphosphine oxide are formed,[76] but in some cases the cyclic triphenylphosphorane is stable enough to be characterised by ^{1}H and ^{31}Pn.m.r. spectroscopy.[75]

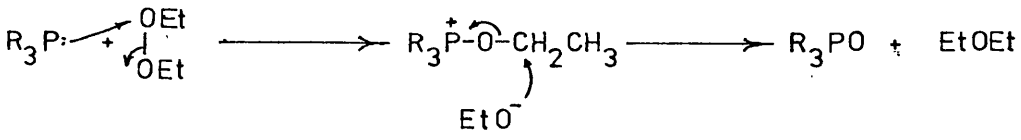
Pentaphenoxyphosphorane is prepared by treating phosphorus pentachloride with phenol in the presence of a tertiary amine.[67,74] Catechol can displace the phenoxy groups forming either a cyclic-phosphorane 27 or a spirophosphorane 28. This is a convenient synthesis of spirophosphorane 28 because its preparation from catechol, phenol and phosphorus pentachloride in the presence of a tertiary amine can result in the formation of hexacoordinate compounds.[77]

Denney extended his work with diethyl peroxide and prepared a number of cyclic phosphoranes by using cyclic trivalent



phosphorus compounds.[40,78,79]

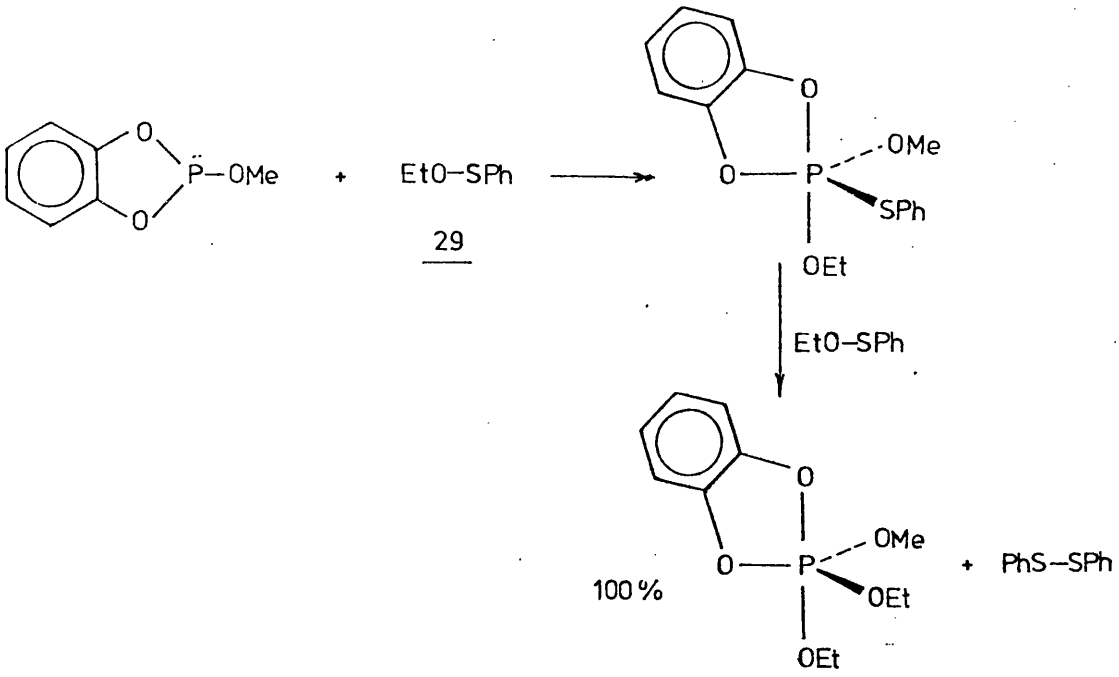
One drawback to this reaction, besides being slow, is that up to 25% of the reaction is an oxidation process where the P(III) compound reduces the diethyl peroxide to diethyl ether (scheme 12).



Scheme 12.

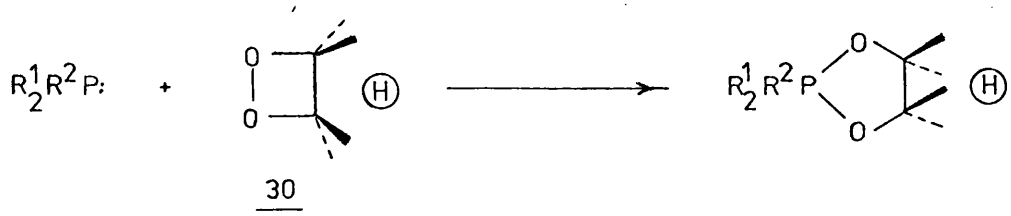
This problem can be overcome by using two moles of ethyl benzenesulphenate (29) in place of diethyl peroxide.[80] The ethyl

benzenesulphenate forms a 1:1-adduct with the P(III) compound



which then reacts with a further mole of the sulphenate forming a diethoxyphosphorane and diphenyl disulphide. Recently a large number of penta-alkoxyphosphoranes have been prepared using varicus alkyl benzenesulphenates.[81]

Bartlett et al. have made phosphoranes containing 4,4,5,5-tetramethyl-1,3,2-dioxaphospholan rings by treating trivalent phosphorus compounds with tetramethyl-1,2-dioxetan (30).[82,83]

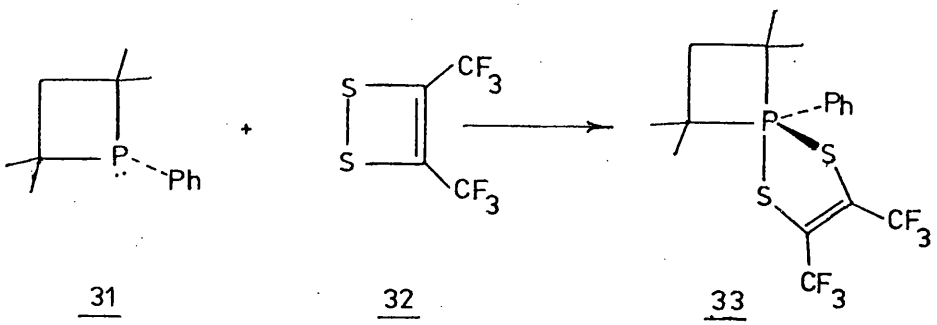


30

$R^1 = R^2$ = Ph, OMe, OEt.

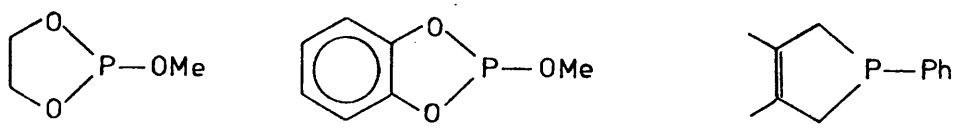
R^1 = Ph, R^2 = OMe.

Phosphorane 33 can be prepared by treating phosphetan 31 with 3,4-bis(trifluoromethyl)-1,2-dithieten (32) in dichloromethane at low temperature.[84] Phosphoranes can also



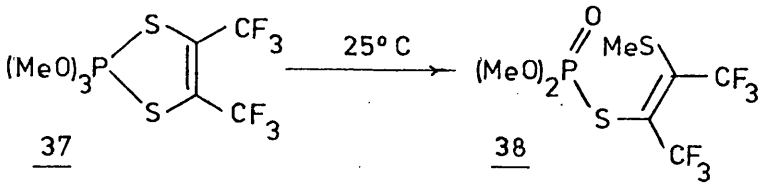
31 32 33

be prepared by the reaction of 32 with dioxaphospholan 34 and benzodioxaphosphole 35.[84] With triphenylphosphine[84] and



34 35 36

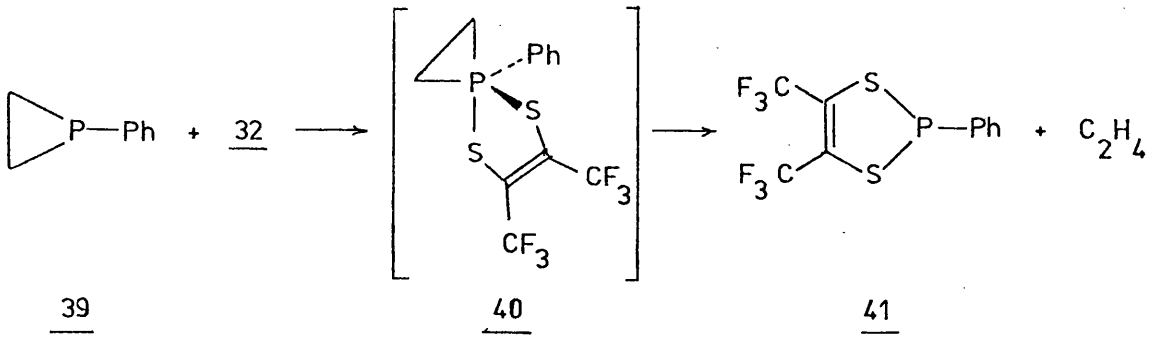
phospholene 36,[85] the corresponding phosphine sulphides are obtained when treated with 32. Dithieten 32 forms a cyclic



37 38 (cis & trans).

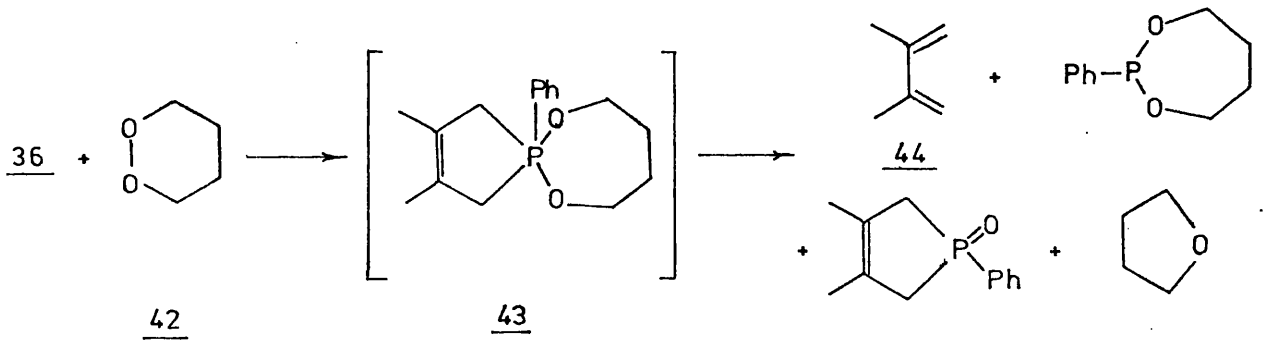
phosphorane (37) with trimethyl phosphite at low temperatures which rearranges to a mixture of cis and trans isomers of 38 at room temperature.[84]

Phenylphosphiran (39) reacts with 32 forming ethylene and 1,3,2-dithiophospholene 41 at low temperatures.[86] This is presumably formed by the decomposition of phosphorane 40 which might be expected to be unstable.

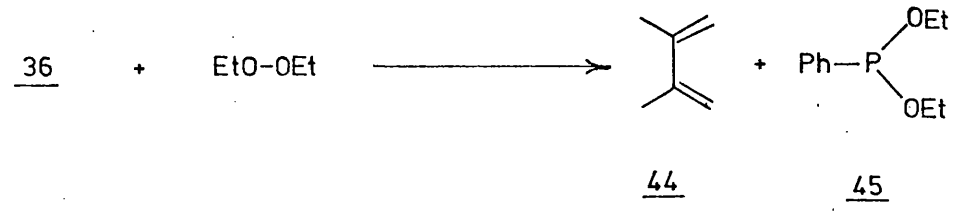


39 40 41

Phospholene 36 reacts with 1,2-dioxan (42) to give a variety of products which are thought to arise from the



42 43 44

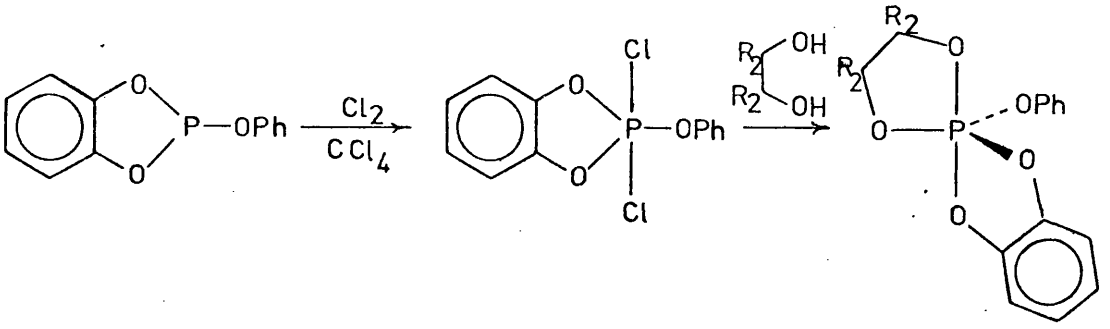


44 45

Scheme 13.

intermediate phosphorane 43.[85] With diethyl peroxide phospholene 36 forms 2,3-dimethylbutadiene (44) and diethyl phenylphosphonite (45).[85]

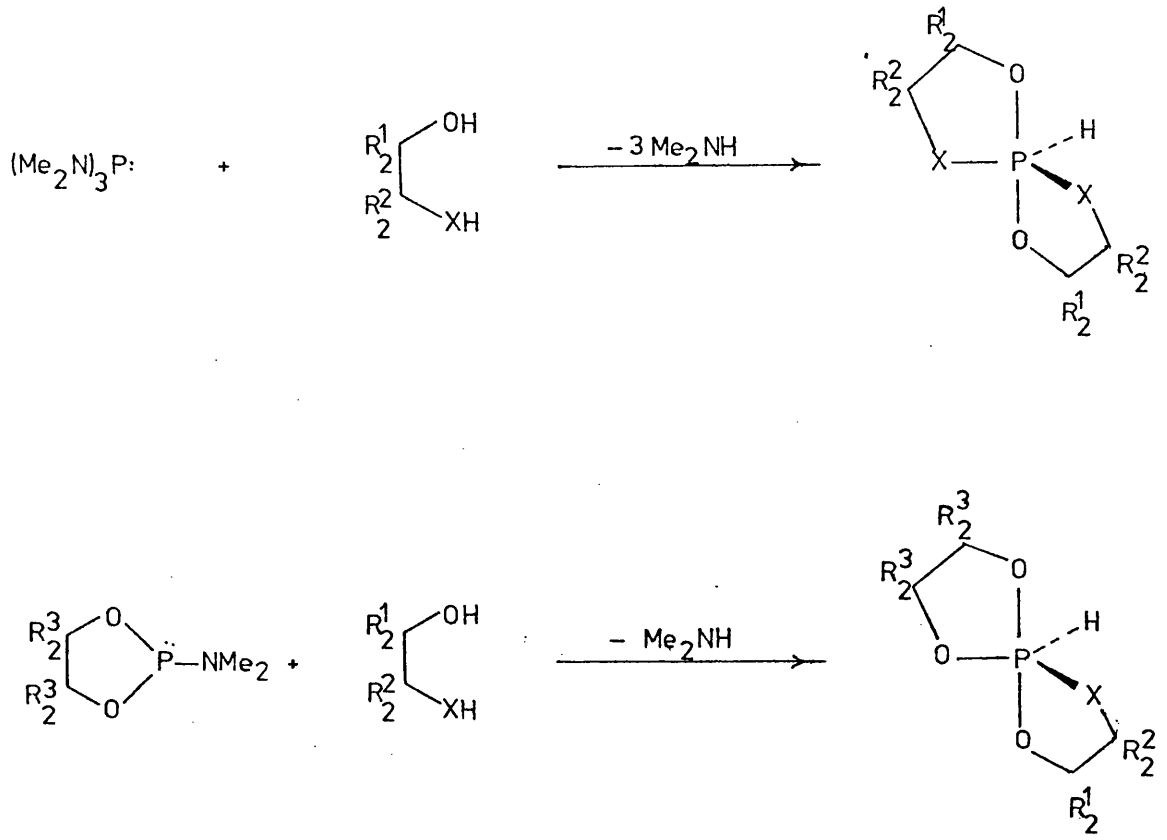
Halogens react with trivalent phosphorus compounds forming dihalophosphoranes. These can react with diols to form spirophosphoranes[48,55] (scheme 14).



Scheme 14.

d) Phosphoranes from Halo-or Amino-Phosphines and Diols or Related Compounds.

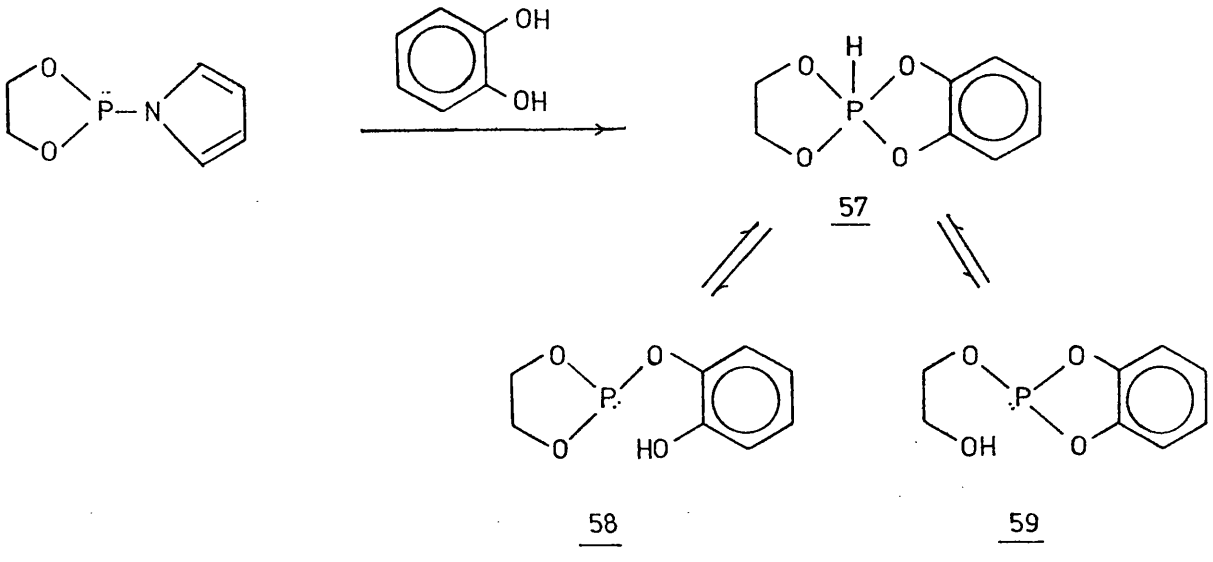
In 1968 Sanchez et al.[87] discovered that spirophosphoranes containing P-H bonds are formed when trivalent phosphorus compounds, containing amino or halogen groups, are treated with diols or 2-aminoalcohols (scheme 15). This is a general method for preparing spirophosphoranes with P-H bonds and works with 1,2-diols,[87] 2-aminoalcohols (55)[88] especially ephedrine (48, R = Me)[89] and norephedrine (48, R = H),[89] 2-hydroxy acids (51),[90,91] amino acids (53),[92] amidoximes (52),[93,94] acylhydrazides (50),[95,96] amidrazones (49),[97,98] diamines (56)[98] and hydroxamic acids (54)[99] (scheme 16).



X = O, NH or NMe

Scheme 15.

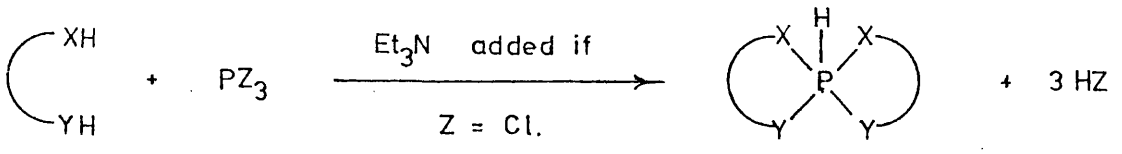
In some cases the phosphorane is in equilibrium with a trivalent phosphorus compound e.g. the ^{31}Pn.m.r. spectrum of phosphorane 57 shows the presence of both cyclic phosphites 58 and 59.[100]



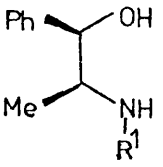
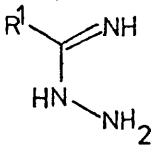
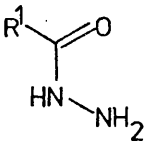
57

58

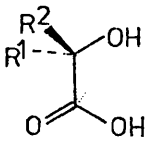
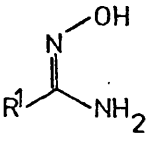
59



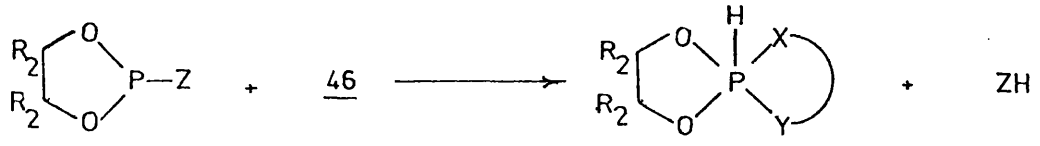
46

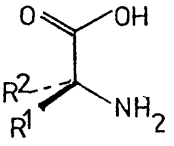
Z = NMe_2, 46 =  ,  ,  .

48 49 50

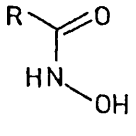
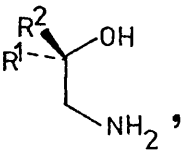
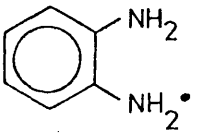
Z = Cl, 46 =  ,  .

51 52



R = H, Z = NMe_2, 46 = 49, 51,  .

53

R = H, Z = Cl, 46 = 51, 53,  ,  ,  .

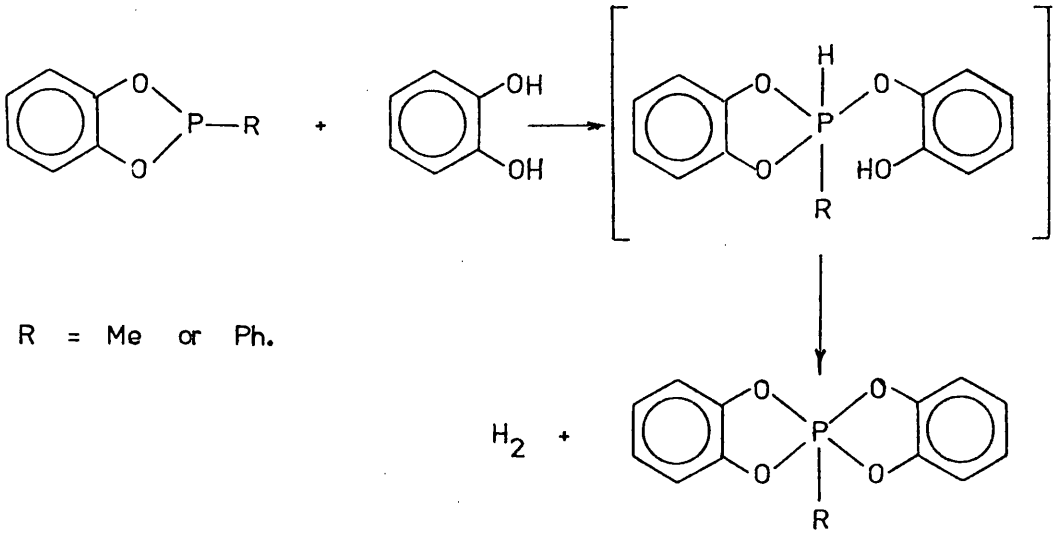
54 55 56

R = H, Z = OAc, 46 = 51, 55. R = Me, Z = NMe_2, 46 = 50.

Z = Cl, NMe_2.

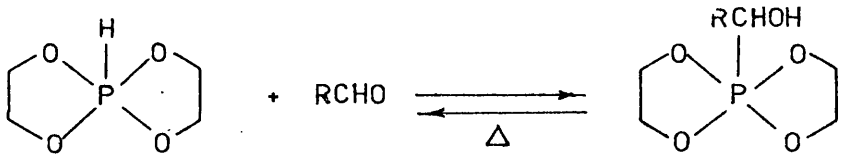
Scheme 16.

When trivalent phosphorus compounds that have no leaving groups react with diols, phosphoranes can be formed by loss of gaseous hydrogen[101] (scheme 17).



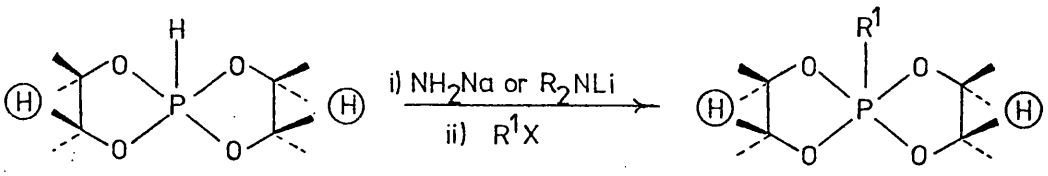
Scheme 17.

Some unsaturated compounds e.g. aldehydes[102] or imines[103] can insert reversibly into the P-H bond on this type of phosphorane, e.g. 60.[102]

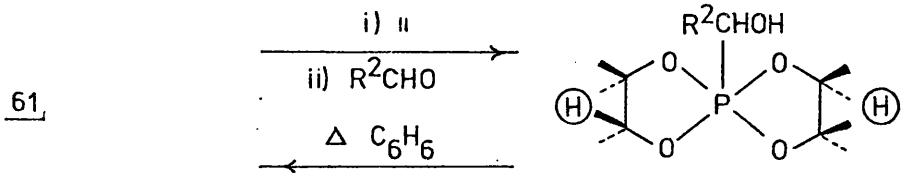


60

Strong bases such as lithium dialkylamides [104,105] or sodamide[105] can metallate phosphorane 61 and subsequent treatment with alkyl halides, aldehydes or acid chlorides produces P-substituted phosphoranes. The structure of the intermediate metallated phosphorus compound is uncertain. Addition of trimethylchlorosilane to the intermediate results



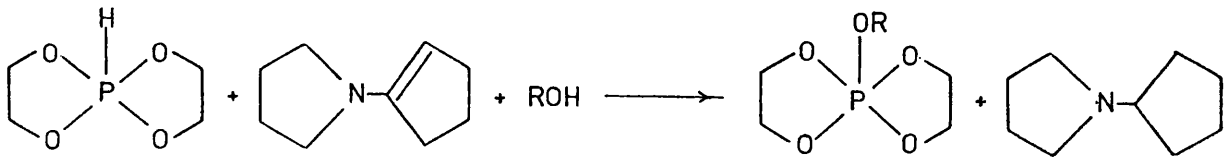
61



61

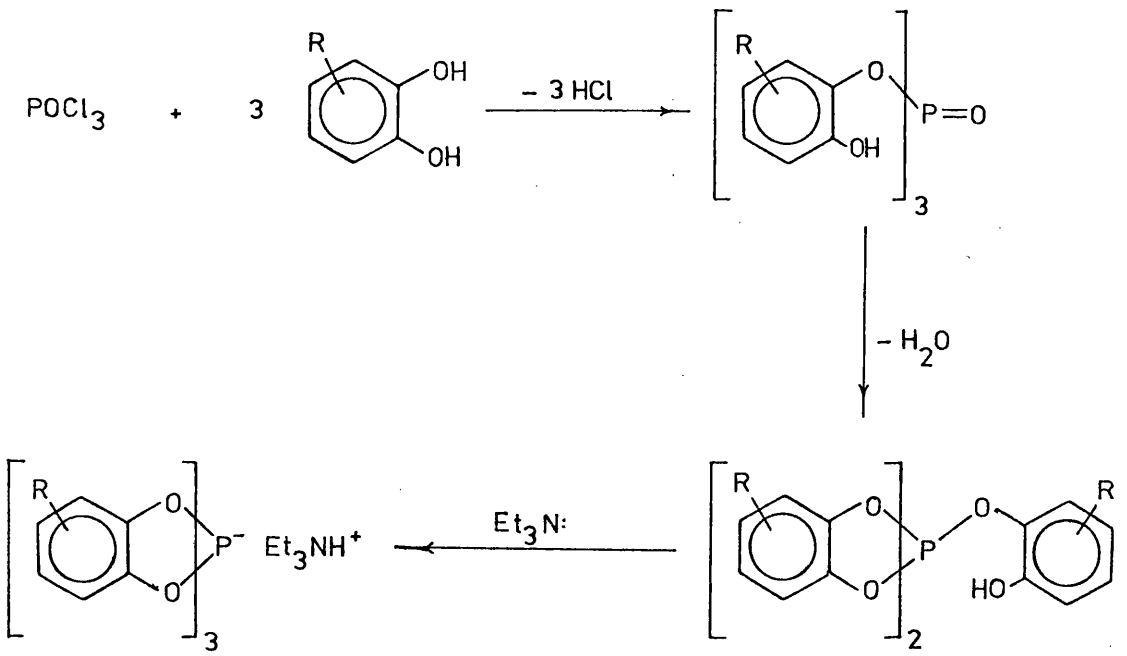
in silylation on oxygen implying that the intermediate is an oxygen anion rather than a phosphorus anion[105] but there is some evidence that the trimethylsilyl group on pentacoordinate phosphorus is inherently unstable.[42]

Alkoxyphosphoranes can be prepared from phosphorane 60 and alcohols by treating the mixture with enamine 62.[106] In



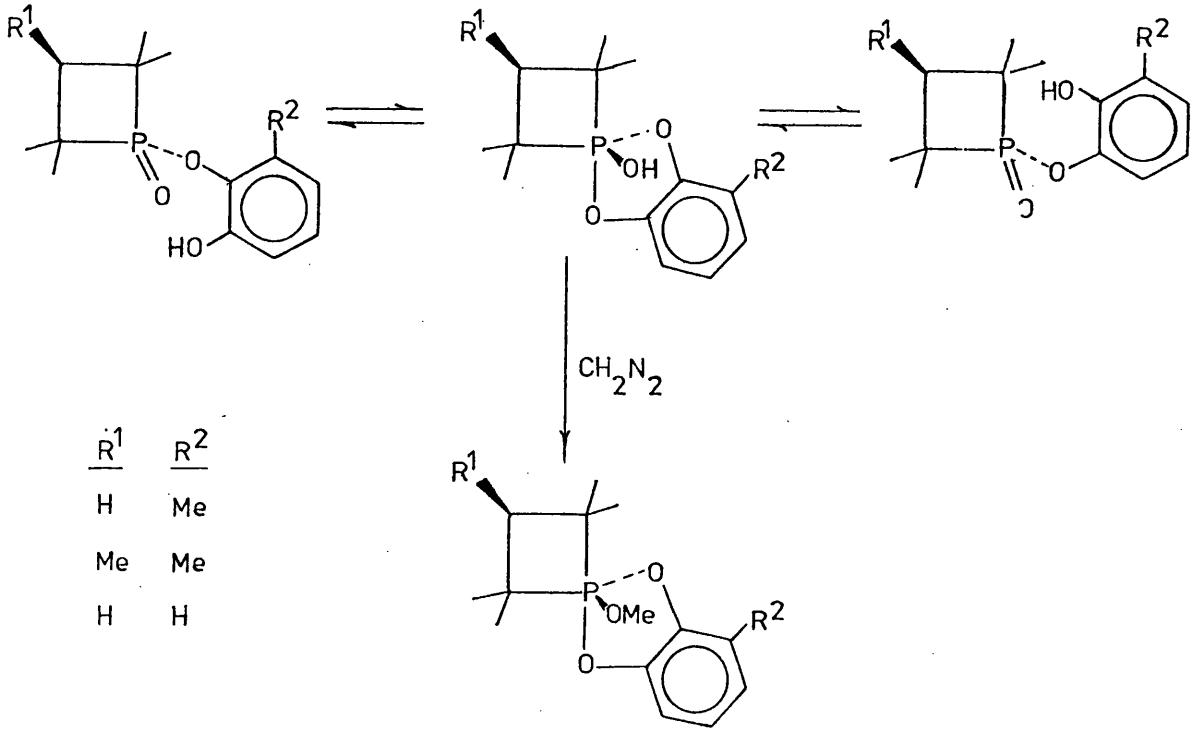
60 62 63

this reaction the enamine is reduced to an amine showing that it is acting as an oxidising agent.



R = H, 3-Me or 4-Bu^t.

Scheme 18.



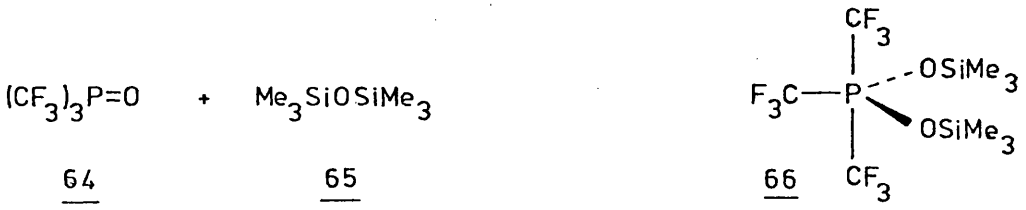
R^1	R^2
H	Me
Me	Me
H	H

Scheme 19

Phosphoranes can be prepared form diols and trivalent phosphorus compounds by using diethyl azodicarboxylate[107] or N-chlorodi-isopropylamine.[108,109] These reactions are discussed more fully in chapters 7 and 2 respectively.

e) Phosphoranes from Phosphorus Oxides.

The first direct preparation of a phosphorane from a phosphine oxide was carried out by Cavell and Leary[110] who treated tris(trifluoromethyl)phosphine oxide (64) with hexamethyldisiloxane (65) producing high yields of phosphorane 66.

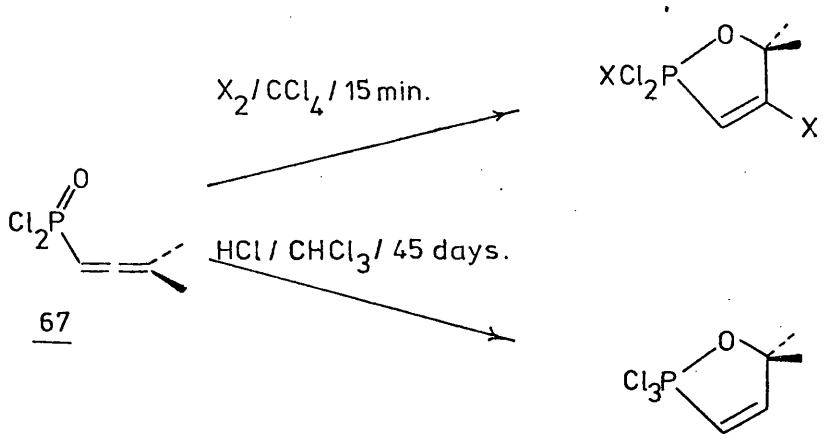


64 65 66

A more recent direct preparation involves the reaction of catechols with phosphorus oxychloride or phosphonic acid.[111] Phosphoranes and hexacoordinate compounds can be prepared in this way (scheme 18).

Hydroxyphosphoranes derived form phosphetan oxides, can be trapped as methoxyphosphoranes by using diazomethane[112] (scheme 19).

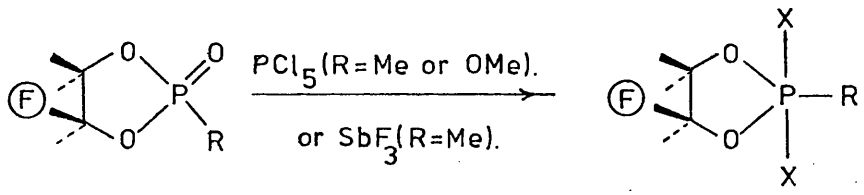
Halogenation[113] or hydrochlorination[114] of the allenyldichlorophosphine oxide 67 forms cyclic trihalophosphoranes in high yields (scheme 20) (see Chapter 6).



67

Scheme 20.

Halogenation of oxide 68 with phosphorus pentachloride or antimony trifluoride gives dihalophosphoranes.[115]

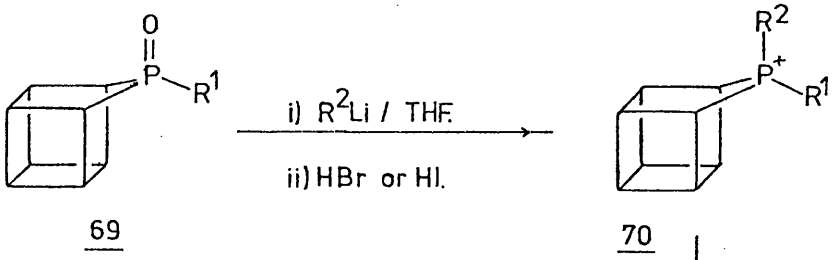


68 X = Cl or F.

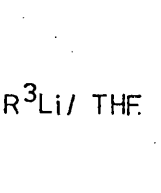
Homocubylphosphoranes (71) can be prepared by the action of alkyl- or aryl-lithium compounds on the corresponding oxides (69).[116-119]

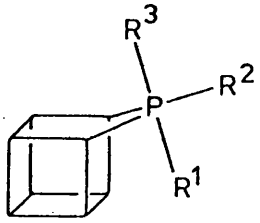
The intermediate phosphonium halide 70 can also be prepared by quaternising the corresponding phosphine with alkyl halides.[119]

This was the first preparation of a penta-alkylphosphorane[117] because the treatment of phosphonium salts with alkyl-lithium reagents usually results in the formation of ylids.[120] The stability of the penta-alkylphosphorane (71, $R^1 = R^2 = R^3$ = Me)



69 70





71

R^1 = R^2 = R^3 = Ph.

R^1 = R^2 = Ph, R^3 = Me.

R^1 = Ph, R^2 = R^3 = Me.

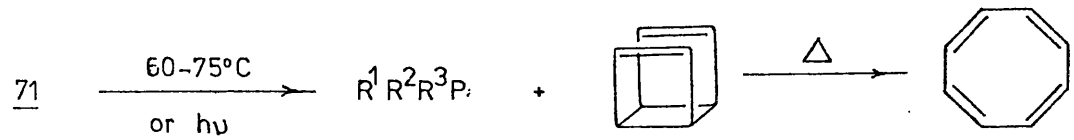
R^1 = R^2 = R^3 = Me.

R^1—R^2 = biphenyl-2,2'-yl, R^3 = Me.

R^1—R^2 = biphenyl-2,2'-yl,
R^3 = biphenyl-2-yl.

is probably due to the relief of strain in the phosphonium salt (70). The angle at phosphorus in the ring is less than the tetrahedral angle required by a phosphonium salt or an ylid and the strain in the ring is greatly reduced when pentacoordinate compounds are formed.

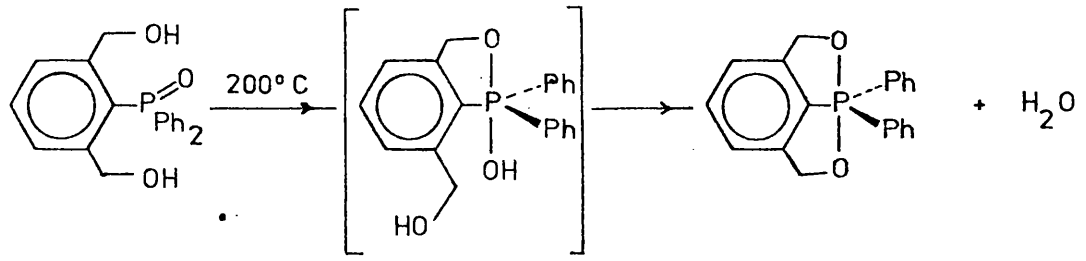
Alkoxyhomocubylphosphoranes are unknown. The treatment of oxide 69 (R^1 = Me) with methanesulphonyl fluoride gives a methoxyphosphonium salt (70 R^1 = Me, R^2 = OMe), but with methyl-lithium this forms trimethylhomocubylphosphorane (71, R^1 = R^2 = R^3 = Me) in higher yields than before[119].



72

These homocubylphosphoranes decompose either thermally or photochemically to acyclic phosphines and diene 72 which subsequently rearranges to cyclo-octatetraene.[119] This reaction was carried out in an attempt to prepare cubane.

Phosphine oxide 73 is thermally dehydrated to form phosphorane 75 which is extremely thermally stable. The



73 74 75

mechanism of this reaction is not known but is thought to involve an intermediate hydroxyphosphorane 74.[121]

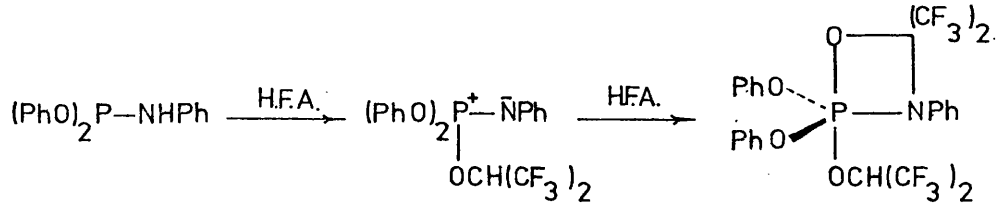
The preparation of phosphoranes from phosphine oxides by using trifluoromethanesulphonic anhydride is described in chapter 3.

f) Miscellaneous Methods for Preparing Phosphoranes.

The reaction of hexafluoroacetone (H.F.A.) with trivalent phosphorus compounds to form 1,3,2- and 1,4,2-dioxaphospholans, has been reviewed in section b. In some cases, however, other phosphoranes are formed. This usually occurs when one of the groups on phosphorus contains an active methylene group (see chapter 1, section b) or a 2,3-unsaturated group, i.e. it is an alkene,[122] alkyne,[123] isocyanate[122] or isothiocyanate[122] (scheme 21).

The tricyclic phosphoranes 76 formed by the action of H.F.A. on alkynyl phospetans are the only known examples of trigonal bipyramidal phosphoranes with diequatorial phosphetan rings. Because of the four membered ring, however, the trigonal bipyramid is slightly distorted.[123]

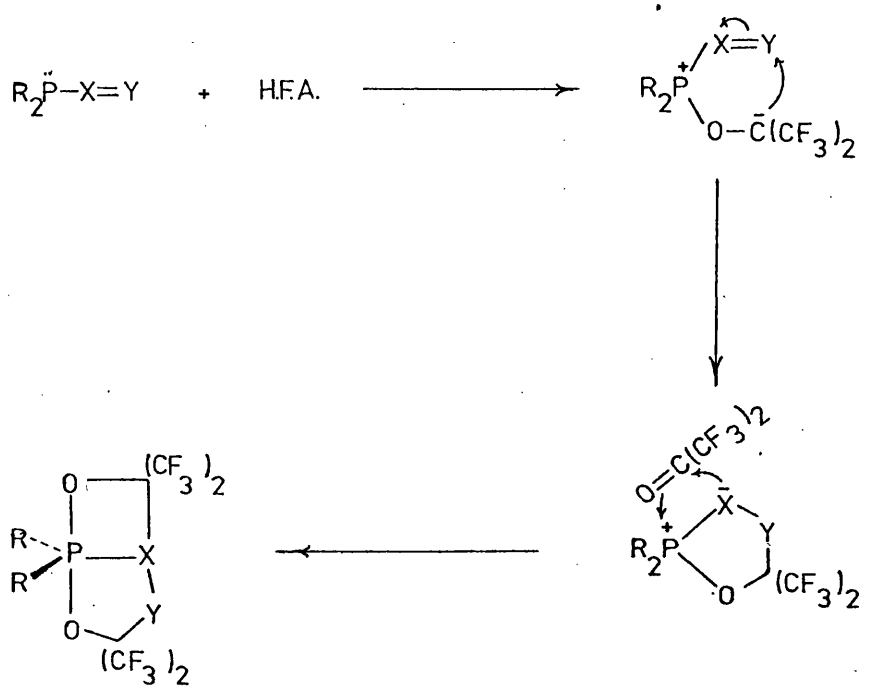
In a similar way phosphoramidite 77 reacts with H.F.A. to form 1,3,2-oxazaphosphetan 78.[122]



77 78

Diphenylphosphine reacts with H.F.A. to form phosphine 18[57] (chapter 1, section b). This phosphine, when treated with alkyl halides, quaternises and rearranges to phosphonium salt 79.

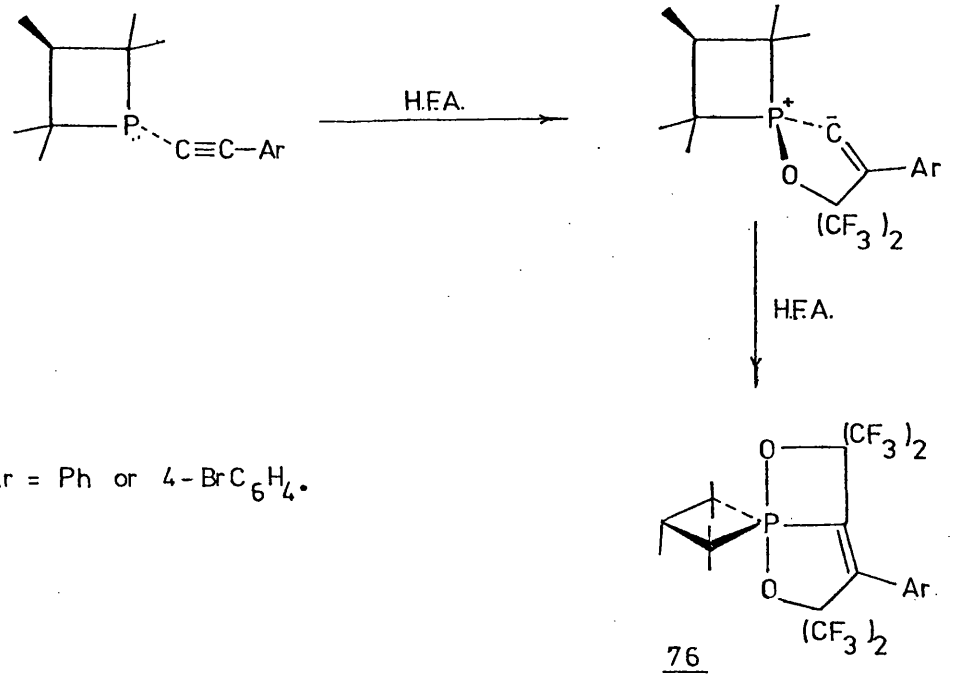
Treatment of this with a further mole of H.F.A. in the presence of a base produces 1,2-oxaphosphetans.[124] The products are the same as those formed by the direct reaction of H.F.A.



R = Ph, X = CH, Y = CH_2.

R = EtO, X = N, Y = CO or CS.

R = PhO, X = N, Y = CO.

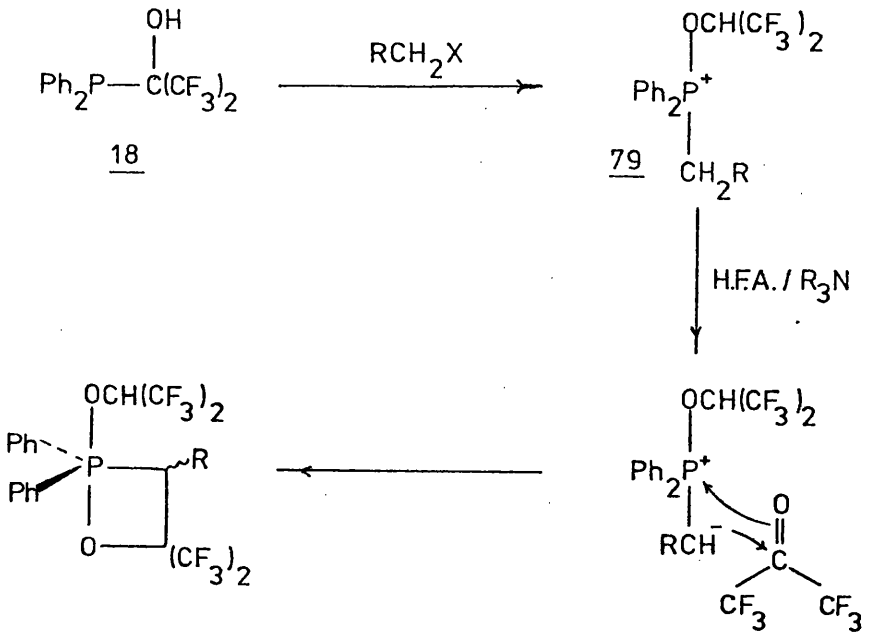


Ar = Ph or 4-BrC_6H_4.

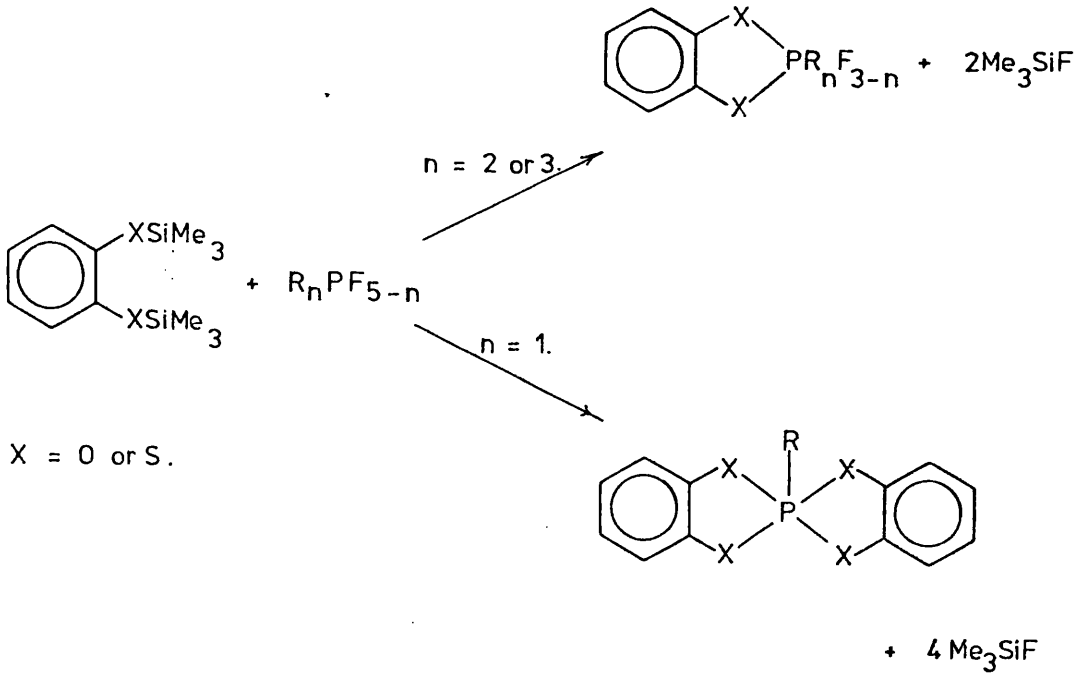
76

Scheme 21.

with alkyldiphenylphosphines (scheme 9).[59,60]



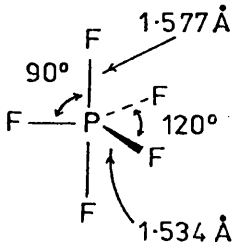
Cyclic phosphoranes can be prepared by treating fluorophosphoranes with disilyl ethers.[125-127] Fluorotrimethylsilane is lost in this reaction.



The reaction of ylids with epoxides to form phosphoranes is discussed in chapter 6.

ii. The Structure of Phosphoranes.

Molecular orbital calculations[128] and electron pair repulsion theory[129] predict that the most stable configuration for simple pentacoordinate molecules, e.g. PF_5 or PH_5 is the trigonal bipyramid (T.B.P.). Other geometries, e.g. the square based pyramid, are less stable.[128] Unsymmetrically substituted phosphoranes show slight distortions away from the T.B.P. geometry, e.g. 80,[129] 81[129,130] and 82.[131]



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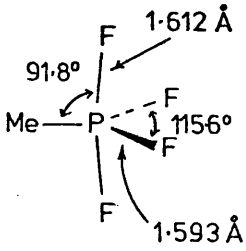

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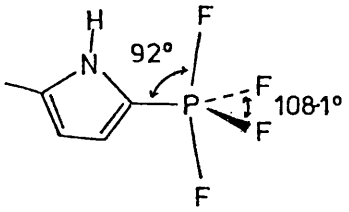
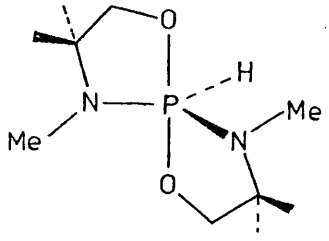


82

Steric interactions[130] are thought to be responsible for this but the distortions can also be explained in terms of electron pair repulsion theory.[129] The apical bonds in a perfect T.B.P. are longer and therefore weaker than the equatorial bonds. Unsymmetrical substitution tends to slightly increase the bond lengths,[129] e.g. 80 and 81.

In cyclic or spirophosphoranes the distortions can be quite severe. X-ray studies show that phosphoranes 83[132] and 84[133] are almost perfect T.B.Ps. whereas 85[134] is very nearly a square based pyramid with the p-bromophenyl group occupying the apical position.



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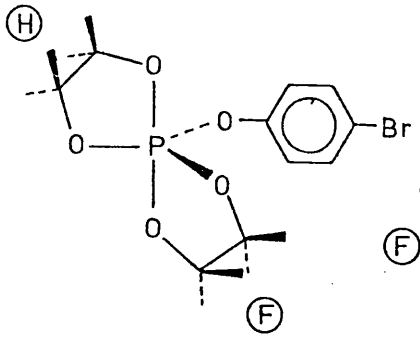

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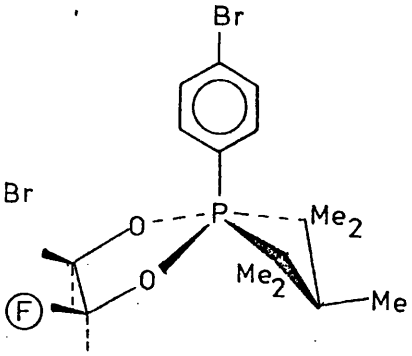


85

These T.B.Ps. are non rigid and are usually undergoing ligand reorganisations (see next section). The preferred position of a ligand in a phosphorane depends on many factors which can be summarised as follows:

a) The preference of a ligand to occupy an apical position depends on the relative apicophilicity[135] of the ligand. The relative apicophilicity (A) of a ligand L is defined as the difference in energy between two isomers where L is apical in one isomer (87) and a reference ligand R is apical in the other (86), providing that no other energy factors, e.g. ring strain, are contributing to the relative energies of the isomers.

86 87

A(L) = Energy (87) — Energy (86).

The following general rules can be used in predicting the relative apicophilicities of ligands:

i) Electronegative ligands or ligands with low lying vacant orbitals (π-acceptors) will prefer to occupy apical positions in T.B.Ps. or basal positions in square based pyramids.

ii) Ligands with lone pairs of electrons (π-donors) will prefer to occupy equatorial positions in T.B.Ps. and apical positions in square based pyramids.

iii) Hydrogen has an anomalously high apicophilicity.[136]

b) Calculations[128] and X-ray studies[133] show that in T.B.Ps., equatorial π-donors (e.g. NMe_2) prefer to be sp^2 hybridised

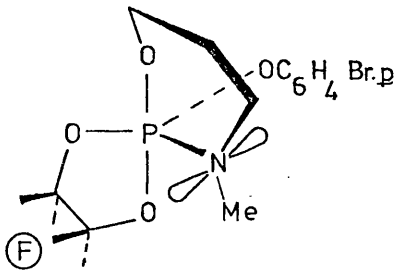
Favoured 88 Unfavoured

with the p orbital lying in the equatorial plane (88).

c) Small (4 or 5-membered) rings prefer to span the apical-equatorial positions of T.B.Ps. Inspection of models shows that small rings are less strained in this position, and this is confirmed by n.m.r. studies of cyclic fluoro-[137] and oxyphosphoranes,[34,37,138] by kinetic studies of substitutions in cyclic and acyclic tetracoordinate phosphorus compounds[7,139] and by X-ray studies of many cyclic and spirophosphoranes.[56, 59,132,133,140.]

d) Larger (6-membered) rings have very little, if any, ring strain in either the apical-equatorial position or the diequatorial position but if they contain hetero atoms with lone pairs of electrons they prefer to be apical-equatorial

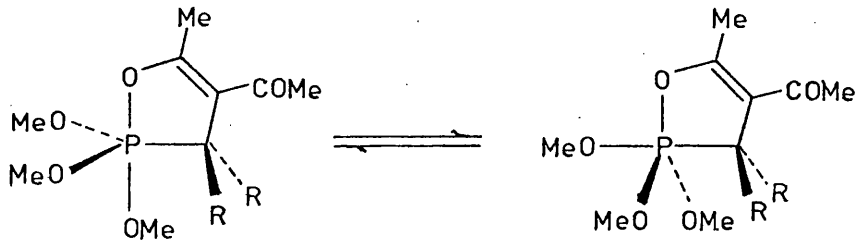
because this allows the lone pair to lie in the equatorial



89

plane, e.g. 89.[133] This is confirmed by X-ray studies which also show that the six-membered ring adopts a boat conformation.[133] Lone pair orientation in the equatorial plane also contributes to the apical-equatorial positioning of five-membered rings with hetero atoms next to phosphorus.[48]

e) Equatorial sites are less sterically hindered than apical sites in T.B.Ps.[137] but this does not have a large effect on the positioning of ligands in phosphoranes. The main steric interactions are between equatorial ligands and substituents on the apical ligand when it is part of a small ring. For the pseudorotation 90 to 91[37] the activation energy (see next section) should be the same for 90 (R = Me) as it is for 90 (R = H) if the eclipsing interactions in 91 are small. When



90 91

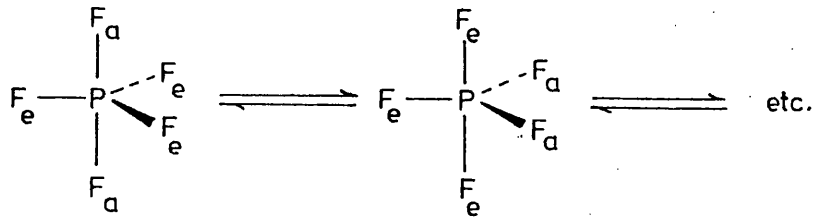
R = Me or H.

R = Me the free energy of activation is 4.9 k.cal.mol^{-1} higher than when R = H showing that the eclipsing interactions are important in determining the configuration of phosphoranes.

Experiments by Stewart and Trippett[47] suggest that tertiary butyl groups in phosphoranes are thermodynamically more stable in the equatorial position.

iii. Ligand Permutational Isomerism in Phosphoranes.

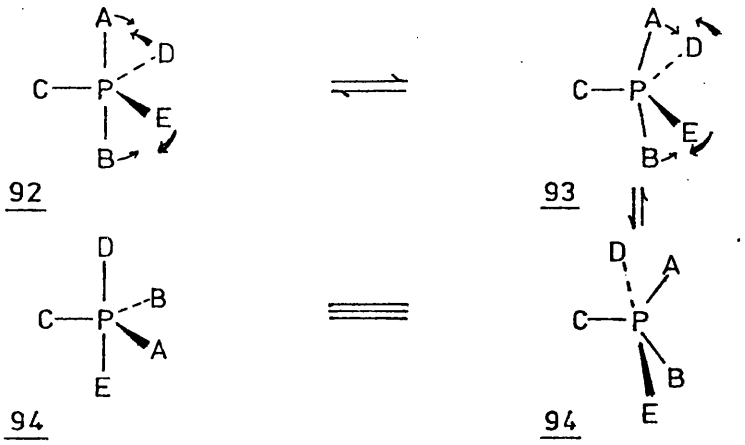
Phosphorus pentafluoride has been studied by electron diffraction techniques[130] and infra-red spectroscopy[141,142] and found to have a trigonal bipyramidal structure. The ^{19}Fn.m.r. spectrum, however, shows only one type of fluorine atom,[142] i.e. a doublet due to PF spin-spin coupling which remains intact throughout the range 60 to -197°C. This data suggests that the T.B.P. is exchanging its apical and equatorial fluorine atoms at a rate that is fast on the n.m.r. time scale but slow on the infra-red and electron diffraction time scale (scheme 22).



Scheme 22.

In 1960 Berry[143] proposed a mechanism to explain this equilibration of the fluorine atoms. This has become known as the Berry Pseudorotation (B.P.R.) and can be used to explain ligand reorganisations in all known phosphoranes and other non rigid T.B.Ps. except where other mechanisms for

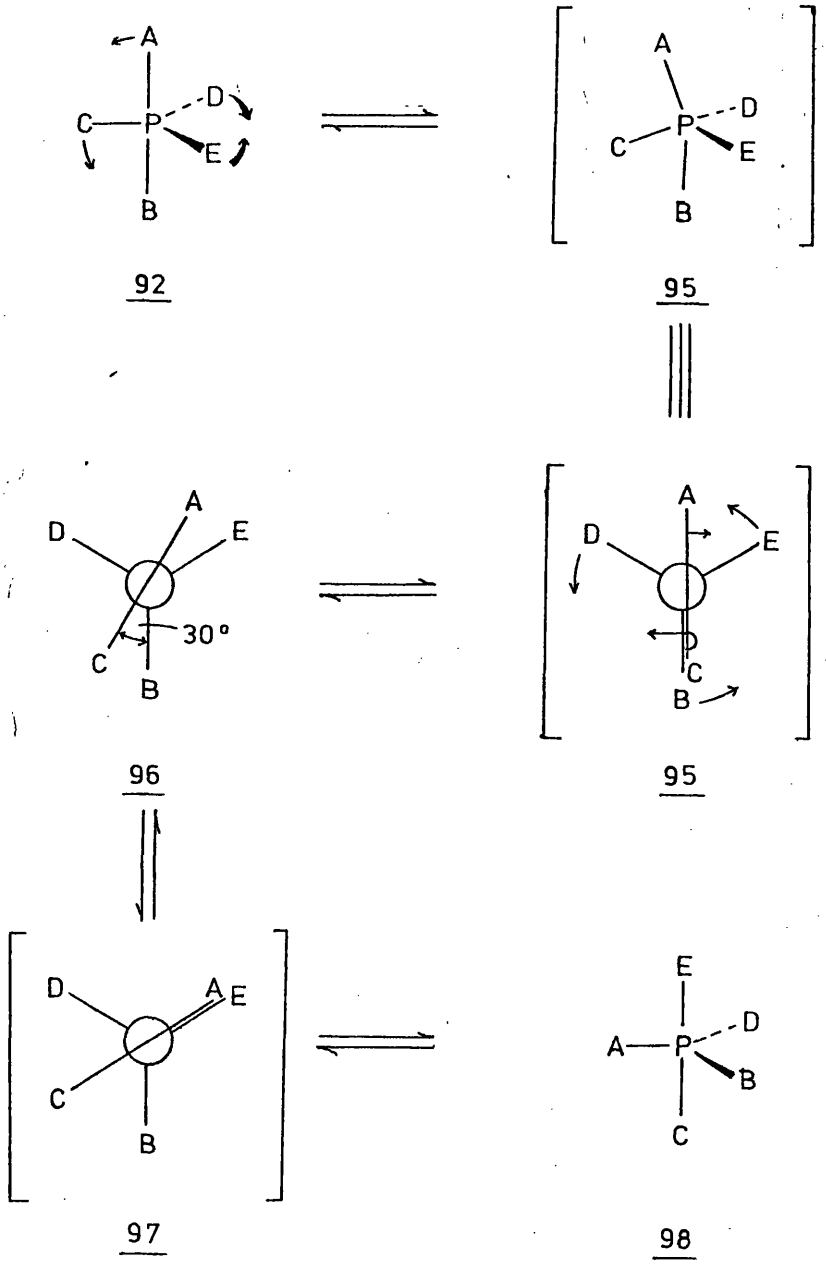
isomerisation are occurring, e.g. bond making and breaking processes. The mechanism of the B.P.R. is outlined in scheme 23.



Scheme 23.

In T.B.P. 92 one equatorial ligand is termed the pivot (C). The apical ligands, A and B, bend away from the pivot C, and towards each other in the vertical plane. At the same time the two equatorial ligands, D and E, bend towards C and away from each other in the horizontal plane. The P-A and P-B bonds shorten slightly and the P-D and P-E bonds lengthen slightly during this bending process, until a point is reached where an intermediate square pyramid 93 is formed. The pivot occupies the apical position in this square pyramid. The direction of bending can reverse to reform T.B.P. 92 or it can continue in the same direction to form a new T.B.P. 94 where D and E are the new apical ligands and A and B are the new equatorial ligands. The new T.B.P. is now free to undergo further B.P.Rs. to form other isomers. In summary, the B.P.R. involves two apical ligands exchanging positions with two equatorial ligands.

An alternative mechanism for this isomerisation was proposed by Ugi and Ramirez[144,145] and is called the Turnstile Rotation (T.R.). The mechanism of the T.R. is outlined in scheme 24.

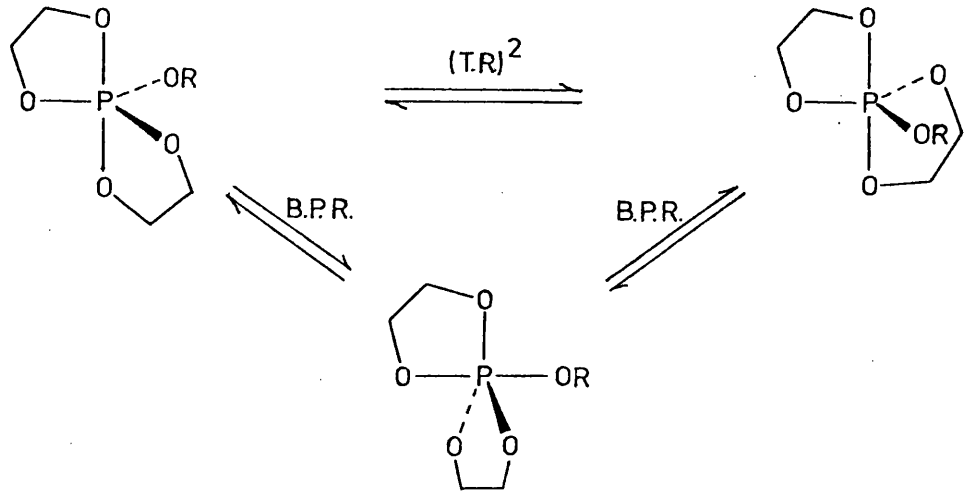


Scheme 24.

One apical and one equatorial ligand (A and C) each move down about 9° in the vertical plane. At the same time

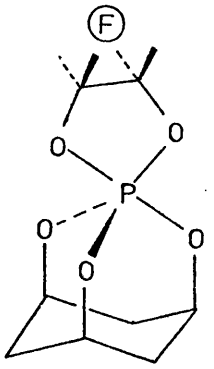
the two remaining equatorial ligands (D and E) move towards each other in the horizontal plane until a 90^{o} angle is formed between them. A and C are called the pair and B, D and E are called the trio. This deformation should give rise to intermediate 95 but this is not formed because at the same time as the bonds are bending the pair and the trio rotate 30^{o} relative to each other forming intermediate 96 which is called a 30^{o} (2 + 3). The pair and the trio in intermediate 96 can now rotate 30^{o} relative to each other in either direction forming either of the hypothetical intermediates 95 or 97. The reverse of the initial bond deformation occurs which either reforms T.B.P. 92 or forms a new T.B.P. 98.

The T.R. 92 to 98 has exactly the same overall effect as a B.P.R. using D as the pivot in 92. Ramirez[145] claims that highly strained spirophosphoranes with small rings spanning two equatorial positions which are formed as intermediates in some B.P.Rs., can be avoided by carrying out multiple T.R. processes, i.e. when the pair and the trio in the 30^{o} (2 + 3) intermediate rotate more than 30^{o} relative to each other before reforming a T.B.P., e.g. scheme 25.



Scheme 25.

He also claims that equivalence in the ^{19}F and ^{1}H n.m.r. spectrum of 99 above -120°C, shows that a rapid T.R. process



99

occurs because molecular models suggest that the system is too constrained for B.P.Rs. to occur.[135] This, however, is largely a matter of opinion and there is no evidence that B.P.Rs. cannot occur in 99 because the structural difference between a Berry square pyramidal intermediate and a Turnstile 30°(2 + 3) is very small.

A recent theoretical comparison of the T.R. and B.P.R. in structurally flexible T.B.Ps., e.g. PH_5, concludes that T.R. intermediates should be regarded as vibrationally excited modes of B.P.R. intermediates.[146] This is because the activation energy for a T.R. process was calculated as 10.05 k.cal.mol.$^{-1}$ whereas for the same process based on a B.P.R., the activation energy was calculated as 1.95 k.cal.mol.$^{-1}$, which is a more acceptable figure.

This treatment only applies to flexible, undistorted T.B.Ps. For distorted T.B.Ps. this treatment does not work. Holmes and Deiters[140] have made a comparison of the actual shapes of several spirophosphoranes and compared these with the intermediates required for T.R. and B.P.R. processes. They made the assumption that the phosphoranes would isomerise by the mechanism which had intermediates most closely resembling the observed structure

of the distorted phosphorane. In the range of phosphoranes studied they concluded that the most favourable process was the Berry mechanism.

The overall result of a T.R. or a B.P.R. is the same and the distinction between the two is only of academic interest. Throughout this thesis all isomerisation processes will be discussed in terms of the B.P.R.

Muetterties[147] has considered several other mechanisms for ligand reorganisations in T.B.Ps. but experimental evidence[148] has discounted all of these except the B.P.R. and T.R. Another mechanism which can operate involves a bond breaking and reforming process. This can usually be detected because the activation energy which is usually measured by dynamic n.m.r. techniques, will be solvent dependent. As the solvent becomes more polar the dissociated phosphorus intermediate is more favoured and the activation energy appears to decrease. The ^{31}P n.m.r. chemical shifts also move to lower fields as solvent polarity increases, when dissociation occurs.

iv. The Calculation of Activation Energies for Berry Pseudorotations.

For the pseudorotation 100 to 101, there are three factors which contribute to the activation energy for the process. These can be summarised as follows.

100 101

a) Relative Apicophilicity (A)

If ring A in 100 is a dioxaphospholan ring the B.P.R. 100 to 101 will replace an apical ring oxygen for the R group. This will introduce an energy term which will be the difference in relative apicophilicity between the ring oxygen and the R group, i.e. A(ring O - R).

Tables of relative apicophilicities[48,136] must be consulted to find this term. If, e.g. R = PhO, this term is usually taken as -1 k.cal.mol.$^{-1}$[48], i.e. the phenoxy group is more apicophilic than a ring oxygen by about 1 k.cal.mol.$^{-1}$.

b) Ring Strain (S)

In going from 100 to 101, the angle at phosphorus in ring A increases from 90^{o} to 120^{o} and so the term S_{90-120} (ring) must be included in the overall energy equation. Experimentally it has been found that for a saturated five-membered ring, e.g. a phospholan ring, this term is about 8 k.cal.mol.$^{-1}$ and for an unsaturated five-membered ring, e.g. a phospholene ring, this term is about 10 k.cal.mol.$^{-1}$[48,53,149].

c) P - X Bond Rotation (RotX)

In 100 where ring A is a dioxaphospholan ring, the lone pair of electrons on the equatorial oxygen atom is in the preferred equatorial plane[128]. In 101, however, the two ring oxygen atoms have their lone pairs in the disfavoured apical plane. It has been found experimentally[48] that about 5 k.cal.mol.$^{-1}$ is required for each ring oxygen to be rotated to place the lone pair apical. The corresponding energy for rotations around each P - N[48] or P - S[150] bond is about 9 k.cal.mol.$^{-1}$. The term nRot(X) must therefore be introduced to the overall energy equation where X defines the heteroatom

and n is the number of heteroatoms with apically orientated lone pairs.

Summarising this for a 1,3,2-dioxaphospholan ring we have the following equation:

$$\Delta G^{*}(\text{calc}) = A(\text{ring O - R}) + S_{90\text{-}120}(\text{dioxaphospholan}) + 2\ \text{Rot(O)}.$$

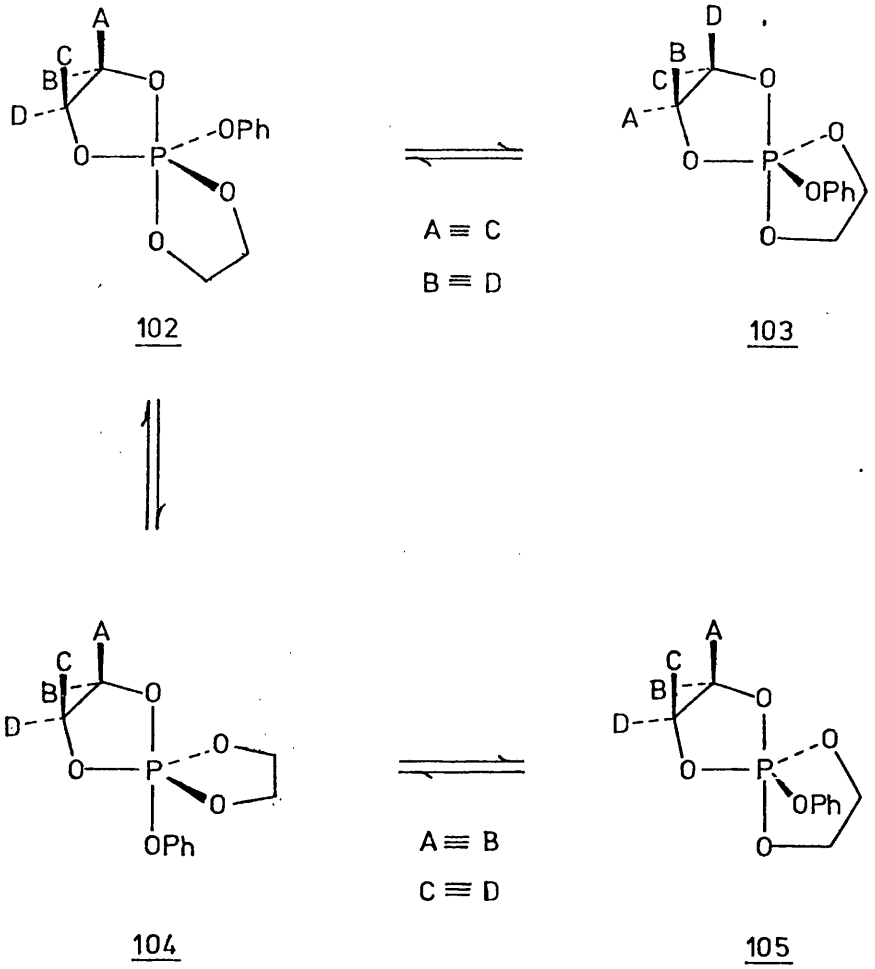
This can be used to calculate the energy difference between the two structures 100 and 101, i.e.:

$$\Delta G^{*}(\text{calc}) \simeq \text{Energy 101} - \text{Energy 100}$$

It is important to note that the calculated activation energy is really the difference between the energies of two isomers and not the true activation energy. This is discussed in greater detail in the next section.

v. Measurement of Activation Energies for Berry Pseudorotations.

Activation energies for B.P.Rs. have been obtained by kinetic studies using n.m.r. techniques[42] and by monitoring the epimerisation of optically active ephedrine adducts by polarimetry[151,152]. A more widely used technique is dynamic n.m.r.(d.n.m.r.). Consider phosphorane 102 where each of the groups A, B, C and D are the same, i.e. CH_3 or CF_3 groups. In the frozen state all of the groups A - D are in different environments and so each should appear as a separate n.m.r. signal. A rapid (low energy) B.P.R. between mirror images 102 and 103 will occur equilibrating groups A & C and B & D thus reducing the four n.m.r. signals to two. A higher energy pseudorotation 102 to 105, will coalesce the two n.m.r. signals to one because this B.P.R. equilibrates groups A & B and C & D. This is because the high energy intermediate 104 in this B.P.R. has a plane of symmetry.



102 103

104 105

The low energy B.P.R. 102 to 103 will always be faster than the higher energy pseudorotation 102 to 105. The n.m.r. spectrum of this phosphorane will only be a singlet when the high energy B.P.R. is fast on the n.m.r. time scale, i.e. when the two isomers are interconverting so rapidly that the n.m.r. spectrometer cannot distinguish between them, and so only sees a time average of the two signals. If the temperature of the n.m.r. tube is reduced the B.P.R. will slow down. When the pseudorotation becomes slow on the n.m.r. time scale the machine will be able to distinguish between the two isomers and therefore shows two separate signals. If the maximum separation of these two signals and the temperature at which coalescence occurs are

measured, the activation energy for the process can be obtained by using the Gutowsky-Holm[153] approximation (equation 1):

$$k_1 = \frac{\pi \Delta \nu}{\sqrt{2}} \qquad \text{Equation 1.}$$

where k_1 is the rate of the pseudorotation and is given by:

$$k_1 = \frac{k\,Tc}{h} \exp -\frac{\Delta G^*}{R\,Tc} \qquad \text{Equation 2.}$$

$\Delta \nu$ = Maximum separation of signals before coalescence in Htz.

k = Boltzmann's constant

Tc = Coalescence temperature

h = Planck's constant

R = Gas constant.

Substituting the numerical values of the constants and combining equations 1 and 2 gives:

$$\Delta G^* = 4.576 \times 10^{-3} Tc(9.97 + \log_{10} Tc - \log_{10} \Delta\nu)$$

This equation is a good approximation if the following valid assumptions are made:

a) The entropy of activation is small and can be ignored.

b) The observed coalescence is between equal amounts of the two isomers being observed. If, for reasons of asymmetry, the two isomers are not in equal amounts the Gutowsky-Holm equation is still a good approximation but it can be modified to deal with this problem.

c) The coalescence must be reversible to ensure that the equilibrium of the n.m.r. signals is not caused by decomposition of the phosphorane.

For phosphorane 102 where A - D are CF_3 groups the measured[48] activation energy is 17.4 k.cal.mol.$^{-1}$. The activation energy can be calculated as follows:

$$\Delta G^*(\text{calc}) = A(\text{ring O - OPh}) + S_{90-120}(\text{dioxaphospholan}) + 2\ \text{Rot O}$$

$$= -1 + 8 + 10$$

$$= 17\ \text{k.cal.mol.}^{-1}$$

Thus the calculated and the measured values are very close.

One final point must be considered. The calculated activation energy is really the energy difference between two isomers whereas the measured activation energy is the energy barrier between these two isomers (figure 1). This means that

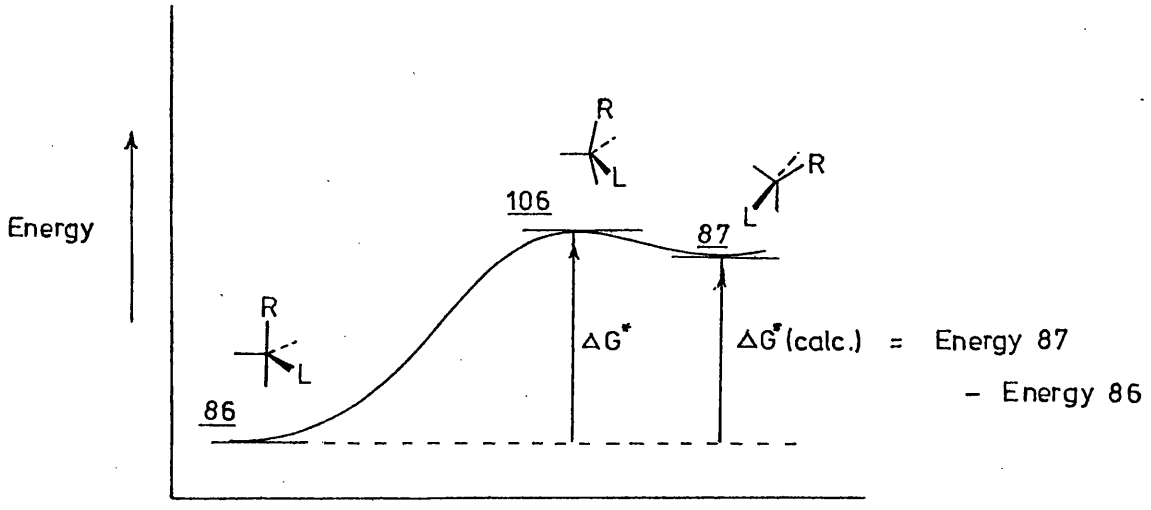


Figure 1.

the calculated activation energy will usually be an underestimate of the actual activation energy, i.e.:

$$\Delta G^* \geq \Delta G^*(\text{calc})$$

This difference will, however, be very small because the transition state 106 is not very different in structure to phosphorane 87.

By measuring the ΔG^* values for a large number of phosphoranes a scale of relative apicophilicities[42,48,136], ring strains[48,53] and P — X bond rotation energies[48,136,150] have been compiled.

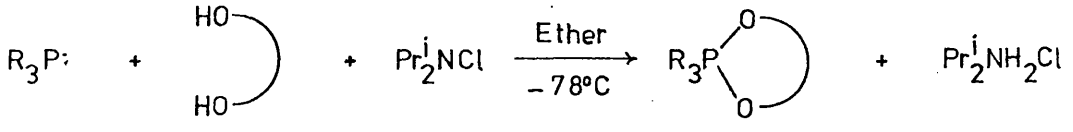
CHAPTER 2. PHOSPHORANES PREPARED BY USING N-CHLORODI-ISOPROPYLAMINE

In 1974 Castro et al.[154] used N-chlorodi-isopropylamine (N.C.D.) to prepare alkoxyphosphonium salts from trisdimethylaminophosphine and alcohols (scheme 26).

$$(Me_2N)_3P + Pr^i_2NCl + ROH \xrightarrow[ii)\ NH_4ClO_4\ (aq).]{i)\ -40°C/\ CH_2Cl_2} (Me_2N)_3\overset{+}{P}OR\ ClO_4^-$$

Scheme 26.

Bone and Trippett[108] have applied this reaction to the synthesis of spirophosphoranes and it has since been used to prepare a large number of phosphoranes from 1,2- or 1,3-diols and cyclic trivalent phosphorus compounds.[42,48,109,155] This reaction is essentially an oxidation where two atoms of hydrogen are removed from a 1:1 mixture of a diol and a P(III) compound which is oxidised to a P(V) compound. The overall stoichiometry of the reaction is outlined in scheme 27.



Scheme 27.

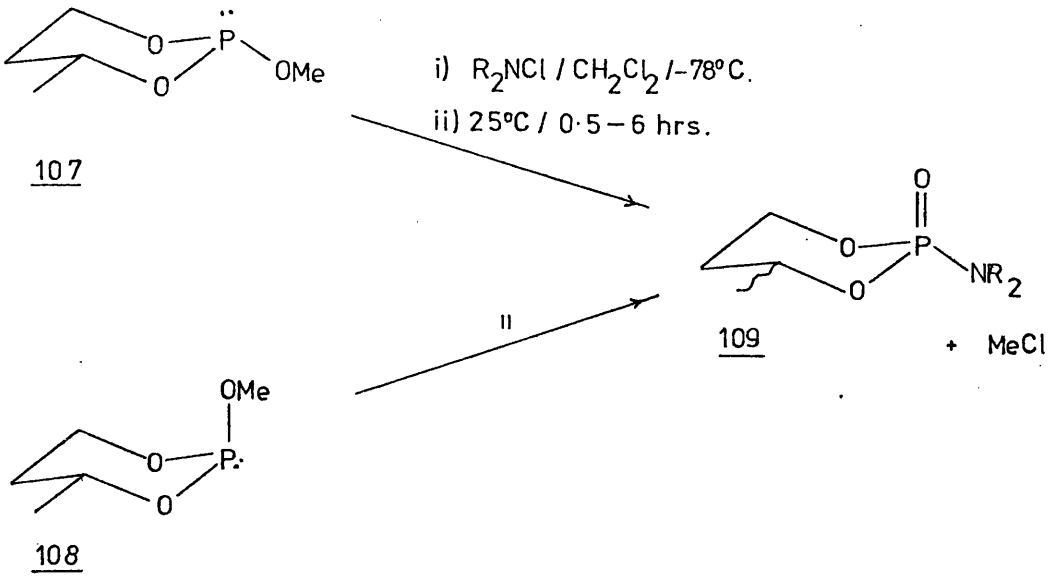
A solution of N.C.D. in ether is added to equimolar quantities of the P(III) compound and the diol in ether at -78°C and usually allowed to warm up to room temperature slowly, and stirred overnight.

Filtration of the insoluble amine hydrochloride, and evaporation of the solvent, yields the crude phosphorane which can usually be crystallised from light petroleum.

The main advantages of this synthesis are the mild conditions under which it is carried out and the ease of isolation of the products, since many phosphoranes are thermally unstable and most are hydrolytically unstable.

Phosphoranes have been prepared from cyclic phosphines (phosphetans), phosphonites, phosphites, phosphoramidites and phosphorothioites.[109] The reaction works well with 1,2- and 1,3-diols especially ethane-1,2-diol, pinacol, perfluoropinacol, neopentylglycol, catechol and substituted catechols.[109] It also works with 2-mercaptoethanol, 2-amino- and 2-dimethylamino-ethanol, 2-mercapto- and 2-amino-phenol, 2-mercaptoanilines, o-phenylenediamine and benzoyl hydrazide,[156] although these reactions are not always so clean as with diols and the products require more careful purification.

Surprisingly little is known about the mechanism of the N.C.D. synthesis of phosphoranes, and all of the information so far obtained suggests that the mechanism is either very complicated or that two or more different mechanisms are in competition. N-Chlorodialkylamines are known to form phosphoranes with trivalent phosphorus compounds[157] and Denney[158] has recently shown that stereoisomers of 2-methoxy-4-methyl-1,3,2-dioxaphosphorinan, 107 and 108, form 2-dialkylamino-4-methyl-1,3,2-dioxaphosphorinan-2-oxides (109) with N-chloro-dimethylamine, diethylamine and -piperidine, with loss of stereochemistry.



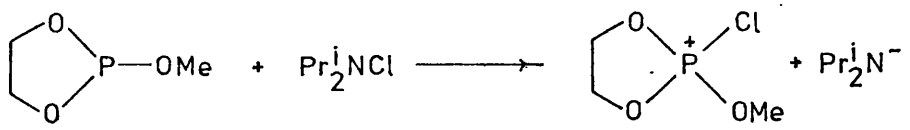
R_2 = Me_2, Et_2 or cyclo-C_5H_{10}

He explains the loss of stereochemistry in this reaction in terms of pseudorotations in intermediate phosphoranes before the products are formed, but there is also a possibility of ionic reactions taking place. N-Chlorodi-isopropylamine, however, does not bring about the same reaction. In fact cyclic phosphites 107 and 108 or trimethyl phosphite, remain unchanged after fourteen days at room temperature with N.C.D.

Waddling[156] has also shown that no reaction between 1,3,2-dioxaphospholans and N.C.D. can be detected by Fourier-Transform ^{31}Pn.m.r. spectroscopy, but as soon as a diol is added a phosphorane is rapidly formed. Other work by Castro[154,159] suggests that trivalent phosphorus compounds attack the chlorine of N.C.D. forming a chlorophosphonium intermediate, which can react with alcohols[154] or diols[159] forming alkoxyphosphonium salts (scheme 26).

Since a large number of phosphoranes have been prepared from 1,3,2-dioxaphospholans and phosphorinans, and these are apparently inert towards N.C.D., a mechanism which does not involve

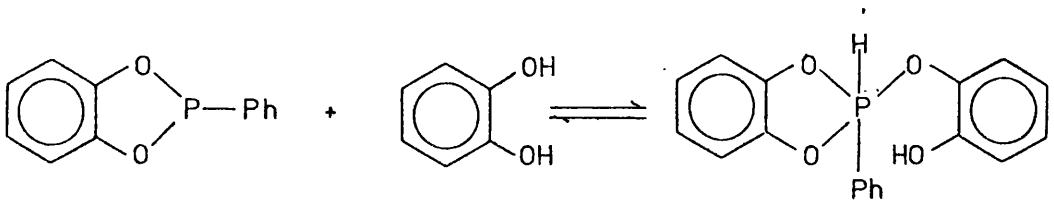
nucleophilic attack of phosphorus on chlorine must be proposed. This, however, does not rule out the formation of chlorophosphonium intermediates because the di-isopropylamide anion, which is formed when the phosphorus atom attacks N.C.D., is a very poor



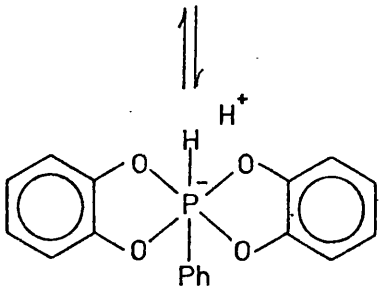
110 111

nucleophile and would probably not attack the intermediate 111 to form a phosphorane or a phospholan oxide. If the equilibrium lies to the left the phosphonium intermediate may be present in concentrations too low to be seen in the n.m.r. spectrum. If the reactions in the equilibrium are fast on the n.m.r. time scale, i.e., if 110 and 111 are interconverting rapidly and 111 is in low concentrations, the n.m.r. spectrum would only show a time-average signal for the two phosphorus compounds 110 and 111 which would be close to the signal for 110. The di-isopropylamide anion is a strong base and would easily remove a proton from a diol leaving an alkoxide which would rapidly attack the phosphonium intermediate and form an alkoxy-phosphonium salt and subsequently a phosphorane.

An alternative mechanism could possibly involve P-H phosphoranes or hexacoordinate phosphorus anions. Alcohols or diols are known to react with trivalent phosphorus compounds forming P-H phosphoranes or hexacoordinate species such as 112 or 113.[160] N.C.D. acts as an oxidising agent and could possibly remove two hydrogen atoms from compounds such as 112 or 113 to form spirophosphoranes.

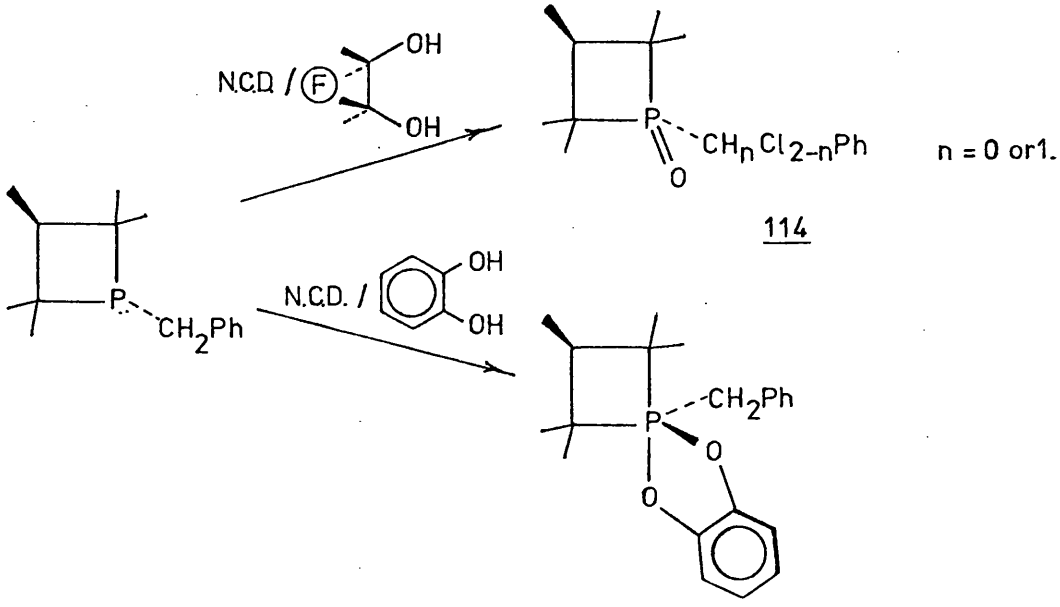


112



113

There are surprisingly few facts known about the N-chlorodi-isopropylamine synthesis of phosphoranes. When phosphoranes derived from cis- or trans-phenyl-2,2-r-3,4,4-pentamethyl-phosphetans are prepared the stereochemistry is retained.[42,109] The corresponding trans-benzylphosphetan gives the trans-benzylphosphorane with catechol but chloro derivatives of the phosphetan oxide (114) are formed with perfluoropinacol.[42,109]



114

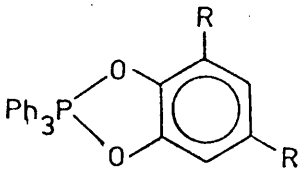
An empirical experimental observation regarding the rate of reaction of various diols can be made. All diols add on to P(III) compounds at approximately the same rate, with the exception that catechols react very much faster and pinacol reacts very much slower than other diols. Some reactions with pinacol take several days to go to completion. This can be explained in terms of the orientation of the hydroxyl groups on the diol. Catechols have both hydroxyl groups held in a perfect orientation for phosphorane formation, whereas the eclipsing interactions of the methyl groups on pinacol stagger the two hydroxyl groups to the gauche or anti conformation, making phosphorane formation more difficult. It would be interesting to compare the rate of addition of cis-cyclopentane-1,2-diol and catechol to a P(III) compound, to see if any factors, other than orientation of hydroxyl groups, effect the rate of addition, since there will be the same relative orientation of hydroxyl groups in both compounds.

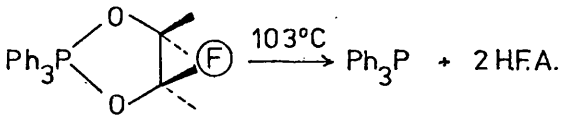
The only conclusion that we can draw about the mechanism of this reaction at present, is that many more experiments will have to be carried out before any firm conclusions can be made.

Phosphoranes prepared from Acyclic Trivalent Phosphorus Compounds.

Most of the phosphoranes so far prepared using N-chlorodi-isopropylamine (N.C.D.) have been derived from cyclic phosphites, phosphonites, phosphoramidites or phosphorothioites.[42, 48,108,109,155.] Since very little was known about the preparation of phosphoranes from acyclic trivalent phosphorus compounds or cyclic phosphines or phosphinites using N.C.D., a number of phosphoranes were prepared and the variable temperature n.m.r. spectra and thermal reactions of some of these were investigated.

Crystalline phosphoranes were prepared from triphenylphosphine and catechol, 3,5-ditertiarybutylcatechol and perfluoropinacol in good yields, but no phosphorane was formed with pinacol. The





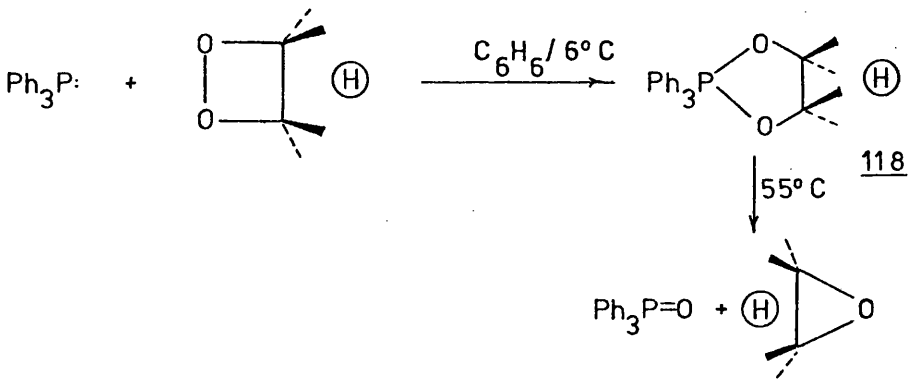
115 R = H, 62%.

116 R = Bu^t, 70%.

117 81%.

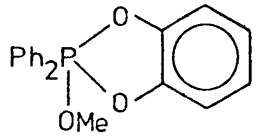
perfluoropinacol adduct 117 has been prepared by Ramirez[22,161] from hexafluoroacetone (H.F.A.) and triphenylphosphine, and decomposes to these compounds at its melting point.

The pinacol derivative (118) was prepared in an n.m.r. tube experiment by Bartlett et al.[83] from triphenylphosphine and tetramethyl-1,2-dioxetan. This adduct is reported to be very

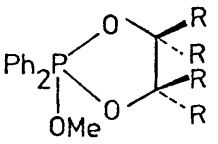


unstable, decomposing to triphenylphosphine oxide and tetramethylethylene oxide above 55°C in benzene, or at room temperature in more polar solvents.

Phosphoranes 119-121 were prepared as crystalline solids in good yields from methyl diphenylphosphinite and the corresponding diols.

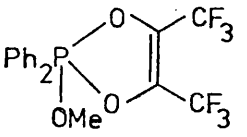


119 84 %



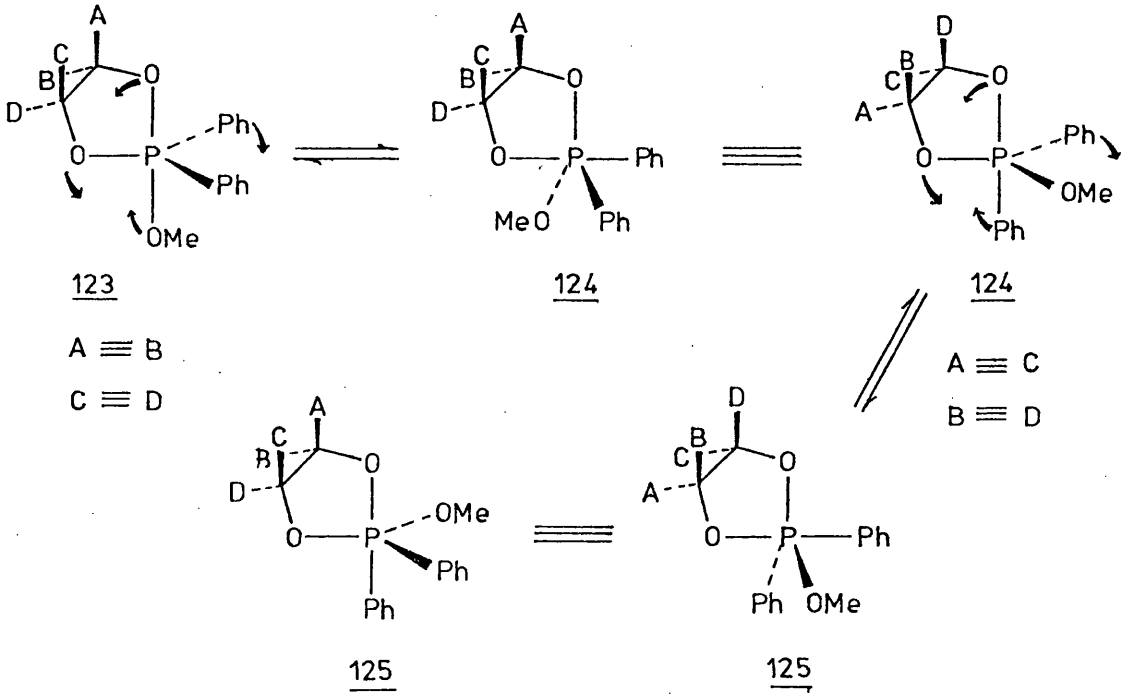
120 R = CF_3, 93 %

121 R = Me, 79 %



122

The variable temperature n.m.r. spectra of 120 and 121 were recorded to obtain the difference in apicophilicity between phenyl and methoxy groups in phosphoranes.



123

A ≡ B

C ≡ D

124

124

A ≡ C

B ≡ D

125

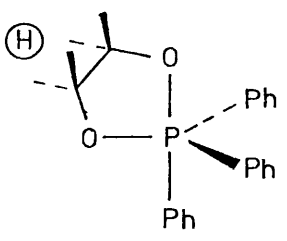
125

Phosphorane 123 has a plane of symmetry making groups A and B equivalent and groups C and D equivalent. This T.B.P. can pseudorotate to T.B.P. 124 which can undergo a low energy, topomeric

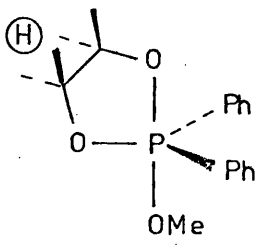
pseudorotation to phosphorane 125. Structures 124 and 125 are mirror images and therefore any pseudorotation between these two equivalent structures will be a low energy process. This low energy B.P.R. 124 to 125 makes groups A and C equivalent and groups B and D equivalent. When the high energy B.P.R. 123 to 124 is fast on the n.m.r. time scale the spectrum should show a singlet, which should split out to a doublet when the temperature of the system is reduced and this pseudorotation is slowed down. The coalescence temperature can be used to find the activation energy for the interconversion of 123 and 124, which is approximately the same as the difference in energy between these two structures, which is the same as the difference in apicophilicity between phenyl and methoxyl.

No splitting out of the CF_3 groups in phosphorane 120 could be seen above $-90^{o}C$ in dichloromethane, but 121 (R=Me) showed reversible coalescence at $-82 \pm 2^{o}C$ corresponding to a difference in apicophilicity between phenyl and methoxyl of 9.3 k.cal.mol.$^{-1}$. This value is in good agreement with Dickstein and Trippett[43] who found this value to be 9.8k.cal.mol.$^{-1}$ by studying the d.n.m.r. spectrum of the perfluorobiacetyl adduct 122.

The remarkable difference in stability between phosphoranes 118 and 121 can possibly be explained in terms of the difference



118

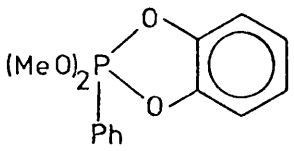


121

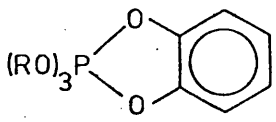
in relative apicophilicity between phenyl and methoxyl groups. The apical position of the phenyl group in 118 is unfavourable because phenyl groups have a low relative apicophilicity, which might destabilise this phosphorane relative to phosphorane 121, where the apical methoxyl group is much more favourable.

Another possible reason is that 121 has an extra oxygen atom next to phosphorus. An empirical observation is that the presence of oxygen atoms next to phosphorus helps to stabilise phosphoranes. Acyclic penta-alkoxyphosphoranes are known[71,81] compounds whereas acyclic penta-alkylphosphoranes are so far unknown.

Catechol was added to dimethyl phenylphosphonite, trimethyl phosphite and triethyl phosphite, to prepare phosphoranes 126, 127 and 128 respectively. These were all oils and were difficult to



126 90 %

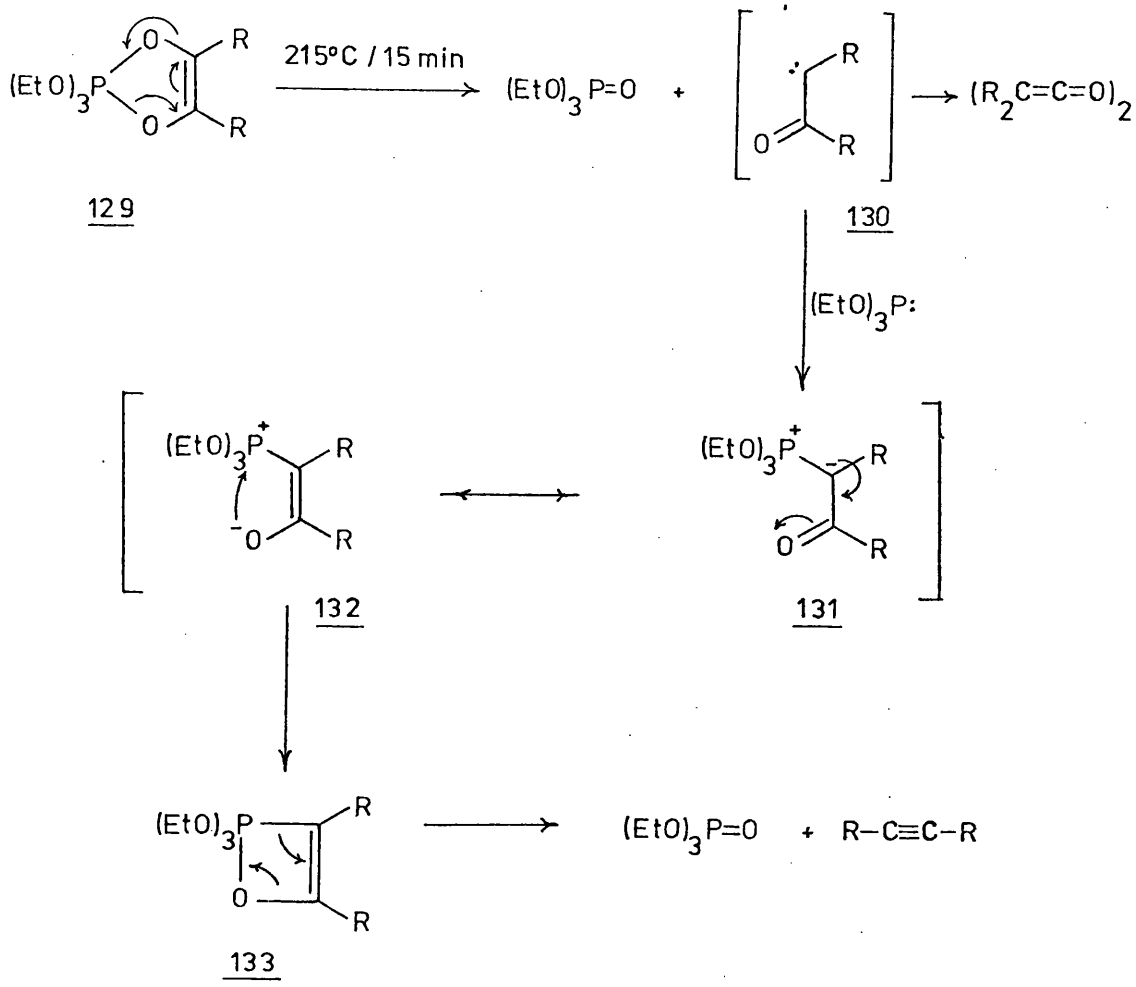


127 R = Me, 24%

128 R = Et, 37%

purify completely, but 127 and 128 were distillable and reasonably pure samples were obtained. Phosphorane 128 has been previously prepared by Denney[79] by adding diethyl peroxide to the corresponding benzodioxaphosphole.

In 1964 Mukaiyama et al.[162] reported the generation of carbenes by thermolysing adducts of triethyl phosphite with 1,2-diketones (scheme 28). The carbenes (130) either rearranged to diaryl ketene dimers, or they were trapped as ylids (131) with triethyl phosphite. These ylids rearranged to Wittig intermediates (133) via betaines

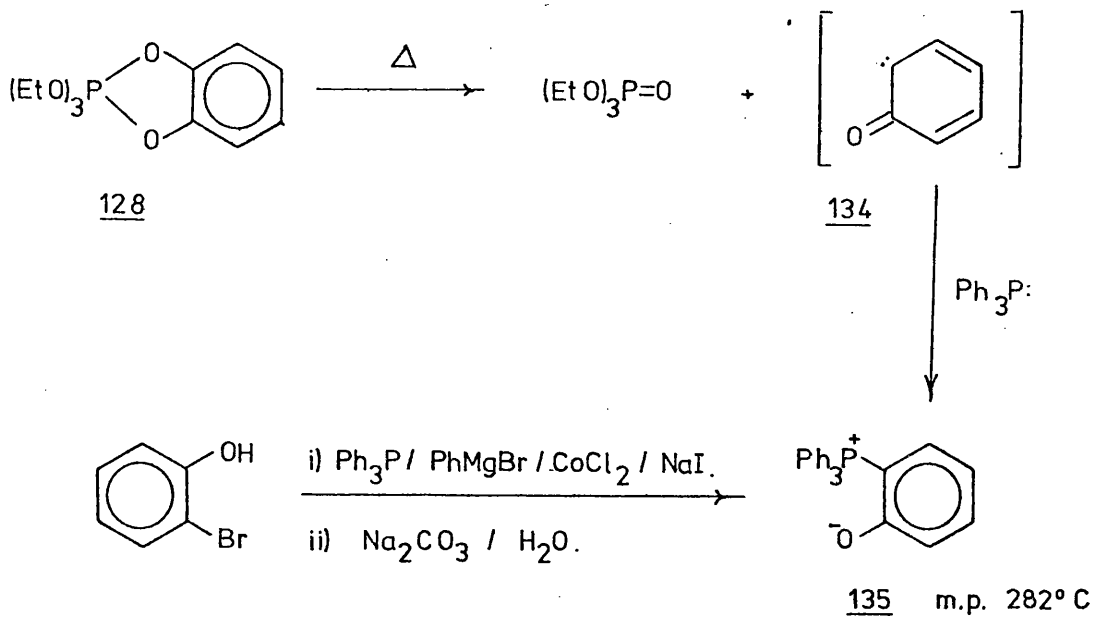


129 130 132 131 133

Scheme 28.

(132), and subsequently decomposed to triethyl phosphate and acetylenes.

In the light of this work the preparation of carbene 134 from phosphorane 128 was attempted. This carbene might be trapped with triphenylphosphine to give the stable betaine 135, which was prepared by Bestmann et al.[163] in the hope that it would undergo a Wittig reaction to produce benzyne.



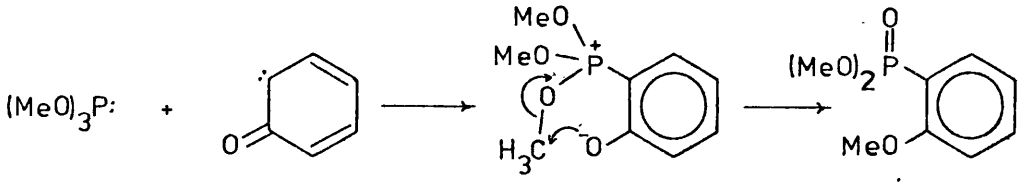
128 134 135 m.p. 282° C

Scheme 29.

When phosphorane 128 was heated with triphenylphosphine between 160 and 180°C for three hours, triethyl phosphate was formed and identified by gas chromatography. An unidentified white crystalline solid was also formed, which had a melting point of 236-7°C, a ^{31}Pn.m.r. chemical shift of -24.2 p.p.m. and a ^{1}Hn.m.r. spectrum showing that only aromatic protons were present. The same compound was obtained when the trimethyl phosphite - catechol adduct 127 was heated with triphenylphosphine. This compound was shown not to be betaine 135 by its inability to react with iodomethane forming a phosphonium iodide.[163]

In order to discover how many of the aromatic protons were phenyl protons and how many were catechol-type protons, the reaction was carried out using tri-p-tolylphosphine instead of triphenylphosphine. This reaction took a different course and the only products containing p-tolyl groups were the unchanged phosphine and its oxide.

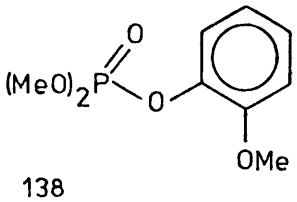
If a carbene (134) was being produced there was a possibility that it could be trapped with trimethyl or triethyl phosphite (scheme 30). The betaine 136 might then undergo an intramolecular Arbuzov reaction producing phosphonate 137.



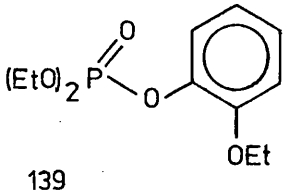
134 136 137

Scheme 30.

When triethoxyphosphorane 128 and excess trimethyl phosphite were heated together, and the products separated by distillation and chromatography on basic alumina, the ^{1}Hn.m.r. spectrum of the product was consistent with phosphonate 137. The mass spectrum, however, had a parent ion and a breakdown pattern consistent with phosphate 138, which was also consistent with the n.m.r. data. This structure was confirmed by comparing the product of the reaction with an authentic sample, which was prepared by the method outlined

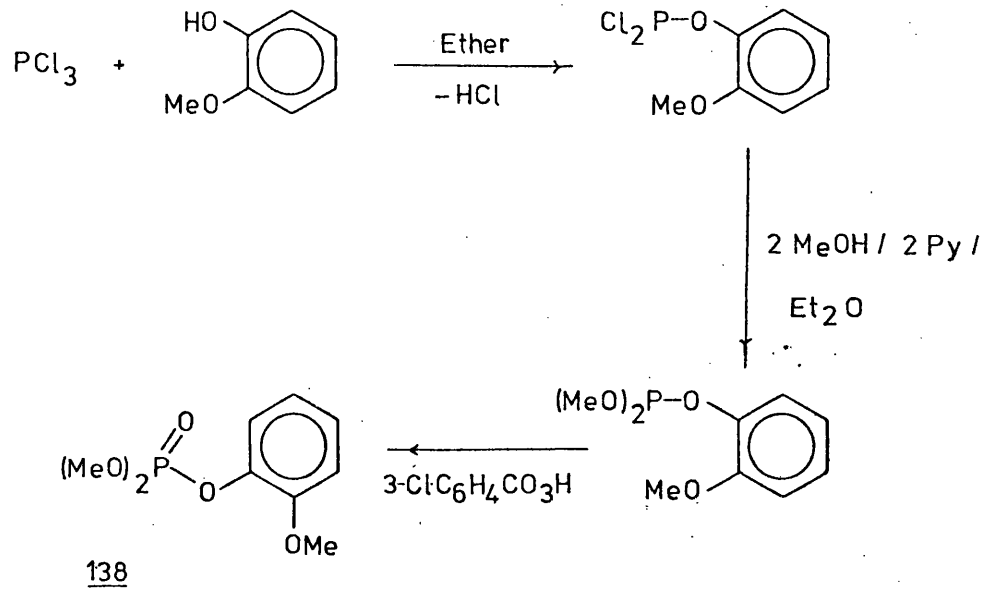


138



139

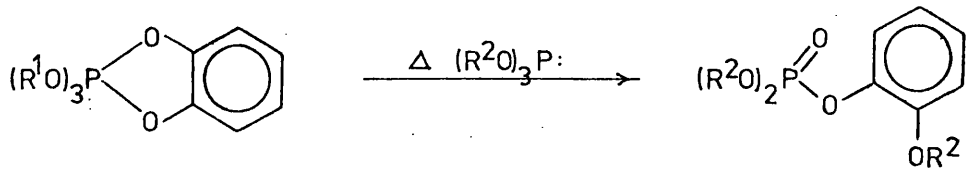
in scheme 31. Product 138 and the authentic sample were identical in all respects.



138

Scheme 31.

In a similar reaction the trimethoxyphosphorane 127, when heated with triethyl phosphite gave the diethyl phosphate 139. The general reactions that occurred are summarised in scheme 32.

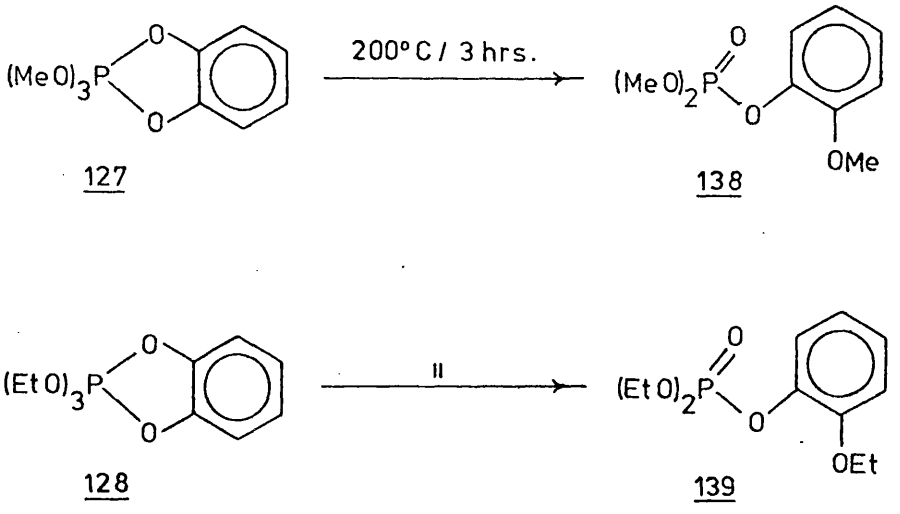


R^1 = Me, R^2 = Et

R^1 = Et, R^2 = Me

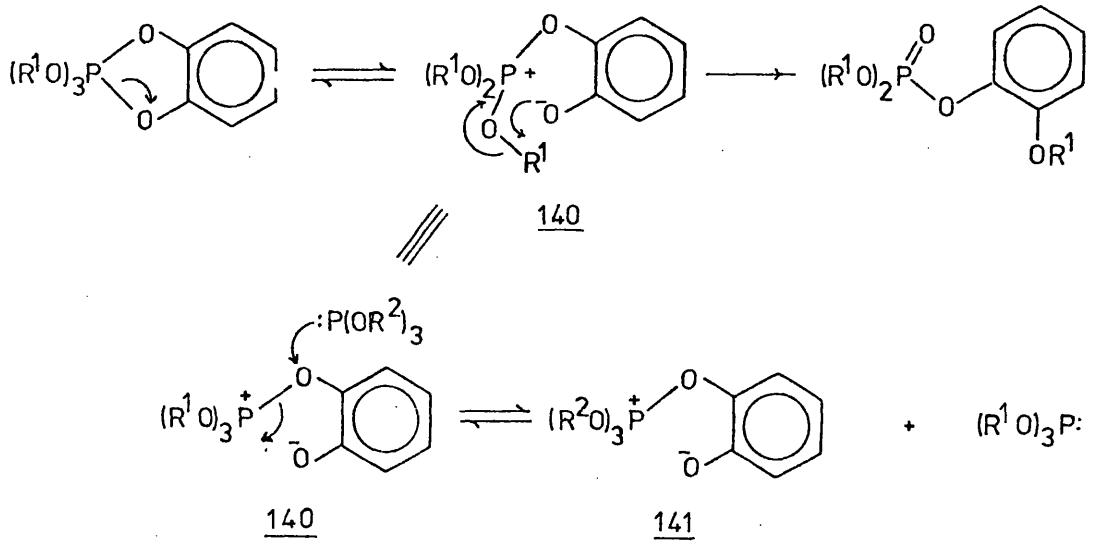
Scheme 32.

In an attempt to explain the formation of these products, phosphoranes 127 and 128 were each heated separately at 200°C for three hours. Under these conditions the phosphoranes rearranged to phosphates 138 and 139 respectively (scheme 33).



Scheme 33.

The mechanism of this rearrangement probably involves a ring opened, dipolar, phosphonium intermediate (140), which can undergo an intramolecular Arbuzov reaction, or it can possibly react with a phosphite forming a new intermediate 141, which can in turn undergo an Arbuzov reaction producing the observed



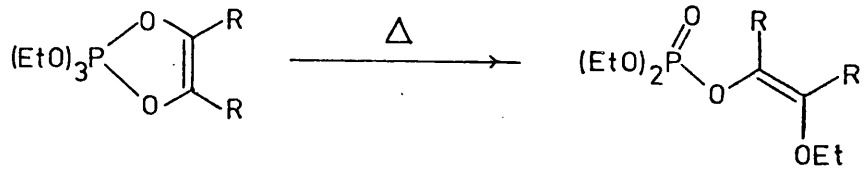
Scheme 34.

products (scheme 34). The equilibrium between 140 and 141 will probably lie to the right because the phosphite was used in large

excess. This means that 141 will be present in higher concentrations than 140 so the product will be derived from the added phosphite rather than the starting phosphorane.

In a final attempt to prepare the carbene 134, the triphenylphosphorane 115 was heated strongly but it was found to be thermally stable when heated at 240°C for thirty minutes, and when it was heated at 240°C for four hours with an equimolar amount of triphenylphosphine, the starting materials were recovered unchanged. The thermal stability of this phosphorane is in direct contrast with that of the corresponding pinacol adduct 118 which decomposes above 55°C in solution.

A possible explanation of why carbene formation does not occur with these catechol adducts, is that the aromatic delocalisation in the catechol ring would be lost in this reaction, making it unfavourable. In the 1,2-diketone adducts (129) which do give carbenes on thermolysis, it would be interesting to see if there are any products of simple rearrangement of this phosphorane (scheme 35).

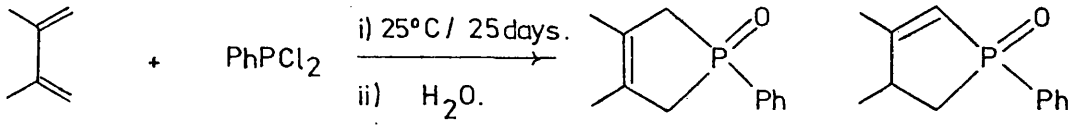


Scheme 35.

Phosphoranes prepared from Phospholenes.

A series of phosphoranes containing a 3,4-dimethylphosphol-3-ene ring was prepared in order to investigate the synthesis of these compounds by using N.C.D., and to investigate the chemistry of these phosphoranes.

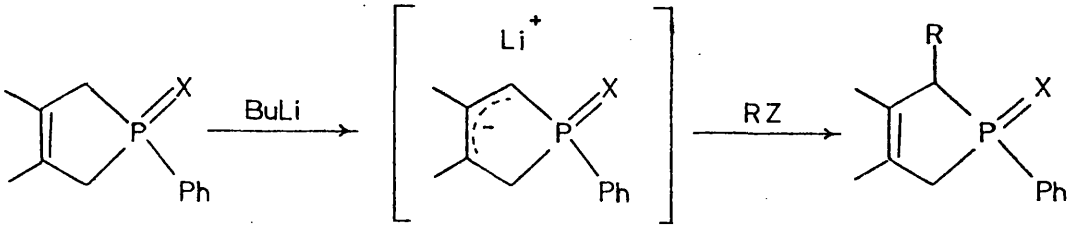
MacCormack[164] reported the preparation of phospholene oxide 143 from phenylphosphonous dichloride and 2,3-dimethylbutadiene (142). On two occasions, however, the product of this reaction contained



142 143 144

60% of the reported Δ,3 -isomer and 40% of the unwanted Δ,2-isomer. Chromatographic separation of these isomers proved to be inefficient.

Lampin et al.[165] have reported the metallation, and subsequent alkylation or acylation at the 2-position, of phospholene oxides and sulphides, (scheme 36).

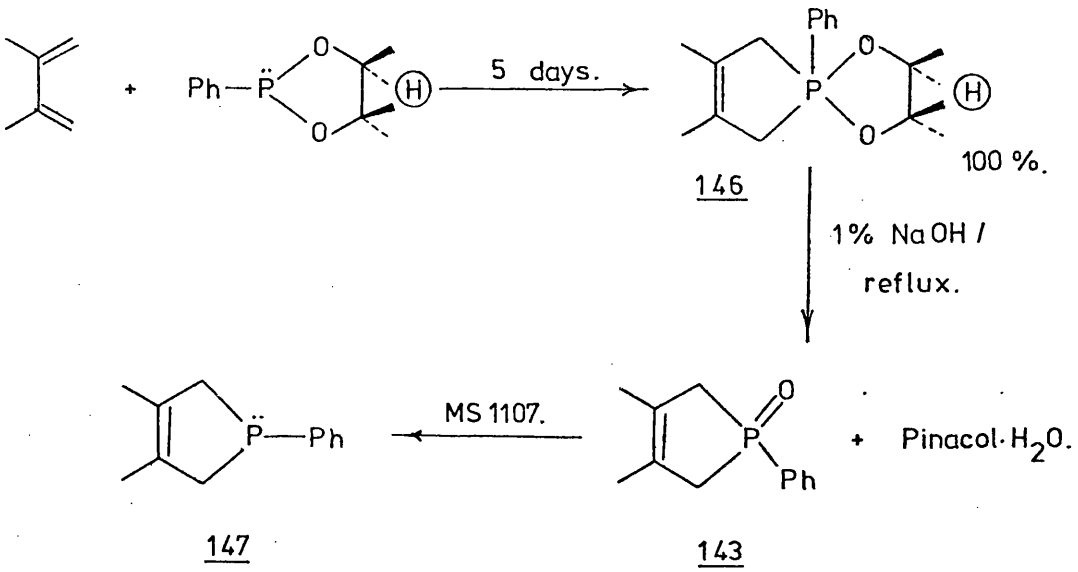


X = O or S.

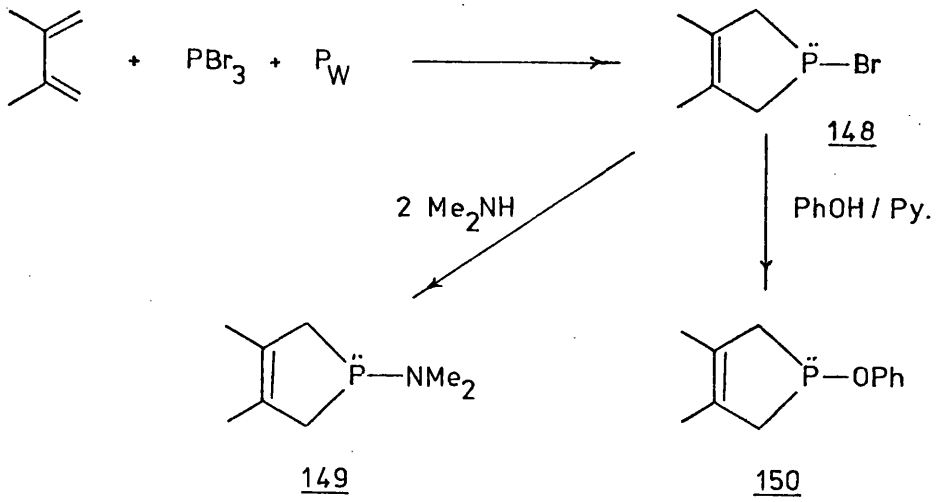
Scheme 36.

An isomerisation of 144 to 143 was attempted by treating the phospholene mixture with lithium di-isopropylamide in ether and working up the reaction with water. In this way the percentage of the Δ,3-isomer was increased to 88% but it could not be improved beyond this point with longer reaction times or different conditions.

A pure sample of the phosphol-3-ene oxide 143 was prepared by hydrolysing a spirophosphorane (146) which was prepared by treating 4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaphospholan with 2,3-dimethylbutadiene. The phospholene oxide was reduced to the corresponding phospholene (147) in almost quantitative yields, by distilling it from MS1107 silicone fluid.



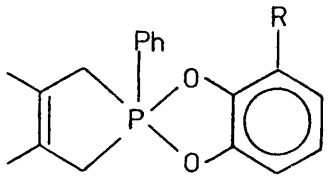
In 1972, Vizel et al.[166] reported the preparation of halophospholenes from phosphorus trihalides, white phosphorus and dienes. This reaction was used to prepare bromophospholene 148, which in turn was used to prepare phospholenes 149 and 150 (scheme 37).

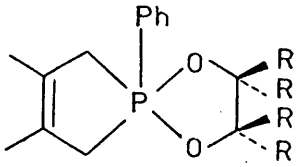


Scheme 37.

Phospholene 147 was used to prepare stable, crystalline phosphoranes with catechol (151) and pinacol (146). With

perfluoropinacol, a phosphorane (153) was prepared as a stable, distillable oil.





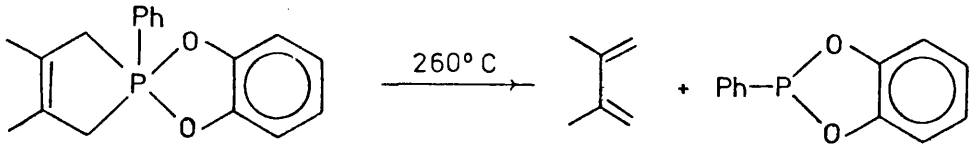
151 R = H, 70 %

152 R = Me —

146 R = Me, 30 %

153 R = CF_3, 89 %

The catechol adduct 151, was found to be fairly stable to hydrolysis and thermolysis. An analytical sample was prepared by sublimation at 100°C and after a sample of it was heated at 260°C for two hours, it had only partly decomposed to 2,3-dimethylbutadiene and 2-phenyl-1,3,2-benzodioxaphosphole (154).



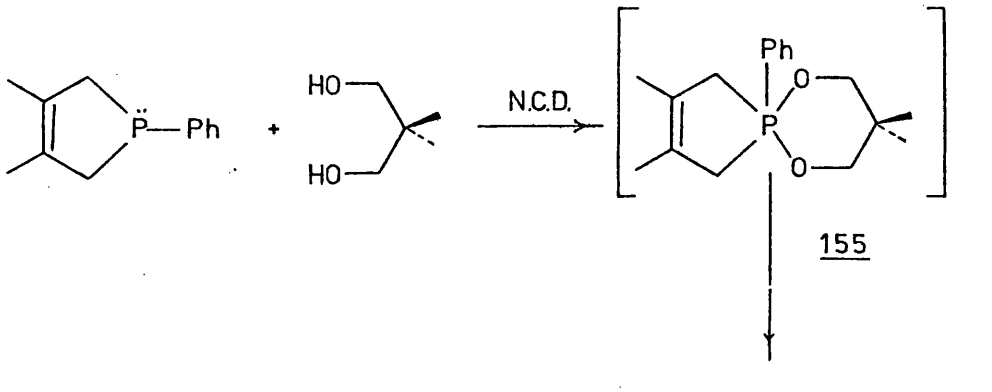
151 154

Despite the apparent stability of this compound, however, the ^{31}Pn.m.r. spectrum of a sample that had been stored in a stoppered flask and sealed with para-film for nine months, showed that large amounts of phospholene oxide 143 were present. This was presumably caused by small amounts of water vapour, or water adsorbed on the surface of the glass, hydrolysing the phosphorane.

Attempts to prepare phosphorane 152, using 3-methylcatechol, failed. Other methods (see chapter 3) also failed to prepare this compound.

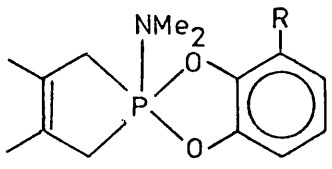
The d.n.m.r. spectra of phosphoranes 146 and 153 are discussed in chapter 3.

Acyclic phosphoranes[167] and spirophosphoranes containing larger than five-membered rings,[85] derived from phospholenes, are apparently unstable (scheme 13, chapter 1). Attempts to add neopentyl glycol to phospholene 143 using N.C.D., resulted in the isolation of dioxaphosphorinan oxide 157. This was presumably formed by atmospheric oxidation, during work-up, of the corresponding dioxaphosphorinan (156) formed by elimination of butadiene 142 from the unstable phosphorane 155.



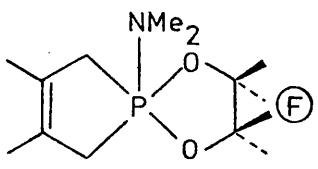
157 156

The dimethylaminophospholene 149 was used to prepare phosphoranes with catechol, 3-methylcatechol and perfluoropinacol



158 R = H, 81 %.

159 R = Me, 79%

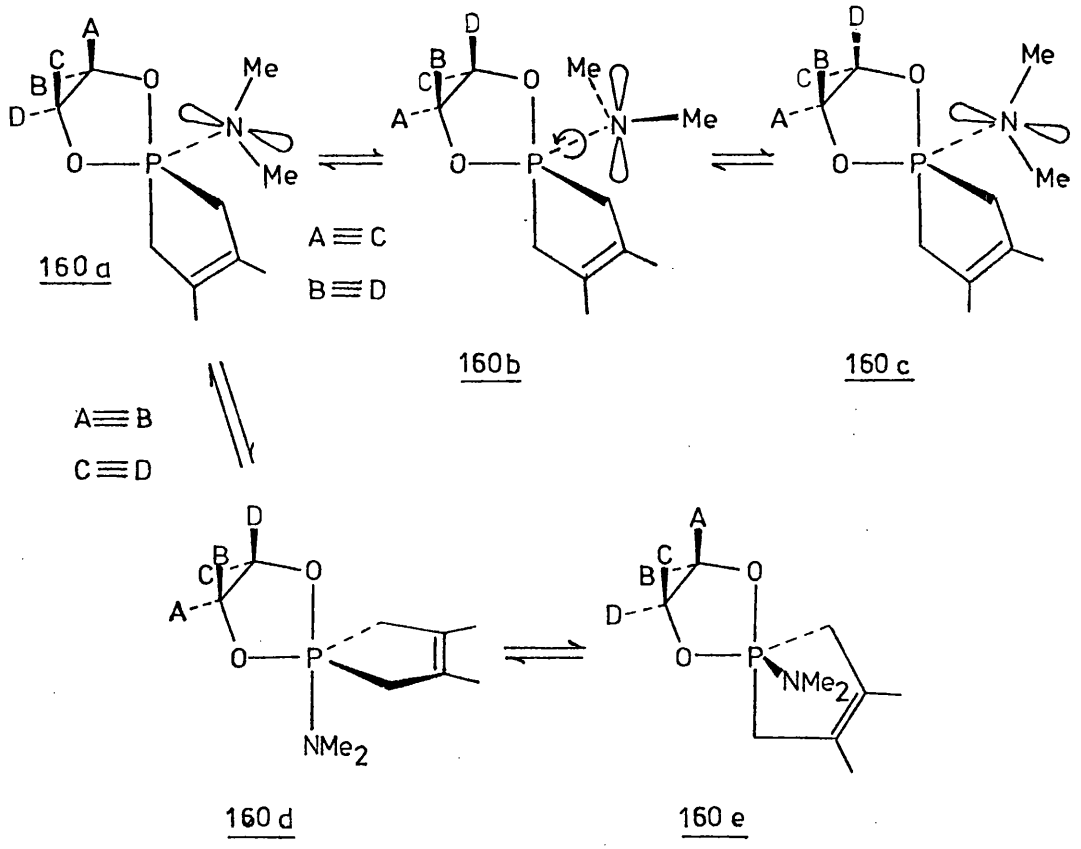


160 89 %.

using N.C.D. The two catechol adducts, 158 and 159, were both very unstable at room temperature but they were stable enough to be characterised by their mass spectra, ^{1}H and ^{31}Pn.m.r. and i.r.

spectra. The 3-methylcatechol phosphorane (159) was very much less stable than the catechol adduct (158), decomposing to a brown oil in two days at -40°C. The decomposition products were not identified but they were probably polymeric since they were insoluble in light petroleum or ether.

The perfluoropinacol phosphorane 160 was a stable distillable oil which became yellow on exposure to daylight. The ^{19}Fn.m.r. spectrum showed a sharp singlet at room temperature, splitting into a doublet, reversibly at approximately -75°C. The B.P.Rs. which this phosphorane can undergo are shown in scheme 38.



Scheme 38.

The frozen structure 160a should show four separate n.m.r. signals for groups A-D. The pseudorotation 160a to 160c makes groups A and C equivalent and groups B and D equivalent, and the B.P.R. 160a to 160e makes groups A and B equivalent and groups C and D equivalent. When both of these B.P.Rs. are fast on the n.m.r. time scale only one signal will be seen because all of the groups will be equivalent.

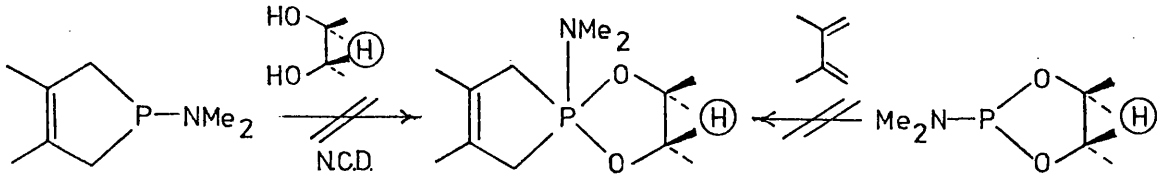
The B.P.R. 160a to 160c is essentially a topomeric pseudorotation between two identical structures and will therefore be of low energy. This pseudorotation, however, is accompanied by a rotation around the P-N bond. This is necessary because a simple B.P.R. 160a to 160b will produce a phosphorane with the lone pair on nitrogen in the disfavoured apical plane. A rotation of 90^{o} around the P-N bond must therefore occur in order to put the lone pair back into the favoured equatorial plane. This P-N bond rotation is probably synchronous with the pseudorotation. The energy barrier to P-N bond rotation has been measured as approximately 9 k.cal.mol.$^{-1}$ [48] and slowing down this bond rotation will effectively slow down the topomeric B.P.R. 160a to 160c. This will cause the singlet in the ^{19}Fn.m.r. spectrum to split into a doublet, which occurs at approximately -75^{o}C, corresponding to an activation energy of 9.4 k.cal.mol.$^{-1}$ for P-N bond rotation in this phosphorane.

If slowing down the P-N bond rotation also makes the high energy B.P.R. 160a to 160e slow down, the spectrum should split out to a quartet. This, however, does not occur. The spectrum remains a doublet at -141^{o}C in liquid propene/diethyl ether. This means that there is either an accidental coincidence of the n.m.r. signals or the poor resolution, caused by the low temperature, makes any small splitting difficult to see. It could also mean that the high energy B.P.R. 160a to 160e is independent of the P-N bond rotation process, and is still fast on the n.m.r. time scale at this

temperature. Very little is known about orientations for lone pairs on apical ligands so it is possible that this high energy B.P.R. is still fast even when the low energy B.P.R. is slow.

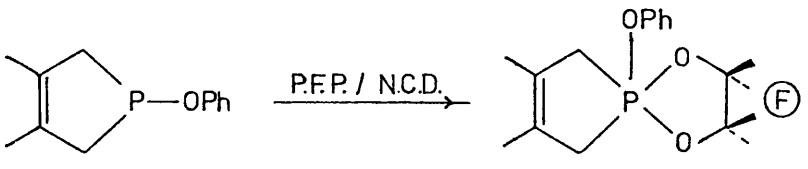
It is unlikely, however, that the high energy B.P.R. will be fast at -141°C because Brierley[42] has shown that the apicophilicity of the dimethylamino group is similar to the apicophilicity of the phenyl group and the phenylphospholene-perfluoropinacol adduct (154) has a coalescence temperature of -78°C (see chapter 3). This suggests that all B.P.Rs. for this phosphorane, will be slow at -141°C, and that accidental coincidence or poor resolution is responsible for the persistent doublet.

Pinacol could not be added to the aminophospholene 149. Similarly, 2,3-dimethylbutadiene could not be added to dioxaphospholan 161, suggesting that phosphorane 162 is inherently unstable and cannot easily be prepared.



149 162 161

Perfluoropinacol (P.F.P.) was added to phospholene 150 giving phosphorane 163 as a distillable oil which later crystallised.

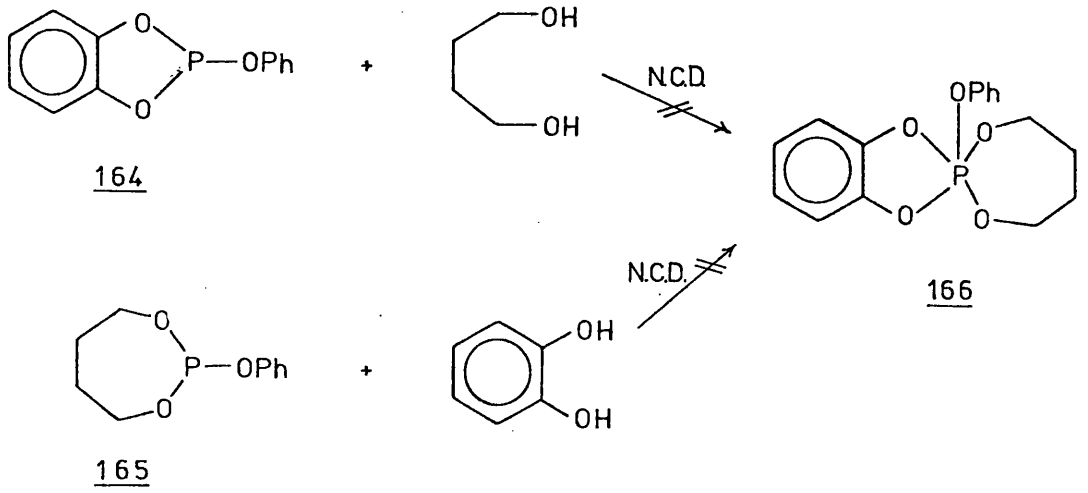


150 163 89 %

The d.n.m.r. of this compound is discussed in chapter 3.

Phosphoranes Containing Seven-Membered Rings.

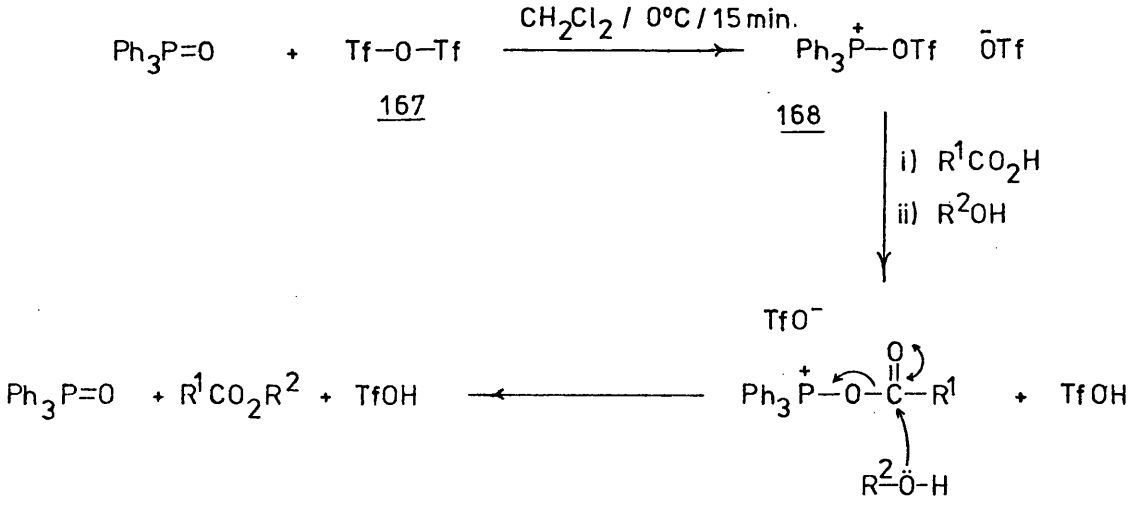
To date, there are no known examples of phosphoranes containing seven-membered rings. Attempts to add butane-1,4-diol to benzodioxaphosphole 164, or catechol to dioxaphosphepane 165, using N.C.D., have both failed to prepare a phosphorane with a seven-membered ring (166). N-Chlorodi-isopropylamine also failed to add cis-but-2-ene-1,4-diol to trivalent phosphorus compounds.



Hexafluoroacetone reacted with phosphepane 165 to give a heavy, colourless oil which had a ^{1}Hn.m.r. spectrum that was similar to the starting material, and an i.r. spectrum that showed the presence of trifluoromethyl groups, i.e. broad, strong bands between 1100 and 1250 cm^{-1}. The ^{19}Fn.m.r. spectrum was complex and suggested that several compounds were present and the ^{31}Pn.m.r. spectrum could not be found. Phosphepane 165 gave only thick, black polymers with tetrachloro-ortho-benzoquinone.

CHAPTER 3. Phosphoranes prepared by using Trifluoromethanesulphonic Anhydride.

There are many good preparations of phosphoranes starting from trivalent phosphorus compounds but there are no general syntheses starting from phosphorus oxides. In 1975, Hendrickson and Schwartzman[168] described the preparation of triphenylphosphine ditriflate (168) from triphenylphosphine oxide and trifluoromethanesulphonic anhydride, (triflic anhydride, 167). This was subsequently used to condense carboxylic acids with various nucleophiles, e.g. alcohols or amines.

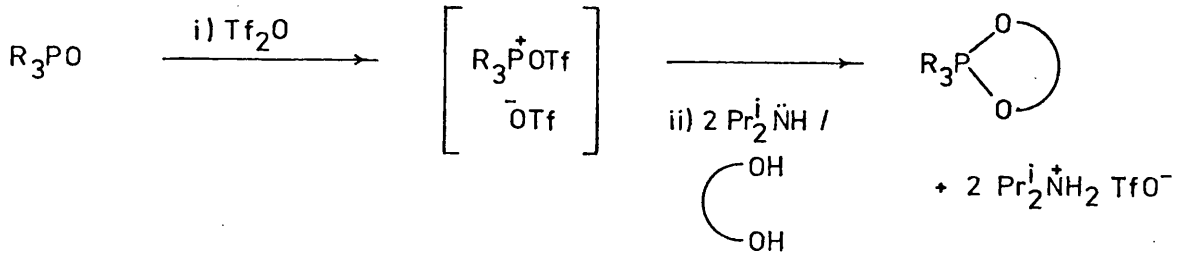


Tf = CF_3SO_2.

This reaction has now been applied to the synthesis of phosphoranes from acyclic phosphine oxides, phospholene oxides and phosphetan oxides. The triflic anhydride is added to a solution of the phosphorus oxide in dichloromethane at 0^oC, and allowed to stand at this temperature until there is no sign of the oxide in the ^{1}Hn.m.r. spectrum of the reaction mixture. This is approximately fifteen minutes for acyclic phosphine oxides and phospholene oxides, and three hours for phosphetan oxides. This solution is then

cooled to -78°C and a mixture of 1 equivalent of a diol and 2 equivalents of di-isopropylamine, in ether, is added. The mixture is allowed to warm up to room temperature and ether is added to precipitate the di-isopropylammonium triflate. Filtration, followed by evaporation of the solvent yields the crude phosphorane which can be extracted with, or crystallised from, light petroleum.

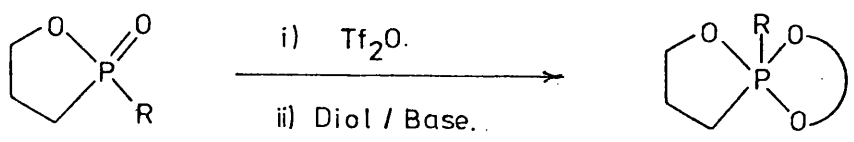
Overall the reaction is a condensation, where the elements of water are removed from a diol and a phosphine oxide by an anhydride, which is converted into two moles of the corresponding acid (scheme 39). The reaction has been used successfully to add catechols,



Scheme 39.

pinacol and perfluoropinacol to phosphine oxides but, so far, has not been applied to 1,3-diols.

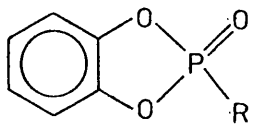
The reaction was developed with the intention that spirophosphoranes, containing a 1,2-oxaphospholan ring, could be prepared. Cyclic phosphonate and phosphinate esters such as 169 and 170 are known compounds but the corresponding trivalent compounds



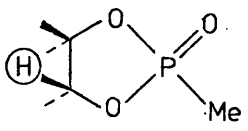
R = Ph, 169

R = OEt, 170

are either unknown or difficult to prepare. Unfortunately this reaction fails to work with these oxaphospholan oxides (169 and 170) and it also fails to work with other cyclic phosphonate esters, e.g. 171 and 172, the diol usually being recovered unchanged after

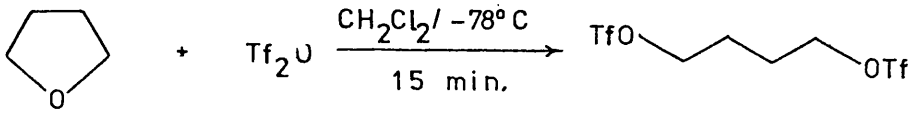


171 R = Ph, Me.



172

the reaction. This is hardly surprising because triflic anhydride is known to ring-open tetrahydrofuran, forming butane-1,4-ditriflate (173) under very mild conditions.[169] Similar ring-opening reactions

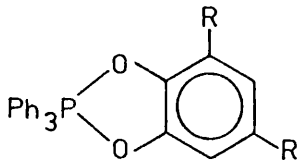


173

could possibly occur for cyclic phosphorus esters.

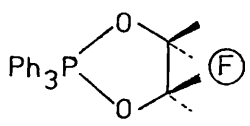
Phosphoranes prepared from Acyclic Phosphine Oxides.

Triphenylphosphine oxide was condensed with perfluoropinacol and 3,5-di-t-butylcatechol to give phosphoranes 117 and 116 respectively, but the thermally stable phosphorane 115 could not be prepared by this method.



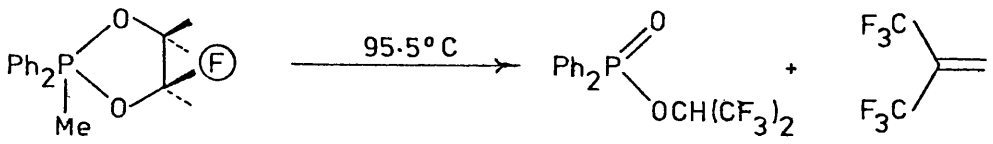
115 R = H, —

116 R = Bu^t, 92 %



117 71 %

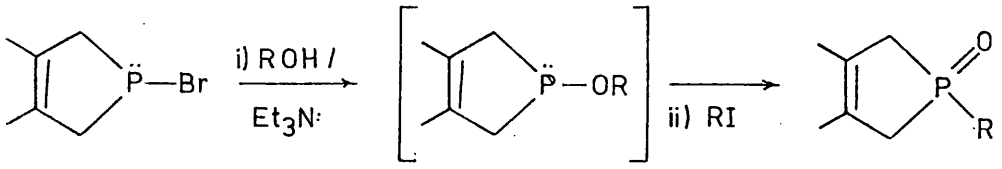
Methyldiphenylphosphine oxide formed an unstable phosphorane with 3,5-di-t-butylcatechol, that could only be detected by its ^{1}H and ^{31}P n.m.r. spectra. With perfluoropinacol a stable, crystalline phosphorane (174) was formed, which decomposed to 1,1-bistrifluoromethyl-ethylene (175) and hexafluoroisopropyl diphenylphosphinate (176) at its melting point, in a similar way to the reactions described by Ramirez,[59,60] (see chapter 1, section 2).



174 176 175

Phosphoranes prepared from Phospholene Oxides.

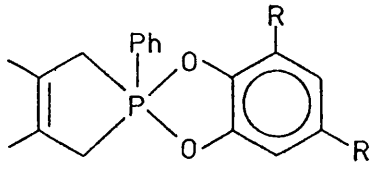
Phospholene oxides were conveniently prepared from bromophospholene 148 by treating it with an alcohol in the presence of triethylamine, to prepare alkoxyphospholenes (177) which, without isolation, were refluxed with iodoalkanes to carry out Arbuzov rearrangements to phospholene oxides. Methyl- and ethyl-phospholene oxides were prepared in this way.



148 177 178 R = Me

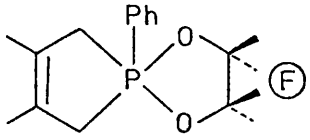
179 R = Et

Phenylphospholene oxide 143 was condensed with catechol and perfluoropinacol to give phosphoranes 151 and 153 respectively. The 3-methylcatechol adduct (152) could not be prepared by this method



151 R = H, 80 %

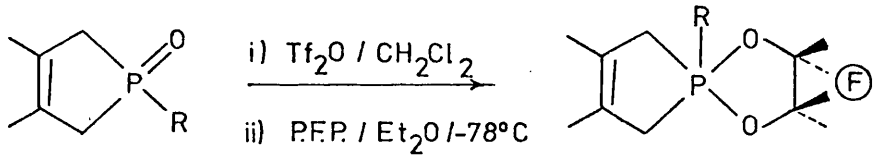
152 R = Me, ——



153 85 %

and the N-chlorodi-isopropylamine method also failed to prepare this compound, which could suggest that it is inherently unstable, although no reason can be found for this since other stable phosphoranes have been prepared from 3-methylcatechol.[42,109]

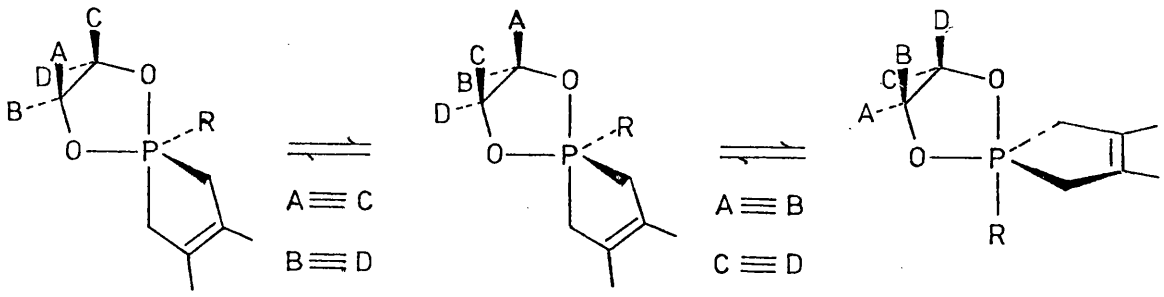
Catechol failed to condense with methylphospholene oxide 178 but perfluoropinacol condensed with both methyl- and ethyl-phospholene oxides (178 and 179) to give stable phosphoranes 180 and 181 respectively.



180 R = Me, 69 %

181 R = Et, 66%

The pseudorotation pathways that are available to phosphorane 182 are outlined in scheme 40. B.P.R. 182 to 182a is a topomeric pseudorotation and will therefore be a low energy process. This makes groups A and C equivalent and groups B and D equivalent. The higher energy B.P.R. 182 to 182b makes groups A and B equivalent and groups C and D equivalent. When both of these B.P.Rs. are fast



182a 182 182b

Scheme 40.

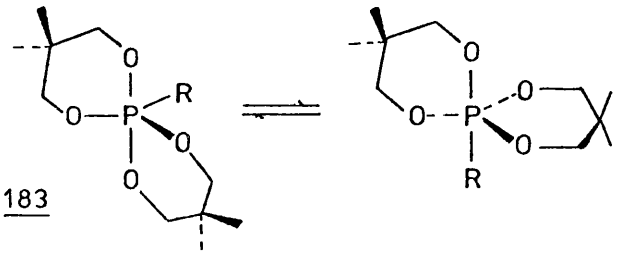
on the n.m.r. time scale the n.m.r. signal for groups A-D will be a singlet because they all become equivalent. Cooling the system will make B.P.R. 182 to 182b slow on the n.m.r. time scale causing the singlet to split into a doublet, allowing the activation energy for the process to be measured. If this activation energy is found for a series of phosphoranes with different R groups, the approximate difference in apicophilicity between the R groups, can be found for this system.

White[53] found this activation energy, for phosphorane 146, (182, R=Ph, A-D=Me) to be approximately 9.6 k.cal.mol.$^{-1}$. The corresponding perfluoropinacol phosphorane 153, (182 R=Ph, A-D=CF_3) showed a reversible coalescence at -78 ± 2^{o}C in dichloromethane, corresponding to an activation energy of 9.0 ± 0.1 k.cal.mol.$^{-1}$, which is in reasonably good agreement with White's value.

Phosphorane 180 (182, R=Me, A-D=CF_3) showed a reversible coalescence at -125 ± 1^{o}C in ether/petrol, corresponding to an activation energy of 7.3k.cal.mol.$^{-1}$. This means that the methyl group is more apicophilic than the phenyl group, by 1.7k.cal.mol.$^{-1}$, in this system.

Phosphorane 181(182, R=Et, A-D=CF_3), did not show any coalescence above -148°C in liquid propene/ether. This means that either there is an accidental equivalence of the CF_3 groups in the ^{19}Fn.m.r. spectrum or assuming $\Delta\upsilon$ is 100Hz, the activation energy is less than 5.8 k.cal.mol.$^{-1}$, i.e. the ethyl group is at least 1.5 k.cal.mol.$^{-1}$ more apicophilic than the methyl group, or at least 3.2 k.cal.mol.$^{-1}$ more apicophilic than the phenyl group in this system.

TABLE 2. Relative Activation Energies for Pseudorotations in Phosphoranes.



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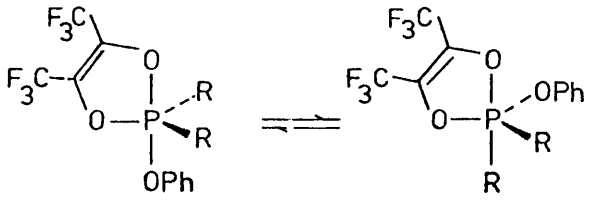
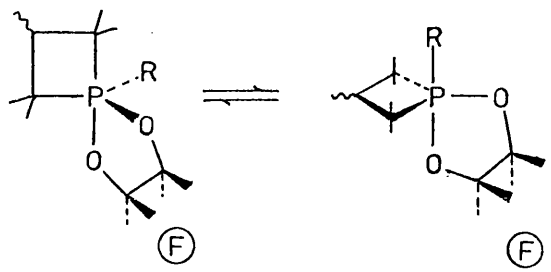


184

R	ΔG^* (k.cal.mol.$^{-1}$)	Ref.
Ph	13.2	48
Me	12.7	48
Bz	12.2	48
Pr^i	12.9	170
Ph	12.6	43

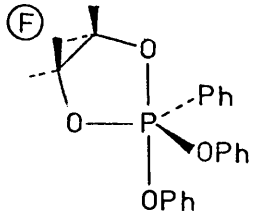


185

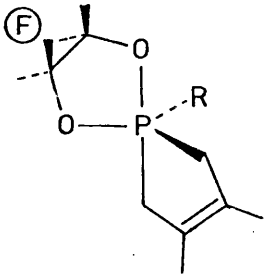
Me	16.9	58
Pr^i	17.8	58
Ph(cis)	19.6	58
Ph(trans)	>22	58

This latter explanation seem unlikely, however, because there is some evidence that the relative apicophilicities of phenyl and alkyl groups are fairly similar. Some of these results are summarised in Table 2 but there is little known about the relative apicophilicities of the ethyl group. The reason why the phenyl group has a lower apicophilicity in the phosphetan series (185) than in other phosphoranes, is unknown.

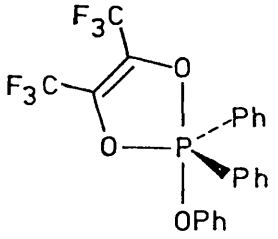
Phosphorane 163, (182, R=OPh, A-D=CF_3), poses an interesting problem. Whittle,[170] by studying the d.n.m.r. spectrum of the H.F.A. adduct 186, has shown that the phenoxy group is 7.9 k.cal.mol.$^{-1}$ more apicophilic than the phenyl group in this system. Using this value, and comparing phosphoranes 153 and 163, it could



186



153 R = Ph.
163 R = OPh.



187

be predicted that the energy barrier to pseudorotation is 7.9 k.cal.mol.$^{-1}$ less for 163 (R=OPh) than for 153 (R=Ph). Since the activation energy for 153 is approximately 9.0 k.cal.mol.$^{-1}$ the predicted activation energy for 163 would be 1.1 k.cal.mol.$^{-1}$ which could not be measured by d.n.m.r. techniques.

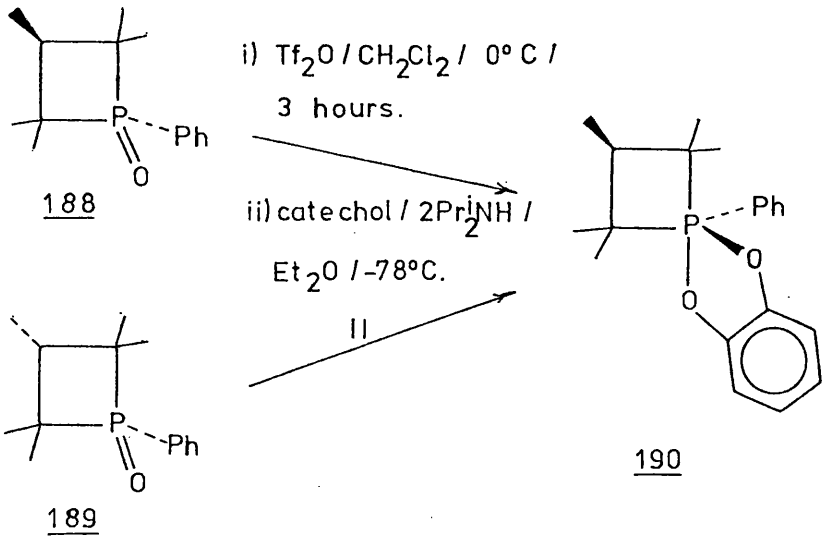
Dickstein and Trippett[43] have measured the difference in apicophilicity between phenyl and phenoxy in phosphorane 187, as 12.6 k.cal.mol.$^{-1}$. Using this value to predict the activation energy for 163 we get -3.6 k.cal.mol.$^{-1}$. This, of course, is a meaningless statement. It could mean that in phosphorane 163 the

phenoxy group prefers to be apical and the phospholene ring is forced to span a diequatorial position, which would probably result in a distortion of the geometry of this phosphorane, towards a square based pyramid. Holmes[171] has calculated that the presence of a highly electronegative ligand in a spirophosphorane, will distort the structure towards a square based pyramid, because this reduces the ring strain and improves the electronic balance in the phosphorane. X-ray structures were used to demonstrate the validity of this argument.

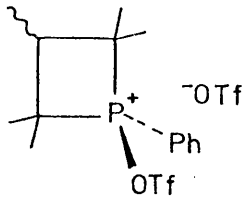
The ^{19}F.n.m.r. spectrum of phosphorane 163 was a sharp singlet between 20 and -145°C in ether or liquid propene/ether, showing that the activation barrier to pseudorotation is very low for this phosphorane.

Phosphoranes prepared from Phosphetan Oxides.

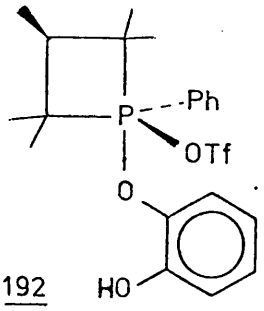
The preparation of phosphoranes from phosphetan oxides, by using triflic anhydride, revealed some interesting aspects of this reaction. Both the cis- and the trans-phenylphosphetan oxides, 188 and 189, gave the trans phosphorane 190, in good yields, with catechol.



This result suggests that there is a mechanism available to the ditriflate intermediate 191, by which it can interconvert the cis and trans isomers, or alternatively, an intermediate phosphorane, such as 192, rapidly pseudorotates to the trans isomer before the final spirophosphorane is formed.

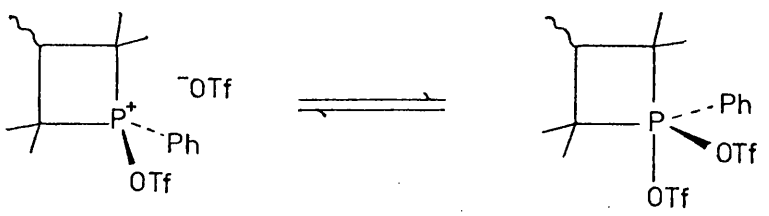


191



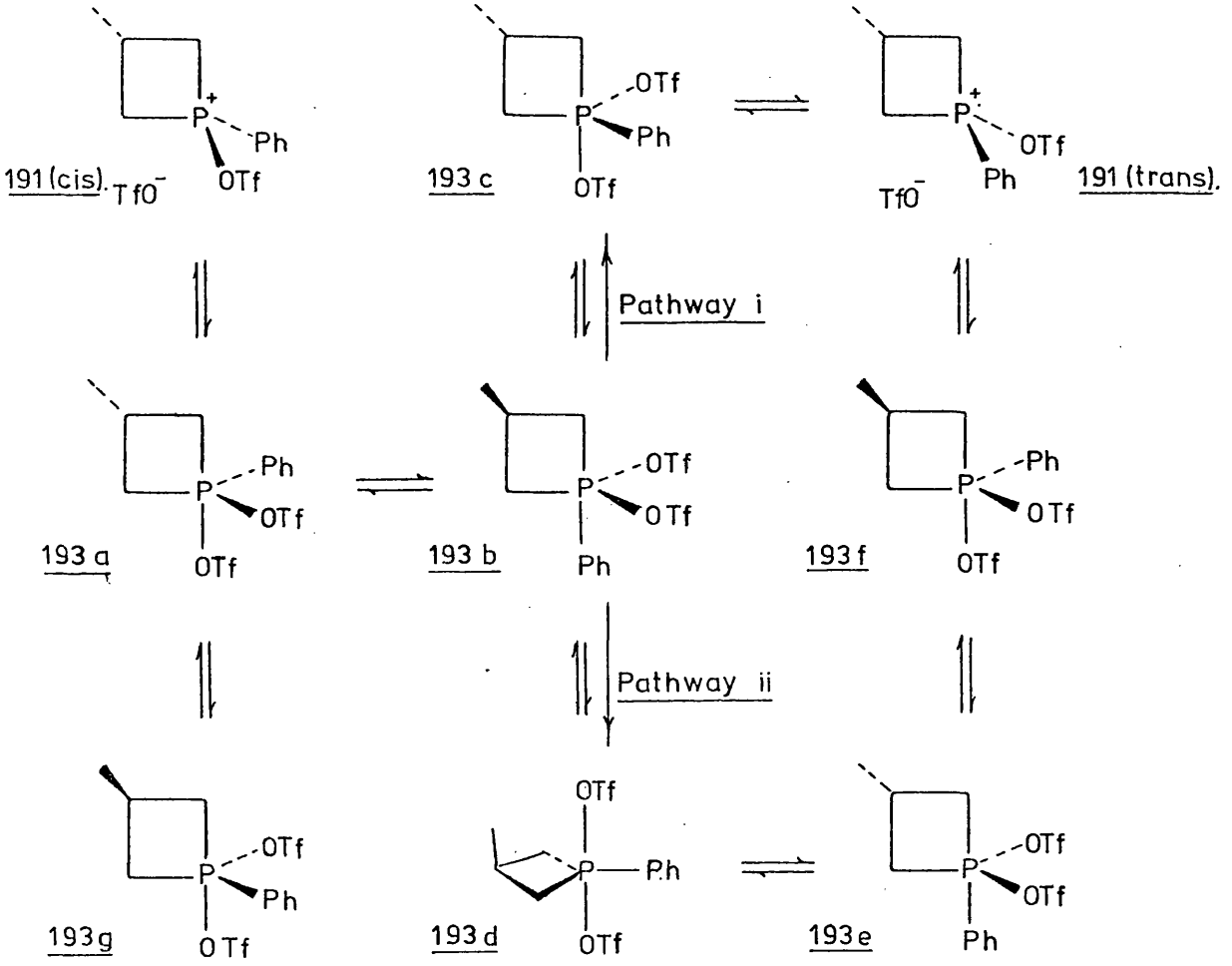
192

The ^{1}Hn.m.r. spectrum of the ditriflate intermediate (191) suggest that the isomerisation takes place at this stage of the reaction. After three hours in dichloromethane at 0°C, the n.m.r. spectrum of the intermediate ditriflate salts from the cis- and trans- phosphetan oxides, are identical, showing that the same intermediate is present in each case. The ^{31}Pn.m.r. chemical shift of the intermediate is solvent dependent, i.e. -110 p.p.m. in dichloromethane and -79 p.p.m. in $CDCl_3$ relative to 85% H_3PO_4. The ^{19}Fn.m.r. spectrum shows a sharp singlet between 20 and -97°C in dichloromethane. These last two observations suggest that there is a rapid exchange of the OTf groups, probably via a pentacoordinate intermediate (193), and that the n.m.r. spectra are averages of the two in solution.



191 193

If the pentacoordinate intermediate 193 has a sufficiently long lifetime, it could pseudorotate and isomerise the cis and trans isomers. The two possible pseudorotation pathways available to 193 are outlined in scheme 41. (The α-methyl groups have been omitted, in scheme 41, to simplify the diagrams).



Scheme 41.

In order to explain some experimental observations, Westheimer[7] proposed that when a nucleophile attacks a tetracoordinate phosphorus compound to form a phosphorane, the nucleophile initially occupies an apical position in the T.B.P.

Similarly, when an anion leaves from a phosphorane to form a tetracoordinate phosphorus compound, it does so from an apical position of the T.B.P. Boyd[172] has confirmed this apical attack or loss from T.B.P.s using M.O. calculations. Assuming this to be correct the triflate anion will attack the phosphonium cation 191 in either one of the two positions that will allow the phosphetan ring to span the apical-equatorial positions, in the intermediate phosphorane 193. Attack in either of the other two positions will produce a phosphorane with a diequatorial four-membered ring, which would probably be unfavourable.

Pathway i). The initially formed cis-phosphorane (193a) can undergo a rapid topomeric pseudorotation to its mirror image (193g), but this plays no part in the cis-trans isomerisation. Phosphorane 193a can pseudorotate to 193b which has the two triflate groups equatorial and the phenyl group apical. Nothing is known about the relative apicophilicity of the triflate group but it is probably fair to assume that it will be at least as apicophilic as an alkoxy or phenoxy group and possibly more so. Denney et al.[173] have shown that the pseudorotation 194a to 194b is fast on the n.m.r. time scale above -51°C, so it seems likely that the pseudorotation 193a to 193b will be fairly rapid at 0°C.

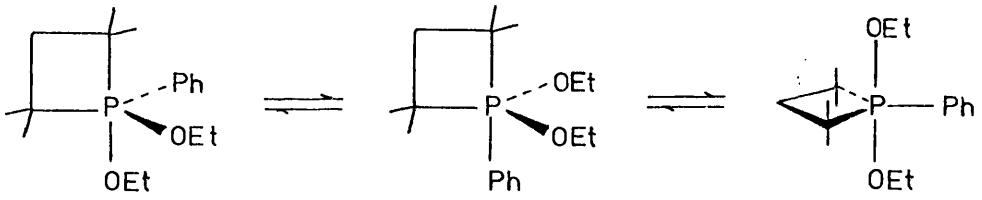
194 a 194 b

Phosphorane 193b can now pseudorotate to 193c which is effectively the trans isomer of 193a, i.e. a cis-trans isomerisation takes place in going from 193a to 193c via 193b. This trans isomer can

now lose an apical triflate group forming the same phosphonium intermediate as would be formed by the reaction of the trans-phenylphosphetan oxide with triflic anhydride.

Pathway ii). An alternative pseudorotation is available to phosphorane 193b. This involves a phosphorane with a diequatorial phosphetan ring (193d), which can, in turn, pseudorotate to 193f via 193e, resulting in a cis-trans isomerisation. Phosphorane 193f is the mirror image of phosphorane 193c. The intermediate with a diequatorial ring makes this a relatively high energy pathway but it is possible that it makes a contribution to the isomerisation process.

Denney[173] has observed a rapid pseudorotation for phosphorane 194 involving an intermediate with a diequatorial phosphetan ring (194c). The ethoxy-methylene protons in phosphoranes 194a



194 a 194 b 194 c

and 194b are diastereotopic, and below -20°C, the 100 MHz n.m.r. spectrum clearly shows these two protons. Above 30°C the two diastereotopic protons become equivalent which suggests that, unless an abnormal process is occurring, a pseudorotation involving phosphorane 194c is rapid on the n.m.r. time scale. There is a plane of symmetry through phosphorane 194c which makes the ethoxy-methylene protons equivalent. There is no similar symmetry in any other structure for phosphorane 194.

If triflate groups are more apicophilic than ethoxy groups, it would lower the energy barrier to similar pseudorotations, and make pathway ii available for the isomerisaton process. If the high apicophilicity of the triflate groups make the intermediate 193d, with the diequatorial phosphetan ring, a feasible intermediate, it could possibly be formed directly from 191 by the triflate anion attacking directly behind the triflate group already on the phosphonium cation. This pseudorotation pathway, however, will still be a higher energy pathway than pathway i, and so would play a smaller part in the isomerisation of the cis and the trans isomers.

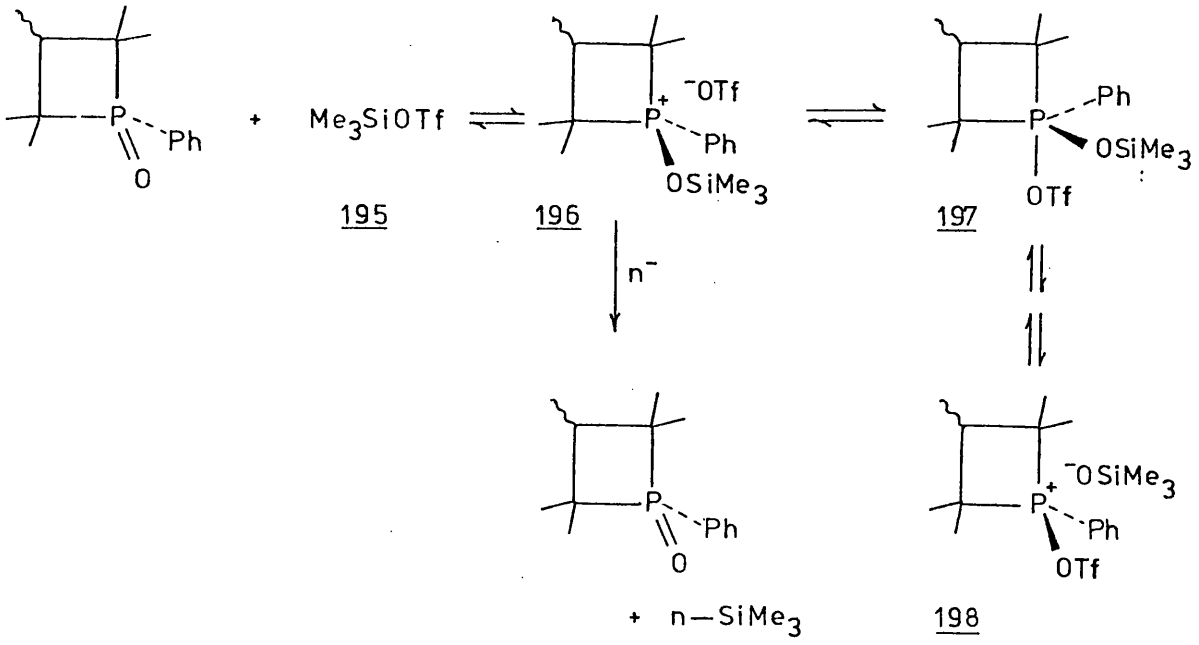
Whichever pathway is operating, the intermediates will be the same whether the cis- or the trans-phosphetan oxide is used, so the same product will be formed in each case. The trans isomer of 191 is probably more stable than the cis isomer because the steric interactions between the 3-methyl and the phenyl group is absent in the trans isomer of 191.

This cis-trans isomerisation proved to be useful. When a mixture of the cis- and the trans-phosphetan oxides were refluxed with 0.2 molar equivalents of triflic anhydride, in benzene for three hours, followed by aqueous work-up, the product contained mainly trans-phosphetan oxide. The preparation of phosphetan oxides always gives a mixture of the cis and the trans isomers which have to be separated by chromatography. If the trans isomer is required the isomerisation reaction makes the chromatographic separation unnecessary.

A similar phosphorane synthesis was attempted using trimethylsilyl trifluoromethanesulphonate (195) and both cis- and trans-pentamethyl-phenylphosphetan oxides. If pentacoordinate species are formed in this reaction similar pseudorotation pathways to those outlined in scheme 41 will be available and allow cis-trans isomerisation to occur.

It was hoped, however, that phosphorane formation would not occur and diols would add on to the intermediate forming phosphoranes with retention of stereochemistry.

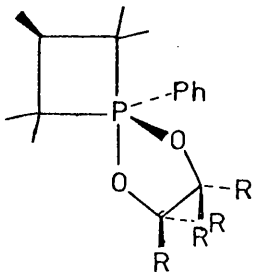
The ^{1}Hn.m.r. spectra of the intermediates were different in each case, the main difference being in the position of the 3-hydrogen on the phosphetan ring. The ^{31}Pn.m.r. chemical shift of the trans intermediate was -81 p.p.m. whereas the starting trans oxide was -53 p.p.m., showing that a reaction had occurred. Treatment of the intermediate with equimolar amounts of catechol and di-isopropylamine at -78°C, resulted in the isolation of phosphetan oxides. The n.m.r. spectra showed that the phosphetan oxides were reformed with only a small amount of isomerisation, showing that very little pseudorotation was occurring in the intermediate, i.e. the intermediate contained mainly tetracoordinate species.



The triflate anion is more stable than the trimethylsiloxy anion so the equilibrium 196 to 198 will favour 196. Any nucleophile can now attack either the phosphorus atom forming a

phosphorane, or it can attack the silicon atom in an Arbuzov type reaction, reforming the phosphetan oxide. The retention of stereochemistry in this reaction suggests that only a small amount of a pentacoordinate intermediate (197) is present, which pseudorotates causing a small amount of isomerisation. Addition of catechol and di-isopropylamine causes a nucleophilic attack on the silicon atom reforming the phosphetan oxide. The other products of this reaction were not identified.

Trans-pentamethylphenylphosphetan oxide was condensed with pinacol and perfluoropinacol using triflic anhydride, forming phosphoranes 199 and 200 respectively. The pinacol derivative



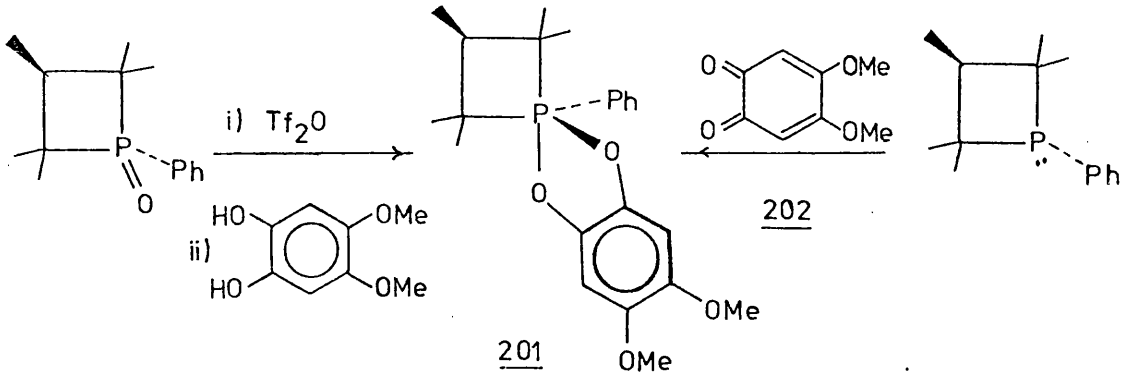
199 R = Me, 34%

200 R = CF_3, 36%

is thermally unstable and can only be stored at low temperature for a short time.

In contrast, the perfluoropinacol derivative is exceptionally stable. This product is known to be the trans isomer because these hexafluoroacetone (H.F.A.) adducts are known compounds,[58] and the structure of the 4′-bromophenyl-cis-adduct has been determined by X-ray crystallography.[134] On the basis that the ^{1}Hn.m.r. spectrum of the trans H.F.A. adduct was similar to the spectrum of the catechol derivative, trans geometry was assigned to this phosphorane. Further evidence for this was obtained by preparing phosphorane 201

by the two independent routes outlined in scheme 42.

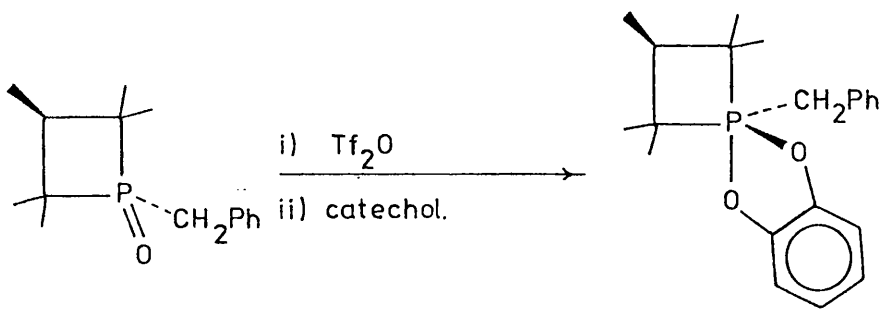


Scheme 42.

It was assumed that the trans phosphetan would retain its stereochemistry when it formed adduct 201 with quinone 202. This adduct was identical in every respect with the phosphorane formed in the triflate reaction so it was concluded that the triflate reaction produces phosphoranes with the trans geometry.

Brierley[42] further proved this geometry by showing that when N-chlorodi-isopropylamine (N.C.D.) was used to add perfluoropinacol to phosphetans, it did so with retention of stereochemistry. The catechol derivative that was prepared from the trans-phenylphosphetan by using N.C.D., was identical in every respect with the corresponding compound formed by the triflate reaction.

Trans-benzylpentamethylphosphetan oxide (203) condenses with catechol forming phosphorane 204 but no phosphorane is formed with



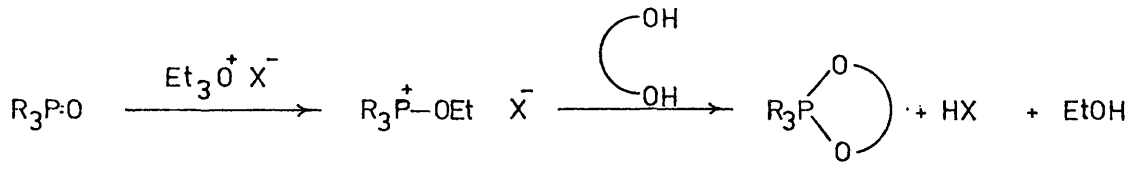
203 204 51%.

perfluoropinacol. So far three different reactions have failed to prepare the H.F.A. adduct. These are the N.C.D. reaction, the triflate reaction and the addition of H.F.A. to the benzylphosphetan.

The triflate method for preparing phosphoranes appears to be a good synthetic method for converting tertiary phosphine oxides into phosphoranes because it avoids the need to use trivalent phosphorus compounds with the attendent problems of oxidation. The reaction is, however, limited to phosphine oxides and fails to work for cyclic phosphonate or phosphinate esters.

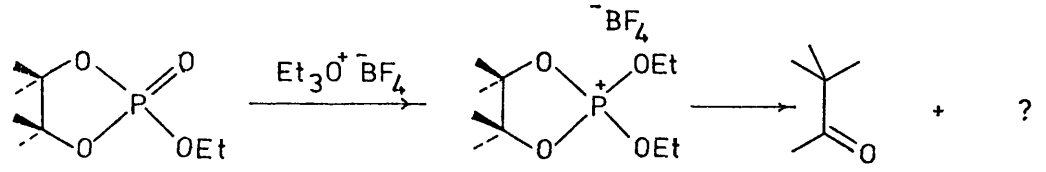
CHAPTER 4. Preparation of Phosphoranes from Phosphonium Compounds.

With the goal of phosphorane preparation from phosphorus oxides still in mind, the alkylation of phosphorus oxides and subsequent reactions with diols, was investigated. It was hoped that reactions of the type outlined in scheme 43 would be possible.

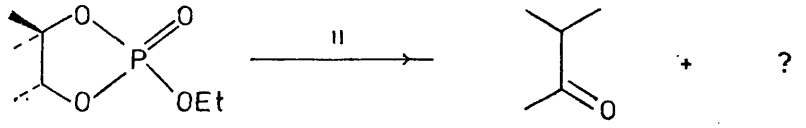


Scheme 43.

There are many examples of alkylations of acyclic phosphorus oxides in the literature[174,175] but there are very few examples of 1,3,2-dioxaphospholan-2-oxides or similar systems, being successfully alkylated. Finley et al.[175] reported the alkylation of cyclic phosphate ester 205 but similar reactions on 207 led only to



205 206

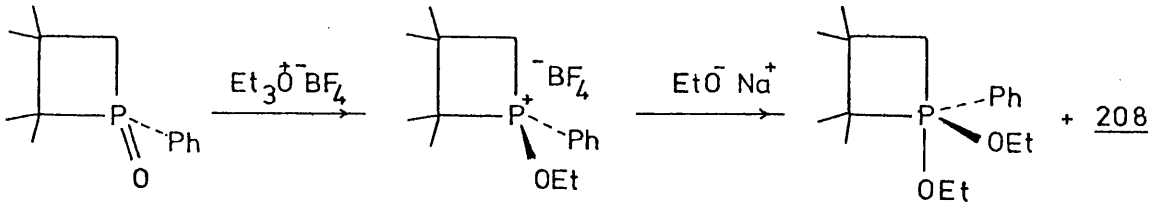


207

decomposition products. The phosphonium salt 206 decomposes slowly to pinacolone and other unidentifiable products. In contrast, the phosphonium salts prepared from acyclic phosphorus oxides and dioxaphosphorinan oxides are thermally stable but hydrolyse very easily, e.g. tetraethoxyphosphonium hexachloroantimonate is a crystalline solid m.p. 116-7°C.

Attempts to prepare pentaethoxyphosphorane from tetraethoxyphosphonium tetrafluoroborate result in Arbuzov reactions[174] (scheme 44). Denney[167] reports the preparation of

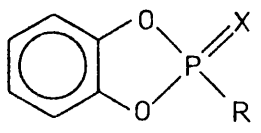
$$(EtO)_4P^+\,BF_4^- + EtOH \longrightarrow (EtO)_3P{=}O + Et_2O + HBF_4$$



208 209 210

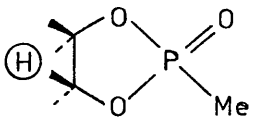
Scheme 44.

phosphorane 210 from phosphonium salt 209 but this was only seen as a ^{31}Pn.m.r. signal in an n.m.r. tube experiment, and the products also contained the starting phosphetan oxide 208. The considerable reduction in ring strain in going from phosphonium salt 209 to phosphorane 210 is, presumably, the driving force for this reaction. It was hoped that phosphonium salts similar to 206 could be prepared and that they would react with diols to form spirophosphoranes because there would be a similar reduction in ring strain if phosphorane formation occurs.



171 X = O, R = Me or Ph.

211 X = S, R = Me.



172

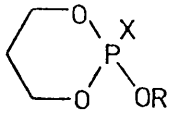
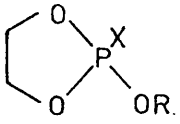
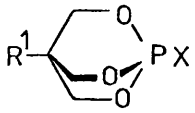
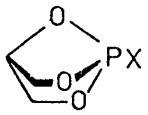
Attempts were made to alkylate phosphonate 171, 172 and 211 using triethyloxonium hexachloroantimonate but both the phosphonate and the oxonium salt were recovered unchanged after several days.

Verkade[176,177] has since explained this behaviour in terms of the basicity of the phosphorus–oxygen double bond (phosphoryl bond). This treatment also applied to the basicity of lone pairs of electrons on trivalent phosphorus atoms.

Verkade's arguments are very simple. Oxygen atoms on phosphorus will withdraw electron density from phosphorus, through the σ bond, because oxygen is more electronegative than phosphorus. The oxygen atoms will, however, be sp^2 hybridised and the oxygen p-electrons can back-donate into empty d-orbitals on phosphorus thus restoring the electronic balance in the system. The σ withdrawal of electrons will tend to increase the effective positive charge on phosphorus and strengthen the phosphoryl bond, i.e. make it less basic, and the pπ-dπ back-donation will have exactly the opposite effect, decreasing the effective positive charge on phosphorus thus weakening the phosphoryl bond, i.e. make it more basic. These two opposite effects must be balanced, one against the other, when predicting the basicity of a phosphoryl oxygen. Exactly the same arguments hold true for lone pairs on trivalent phosphorus atoms.

The next step in the argument considers the bond angles in cyclic phosphate esters. The angle at phosphorus is the same in each of the compounds in table 3 but the angle at oxygen becomes smaller as the constraints exerted by the rings or cages increase. As the angle at oxygen becomes smaller the oxygen atoms loose their sp^2 hybridised character. The sp^3 hybridised oxygens cannot back-donate their lone pairs of electrons, to phosphorus as well as the sp^2 hybridised oxygens so the effective positive charge on phosphorus increases, i.e. the basicity of the phosphoryl group decreases as the oxygen atoms become more sp^3 in character. This is reflected in the inability to alkylate the compounds at the bottom of table 3, and the shifting of the phosphoryl infra-red stretching frequencies to higher wavenumbers, down the table. This behaviour is predicted

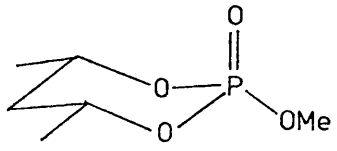
TABLE 3. Relative Basicities of Phosphoryl Bonds.

			$\nu_{max.P=O}$ cm^{-1}.	P-Ô-C Bond Angle
$(RO)_3PX$	P = O Easily Alkylated.	Increasing Basicity of P = O or P:	1260-1290	120°
			1280-1312	120°
			1302	115°
	P = O Cannot Be Alkylated.	Decreasing π Bond Order for P = O.	1327	
			1346-1354	101°

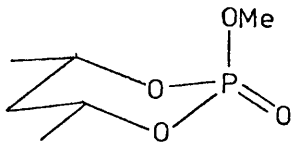
X = Lone Pair or =O

by Extended Hückel M.O. calculations and C.N.D.O./2 calculations.

Work on the cis and trans isomers of dioxaphosphorinan oxides 212 and 213, indicates that the relative orientation of the ring oxygen lone pairs to the phosphoryl group is also an important factor in determining the relative basicities of phosphate esters, since 212 is more basic than 213.[177]



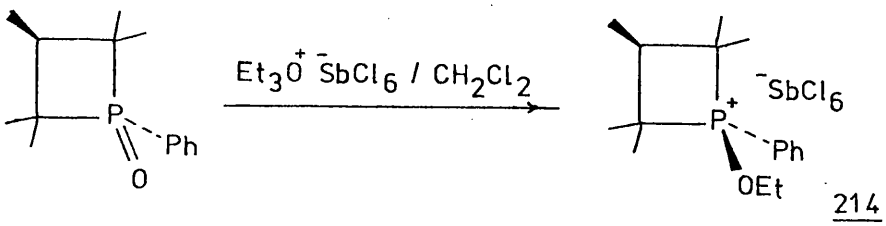
212



213

It must be concluded from this work and from experimental observations, that the preparation of phosphoranes from dioxaphospholan oxides, via tetracoordinate intermediates, is a futile task because the intermediates cannot be easily prepared. Phosphetanium salts derived from phosphetan oxides are known compounds,[178,179] however, and the reactions of these with diols were investigated.

Phosphetanium salt 214 was prepared and treated with diols in the presence of tertiary amines, but under all conditions investigated, the product was the starting phosphetan oxide. The

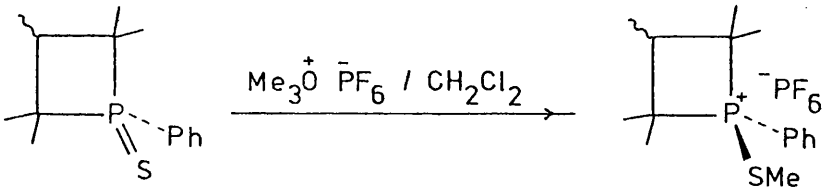


214

diols used were catechol and perfluoropinacol, and the bases were triethylamine, isopropylcyclohexylamine and the non-nucleophilic base D.B.U. (1,5-diazabicyclo[4,5,0]undec-5-ene). These results suggest that Arbuzov type reactions at carbon are more favourable than attack at phosphorus, even though phosphorane formation is favoured because of the relief in ring strain.

Attempts were made to overcome the problem of Arbuzov reactions by using phosphetan sulphides rather than phosphetan oxides since alkylthiophosphonium compounds do not undergo Arbuzov reactions as readily as alkoxyphosphonium compounds. Phosphonium

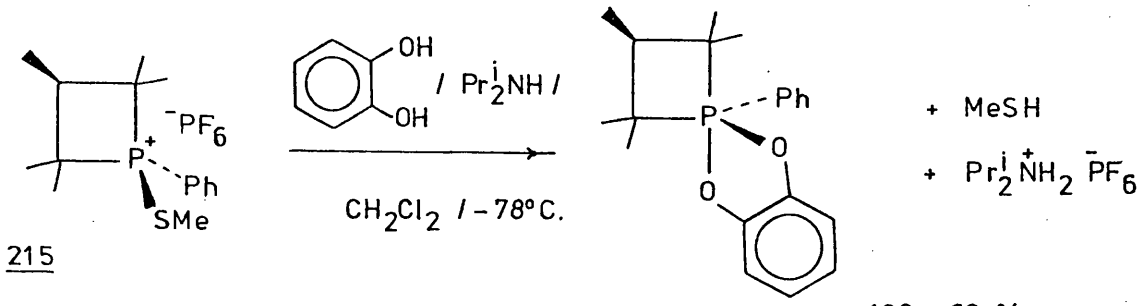
salts 215 and 216 were prepared from the corresponding phosphetan sulphides, and the reactions of these with diols were investigated.



215 trans-3-Me

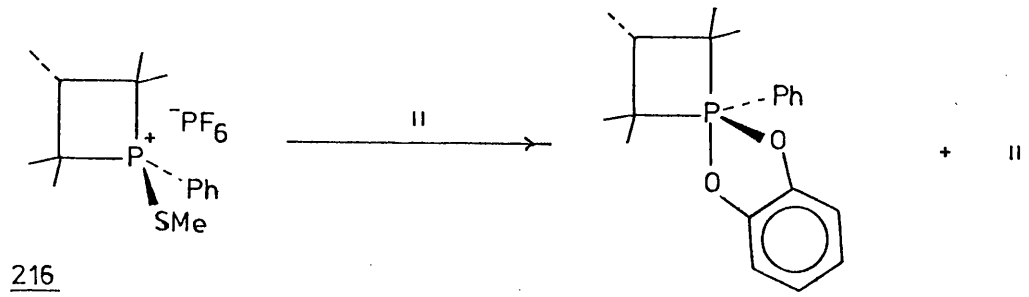
216 cis-3-Me

With catechol in the presence one molar equivalent of di-isopropylamine, both 215 and 216 gave phosphoranes with complete



215

190 60 %



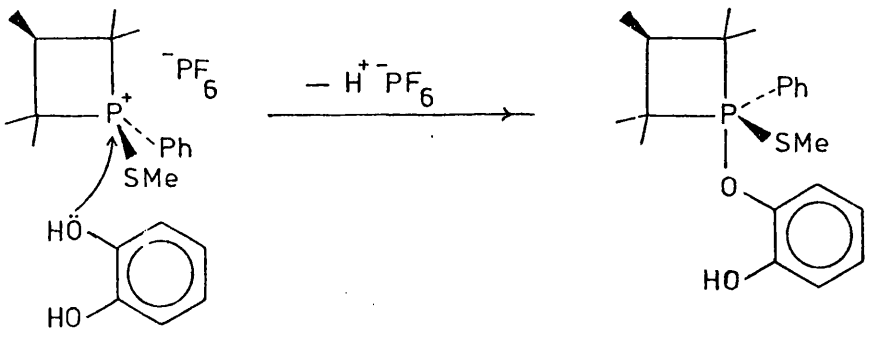
216

217 73 %

retention of stereochemistry in good yields. When this reaction was carried out in n.m.r. tubes, the trans-phosphetanium salt (215) gave only the trans-phosphorane (190, ^{31}Pn.m.r. + 0.4 p.p.m.) and the cis-phosphetanium salt (216) gave only the cis-phosphorane (217, ^{31}Pn.m.r. - 6.25 p.p.m.). The only other products which could be seen in the Fourier-Transform ^{31}Pn.m.r. spectra, were small amounts of phosphetan oxides which were probably formed by a small amount of hydrolysis of the phosphetanium salts.

No reaction occurred between phosphetanium salts 215 and 216, and perfluoropinacol, and after twentyfour hours at room temperature, the starting materials were recovered unchanged. The monosodium salt of perfluoropincaol also failed to react with the phosphetanium salts even after ten days. No reason can be given for this behaviour since the phosphoranes that would have been formed are known compounds and are very stable.[58]

There are several possible mechanisms for the reaction of catechol with phosphetanium salts 215 and 216 but the first step in any mechanism will most probably be nucleophilic attack by one of the catechol hydroxyl groups on phosphorus forming a pentacoordinate intermediate (218). The incoming catechol must initially occupy an apical position in the intermediate phosphorane, and it must attack in a direction that avoids placing the phosphetan ring



218

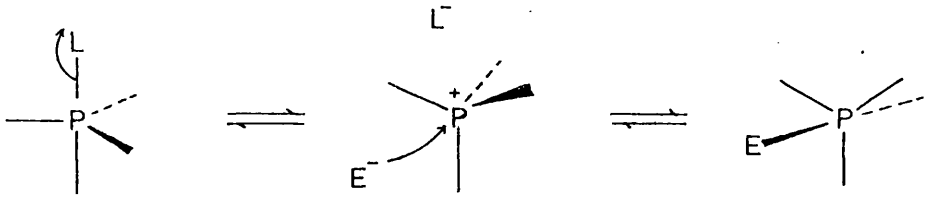
diequatorial in this phosphorane.

The next step is a nucleophilic substitution at pentacoordinate phosphorus where the methylthio group is replaced by the second catechol hydroxyl group. Before this reaction is considered further some aspects of substitution reactions at pentacoordinate phosphorus will be considered.

Substitutions at Pentacoordinate Phosphorus.

Surprisingly little is known about substitution reactions at pentacoordinate phosphorus but the two most likely mechanisms involve either a tetracoordinate intermediate or a hexacoordinate intermediate.

i) Substitutions involving Tetracoordinate Intermediates.



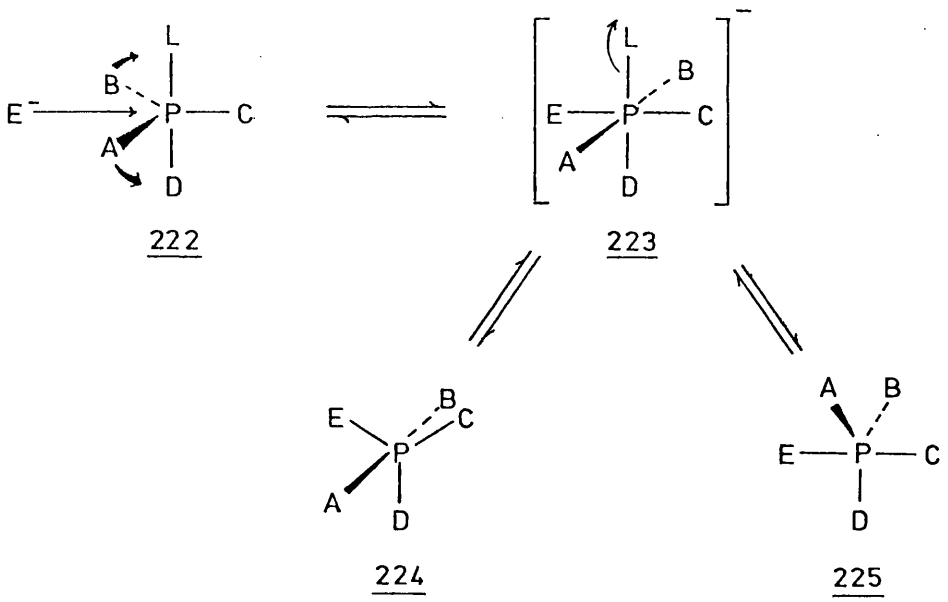
219 220 221

If the leaving group L, leaves phosphorane 219 before the entering group E, attacks phosphorus, a tetracoordinate intermediate (220) is formed. In this mechanism L must leave from an apical position and E must occupy an apical position in the product (221). There are four possible positions for E to attack on intermediate 220. These are the centres of the four faces of the tetrahedron, i.e. attack will occur directly behind one of the ligands on the intermediate thus making this ligand and E, the two new apical ligands in 221. If a small ring is present in the intermediate, i.e. 219 is a cyclic phosphorane, the number of possible positions for E to attack is reduced to the two that will not form a phosphorane with a diequatorial ring.

The presence of small rings will disfavour this mechanism because there will be a large increase in ring strain in going from phosphorane 219 to phosphonium intermediate 220. This mechanism will be favoured by the absence of rings and the presence of very good leaving groups.

ii) Substitutions involving Hexacoordinate Intermediates.

If the entering group E, attacks phosphorus before the leaving group L, leaves, a hexacoordinate phosphorus anion (223) will be formed as an intermediate. Attack of E will probably occur in

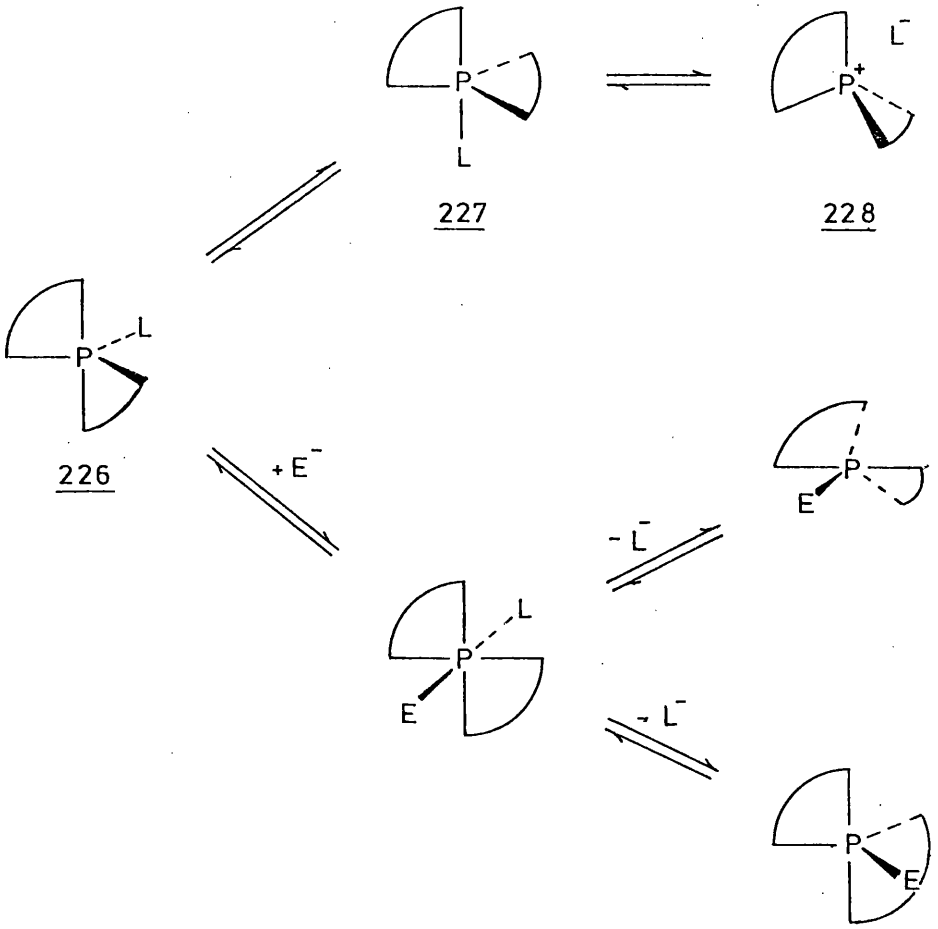


222 223 224 225

the equatorial plane between two ligands, i.e. in the centre of an equatorial edge of the trigonal bipyramid. This is because there is not a great deal of steric hindrance to attack at this position. and only a small amount of ligand reorganisation is required to form the hexacoordinate intermediate, i.e. in phosphorane 222, ligands A and B each have to move 30^{o} back in the equatorial plane.

The hexacoordinate intermediate can now lose any one of the six ligands to form a new phosphorane. If ligand L leaves from 223, two possible phosphoranes can be formed. Either ligands A and B or ligands C and E can occupy the apical positions in the products (224 or 225). Factors such as apicophilicity or ring strain will be important in determining the geometry of the product, e.g. if A and D form part of a small ring, the product will be 224, where the ring spans an apical-equatorial position rather than the diequatorial position in 225.

Spirophosphoranes containing a leaving group are most likely to undergo substitutions via hexacoordinate intermediates for two reasons. Firstly the leaving group, L, will most likely be in an



Scheme 45.

equatorial position so the phosphorane would have to pseudorotate to place L apical before it could leave as an anion. This pseudorotation involves a high energy intermediate with a diequatorial ring (227). Secondly, the tetracoordinate intermediate (228) thus formed will be highly strained because of the two rings, and will therefore be an unfavourable intermediate.

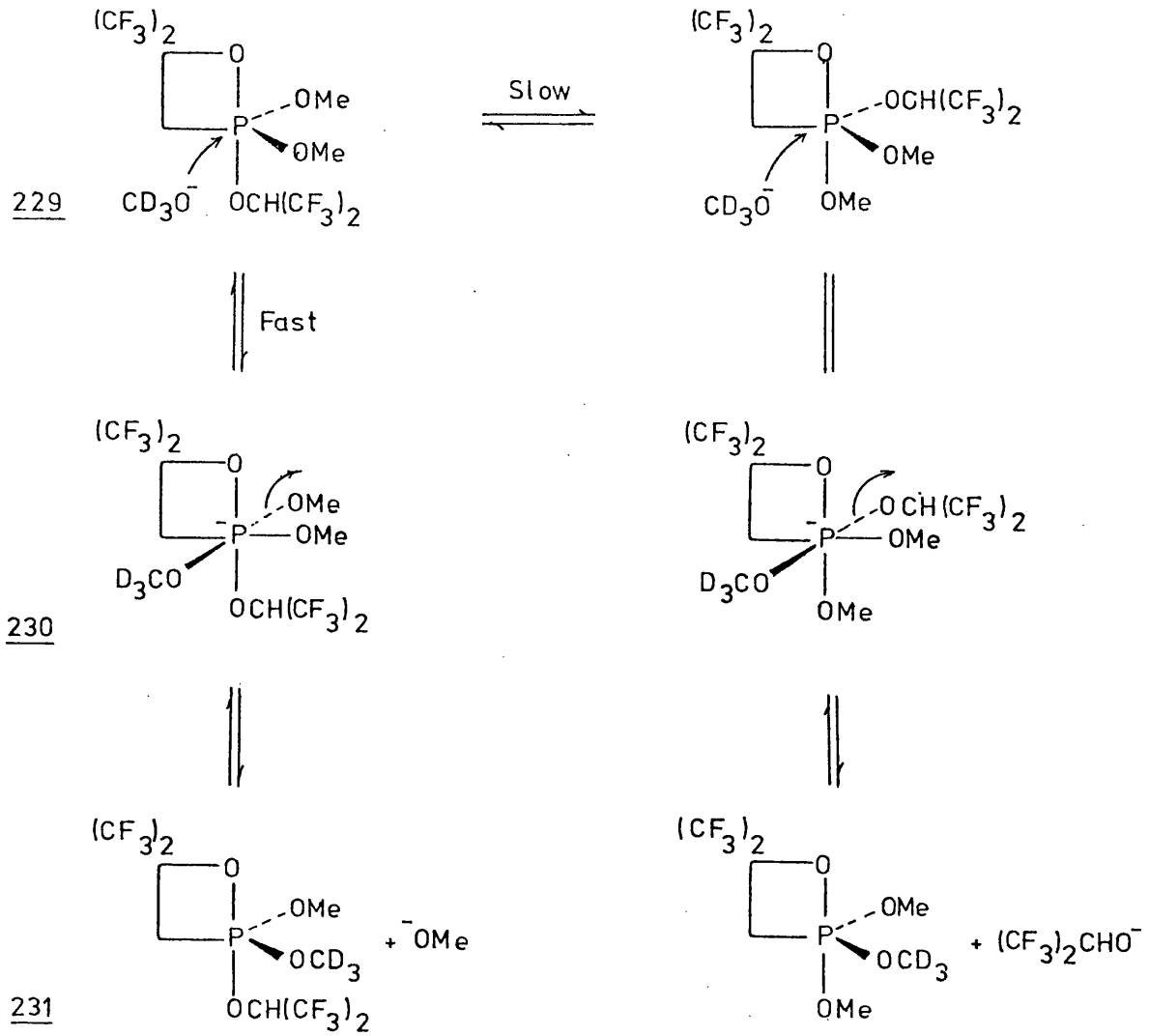
This suggests that for spirophosphoranes, nucleophilic substitution occurs in the equatorial plane where the nucleophile can attack any one of three equatorial edges forming any one of three possible hexacoordinate intermediates. If this attack occurs directly behind the leaving group, as shown in scheme 45, there will be an inversion of configuration at phosphorus, and the reaction will be analogous to an S_N2 substitution at carbon.

It must be stressed that there is very little evidence for these mechanisms and other mechanisms must not be ruled out. Some experiments which have been carried out, in order to find out more about nucleophilic substitutions at pentacoordinate phosphorus, are described below.

Westheimer[180] has studied the kinetics for the hydrolysis of a series of penta-aryloxyphosphoranes by stop-flow techniques, and has concluded that the hydrolysis involves a hexacoordinate intermediate. This result is consistent with the large number of stable hexacoordinate phosphorus anions which have now been prepared.

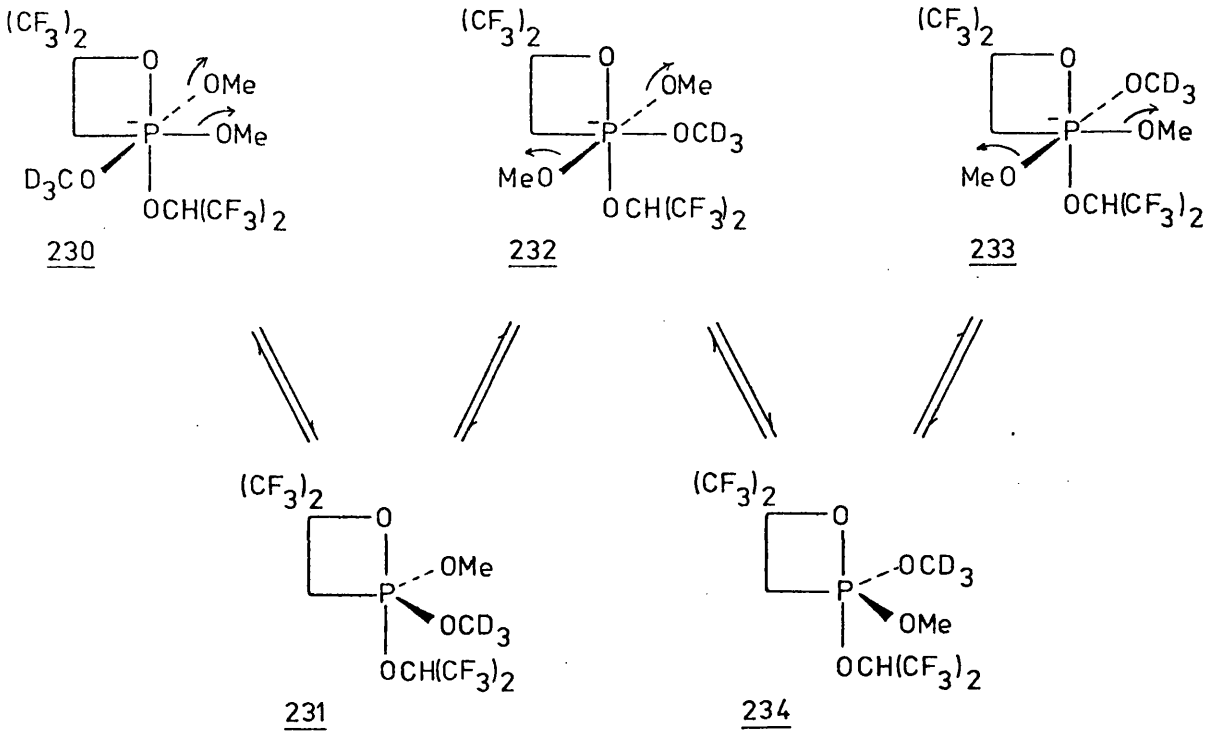
Ramirez[60] has shown that the treatment of oxaphosphetan 229, with one molar equivalent of CD_3OD in the presence of a tertiary amine, results in the initial displacement of a methoxyl group in preference to a hexafluoroisopropoxyl group, in spite of the greater anionic stability of the latter. Ramirez interprets this as an S_N2 type substitution where nucleophilic attack occurs directly behind the leaving group as shown in scheme 46.

Other conclusions can be drawn from this experiment, however, e.g. either of the two methoxyl groups in 230, can leave giving exactly the same product (231), i.e. the nucleophilic attack does not have to occur directly behind the leaving group.

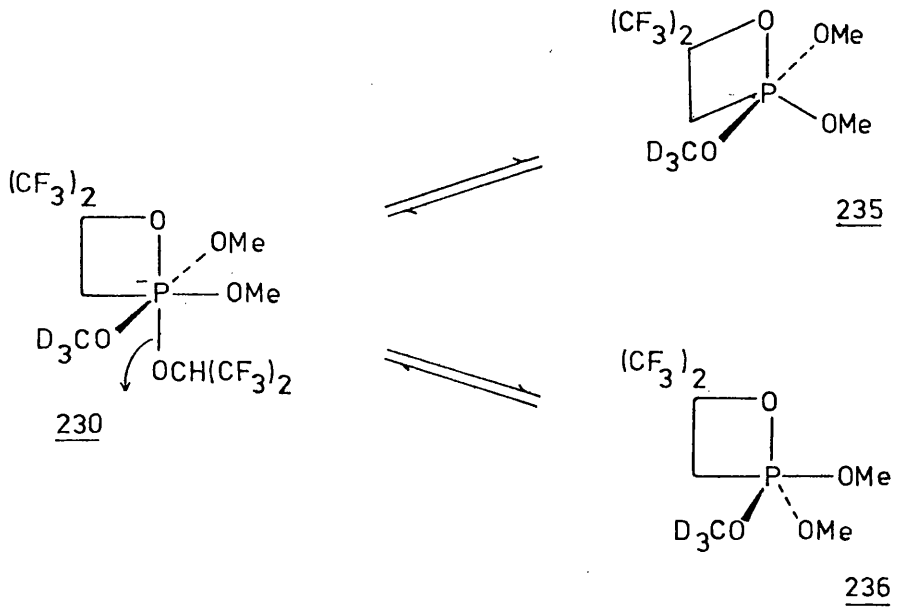


Scheme 46.

Assuming that the hexafluoroisopropoxyl group is more apicophilic than the methoxyl group, phosphorane 229 will be the most predominant isomer. Attack by the CD_3O^- anion can occur in the centre of any one of the three equatorial edges, forming three possible hexacoordinate intermediates (230, 232 or 233). Loss of methoxyl groups from any of these results in the formation of the initially observed product 231, or its mirror image 234.



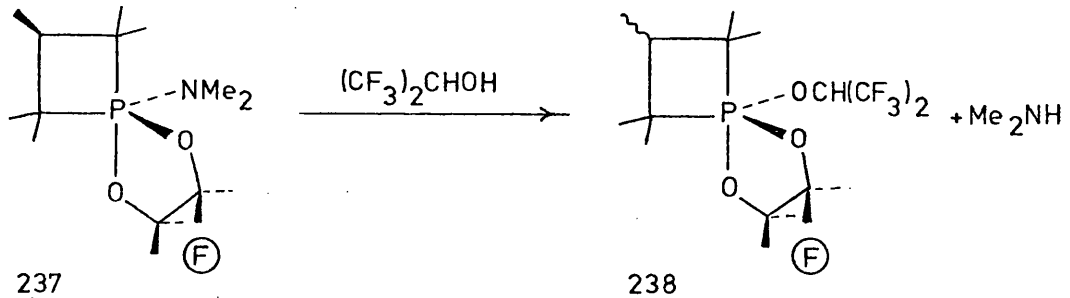
Loss of any of the alkoxy groups in the hexacoordinate intermediate is possible but it is unlikely that the hexafluoroisopropoxyl group will be lost because this will result in the formation of a phosphorane with either a diequatorial oxaphosphetan ring (235) or a



phosphorane with the oxaphosphetan ring-oxygen in an equatorial position (236). Both of these two phosphoranes are high energy species and will therefore probably not be formed in preference to low energy phosphoranes such as 231.

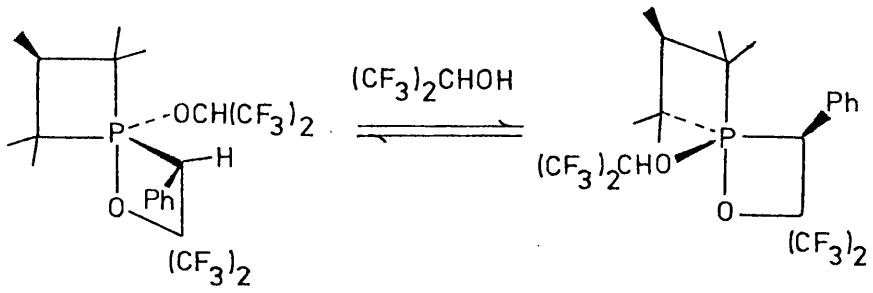
The only conclusion that can be drawn from this experiment is that if nucleophilic attack occurs in the equatorial plane, the leaving group leaves from the equatorial plane in this type of phosphorane. No firm conclusions can be made about the direction of nucleophilic attack relative to the leaving group.

Oram and Trippett[58] have shown that hexafluoroisopropanol will displace a dimethylamino group from the trans-phosphetan adduct 237, to give one pure isomer of phosphorane 238, but the geometry of the product is unknown.



237 238

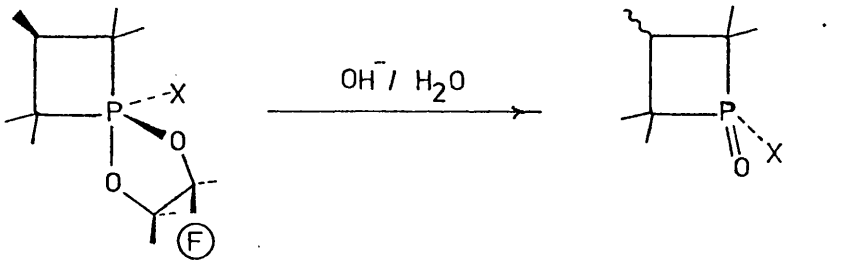
They also found that adduct 239 slowly equilibrates with adduct 240 in the presence of hexafluoroisopropanol. This is an example



239 1 : 10 240

of substitution with inversion of configuration and can only occur if nucleophilic attack occurs directly behind the leaving group.

Whittle[170] has shown that the hydrolysis of the trans-phosphetan adducts 241 and 242 occurs with complete retention of configuration for 241 (X = isopropyl), and with complete inversion of configuration for 242 (X = dimethylamino). This means that the hydrolysis of 242



241 X = Pr^i. X = Pr^i, trans-3-Me.

242 X = NMe_2. X = NMe_2, cis-3-Me.

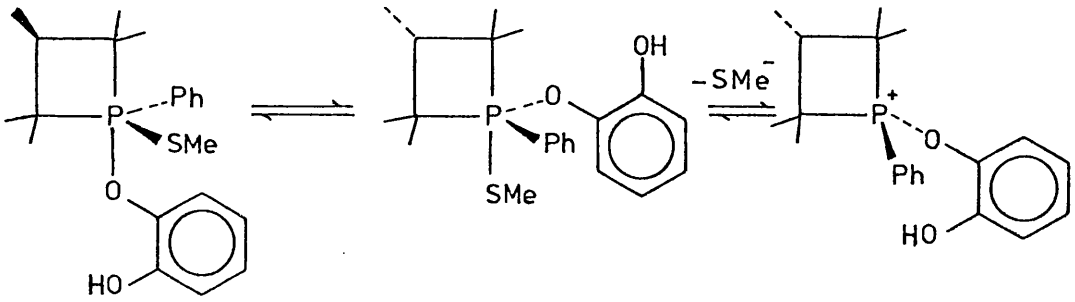
(X = NMe_2) must occur by nucleophilic attack of the hydroxide ion, directly behind the dimethylamino group. Whittle suggests that the π back-donation of electrons from the nitrogen atom to phosphorus may, in some way, inhibit nucleophilic attack on the two equatorial edges adjacent to the dimethylamino group. The opposite must be true for 241 (X = Pr^i), i.e. nucleophilic attack must only occur at the two equatorial edges adjacent to the isopropyl group. An alternative mechanism, which results in retention of configuration, is via a tetracoordinate intermediate, which will be discussed later.

So far, all of the evidence indicates that the precise mechanism of nucleophilic substitution at pentacoordinate phosphorus depends on the particular system that is being studied, but hexacoordinate intermediates, rather than tetracoordinate intermediates, are usually involved. Sometimes substitution occurs in a colinear fashion with inversion of configuration at phosphorus, and sometimes the configuration

is retained.

Referring back to the reaction of the methylthiophosphetanium hexafluorophosphates 215 and 216 with catechol, the intermediate phosphorane 218 can undergo substitution of the methylthio group in several different ways. Only the trans isomer will be considered in detail but similar considerations will apply to the cis isomer.

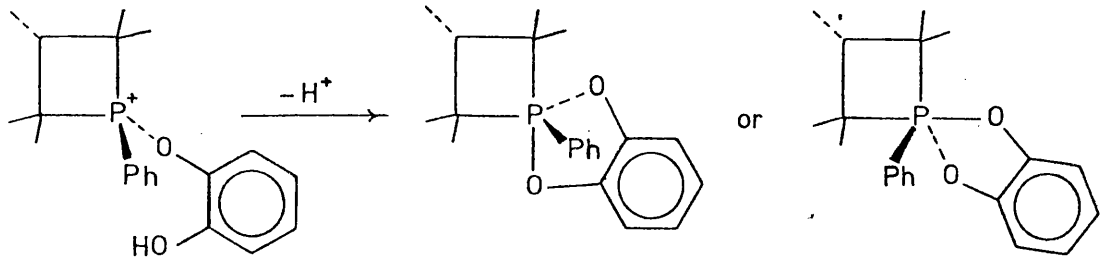
If the methylthio group is replaced by the second catechol hydroxyl group via a tetracoordinate intermediate, phosphorane 218 must pseudorotate to phosphorane 243, placing the methylthio group in an apical position before it can leave. This pseudorotation



218 243 244

will be a low energy process because the relative apicophilicities of alkylthio groups and aryloxy groups are not very different, and no high energy intermediates are involved in this B.P.R. No cis-trans isomerisation can occur in this low energy B.P.R.

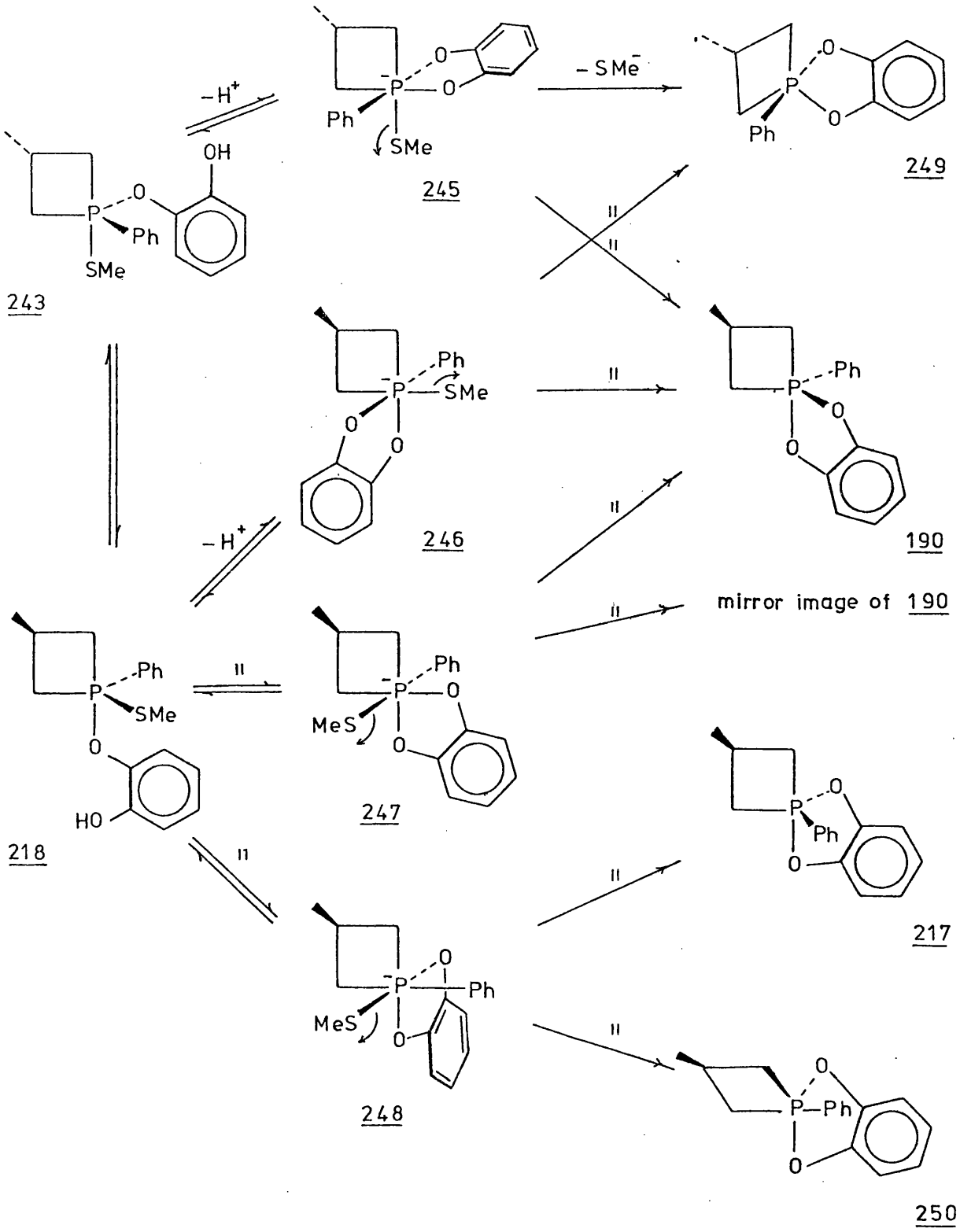
Phosphonium intermediate 244 can now ring-close, with loss of a proton, to form a phosphorane. Once again only two positions are available for apical attack by the second hydroxyl group, to avoid diequatorial phosphetan rings. The two positions for attack result in the formation of two mirror images of phosphorane 190, but the trans configuration is retained.



244 190

The retention of configuration in this mechanism fits in well with the experimental observations, but one drawback is that the formation of phosphetanium salt 244 from phosphorane 243 is an unfavourable reaction because there is a large increase in ring strain in the tetracoordinate intermediate. This problem does not arise in a hexacoordinate mechanism but the observations cannot be explained fully in terms of a hexacoordinate mechanism. The possible hexacoordinate intermediates are shown in scheme 47. The α-methyl groups have been omitted to simplify the diagrams.

If we assume that nucleophilic attack will occur at the centre of an equatorial edge of the T.B.P., four possible hexacoordinate intermediates can be formed. Phosphorane 218, which has an apical catechol ligand, has three equatorial edges available for the second hydroxyl group to attack, giving three possible intermediates, 246, 247 and 248. Alternatively, phosphorane 218 can pseudorotate to phosphorane 243, which now has an apical methylthio group and an equatorial catechol ligand. Inspection of molecular models suggests that only the two equatorial edges which are adjacent to the catechol ligand, are available for attack by the second hydroxyl group. Attack of either of these two edges gives the same hexacoordinate intermediate 245.


-H+
-SMe-
OH
Ph
SMe
245
249
243
246
190
mirror image of 190
MeS
247
218
217
248
250

Scheme 47.

Each of the four possible hexacoordinate intermediates (245-248) can now lose the methylthio group as an anion, each forming two possible phosphoranes. Two of these can be discounted immediately because 249 and 250 each have a diequatorial ring and will therefore be high energy species. In the unlikely event that they are formed, they will rapidly pseudorotate to a more stable (lower energy) phosphorane, but this will result in a cis-trans equilibration which is not observed.

Intermediates 245, 246 and 247 will all give rise to phosphorane 190, the observed product with retained stereochemistry, whereas intermediate 248, which is formed by nucleophilic attack directly behind the leaving group, will give phosphorane 217 where inversion of configuration has occurred. Since the reaction is known to proceed with retention of stereochemistry, the formation of intermediate 248 can be discounted.

If the reaction does proceed via a hexacoordinate intermediate there is no good reason why intermediates 245-247 can be formed whereas intermediate 248 cannot. Molecular models suggest that all four intermediates are equally likely to be formed. One speculative possibility is that the second catechol hydroxyl group forms an intramolecular hydrogen bond with the lone pairs of electrons on the methylthio group and is therefore directed into the positions adjacent to it and preventing attack behind it.

Another possibility is that phosphorane 243 is the preferred conformation in the equilibrium 218 to 243 and so hexacoordinate intermediate 245 is formed in preference to 246, 247 or 248, and therefore the product has retained its stereochemistry. This is unlikely, however, because the difference in relative apicophilicities between the catechol ligand and the methylthio group will be small and so the activation energy for this B.P.R. will be small, i.e. the B.P.R. will be rapid under the reaction conditions making

phosphorane 248 just as likely as phosphorane 243.

Pseudorotations of phosphorane 218, which interconvert cis and trans isomers are possible but these involve high energy intermediates with either apical phenyl groups or diequatorial phosphetan rings. These pseudorotations will therefore be unimportant under the reaction conditions ($-78^{o}C$), and the experimental results show that they are not taking place.

The conclusions that can be drawn from this experiment can be summarised as follows.

i) A mechanism involving a tetracoordinate intermediate is possible but this involves a high energy phosphetanium intermediate.

ii) If a hexacoordinate intermediate is involved, the entering group does not attack directly behind the leaving group in an S_N2 type reaction.

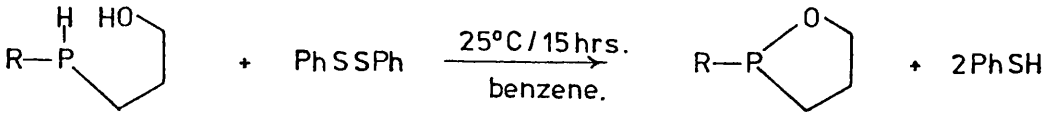
iii) Pseudorotations that can invert the configurations at phosphorus are possible, but they do not occur under the reaction conditions.

The mechanisms do not explain why perfluoropinacol does not form phosphoranes in this reaction. The only possible explanation is that the trifluoromethyl groups offer too much steric hindrance in a hexacoordinate intermediate and is therefore not formed.

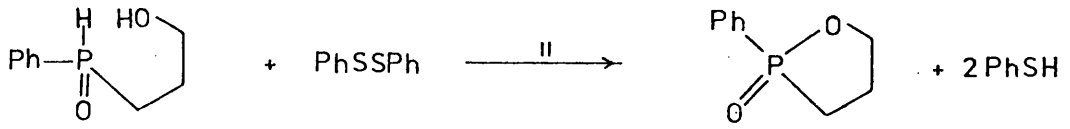
This series of experiments shows that diols prefer to attack carbon atoms of alkoxyphosphetanium salt in an Arbuzov type reaction, but they prefer to attack phosphorus in alkylthiophosphetanium salts, forming phosphoranes.

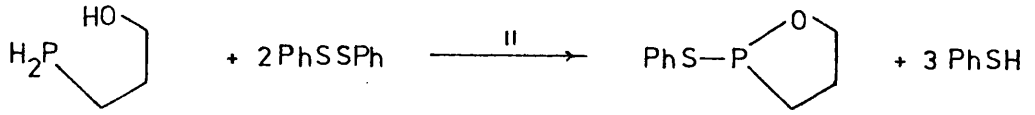
CHAPTER 5. Synthesis of Phosphorus Compounds containing the 1,2-Oxaphospholan Ring.

The preparation of spirophosphoranes containing 1,2-oxaphospholan rings is severely restricted by the lack of trivalent 1,2-oxaphospholans. Grayson and Farley[181] reported the preparation of 1,2-oxaphospholan systems by the oxidation of primary or secondary, 3-hydroxyalkylphosphines or phosphine oxides, using diphenyldisulphide (scheme 48).



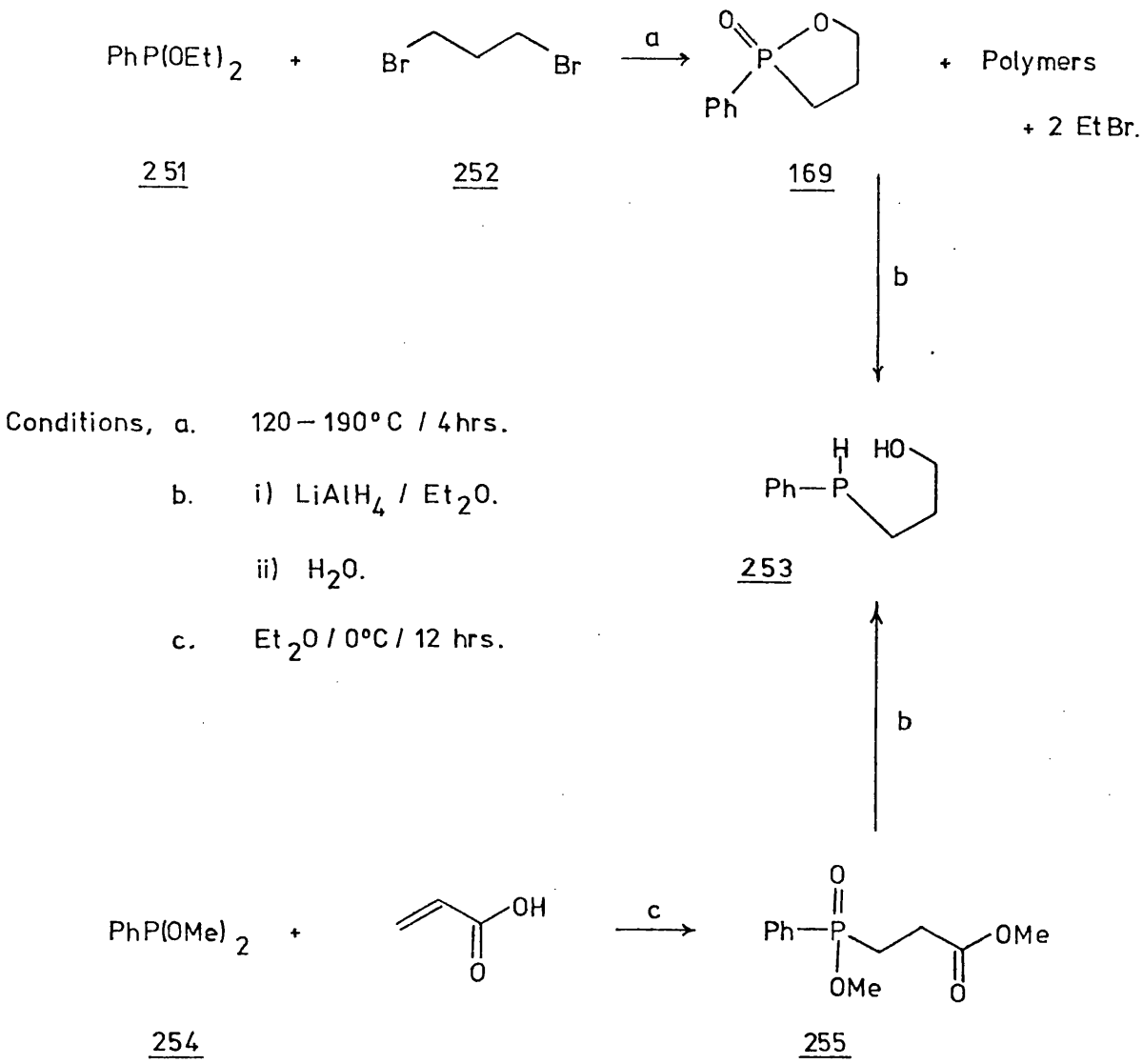
R = Ph or cyclo C_6H_{11}





Scheme 48.

The synthesis of 3-hydroxyalkylphosphines that are reported in the literature are difficult and involve either the treatment of metallated primary phosphines with oxetan[182] or the insertion of olefins into P-H bonds of primary phosphines.[183] In order to avoid the use of these highly reactive primary phosphines, two new syntheses of these compounds were developed and are outlined in scheme 49.

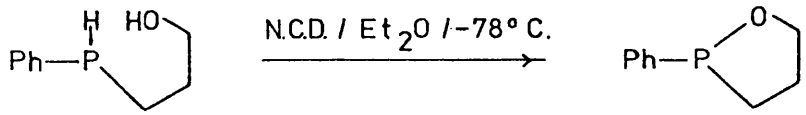


Scheme 49.

The first method involves the treatment of diethyl phenylphosphonite (251) with 1,3-dibromopropane (252) at 120-190°C for four hours. The product is a mixture of oxaphospholan oxide 169 and polymers. Lithium aluminium hydride reduction of the mixture of products gives phosphine 253 in 28% yield. An alternative method involves the formation of ester 255 from acrylic acid and dimethyl phenylphosphonite, and subsequent reduction

with lithium aluminium hydride giving phosphine 253 in 29% yield.

The reported cyclisation[181] of phosphine 253 using diphenyldisulphide could not be made to work. On two occasions large amounts of thiophenol were formed, showing that an oxidation of some description had taken place, but the only phosphorus containing products were involatile polymers. Cyclisation was achieved, however, by treating a solution of phosphine 253, in ether at -78°C, with one molar equivalent of N-chlorodi-isopropylamine (N.C.D.). A precipitate of di-isopropylammonium chloride was formed and subsequent filtration, evaporation and distillation gave the cyclic phosphinite ester 256 in 20% yield.

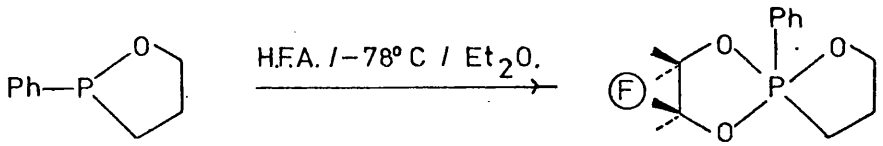


253 256

When 1,2-oxaphospholan 256 was treated with perfluoropinacol and N.C.D., a spirophosphorane was not obtained but instead, the corresponding 1,2-oxaphospholan-2-oxide was formed in almost quantitative yield. This is one of the few examples of an N.C.D. reaction that failed to work. A precipitate of di-isopropylammonium chloride was formed, suggesting that a reaction had occurred, and the perfluoropinacol was not recovered from the reaction mixture, but since it is fairly volatile it could have been evaporated with the solvent. Oxidation by molecular oxygen dissolved in the solvent is another possible explanation but this is unlikely because the solvent was purged with dry nitrogen before the reaction was carried out. The most likely explanation is that either an anomalous reaction occurred with the perfluoropinacol or a small amount of water was accidentally introduced into the reaction flask and reacted with the

1,2-oxaphospholan and N.C.D. in preference to the perfluoropinacol. This explains the formation of the amine hydrochloride whereas oxidation with molecular oxygen does not.

With excess hexafluoroacetone (H.F.A.), oxaphospholan 256 gave spirophosphorane 257 as a white crystalline compound in 47% yield. This phosphorane is the first example of a spirophosphorane

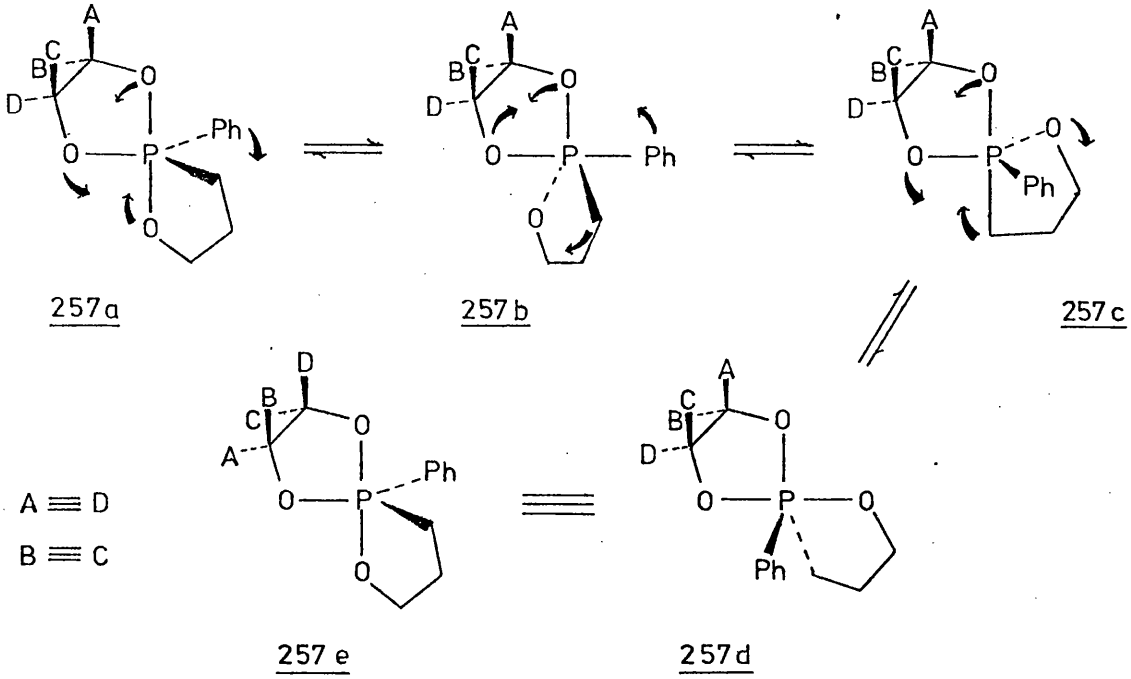


256 257

containing both a 1,3,2-dioxaphospholan ring and a 1,2-oxaphospholan ring.

Structure 257a will probably be the most stable conformation for this phosphorane since both rings span apical-equatorial positions, the phenyl group is equatorial and the oxygen atom in the 1,2-oxaphospholan ring is apical. There is no symmetry in this conformation so each of the four trifluoromethyl groups should appear as a separate signal in the ^{19}Fn.m.r. spectrum. Partial equivalence of the trifluoromethyl groups can be achieved by the multistep pseudorotation process shown in scheme 50, which makes groups A and D equivalent and groups B and C equivalent.

This pseudorotation pathway involves a high energy intermediate 257b that has a diequatorial oxaphospholan ring and an apical phenyl group. The temperature at which the four n.m.r. signals coalesce to two can be used to determine the activation energy for the B.P.R. 257a to 257b. The activation energy can also be



Scheme 50.

calculated by using the equation:

$\Delta G^* \geqslant \Delta G$ = A(ring O-Ph) + S_{90-120}(oxaphospholan) + Rot. O.

(see chapter 1, section iv).

The term Rot. O, is usually given the value of 5 k.cal.mol.$^{-1}$, and since the ring strain of both phospholans and 1,3,2-dioxaphospholans are usually taken as 8 k.cal.mol.$^{-1}$, it seems reasonable that the ring strain for a 1,2-oxaphospholan ring will also be approximately 8 k.cal.mol.$^{-1}$. The apicophilicity of a ring-oxygen will probably be similar to the apicophilicity of an alkoxy group. The difference in apicophilicity between phenyl and methoxyl groups is 9-10 k.cal.mol.$^{-1}$, (see chapter 2), and the difference between phenyl and phenoxy is in the range 8-12.6 k.cal.mol.$^{-1}$, (see chapter 3), so a good range for the term A(ring O-Ph) would be 8-12 k.cal.mol.$^{-1}$.

Substituting these values into the energy equation we get:

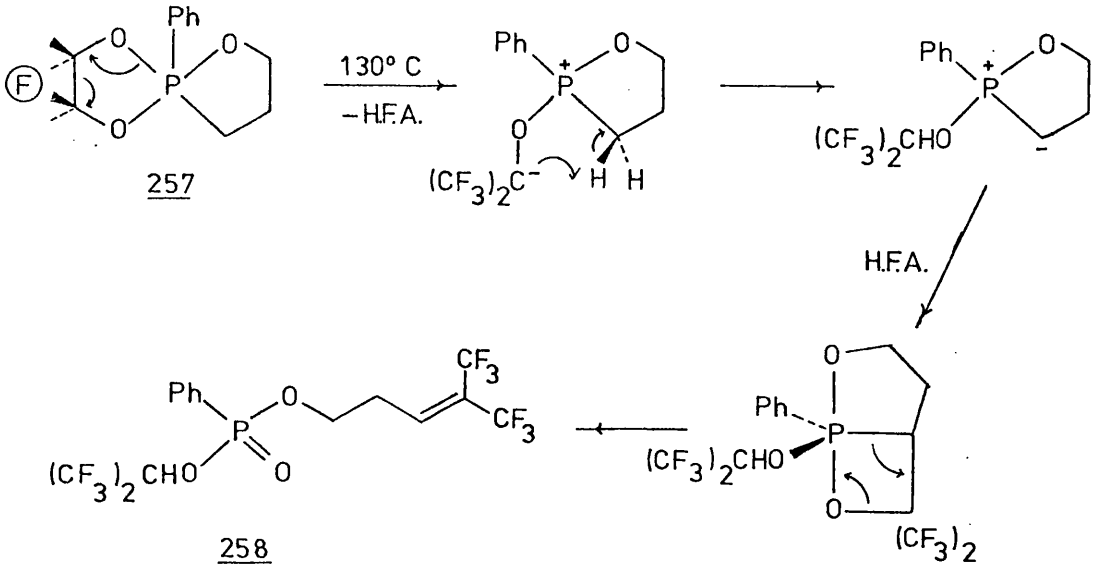
$\Delta G^* \geq \Delta G \doteq (8 \text{ to } 12) + 8 + 5$

$= 21 \text{ to } 25 \text{ k.cal.mol.}^{-1}$

This means that the activation energy for the B.P.R. 257a to 257b will be in the range 21 to 25 k.cal.mol.$^{-1}$. Activation energies this large cannot easily be measured using d.n.m.r. techniques since the coalescence temperature corresponding to this energy is higher than the maximum temperature obtainable on the n.m.r. spectrometers in these laboratories. This calculated activation energy is based on assumptions about apicophilicity differences in other systems, and on the ring strain of a 1,2--oxaphospholan ring, so an attempt was made to measure the activation energy for this B.P.R. in case the calculated value was significantly overestimated.

The ^{19}Fn.m.r. of phosphorane 257 was a multiplet at room temperature in 1-bromonaphthalene. This was apparently caused by the four separate signals being nearly superimposed, and to complicate the spectrum further, each signal was split into a quartet by FF spin-spin coupling between adjacent trifluoromethyl groups. Attempts to separate the signals using lanthanide shift reagents only resulted in a lowering of the resolution of the spectrum.

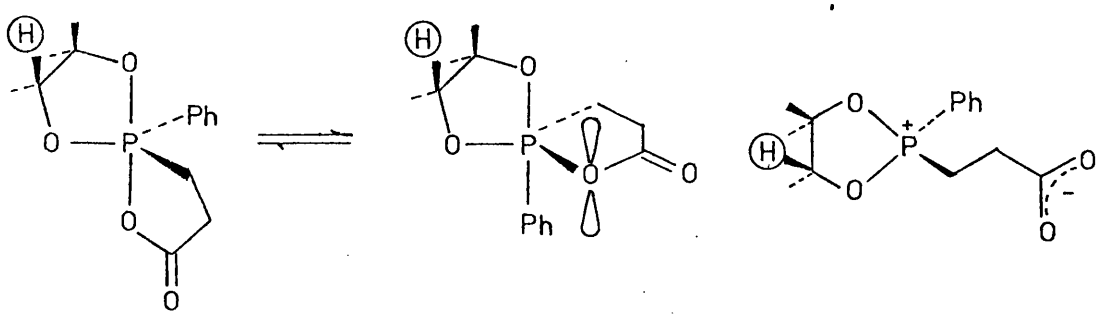
A coalescence was attempted in the hope that the number of lines in the multiplet would be reduced but before any coalescence was observed the phosphorane decomposed to phosphonate 258 at 130^{o}C.



This rearrangement was carried out on a preparative scale by heating the phosphorane by itself at 140°C for half an hour. The product was a colourless, mobile oil and all of the spectral data were consistent with structure 258.

The high energy barrier to this pseudorotation can be lowered if the phenyl group is replaced by a more apicophilic group, e.g. phenoxy. The difficulty in preparing the required starting trivalent phosphorus compound, however, means that either new methods for preparing 1,2-oxaphospholans or new methods for preparing this type of phosphorane from more easily accessible trivalent phosphorus compounds are needed. Some possible reactions are discussed in chapter 6.

Brierley[42] has measured the activation energy for pseudorotations of a phosphorane similar to 257, and found this barrier to be 17.6 k.cal.mol.$^{-1}$ for the acrylic acid adduct 259. The calculated activation energy for pseudorotations of this phosphorane should be approximately the same as for phosphorane 257. Three possible



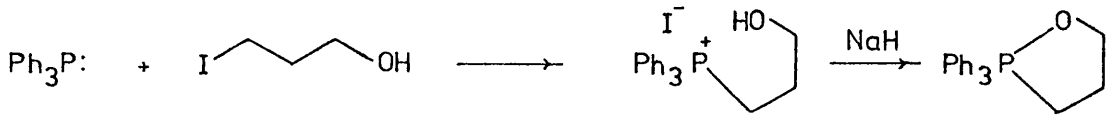
259 260 261

reasons why the measured value is much lower than is calculated for 257 could be that an abnormal ligand reorganisation process occurs via a ring-openend dipolar compound 261. The carboxylate anion will be delocalised and therefore relatively stable, and it will also be a good leaving group making this process more favourable. Another possible reason is that ring strain for this type of ring is not known and could be rather less than 8-10 k.cal. $mol.^{-1}$, thus reducing the activation energy. A final possibility is that the delocalisation of the lone pair of electrons on the ring--oxygen atom, with the carbonyl group, reduces the term Rot.O in the energy equation. When the ring is diequatorial (260) the lone pair is in the disfavoured apical plane. If these electrons are withdrawn by the carbonyl group the interactions of the lone pair with phosphorus are reduced lowering the barrier to rotation around the P-O bond.

A comparison of this acrylic acid adduct with phosphorane 257 is not valid because nothing is known about the effects of the carbonyl group in an oxaphospholan ring and also very little is known about 1,2-oxaphospholan rings in spirophosphoranes.

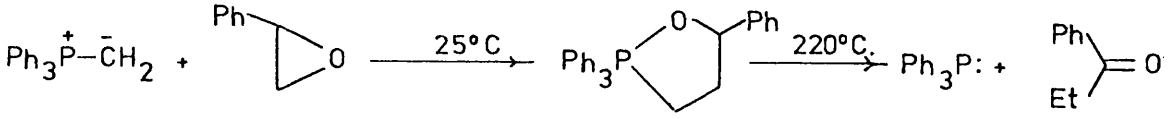
CHAPTER 6. Attempts to Prepare Phosphoranes containing a 1,2-Oxaphospholan Ring.

In 1967, Hands and Mercer[184] prepared P,P,P-triphenyl-1,2--oxaphospholan (263) in high yields, by treating phosphonium salt 262 with sodium hydride. The reaction between epoxides and ylids



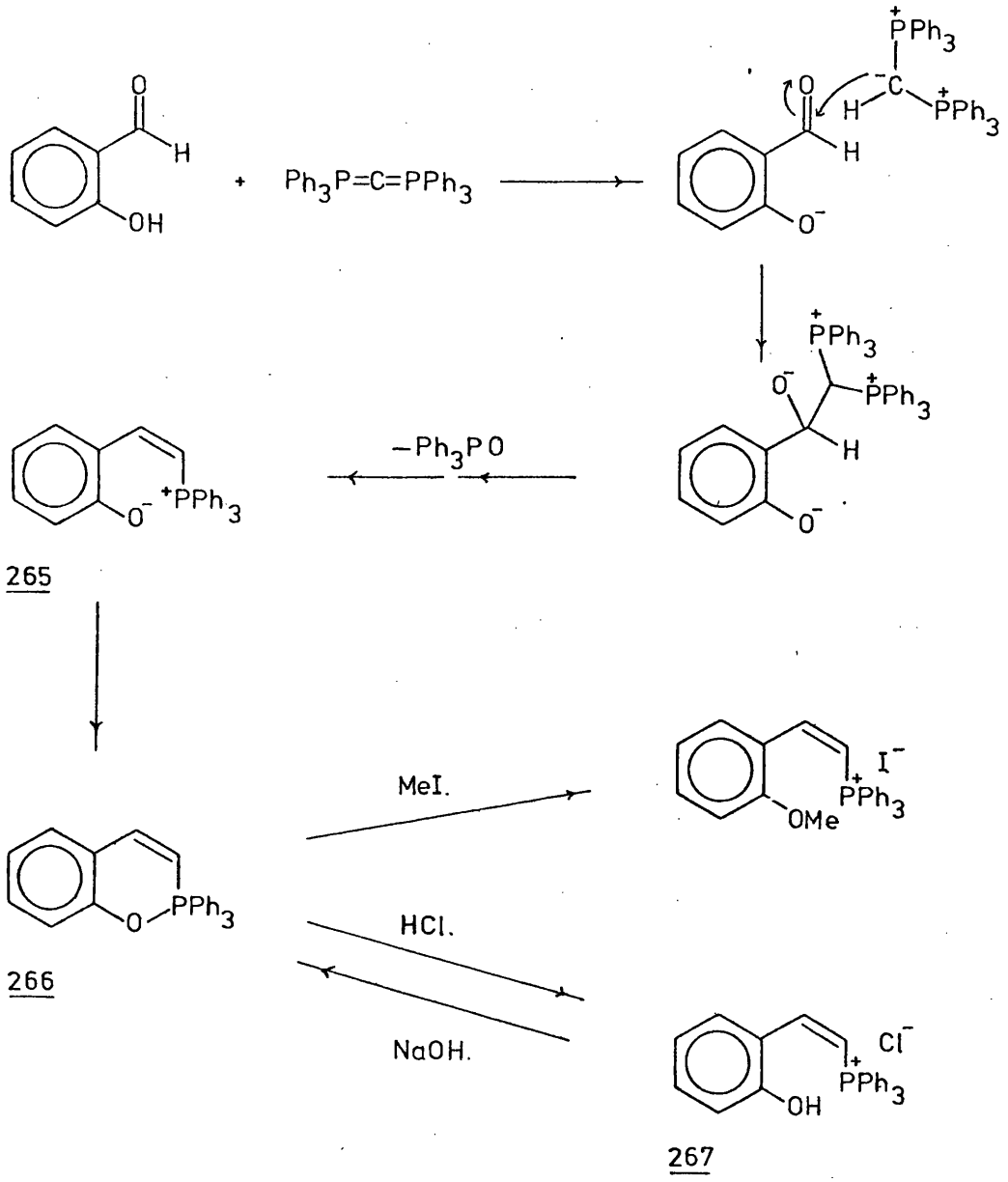
262 263

has been used to prepare oxaphospholan rings.[185-188]



264

These phosphoranes are usually crystalline solids that can easily be converted into phosphonium salts by treatment with alkyl halides or hydrogen halides. The ring opening reaction with hydrogen halides is reversible, e.g. phosphorane 266 can be ring opened with hydrogen chloride to give phosphonium salt 267, which in turn can be cyclised by treatment with sodium hydroxide.[188] The ring opening reaction with iodomethane implies that either the lone pair of electrons on the ring-oxygen atom is very nucleophilic or that the phosphorane is in equilibrium with a ring opened, dipolar form of the compound (265). The latter explanation, however, does not account for the very positive ^{31}Pn.m.r. chemical shifts for



265

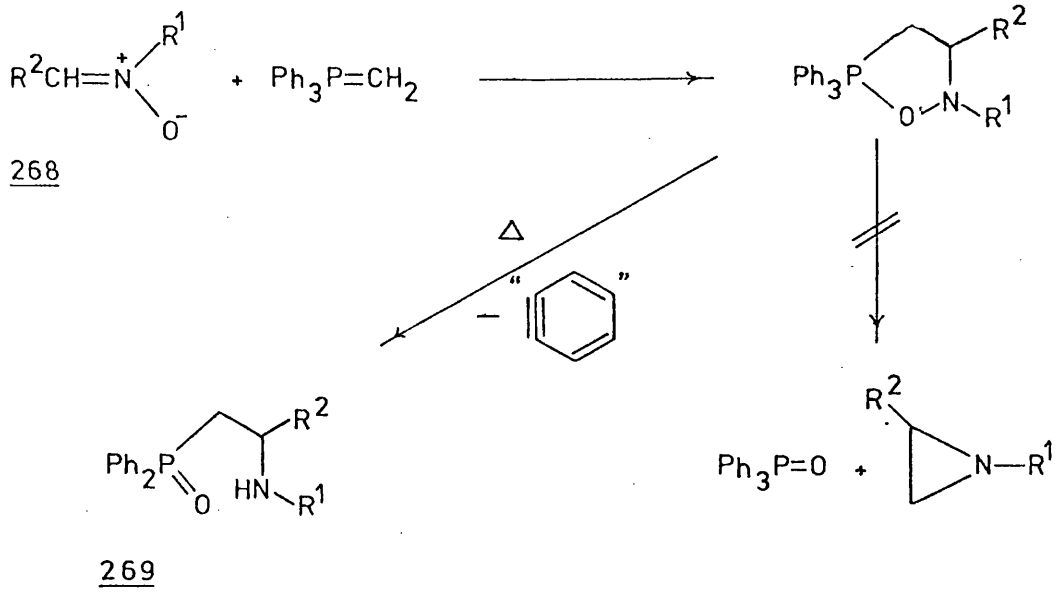
266

267

this type of phosphorane, e.g. 264, ^{31}P = +55.2 p.p.m. & 266, ^{31}P = +51 p.p.m. relative to 85% H_3PO_4.

Imine oxides (268) also form phosphoranes with ylids.[189] These phosphoranes were prepared in the hope that they would decompose to aziridines but in fact they decomposed, with formal loss of benzyne, by an unknown mechanism, forming phosphine oxides (269).

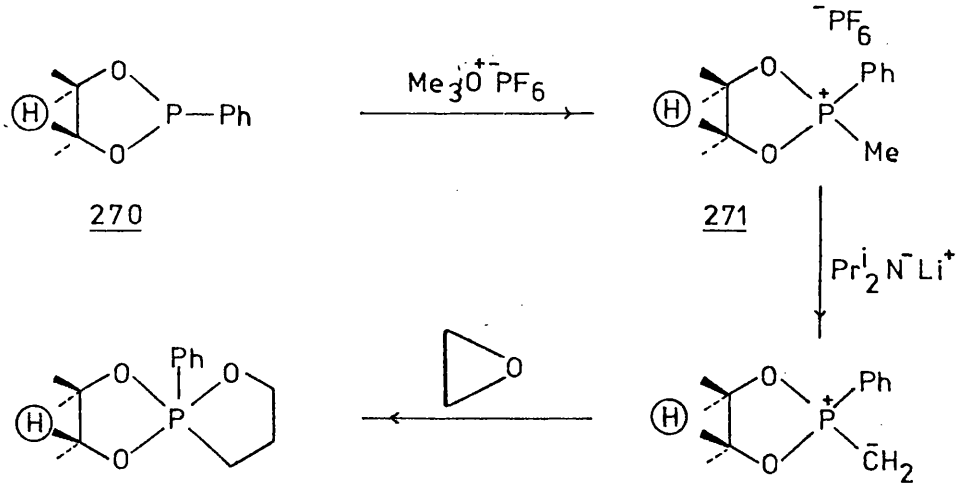
With this work in mind, attempts were made to adapt the reaction of ylids with epoxides to the preparation of spirophosphoranes



268

269

containing a 1,2-oxaphospholan ring by the route outlined in scheme 51. It was realised that the quaternisation of

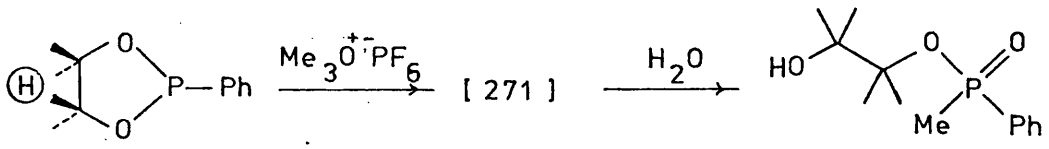


Scheme 51.

dioxaphospholan 270 would be difficult because of the increase in ring strain in going from 270 to 271, and also that phosphonium salt 271 would be very hydrolytically unstable because of the relief of ring strain when pentacoordinate intermediates in the hydrolysis reaction were formed. For these reasons

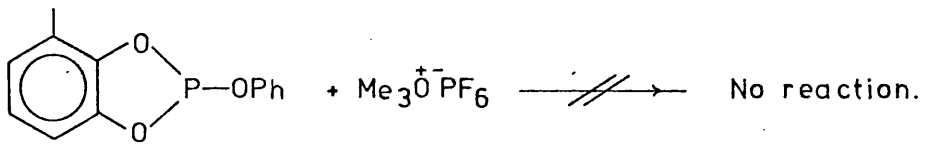
trimethyloxonium hexafluorophosphate was used as the alkylating agent because it was a powerful alkylating agent thus making the formation of 271 more likely and also, phosphonium hexafluorophosphates are usually considered to be less hygroscopic than phosphonium salts with other anions.[190]

When this reaction was carried out the only product that was obtained from the reaction of dioxaphospholan 270 with the oxonium salt was phosphinate 272. This was presumably formed by the accidental hydrolysis of phosphonium salt 271 even though stringent conditions of dryness were used.



270 272

A similar series of reactions was attempted using the cyclic phosphite ester 273 but this could not be alkylated with trimethyloxonium hexafluorophosphate, the starting materials being recovered unchanged after several weeks. The low nucleophilicity of this type of phosphorus compound is consistent with the predictions of Verkade,[176] (see chapter 4).

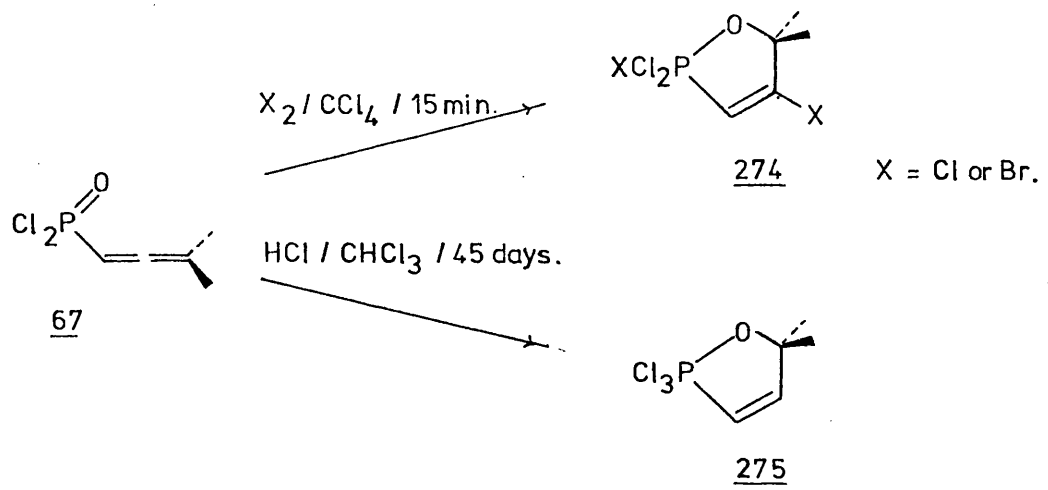


273

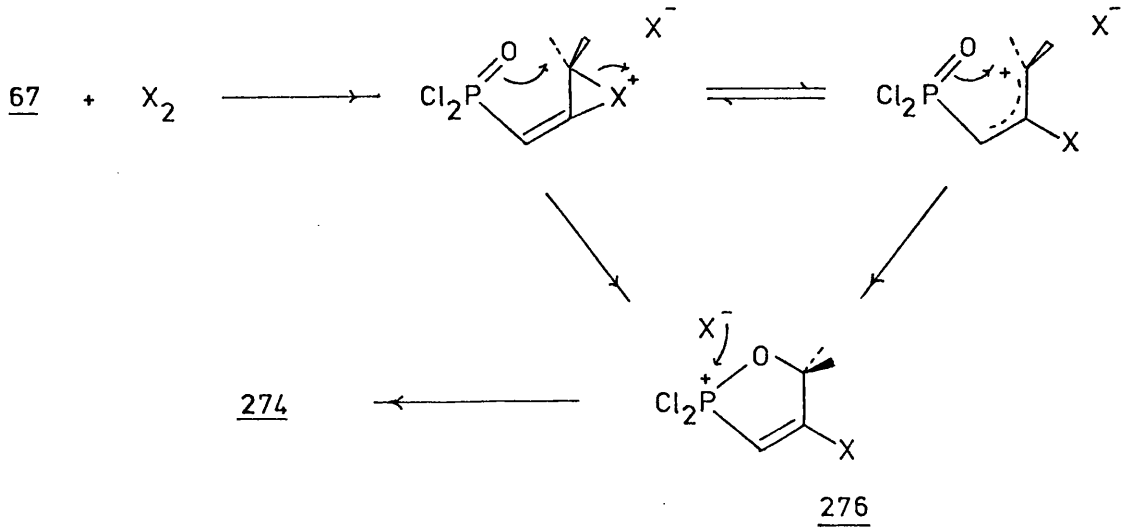
Since quaternisation of these compounds proved to be difficult, together with the inherent instability of the phosphonium intermediates,

the preparation of spirophosphoranes by this method was abandoned.

The synthesis of halophosphoranes containing a 1,2-oxaphosphol-3-ene ring have been reported.[113,114] Phosphoranes 274 and 275 were prepared by the halogenation or hydrochlorination of allenylphosphonic dichloride 67.



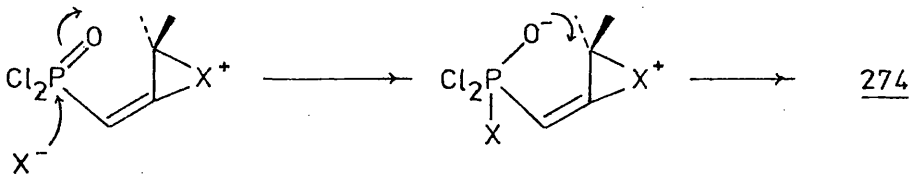
The mechanism of this reaction is thought to involve nucleophilic attack of the phosphoryl group on a carbonium or



Scheme 52.

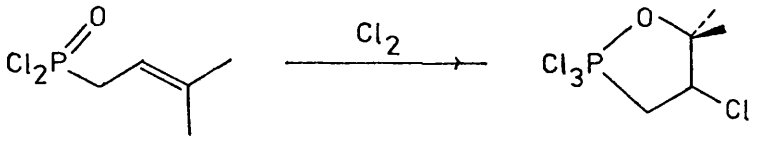
halonium ion intermediate (scheme 52). To avoid the formation of a cyclic phosphonium intermediate (276) in this mechanism, the attack of the halide ion on phosphorus is probably synchronous with the

cyclisation. Another possibility is that cyclisation occurs after the halide ion attacks phosphorus forming an intermediate such as 277.



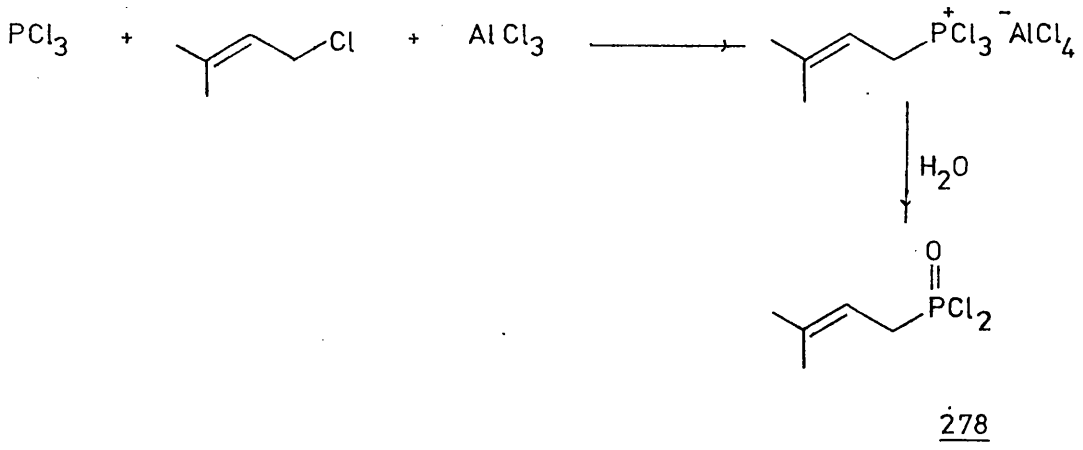
277

An attempt was made to modify this reaction to prepare the saturated analogue (274a) by chlorinating 3-methylbut-2-enylphosphonic dichloride (278). This reaction, however, failed at the outset since the starting phosphonic dichloride (278) could not be prepared.



278 274a

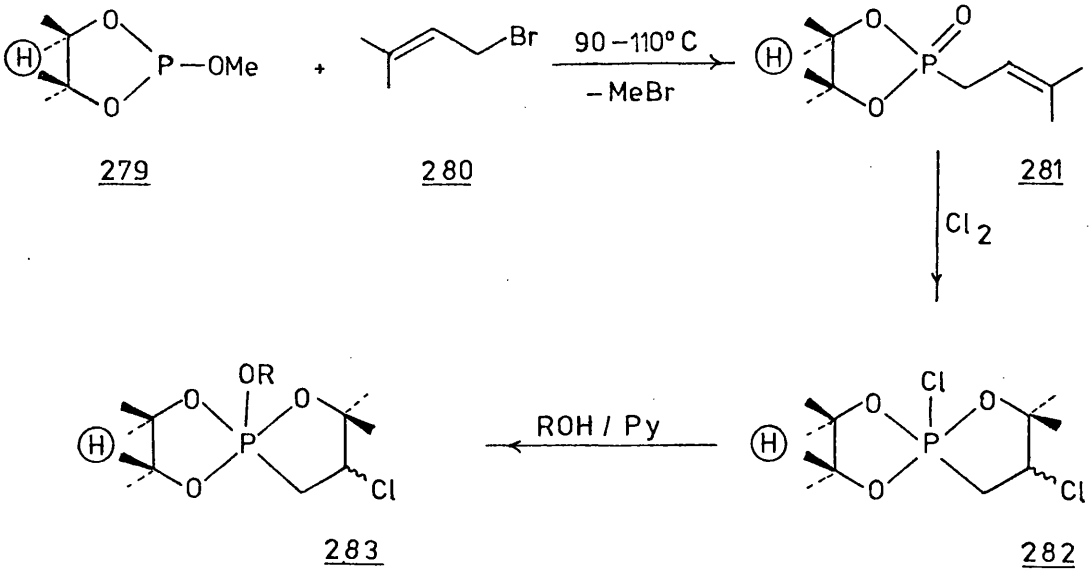
Following the method for the preparation of allylphosphonic dichloride,[191] large amounts of involatile, black polymers were formed and a small yield of a yellow oil was obtained by the route outlined in scheme 53. This oil was very unstable forming a thick purple solid on contact with deuterochloroform. The instability of this compound, assuming that this was the yellow oil, is somewhat surprising since the allyl analogue is a stable, distillable oil.



278

Scheme 53.

An attempt was made to adapt this reaction to the preparation of spirophosphoranes, in one step, by the chlorination of phosphonate 281, which was easily prepared by heating phosphite 279 with 1-bromo-3-methylbut-2-ene, (scheme 54).

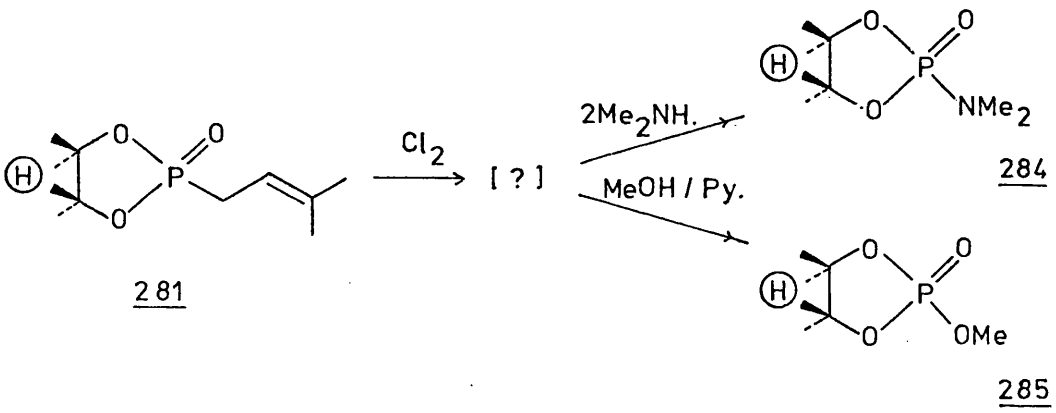


279 280 281 283 282

Scheme 54.

When a standard solution of chlorine in tetrachloromethane was titrated into a weighed amount of phosphonate 281 at $0^{o}C$, the yellow colour was discharged immediately. After one molar equivalent of chlorine was added the yellow colour persisted showing that one mole of 281 reacts with just one mole of chlorine. Subsequent chlorinations were carried out by slowly passing chlorine gas into a solution of 281 in CCl_4 until a yellow colour persisted. The excess chlorine was removed by purging the solution with dry nitrogen.

Immediate addition of either excess dimethylamine or one molar equivalent of each of methanol and pyridine to the chlorinated



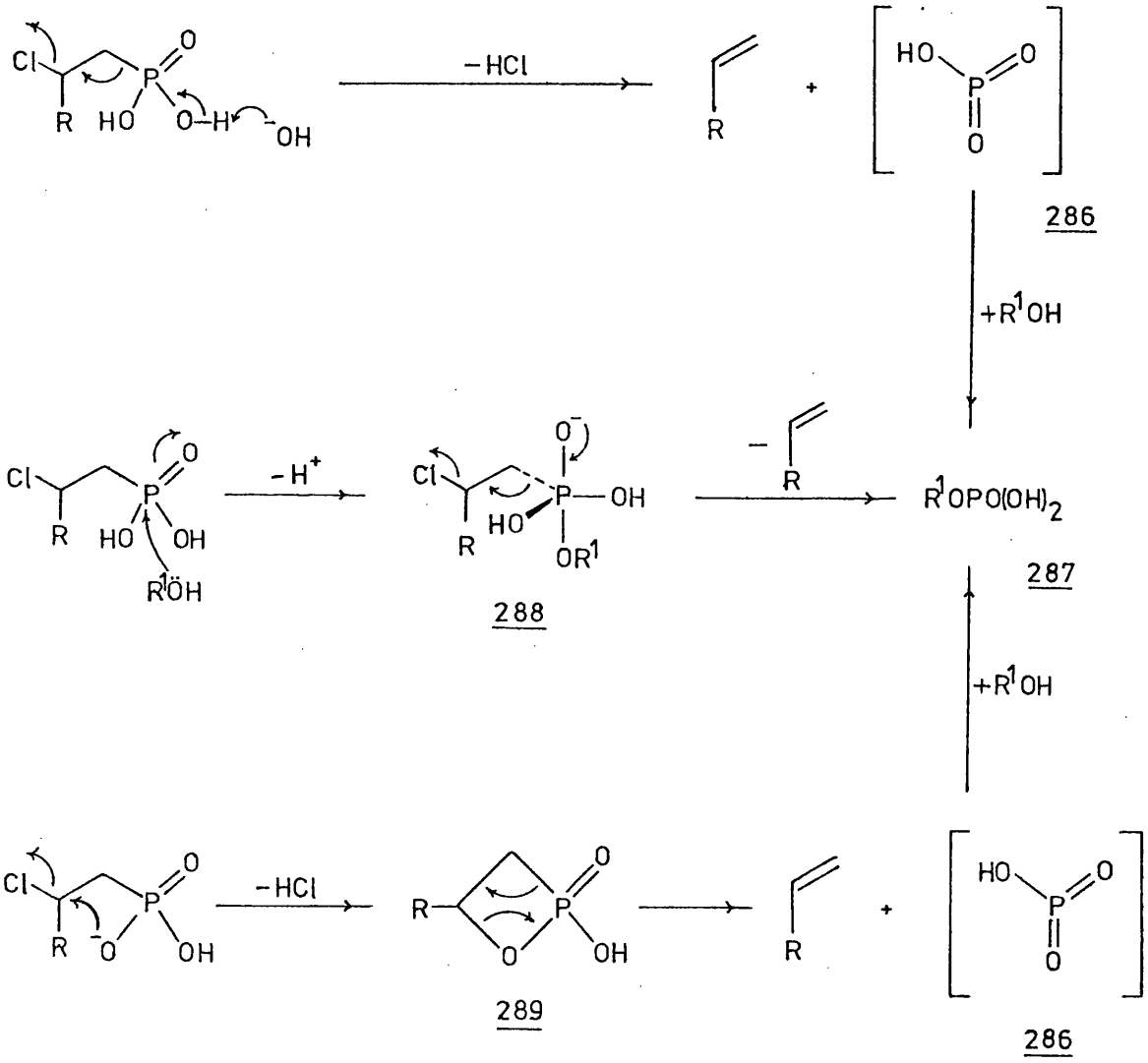
281 284 285

phosphonate resulted in the formation of cyclic phosphoramidate (284) or cyclic phosphate ester (285). This is a very interesting reaction because a carbon-phosphorus bond is broken. Investigations into the mechanism of this reaction have not shed any light on how this bond is broken or what the intermediate in the reaction is. One thing that is clear, however, is that no spirophosphoranes were formed in this reaction.

The stage at which the C-P bond breaks is not known. It is known to be present in the starting material because the ^{1}Hn.m.r. spectrum of 281 clearly shows the presence of a $P\text{-}CH_2\text{-}CH$ group.

Both the α and the β protons are coupled to phosphorus and they can both be decoupled by ^{31}P(INDOR)n.m.r. spectroscopy. The presence of this group in the intermediate, however, is uncertain.

Examples of C-P bond fission can be found in the literature but these are restricted to 2-haloalkylphosphonic acids.[192] These reactions are thought to occur by the three mechanisms shown in scheme 55. The first mechanism is a fragmentation of the monoanion

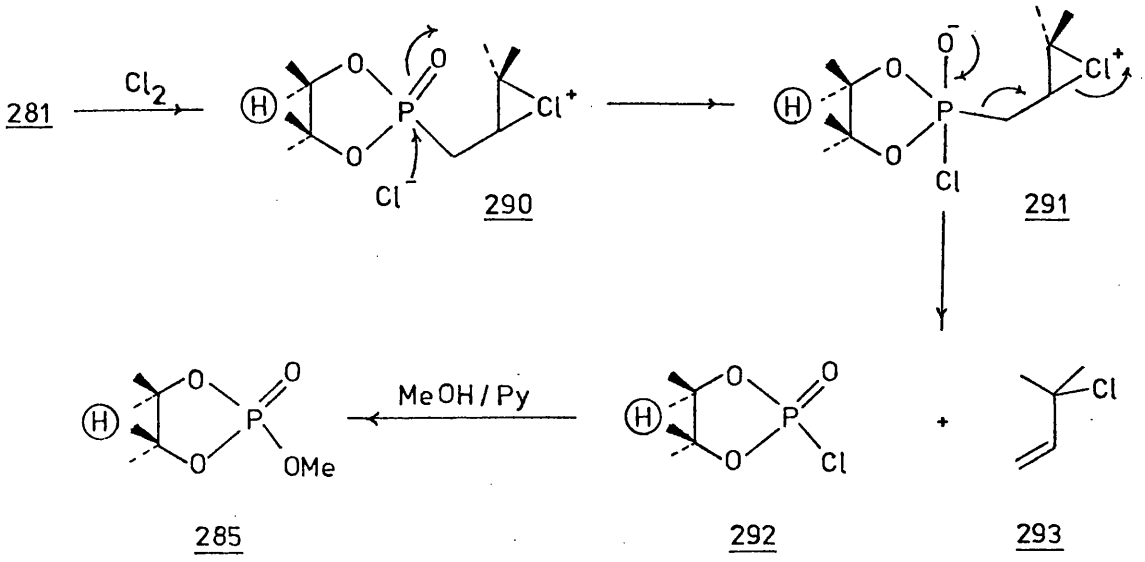


Scheme 55.

of the phosphonic acid forming an alkene and a reactive metaphosphate (286) which is trapped with an alcohol to form a phosphate monoester. The second mechanism involves a pentacoordinate intermediate (288) formed by nucleophilic attack of the alcohol on

the phosphorus atom. Subsequent fragmentation of this phosphorane gives the alkene and the phosphate monoester directly. Finally a Wittig type reaction can occur via an intermediate (289) which is formed by an intramolecular, nucleophilic substitution of the chlorine atom by the phosphonic acid anion. Decomposition of this intermediate gives the reactive metaphosphate 286, which is trapped by the alcohol.

This work on 2-haloalkylphosphonic acids does not help a great deal in sorting out the mechanism of C-P bond fission in phosphonate 281 but there is some circumstantial evidence suggesting that the C-P bond is not broken until the methanol-pyridine or dimethylamine is added. If the bond is broken at the chlorination stage the cyclic phosphorochloridate ester 292 might be expected to be involved in the reaction. A possible mechanism for its formation is given in scheme 56. This involves the fragmentation of a pentacoordinate intermediate (291) which is formed by nucleophilic attack of the chloride ion on phosphonate 290, which would be a favourable reaction because there would be a relief of ring strain

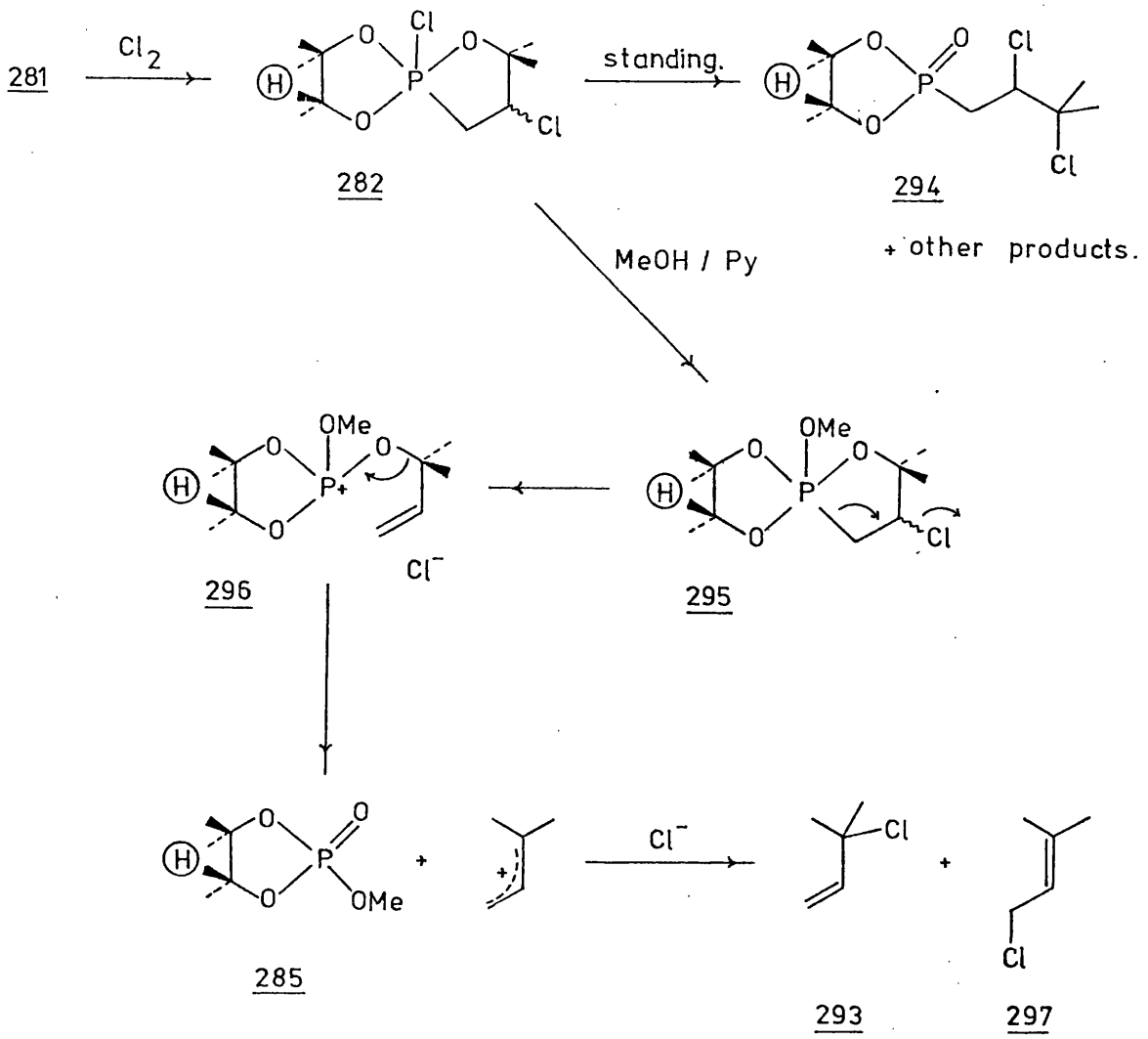


Scheme 56.

in forming this intermediate. The fragmentation of intermediate 291 would not be as simple as scheme 56 suggests because in the initially formed phosphorane the chlorine atom and the oxide anion would occupy the apical positions and pseudorotations would have to occur to place the alkyl group apical before it could leave in the fragmentation reaction.

Phosphorochloridate 292 is a known compound but no trace of it could be found in the ^{31}Pn.m.r. spectrum of the chlorinated intermediate. Similarly no trace of the allyl chloride 293 could be found by gas chromatography suggesting that this type of mechanism does not occur. Another point is that phosphorochloridate 292 is less reactive towards methanol-pyridine than the chlorinated intermediate in the reaction of phosphonate 281, again suggesting that the mechanism outlined in scheme 56 is not operating.

On one occasion only the ^{31}Pn.m.r. spectrum of the chlorinated intermediate showed a signal at -18 p.p.m. which diminished over a period of about fifteen minutes and was replaced by several signals that appeared between -38 and -42 p.p.m. All subsequent attempts to repeat this spectrum have failed. The only signals that are seen are around -40 p.p.m. This mixture of compounds is inactive towards methanol or methanol-pyridine mixture. The reaction with methanol only occurs immediately after the chlorination which suggests, together with the n.m.r. data, that a reactive intermediate is formed which rearranges to non-reactive compounds on standing. These compounds have very similar ^{31}Pn.m.r. chemical shifts to the starting material (-39.1 p.p.m.) and it is therefore likely that they have similar structures. A possible mechanism that takes these observations into account is given in scheme 57.

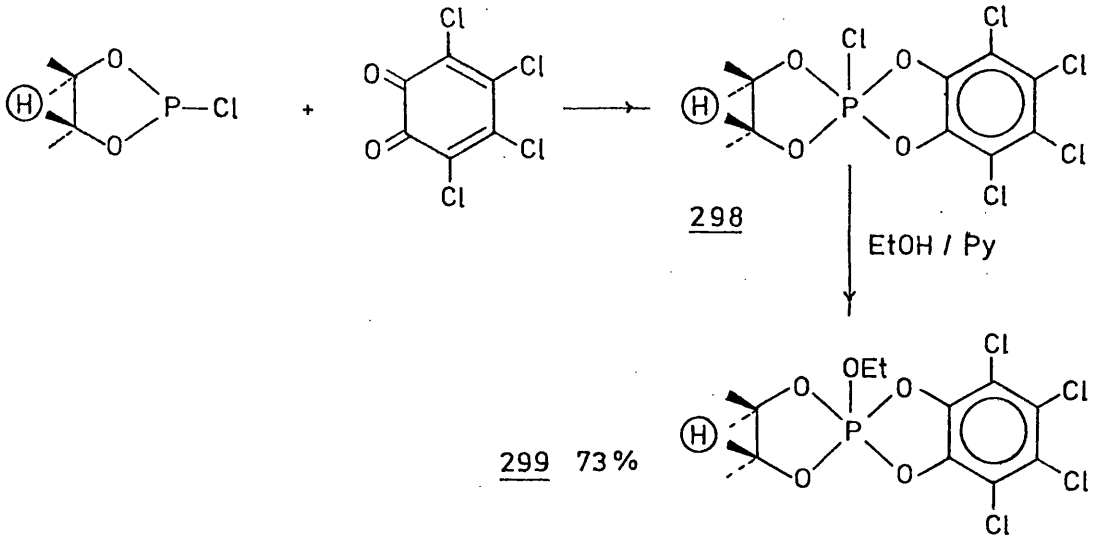


Scheme 57.

This mechanism involves the fragmentation of phosphorane 295 forming a phosphonium intermediate 296, which can lose an allyl carbonium ion to give the observed product 285 and two possible allyl chlorides 293 and 297. The chlorophosphorane 282, is less likely to fragment than phosphorane 295 because the polarisation in the phosphorus-chlorine bond will increase the effective positive charge on the phosphorus atom thus disfavouring the formation of a phosphonium intermediate.

The weaknesses in this mechanism are two-fold. The phosphonium intermediate 296 contains a small ring and will therefore be highly

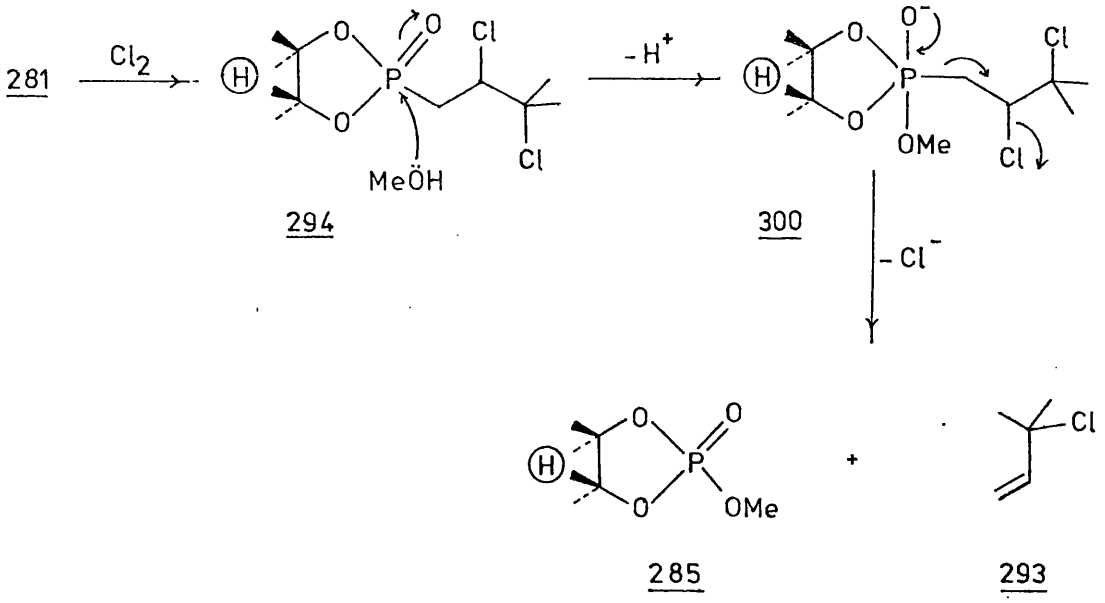
strained thus making its formation unfavourable. Secondly, there is no trace of either of the two allyl chlorides 293 or 297 in the gas chromatogram of the products. Another assumption that is made is that the chlorophosphorane can substitute its chlorine atom under fairly mild conditions. To test this assumption phosphorane 298 was prepared and, without isolation, was treated with ethanol



299 73%

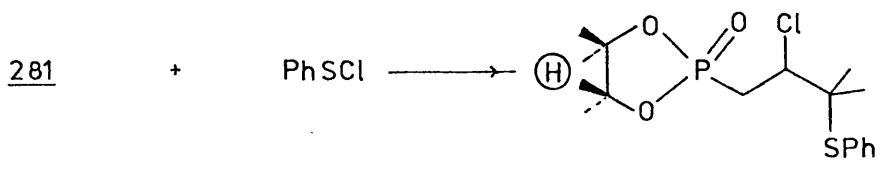
and pyridine in ether at 0°C. The ethoxyphosphorane 298 was formed in 73% yield and was identical in every respect with an authentic sample. This shows that substitution of halides at pentacoordinate phosphorus is a favourable reaction under mild conditions. Since this reaction was carried out, Brierley[42] has carried out other substitutions on this phosphorane.

An alternative mechanism is shown in scheme 58. This involves addition of chlorine to the double bond of 281 followed by nucleophilic attack by methanol on phosphorus forming phosphorane 300. This will be a favourable process because there will be some relief of ring strain in going from 294 to 300. Fragmentation of this phosphorane gives the observed product and allyl chloride 293.



Scheme 58.

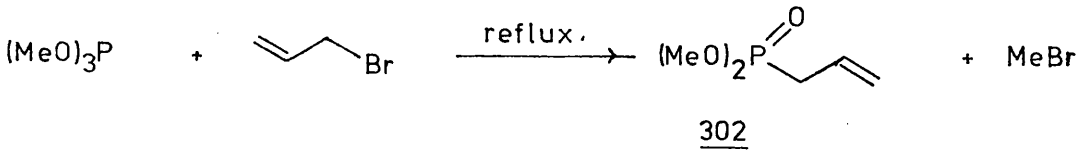
The major objection to this mechanism is that the dichloroalkylphosphonate 294, does not look like a reactive intermediate that decomposes by simply standing at $0^{o}C$ for a few minutes. To test the stability of this type of compound a similar compound (301) was prepared by adding benzenesulphenyl chloride to phosphonate 281. This was found to be a perfectly stable compound and did not react with methanol-pyridine in the manner proposed in scheme 58.



301

In order to learn more about the reactions of allylphosphonates with halogens, compounds 302 and 303 were prepared by the methods

outlined in scheme 59. Chlorination of phosphonate 302 resulted in addition of chlorine across the double bond (304). This was a



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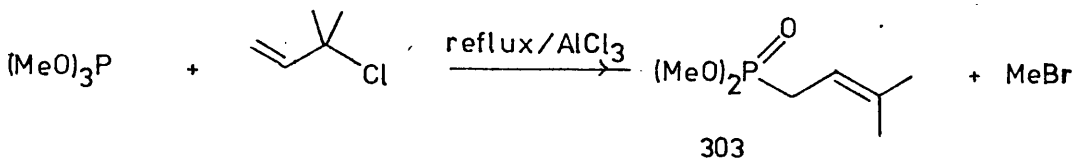
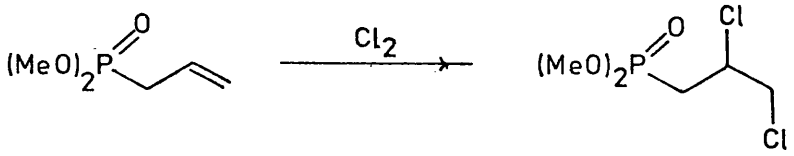


303

Scheme 59.

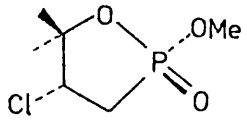


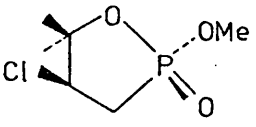
302 304

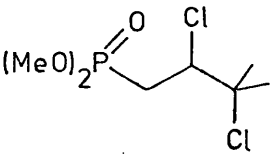
stable, distillable oil but it was only formed in 32% yield, the remainder of the product being a heavy, involatile and probably polymeric material.

Chlorination of phosphonate 303 gave a number of compounds that could not be fully characterised. Gas chromatography showed that six compounds were formed but g.l.c./mass spectroscopy showed that the first two compounds, the major products on the gas chromatogram, had identical mass spectra and similarly the last two compounds on the gas chromatogram, had identical mass spectra. The mass spectra suggested that the major products were two isomers of the cyclic phosphonate 305, which would account for the identical mass spectra of these compounds, and the next important product 306, was formed by simple addition of chlorine across the double bond.

The other products were formed in very low yields and are possibly formed by elimination of HCl from phosphonate 306.







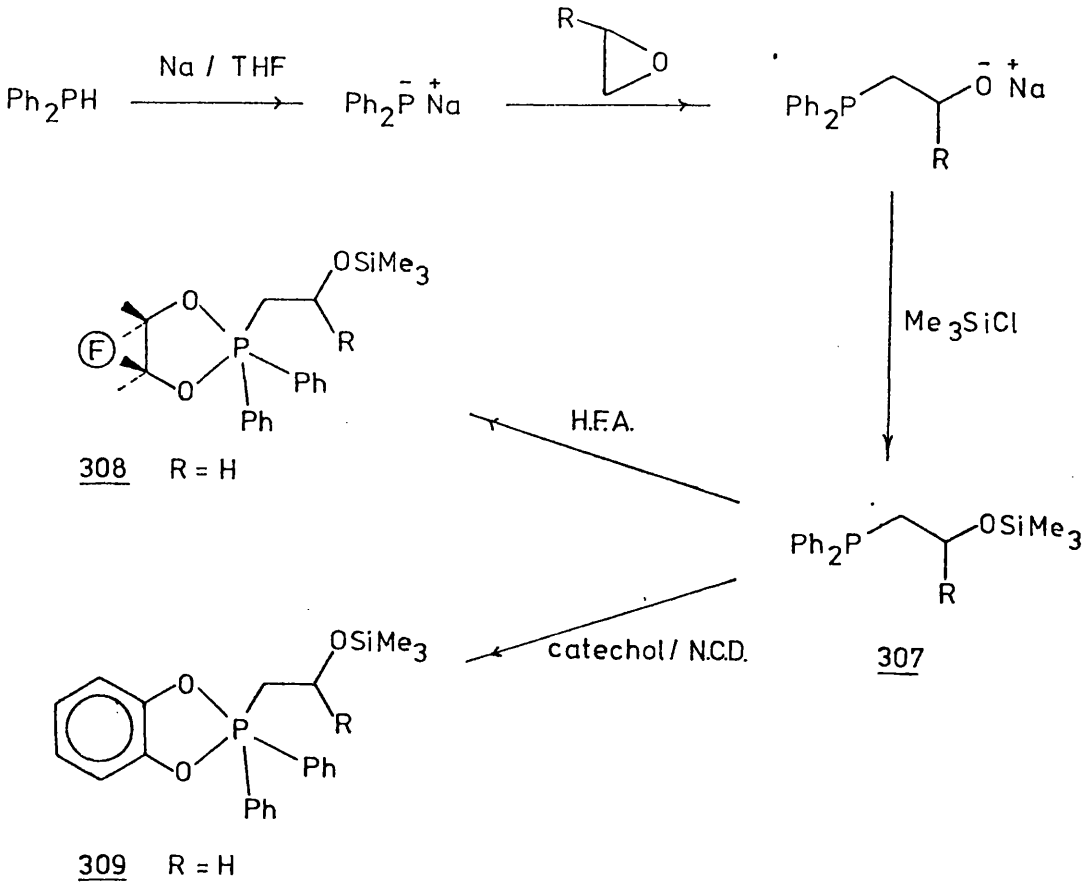
305 65%

306 26%

Preparative g.l.c. gave samples of the major products which allowed the ^{1}Hn.m.r. spectra to be recorded. The n.m.r. spectrum of 305, however, was not consistent with the cyclic structure given and an alternative structure could not be assigned. The n.m.r. spectrum of 306 was consistent with addition of chlorine across the double bond of phosphonate 303.

These last two experiments did not help a great deal in the understanding of the reaction between cyclic phosphonate 281 and chlorine. They did show, however, that the reaction was probably very complicated and that several possible products could be formed in this chlorination.

In order to investigate the proposed fragmentation of phosphorane 295 (scheme 57), two phosphoranes containing β-leaving groups were prepared as shown in scheme 60. Phosphine 307 reacted with hexafluoroacetone (H.F.A.) forming an adduct (308) which was isolated as a colourless oil and was fairly thermally stable but hydrolysed rapidly. Phosphorane 309 was formed in an N-chlorodi-isopropylamine (N.C.D.) reaction with catechol. This was also fairly thermally stable but extremely hydrolytically unstable. Neither phosphorane showed any tendancy to undergo C-P bond fission and hydrolysis resulted in a loss of the trimethylsiloxy group but the



Scheme 60.

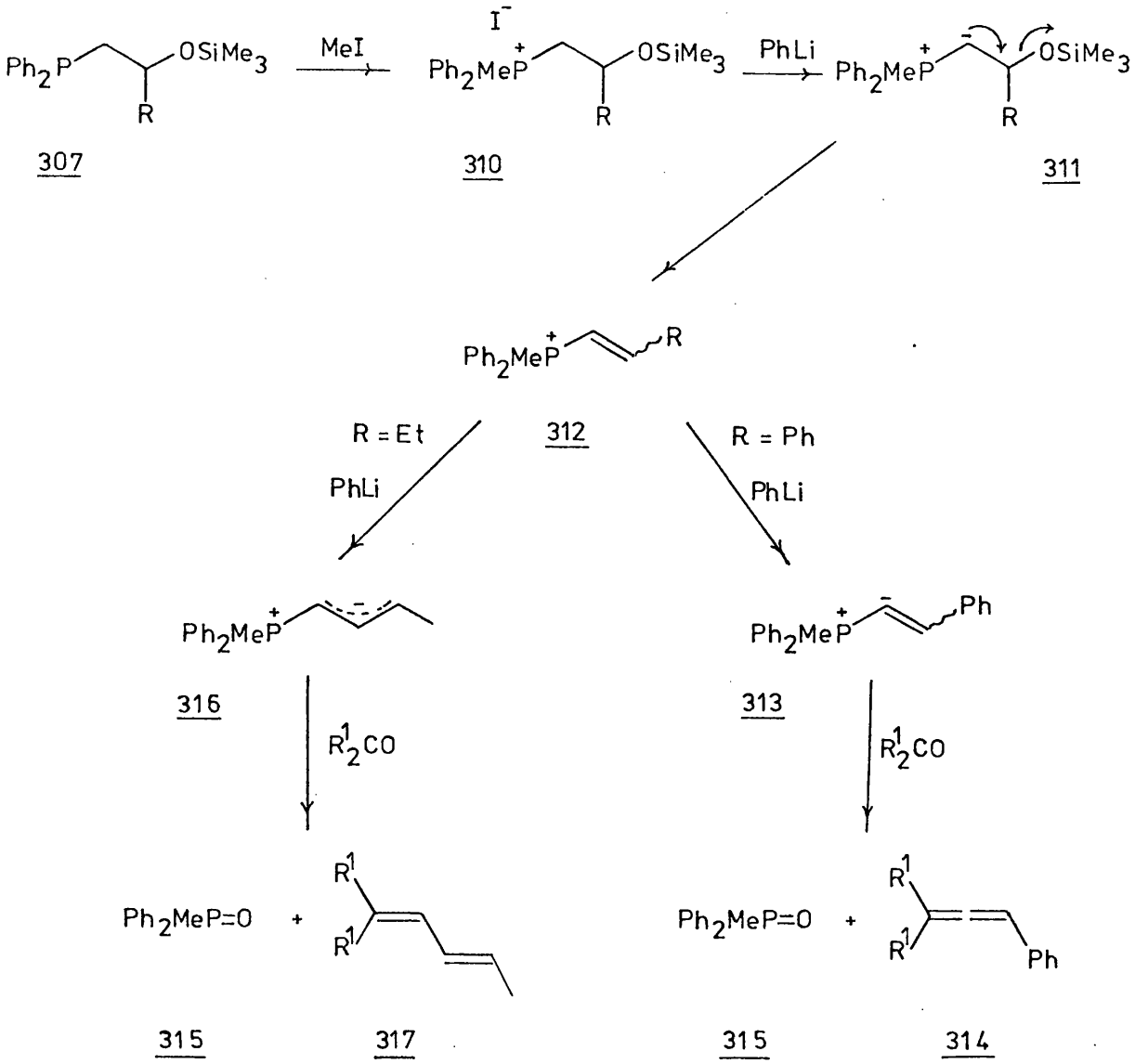
P-CH_2-CH_2 group remained intact and was clearly seen in the ^{1}Hn.m.r. spectrum. This suggests that phosphoranes with β-leaving groups do not fragment easily and therefore the mechanism in scheme 57 is unlikely.

The only conclusions that can be drawn from this series of experiments are that C-P bond fission occurs by an unknown mechanism via unknown reactive intermediates. The fate of the allyl group of 281 is unknown.

Organophosphorus Compounds containing a 2-Trimethylsiloxyethyl Group.

Phosphorus compounds containing a 2-trimethylsiloxyethyl group were found to undergo some interesting reactions. Phosphonium salts (310, R=Ph or Et) were investigated for their potential use in the Wittig olefin synthesis. It was hoped that the reactions

outlined in scheme 61 could be made to work.

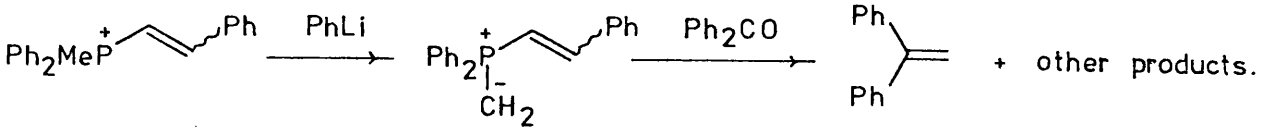


Scheme 61.

The ylid 311 could possibly eliminate the trimethylsiloxy anion forming a vinylphosphonium salt 312. This could now undergo other Wittig reactions depending on the nature of the R group. If R = Ph a vinylylid 313, could be formed which would react with ketones to give allene 314 and methyldiphenylphosphine oxide 315. If, on the other hand, R = Et, an allylylid 316, could be formed which would react with ketones forming 1,3-dienes 317, and phosphine oxide 315.

When these reactions were attempted the phosphonium salts 310, were found to be very hydrolytically unstable. This meant that the purification of these phosphonium salts was difficult and the reactions had to be carried out with the crude, impure phosphonium salts.

Treatment of phosphonium salt 310 (R=Ph) with one molar equivalent of phenyl-lithium gave vinylphosphonium salt 312 (R=Ph) as expected but a further equivalent of phenyl-lithium resulted in the removal of a proton from the methyl group rather than the vinyl group, forming ylid 318 which, with benzophenone, gave 1,1-diphenylethene. This could probably have been predicted because the



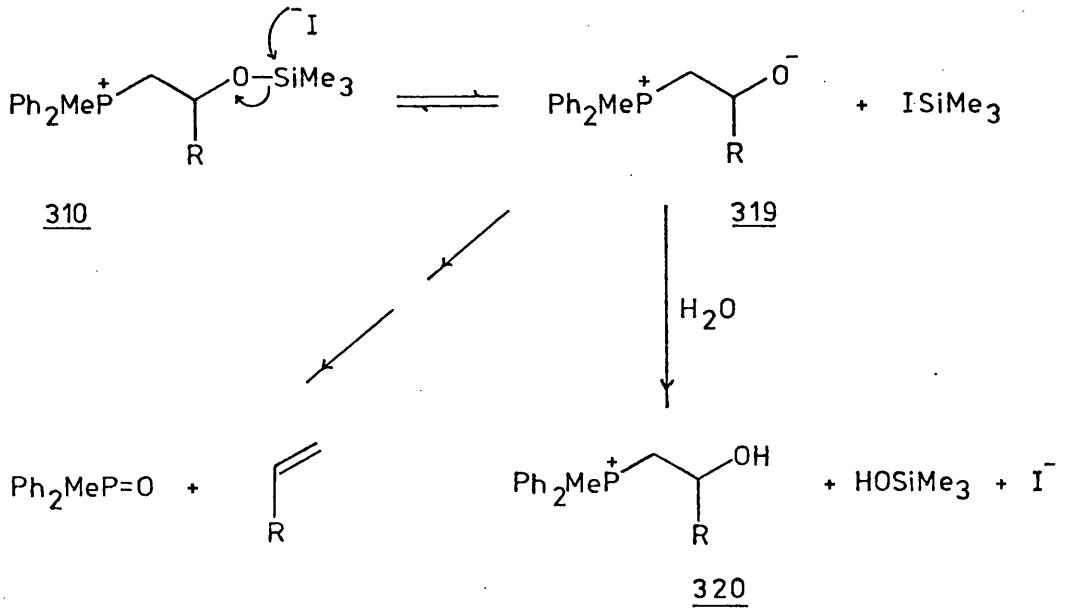
312 318

methyl protons would probably be more acidic than the vinyl proton.

The vinylphosphonium salt 312 (R=Ph) could not be fully characterised and it is quite possible that other reactions were responsible for the observed product. Characterisation was made difficult by the fact that the phosphonium salt was not crystalline which made its purification difficult and also it is known that the alkenyl protons in vinylphosphonium salts have ^{1}Hn.m.r. chemical shifts similar to phenyl groups and cannot be seen when phenyl groups are present in the compound.[193]

Attempts to prepare vinylphosphonium salt 312 (R=Et) by treating phosphonium salt 310 (R=Et) with phenyl-lithium, resulted in the formation of a complex mixture of products which could not easily be separated or identified.

Phosphonium salts 310 (R=Ph, Et or H) were very hydrolytically unstable and attempts to recrystallise them resulted in the isolation of 2-hydroxyalkylphosphonium iodides, 320. It was thought that this occurred by a similar mechanism to the fluoride ion catalysed hydrolysis of silyl ethers, i.e. the iodide ion attacks the silicon atom forming iodotrimethylsilane and an alkoxide. The iodotrimethylsilane is then rapidly hydrolysed by traces of water that accidentally enter the solvent (scheme 62).

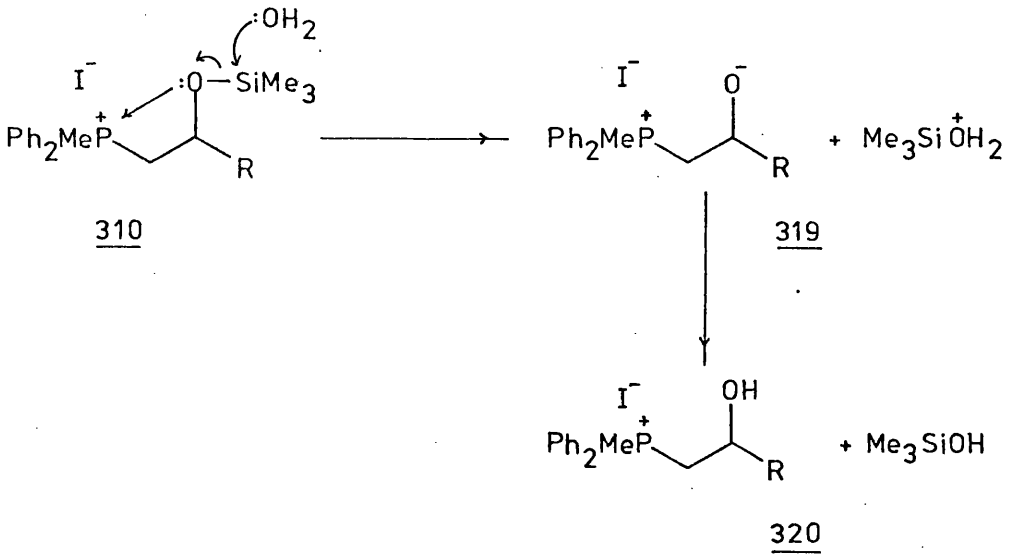


Scheme 62.

The main drawback to this mechanism is that the formation of the alkoxide intermediate 319 depends on the presence of iodide ions and not on traces of water. This means that there will always be some of this alkoxide in the solution and since it is a Wittig intermediate, alkene formation would be expected. Since this does not occur another mechanism must be operating.

Intramolecular electrophilic catalysis is possible in these systems. If the silyl ether-oxygen atom coordinates to the phosphorus atom, attack of water on silicon would be enhanced,

(scheme 63). A Wittig intermediate is also formed in this mechanism but it is always formed in the presence of an acid



Scheme 63.

so the alkoxide would be protonated before alkene formation could occur.

Some evidence to show that iodide ions do not generally catalyse the hydrolysis of silyl ethers was obtained by carrying out an experiment involving the hydrolysis of 1-trimethylsiloxybutane. Three solutions of 0.5g of this silyl ether, in wet acetone were prepared. One solution was kept as a control and 0.1 and 1.0 molar equivalents of methyltriphenylphosphonium iodide were added to the remaining solutions respectively. After three hours gas chromatography showed that no hydrolysis had occurred in any of the solutions and after fortyeight hours each solution contained a very small amount of butan-1-ol. This experiment suggests that phosphonium iodides on their own do not catalyse the hydrolysis of silyl ethers and that an intramolecular electrophilic catalysis probably occurs in phosphonium salt 310.

CHAPTER 7. The Preparation of Heterocyclic Compounds.

Diethyl azodicarboxylate (D.A.D., also called diethyl azodiformate), in conjunction with phosphines, has been widely used as a condensing reagent in the formation of esters[194-199], amides[194,200] and phosphate esters[194,201] and in the alkylation of activated methylene groups.[202] The reaction is usually highly selective, e.g. in the esterification of sugars[195] or steroids[199] the reaction occurs at specific hydroxyl groups. The reaction conditions are usually very mild (e.g. in ether or benzene at room temperature for twelve hours), so this reagent has been used in the chemistry of glycerids[197], nucleosides[200-202], nucleotides[201], steroids[199] and sugars.[195,200]

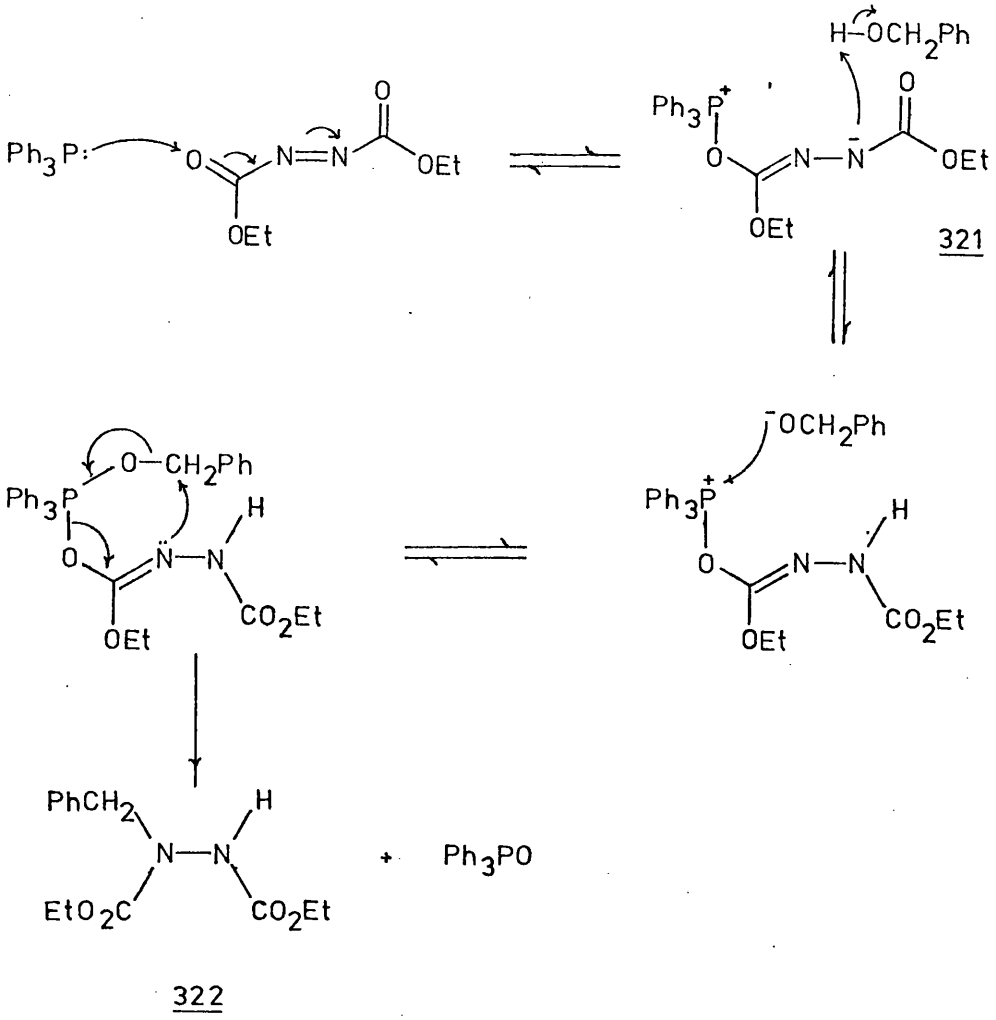
The overall reaction for the condensation of, e.g. a carboxylic acid with an alcohol, is shown in scheme 64. The elements

$$RCO_2H + HOR^1 + (EtO_2CN{:})_2 + Ph_3P \longrightarrow RCO_2R^1 + (EtO_2CNH\cdot)_2 + Ph_3PO$$

Scheme 64.

of water are removed from the acid and the alcohol by the D.A.D.-phosphine mixture, forming a phosphine oxide and diethyl hydrazodicarboxylate. Triphenylphosphine is usually used in this reaction.

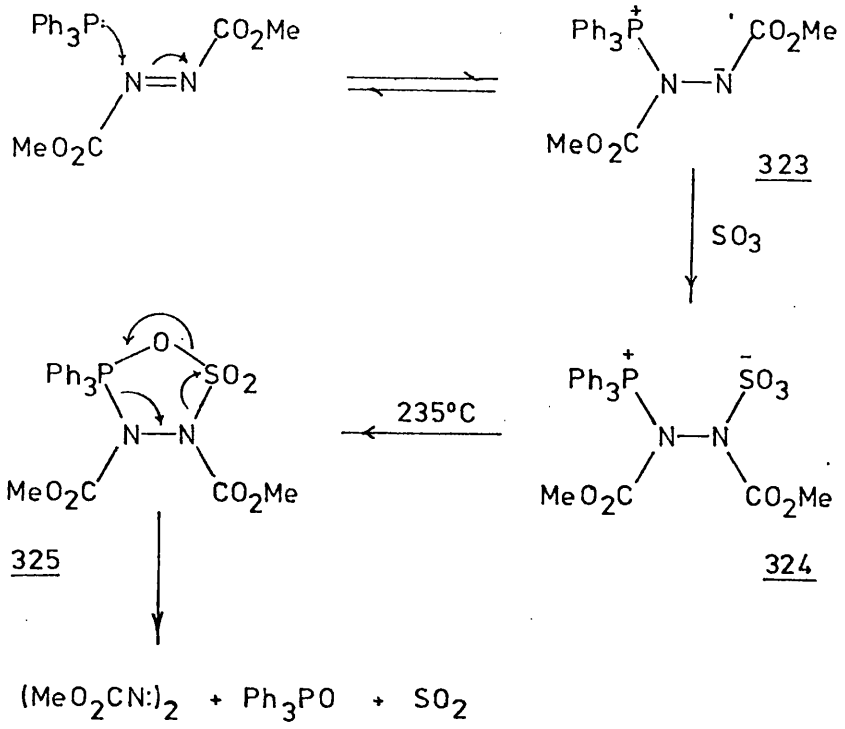
The mechanism of this reaction is in dispute. Early workers[203-205] thought that the initial attack of the phosphine was on the carbonyl-oxygen atom of D.A.D. forming a dipolar species 321, which could be trapped with, e.g. benzyl alcohol[205] forming the substituted hydrazo compound 322.



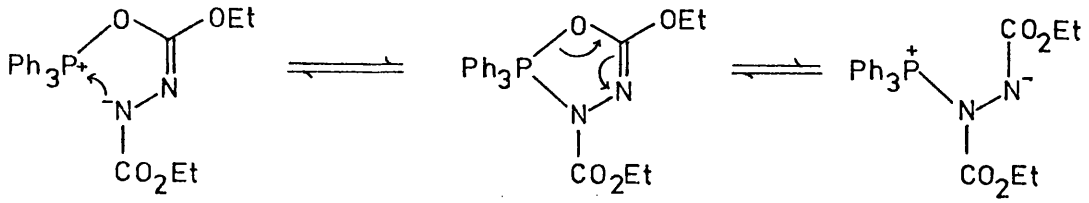
322

More recent work with dimethyl azodicarboxylate[206] suggests that the phosphorus initially attacks a nitrogen atom forming an intermediate dipolar species 323, which can be trapped with sulphur trioxide forming a stable zwitterion 324. This decomposes above 235°C reforming dimethyl azodicarboxylate and liberating sulphur dioxide and a phosphine oxide. The zwitterion 324 has a ^{31}Pn.m.r. chemical shift of -53 p.p.m. showing that it does not exist as the cyclic phosphorane 325.

The overall result of each of these two mechanisms is the same and it is difficult to distinguish between them but since stable adducts such as 324 have been prepared, intermediates such as 323 must be involved in the reaction but these can be formed either by direct attack on the nitrogen atom or by intial attack

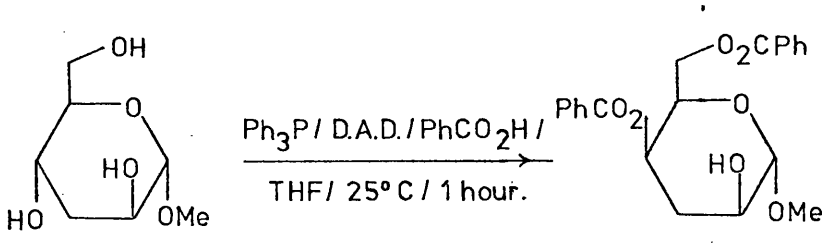


on the carbonyl-oxygen followed by a rearrangement via an intermediate phosphorane, 321a.



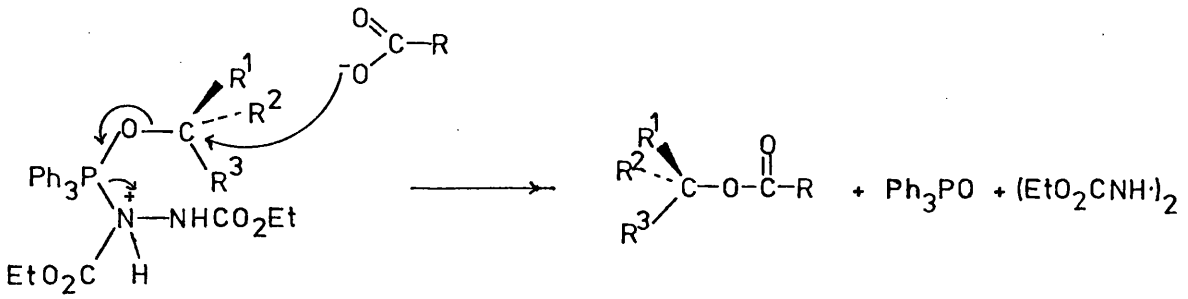
321 321a

Condensation reactions always go with complete inversion of configuration at the alcohol[195,197-200] showing that an S_N2 reaction occurs at the alcohol. This is demonstrated by the esterification of glucoside 326, with complete inversion of configuration in the major product 327. This also demonstrates the specificity of the reaction since the 3-hydroxyl group is not esterified in this reaction. The S_N2 reaction probably occurs as shown in scheme 65.



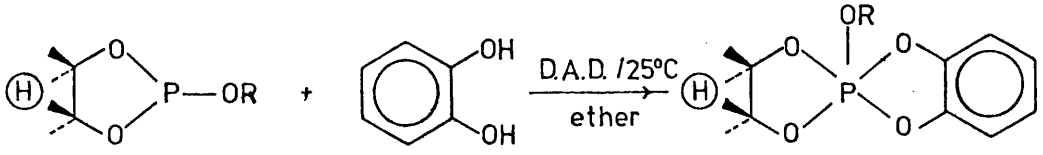
326 327

Bone and Trippett[48,107] have adapted this reaction to the synthesis of spirophosphoranes by treating cyclic trivalent



Scheme 65.

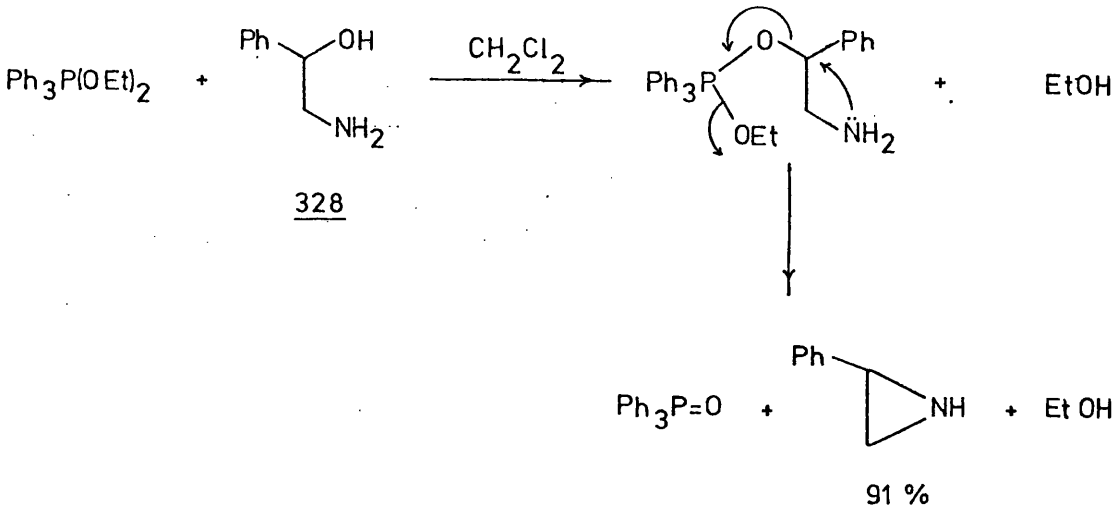
phosphorus compounds with diols in the presence of D.A.D. The hydrazo compound which is produced in this reaction is only slightly soluble in ether at room temperature and facilitates the isolation of the phosphoranes (scheme 66).



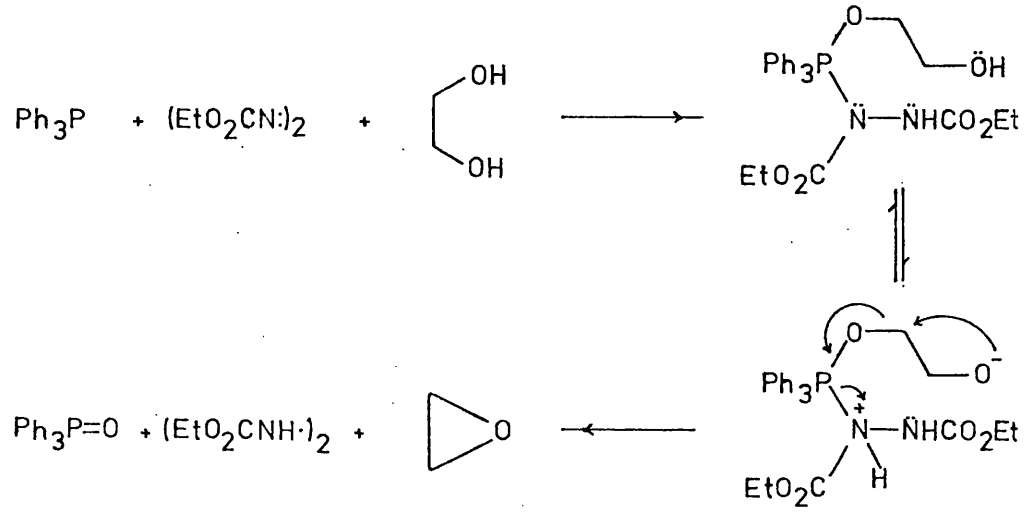
R = Ph or Me.

Scheme 66.

This reaction has now been applied to the synthesis of heterocyclic compounds from diols and related compounds, via unstable triphenylphosphoranes. Denney[75,76] has investigated the formation of heterocyclic compounds rather than cyclic phosphoranes, when diethoxytriphenylphosphorane is treated with diols or related compounds, e.g. 328.



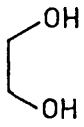
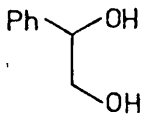
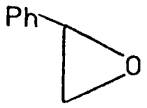
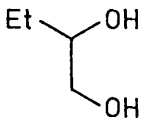
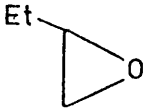
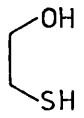
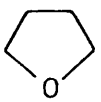
The proposed mechanism for the formation of heterocyclic compounds from diols using triphenylphosphine and D.A.D. is shown in scheme 67. The reaction was usually carried out in ether at



Scheme 67.

room temperature but changing the solvent to benzene, dichloromethane or chloroform, had little effect on the reaction. Trisdimethylaminophosphine was also used with D.A.D. to carry out this reaction and in some cases the yield of the heterocyclic compound was increased, and in other cases the yield was decreased. The results are summarised in table 4.

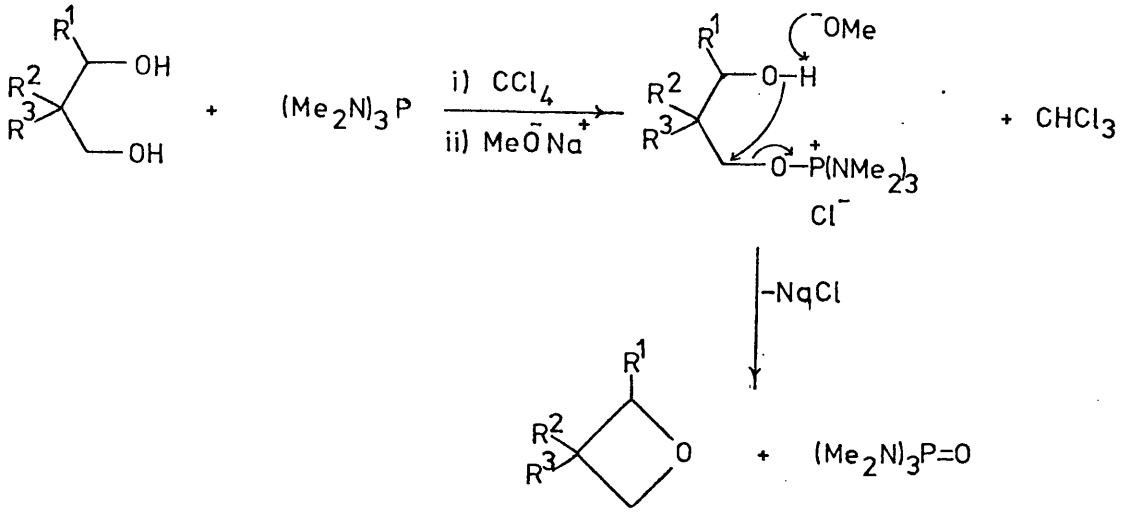
TABLE 4. Table of Heterocyclic Compounds Prepared from Diols and Related Compounds by using Diethyl azodicarboxylate and Phosphines.

Diol	Product	Yield with Ph_3P	Yield with $(Me_2N)_3P$
		High Yields*	-
		73%	Failed
		90%	-
		54%	80%
$HO(CH_2)_4OH$		55%	29%

*Acetaldehyde was also produced in this reaction.

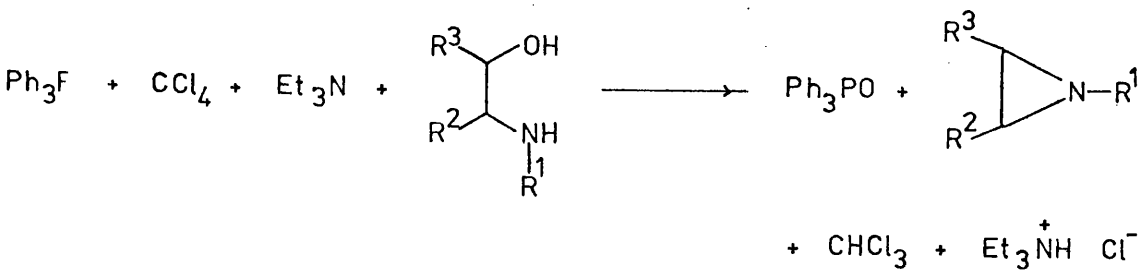
This reaction failed to make four-membered ring heterocyclic compounds from 1,3-diols or 3-aminopropanol, it failed to make

aziridines from 2-aminoethanols and it failed to prepare bicyclic compounds. These compounds can, however, be prepared from diols etc. using organophosphorus condensing reagents, e.g. Castro[207] has prepared oxetans in high yields from various 1,3-diols by treating them with trisdimethylaminophosphine in the presence of CCl_4 (scheme 68).



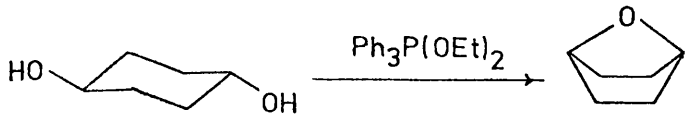
Scheme 68.

Aziridines have been prepared from 2-aminoalcohols, in high yields, by Denney's exchange route[75,76] and Appel[208] has also carried out this reaction by using triphenylphosphine in the presence of triethylamine and CCl_4 as a condensing reagent (scheme 69).



Scheme 69.

Denney's exchange route prepared tetramethylethylene oxide in high yields from pinacol and 7-oxabicyclo [2,2,1]heptane (329) in high yields from trans-cyclohexane-1,4-diol but the D.A.D. reaction failed to prepare either of these heterocyclic compounds. A possible explanation for these failures is that the D.A.D.-phosphine



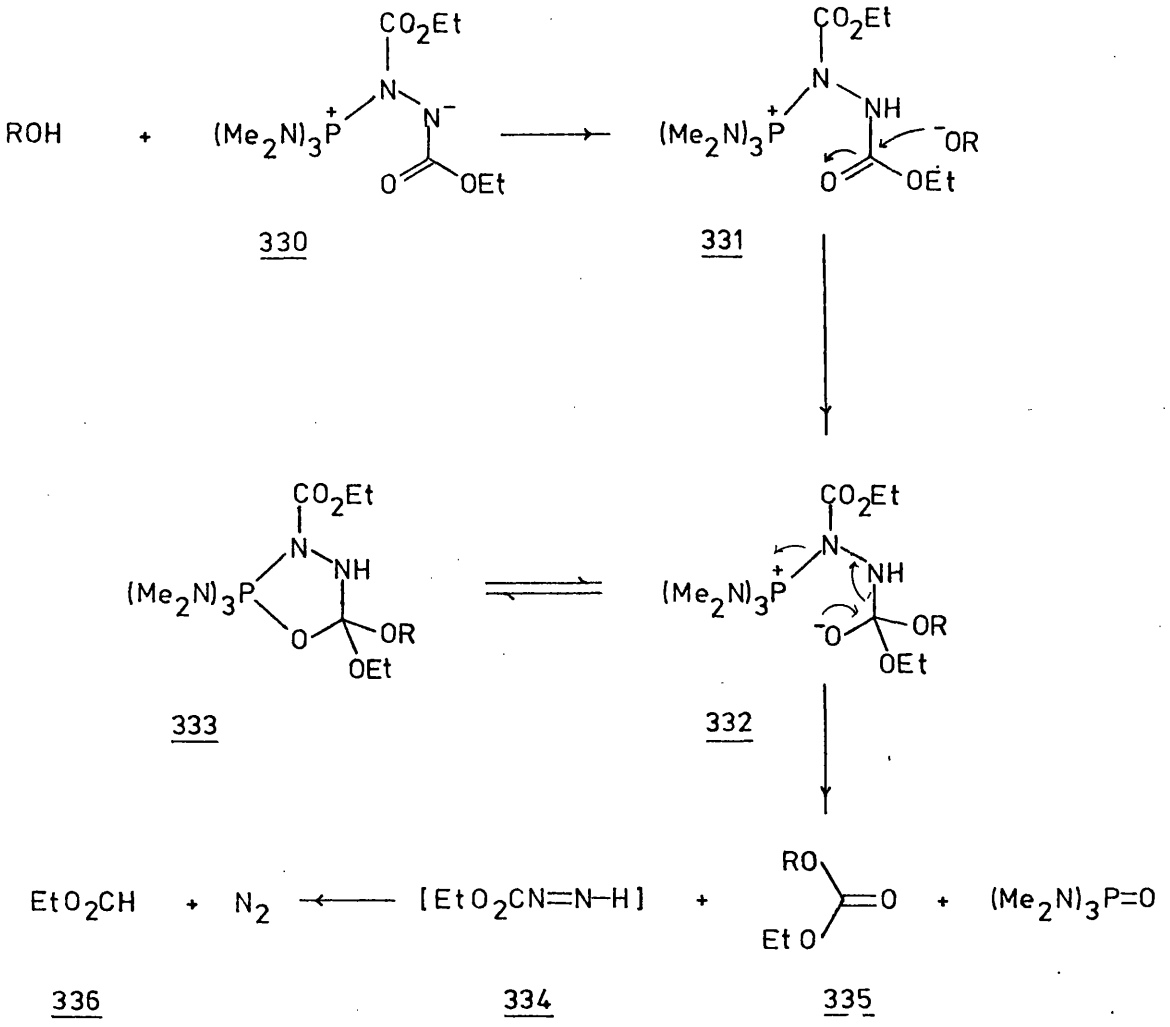
329 80 %

intermediate is very bulky and also both pinacol and cyclohexane-1,4-diol are very bulky and there is possibly some steric hindrance to the reaction. This explanation seems a little unlikely, however, because Bone[48,107] has added pinacol to a cyclic phosphite in high yields by using D.A.D.

The general impression that this investigation gives is that the synthesis of heterocyclic compounds from diols by using D.A.D. and phosphines is unpredictable and not generally applicable. Since there are other, less complicated reagents that do the same job, this reaction is only of academic interest.

The reaction of D.A.D. with alcohols in the presence of trisdimethylaminophosphine takes an unusual course, producing nitrogen, carbonates (335), and ethyl formate (336).[209] The phosphine can be recovered unchanged in this reaction and only 0.25 molar equivalents are required to take the reaction to completion.

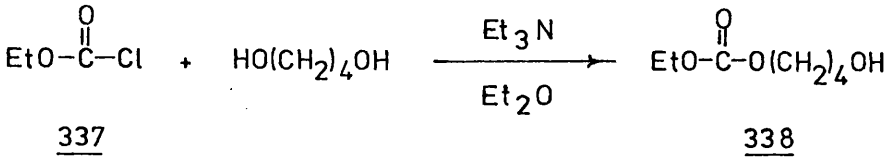
This is thought to occur because the positive phosphorus atom in intermediate 330, is surrounded by four nitrogen atoms which tend to stabilise the positive charge and decrease the chance of the alkoxide ion forming a phosphorane intermediate by attacking phosphorus. The positive charge on phosphorus can be partially reduced by interacting with the carbonyl-oxygen atom. This will make the carbonyl group



more electrophilic thus making the alkoxide ion more likely to attack the carbonyl group, rather than the phosphorus atom, forming intermediate 332. This can now ring-close forming a cyclic phosphorane (333) but it is more likely to remain in the ring-opened form and decompose to the phosphine, carbonate 335 and ethyl azoformate 334, which will spontaneously decompose to ethyl formate and nitrogen.

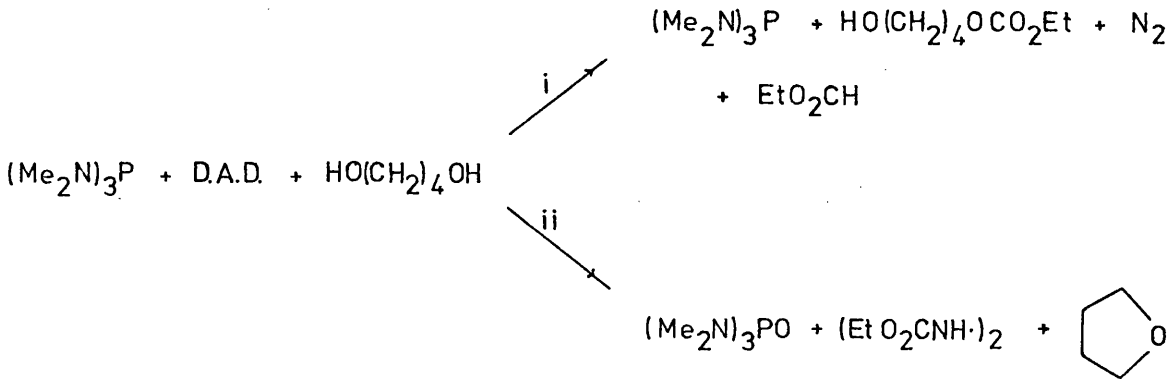
In the light of this work, the preparation of tetrahydrofuran from butane-1,4-diol by using D.A.D. and trisdimethylaminophosphine, was reinvestigated. Equimolar amounts of these reagents were mixed in ether at $0^{o}C$ and after thirty minutes the solvent was removed under vacuum and trapped. Gas chromatography of the solvent showed the presence of T.H.F. and small quantities of other volatile

materials. The ^{1}Hn.m.r. of the residue showed three doublets due to P-NMe_2 groups which had ^{31}P(INDOR) n.m.r. chemical shifts corresponding to the phosphine oxide (-41.3 p.p.m.) the phosphine (-117 p.p.m.) and another compound (-41.7 p.p.m.) which could have been a phosphonium intermediate such as 330 or 331. Thin layer chromatography on basic alumina showed the presence of 4-hydroxybutyl ethyl carbonate (338) which was identical with an authentic sample of this compound prepared by the reaction between ethyl chloroformate (337) and butane-1,4-diol in the presence of triethylamine.



337 338

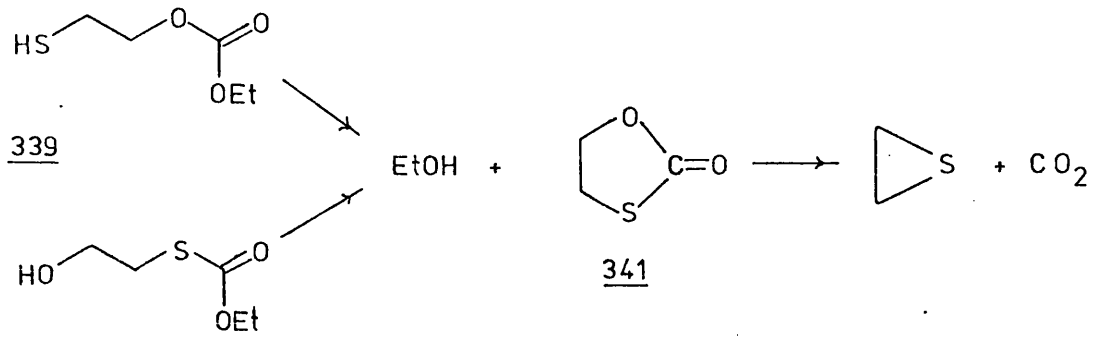
This experiment suggests that part of this reaction goes via route i, (scheme 70) and the other part goes via route ii. This could account for the low yield of T.H.F. in this reaction (see table 4)



Scheme 70.

but it does not explain the high yield of ethylene sulphide which is formed in the reaction of 2-mercaptoethanol with D.A.D. and trisdimethylaminophosphine. One possibility is that a carbonate (339) or more likely a thiocarbonate (340), because the sulphur atom will be more nucleophilic than the oxygen atom of 2-mercaptoethanol,

is formed which subsequently decomposes to ethylene sulphide, ethanol and carbon dioxide.



339

340

341

Both carbonates 339 and 340 are known compounds and they very easily eliminate ethanol forming 1,3-oxathiolan-2-one (341) which, in the presence of small amounts of bases, decomposes to ethylene sulphide and carbon dioxide.[210] This proposed mechanism does not, however, rule out the possibility that the reaction occurs by the normal route (scheme 67). Before any firm conclusions can be drawn for this reaction the reaction mixture must be analysed. The presence of diethyl hydrazodicarboxylate and trisdimethylaminophosphine oxide will show that the normal mechanism is operating whereas the presence of ethanol and ethyl formate will show that carbonates are formed as intermediates. It is also possible that both mechanisms are in competition as in the case of butane-1,4-diol.

EXPERIMENTAL

INSTRUMENTATION.

Infra-red spectra were recorded on Perkin Elmer 237 or 257 spectrometers as nujol mulls, except where otherwise stated. Mass spectra were determined with an A.E.I. MS9 or a V.G. Micromass 16B instrument; in each case the molecular ion is given first, unless otherwise stated, followed by peaks of structural significance. ^{1}Hn.m.r. spectra were recorded on a Varian T-60 spectrometer, in deuterochloroform with tetramethylsilane as internal standard, unless otherwise stated. Where possible ^{31}Pn.m.r. chemical shifts were determined by heteronuclear INDOR spectroscopy using an HD-60 heteronuclear decoupler (N.M.R. Specialties) linked to a Varian T-60 spectrometer. Other ^{31}Pn.m.r., ^{19}Fn.m.r., variable temperature ^{19}F and ^{1}Hn.m.r., and 100 MHz. ^{1}Hn.m.r. spectra were recorded on a Jeol JNM-PS-100 spectrometer. Fourier-Transform ^{31}Pn.m.r. spectra were recorded on a Jeol JNM-FX-60 spectrometer. ^{31}Pn.m.r. chemical shifts are quoted relative to external 85% phosphoric acid. ^{19}Fn.m.r. chemical shifts are quoted relative to external α,α,α-trifluorotoluene. Melting points were obtained using a Kofler heating stage and are uncorrected. Gas chromatography was carried out using a Pye Unicam 104 chromatograph or 105 preparative chromatograph using nitrogen as the carrier gas and flame ionisation detectors.

GENERAL DETAILS

All operations involving air or moisture sensitive compounds were carried out under an atmosphere of dry, oxygen-free nitrogen. Koch-Light 'Celite' was used as a filtering aid, and was heated at approximately 100°C for thirty minutes before use. Small scale

distillations or sublimations were carried out using a Kugelrohr and the boiling points, etc. quoted are the oven temperatures at which the distillation occurred.

Diethyl ether and hydrocarbon solvents were dried over sodium wire. Tetrahydrofuran was refluxed over and distilled from lithium aluminium hydride. Methanol and ethanol were refluxed over and distilled from their magnesium alkoxides. Dichloromethane and tetrachloromethane were refluxed over and distilled from calcium hydride. Pyridine and triethylamine were refluxed over and distilled from potassium hydroxide and the dry reagents were stored over potassium hydroxide pellets. Ethyl acetate was purified by stirring it with anhydrous potassium carbonate and fused calcium chloride followed by distillation from anhydrous potassium carbonate.

Unless otherwise stated, 'light petroleum' refers to petroleum spirit boiling range 60-80°C.

The experiments are numbered in the order in which they are written up. Phosphoranes appear first, followed by other phosphorus compounds. Non-phosphorus compounds appear at the end. As far as possible the experiment numbers have been cross-referenced with the text number for the compound.

Text No.	Expt. No.	Text No.	Expt. No.	Text No.	Expt. No.
115	1a,2i	138	52,55,56	150	13
116	1b,2f	139	53,54	151	1l,51
117	1g,2g	142	72	153	1k,2j
119	1c	143	9,60	154	51
120	1h	144	60	155	1q
121	1i	146	1j,9	157	1q
126	1d	147	10	158	1n
127	1e,52,54	148	11	159	1o
128	1f,53,55	149	12	160	1p

Text No.	Expt. No.	Text No.	Expt. No.	Text No.	Expt. No.
163	1m	201	2d,4	284	48c
165	47	204	2e	285	29,48c
167	70	211	37	292	28
169	44	214	24	293	75
170	143	215	22	297	75
171	35,36	216	23	299	5
172	33	217	8b,8c	301	48d
174	2h,49	251	42	302	31,48a
175	49	253	45	303	32,48b
176	49	254	41	304	48a
178	14	255	45	305	48b
179	15	256	46	306	48b
180	2k	257	6,50	307	62,63,64
181	2l	258	50	308	7
188	16,18	270	25,59	309	1r
189	17	272	59	310	65,66,67
190	2a,8a,8c	273	38	312	68
196	3	279	27	320	65,66,67
199	2c	280	74	338	81
200	2b	281	30,48c		

1. Preparation of Phosphoranes by using N-Chlorodi-isopropylamine.

General directions.

A solution of the diol or catechol (5 mmol.) in 10 cm^3 of ether was added to a solution of the trivalent phosphorus compound (5 mmol.) in 25 cm^3 of ether at -78°C. N-Chlorodi-isopropylamine (0.6 g) in 10 cm^3 of ether was then added slowly and the mixture was stirred at -78°C for 30 minutes after which it was set aside, stirring, overnight at room temperature. Filtration, followed by evaporation gave the crude phosphorane which was crystallised from or extracted with light petroleum.

The following phosphoranes were prepared by this method.

1a. P,P,P-Triphenyl-1,3,2-benzodioxaphosphole (115), was prepared from triphenylphosphine and catechol in 62% yield, m.p. 75°C (decomp.), ν_{max} (CH_2Cl_2) 3050, 1580, 1470, 1420, 1353 & 823 $cm.^{-1}$, m/e 370, 293, 262 & 278, δ 6.5-6.8(4H, m) & 7.0-7.8(15H, m), $^{31}P(CH_2Cl_2)$ +22.9 p.p.m.

1b. 4,6-Di-t-butyl-P,P,P-triphenyl-1,3,2-benzodioxaphosphole (116), was prepared from triphenylphosphine and 3,5-di-t-butylcatechol in 70% yield, m.p. 146-148°C, ν_{max} 1405, 1245, 1110, 1080, 960 & 840 $cm.^{-1}$, m/e 482, 467, 425, 405, 278, 262 & 220, δ 1.13(9H,s),1.15(9H, s), 6.55-6.7(2H, m) & 7.0-7.6(15H, m), $^{31}P(CH_2Cl_2)$ +21.9 p.p.m. Found C, 79.7; H, 7.4; P, 6.3%. $C_{32}H_{35}O_2P$ requires C, 79.65; H, 7.3; P, 6.4%.

1c. P-Methoxy-P,P-diphenyl-1,3,2-benzodioxaphosphole (119), was prepared from methyl diphenylphosphinite and catechol in 84% yield, m.p. 84-85°C, ν_{max} ($CDCl_3$) 3060, 2980, 2940, 2840, 1490, 1440, 1360, 1280, 1255, 1110, 1040(b) & 840 $cm.^{-1}$, m/e 324, 293, 247, 232 & 216, δ 3.3(3H, d, J 11 Hz), 6.6-6.8(4H, m) & 7.1-8.0(10H,m), $^{31}P(CDCl_3)$ + 19 p.p.m. Found C, 70.35; H, 5.4; P, 9.3%. $C_{19}H_{17}O_3P$ requires C 70.4; H, 5.3; P, 9.55%.

1d. P,P-Dimethoxy-P-phenyl-1,3,2-benzodioxaphosphole (126), was prepared as an oil from dimethyl phenylphosphonite and catechol in 90% yield. ν_{max}(Film) 2970, 1600, 1495, 1445, 1260(b), 1135, 1040(b) & 753 cm^{-1}., m/e no molecular ion (278), 232, 155 & 110, δ 3.79(6H, d, J 12 Hz) & 7.0-8.35 (10H, m), $^{31}P(CDCl_3)$ + 29.5 p.p.m.

1e. P,P,P-Trimethoxy-1,3,2-benzodioxaphosphole (127), was prepared as an impure oil from trimethyl phosphite and catechol in 24% yield, $b_{0.3}$ 91°C. ν_{max}(Film) 2980, 2930, 1495, 1260 & 1050 (b) cm^{-1}., δ(CCl_4/TMS) 3.86 (9H, d, J 14Hz) & 7.14(4H, s), $^{31}P(CCl_4)$ + 51.6 p.p.m.

1f. P,P,P-Triethoxy-1,3,2-benzodioxaphosphole (128),[79] was prepared as an impure oil from triethyl phosphite and catechol in 37% yield, $b_{0.5}$ 110°C. ν_{max} 2980, 2940, 1500, 1270 & 1060(b) cm^{-1}., δ(CCl_4/TMS) 1.36(9H, dt, J 7 Hz & 1 Hz), 4.25(6H, quintet, J 7Hz) & 7.17(4H, s), $^{31}P(CCl_4)$ + 49.6 p.p.m.

1g. P,P,P-Triphenyl-4,4,5,5-tetrakistrifluoromethyl-1,3,2-dioxaphospholan (117), was prepared from triphenylphosphine and perfluoropinacol in 81% yield, m.p. 103°C(decomp.). The spectral data and melting point of this compound were consistent with the data given by Ramirez et al.[22,161]

1h. P-Methoxy-P,P-diphenyl-4,4,5,5-tetrakistrifluoromethyl-1,3,2--dioxaphospholan (120), was prepared from methyl diphenylphosphinite and perfluoropinacol in 93% yield, m.p. 75-76°C. ν_{max} 3060, 1440, 1245(b), 1215(b), 1120, 1100, 1055, 1045, 965, 880, 810 & 765 cm^{-1}., m/e 548, 529, 517, 471, 363, 232, 216, 166, 147 & 77, δ 3.45(3H, d, J, 12 Hz) & 7.0-8.0(10H, m), $^{31}P(CDCl_3)$ + 18 p.p.m., $^{19}F(CH_2Cl_3)$ + 3.6 p.p.m.. Found C, 41.4; H, 2.4; P, 5.7%. $C_{19}H_{13}F_{12}O_3P$ requires C, 41.6; H, 2.4; P, 5.65%.

1i. P-Methoxy-P,P-diphenyl-4,4,5,5-tetramethyl-1,3,2-dioxaphospholan (121), was prepared from methyl diphenylphosphinite and pinacol in 79% yield, m.p. 113°C. ν_{max} 3060, 1440, 1380, 1165, 1110, 1100, 1055, 975, 920, 810 & 720 cm^{-1}., m/e no molecular ion (332), 310, 255, 232, 231, 217 & 216, δ 1.11(12H, s), 3.25(3H, d, J 12 Hz) & 7.5-8.5(10H, m), $^{31}P(CDCl_3)$ + 45 p.p.m. The pinacol-methyl group had Δν 14 Hz & Tc -82±2°C in CH_2Cl_2. Found C, 68.6; H, 7.5; P, 9.3%. $C_{19}H_{25}O_3P$ requires C, 68.7; H, 7.6; P, 9.3%. The n.m.r. data for this compound has been reported by Bartlett et al.[83] but it has not previously been isolated.

1j. 2,2,3,3,7,8-Hexamethyl-5-phenyl-1,4-dioxa-5-phospha(5P^{V})spiro[4,4]-non-7-ene (146), was prepared from 3,4-dimethyl-1-phenylphosphol-3-ene (147) and pinacol in 30% yield, m.p. 104-105°C. ν_{max} 3060, 1440, 1390, 1360, 1220, 1160, 1125, 985, 915, 860, 750 & 720 cm^{-1}., m/e 306, 224, 206, 191 & 190, δ 1.0(12H, s), 1.43(6H, s), 2.36(4H, d, J 14 Hz) & 7.26-8.06 (5H, m), $^{31}P(CDCl_3)$ + 17.1 p.p.m. Found C, 70.5; H, 9.0; P, 10.2%. $C_{18}H_{27}O_2P$ requires C, 70.55; H, 8.9; P, 10.1%.

1k. 2,2,3,3-Tetrakistrifluoromethyl-7,8-dimethyl-5-phenyl-1,4-dioxa-5--phospha(5P^{V})spiro[4,4]non-7-ene (153), was prepared from 3,4-dimethyl--1-phenylphosphol-3-ene (147) and perfluoropinacol in 89% yield, $b_{0.2}$ 130°C. ν_{max}(Film) 3060, 2980, 2960, 1440, 1240-1210(b), 1155, 1110, 995, 960, 910, 880 & 740 cm^{-1}., m/e 522, 503, 453, 440, 371, 356, 337 & 190, δ 1.5(6H, s), 2.78(4H, d, J 16 Hz) & 7.26-8.05(5H, m), $^{31}P(CDCl_3)$ -7.8 p.p.m., $^{19}F(CH_2Cl_2)$ + 4.5 p.p.m., Δν 136Hz, Tc-78 ± 2°C. Found C, 41.5; H, 2.9; P, 5.9%. $C_{18}H_{15}O_2F_{12}P$ requires C, 41.4; H, 2.9; P, 5.9%.

1l. 3',4'-Dimethyl-2-phenylspiro[1,3,2-benzodioxaphosphole-2,1'-phosphol--3'-ene] (151), was prepared from 3,4-dimethyl-1-phenylphosphol-3-ene (147) and catechol in 70% yield as monoclinic crystals m.p. 123-124°C, from ethyl acetate-light petroleum. ν_{max} 3060, 1485, 1440, 1355, 1260, 1235

1130, 1110, 1015, 880, 850, 840 & 740 cm^{-1}., m/e 298, 216, 190 & 140, δ 1.63(6H, s), 2.73(2H, d, J 16 Hz), 2.82(2H, d, J 17 Hz), 6.77(4H, s) & 7.26-7.9(5H, m), $^{31}P(CDCl_3)$ -1.1 p.p.m. Found C, 72.4; H, 6.35; P, 10.25%. $C_{18}H_{19}O_2P$ requires C, 72.5; H, 6.4; P, 10.4%.

1m. 2,2,3,3-Tetrakistrifluoromethyl-7,8-dimethyl-5-phenoxy-1,4-dioxa-5-phospha($5P^V$)spiro[4,4]non-7-ene (163), was prepared from 1-phenoxy-3,4-dimethylphosphol-3-ene (150) and perfluoropinacol in 89% yield as very hygroscopic crystals m.p. 57.5 to 58.5°C from petroleum spirit boiling range 40-60°C. ν_{max} 1485, 1300-1200(b), 1110, 1000, 995, 960, 925, 880, 770, 730 & 690 cm^{-1}., m/e 538, 519, 469, 456, 445, 307, 206 & 197. δ 1.73(6H, s), 2.80(4H, d, J 15 Hz) & 6.85-7.5(5H, m), $^{31}P(CDCl_3)$ -18.0 p.p.m., ^{19}F(light petroleum) + 5.1 p.p.m. Found C, 40.15; H, 2.9; P, 5.3%. $C_{18}H_{15}O_3F_{12}P$ requires C, 40.2; H, 2.8; P, 5.75%.

1n. 2-Dimethylamino-3',4'-dimethylspiro[1,3,2-benzodioxaphosphole-2,1'-phosphol-3-ene] (158), was prepared from 1-dimethylamino-3,4-dimethylphosphol-3-ene and catechol in 81% yield. This was a pale brown solid that decomposed to a brown oil at room temperature. $\nu_{max}(CH_2Cl_2)$ 3060, 2980, 2900, 1490, 1350, 1260, 1240, 1210, 1090, 1000, 980 & 830 cm^{-1}., m/e 265, 221, 183 & 139 δ 1.7(6H, s) 2.57(4H, d, J 17 Hz), 2.63(6H, d, J 11 Hz) & 6.8(4H, s), $^{31}P(CDCl_3)$ -14.7 p.p.m.

1o. 2-Dimethylamino-3',4',4-trimethylspiro[1,3,2-benzodioxaphosphole-2,1'-phosphol-3-ene] (159), was prepared from 1-dimethylamino-3,4-dimethylphosphol-3-ene and 3-methylcatechol in 79% yield. This was a pale brown solid that rapidly decomposed to a brown oil at room temperature and slowly decomposed at -40°C. ν_{max} (CH_2Cl_2) 3050, 2980, 2910, 1480, 1465, 1350, 1250(b), 1075, 980, 960 & 860 cm^{-1}., m/e 279, 235, 197 & 153, δ 1.73(6H, s), 2.23(3H, s), 2.58(4H, d, J 18 Hz), 2.63(6H, d, J 11 Hz) &

6.67(3H, s), $^{31}P(CDCl_3)$ -14.5 p.p.m.

1p. 5-Dimethylamino-2,2,3,3-tetrakistrifluoromethyl-7,8-dimethyl-1,4--dioxa-5-phospha ($5P^V$)spiro[4,4]non-7-ene (160), was prepared from 1-dimethylamino-3,4-dimethylphosphol-3-ene and perfluoropinacol in 73% yield, $b_{0.2}$ 110°C, ν_{max}(Film) 2920, 2860, 1450, 1250(b), 1115, 1010, 965, 880, 750 & 710 cm^{-1}., m/e 489, 470, 445, 420, 407, 338, 323, 304, 197 & 157, δ 1.7(6H, s), 2.53(4H, d, J 15 Hz) & 2.67(6H, d, J 11 Hz), $^{31}P(CDCl_3)$ -16.9 p.p.m., ^{19}F(ether-light petroleum) + 6 p.p.m., Δν 76 Hz, Tc 75±3°C. Found C, 33.3; H, 3.0; N, 2.35%, $C_{14}H_{16}O_2F_{12}NP$ requires C, 34.4:, H, 3.3; N, 2.9%.

1q. Attempts to prepare 3,3,8,9-tetramethyl-6-phenyl-1,5-dioxa-6-phospha-($6P^V$)spiro[5,4]dec-8-ene (155), resulted in the isolation of 5,5-dimethyl--P-phenyl-1,3,2-dioxaphosphorinan-2-oxide (157), ν_{max} 3060, 1450, 1230(b), 1150, 1140, 1060, 1010, 970, 750 & 710 cm^{-1}., m/e 226, 159, 143, 141 & 125, δ 0.60(3H, s), 1.36(3H, s), 3.4-4.0(4H, m) & 7.57(5H,s), ^{31}P ($CDCl_3$) -32 p.p.m.

1r. P-[2-Trimethylsiloxyethyl]-P,P-diphenyl-1,3,2-benzodioxaphosphole (309), was prepared as an oil from 2-trimethylsiloxyethyldiphenylphosphine (310), and catechol in 52% yield, ν_{max}(Film) 3060, 2960, 2870, 1615, 1590, 1490, 1440, 1360, 1320, 1250, 1100(b), 1010, 850(b), 790(b) & 700 cm^{-1}., δ -0.06(9H, s), 2.76(2H, dt, J_{PH} 6 Hz, J_{HH} 8 Hz), 3.83(2H, dt, J_{PH} 13 Hz, J_{HH} 8 Hz), 6.55-6.8(4H, m) & 7.1-7.96(10H, m), $^{31}P(CDCl_3)$ + 24.7 p.p.m.

2. Preparation of Phosphoranes by using Trifluoromethanesulphonic Anhydride (167), General directions.

Trifluoromethanesulphonic anhydride (5 mmol) in 5 cm^3 of dichloromethane was added slowly to the phosphine oxide (5 mmol) in

10 cm^3 of dichloromethane at 0^oC. This was maintained at 0^oC for three hours in the case of phosphetan oxides and fifteen minutes for phospholene oxides or acyclic phosphine oxides. The mixture was then cooled to -78^oC and a mixture of the diol or catechol (5 mmol) and di-isopropylamine (10 mmol) in 20 cm^3 of ether was added slowly with rapid stirring. After thirty minutes this was allowed to warm up to room temperature and a further 15 cm^3 of ether was added to precipitate the di-isopropylammonium trifluoromethanesulphonate. Filtration, followed by evaporation, gave the crude phosphorane which was extracted with or crystallised from light petroleum.

The following phosphoranes were prepared by this method.

2a. P-r-phenyl-2',2'-trans-3',4',4'-pentamethyl-1,3,2-benzodioxaphospholen-2-spiro-1'-phosphetan (190), was prepared in two ways;

i) From 2,2-trans-3,4,4-pentamethyl-r-1-phenylphosphetan-1-oxide and catechol in 77% yield, m.p. and mixed m.p. 124-125°C.

ii) From 2,2-cis-3,4,4-pentamethyl-r-1-phenylphosphetan-1-oxide and catechol in 61% yield, m.p. and mixed m.p. 120-123°C.

In each case the phosphoranes were identical with samples prepared by the N-chlorodi-isopropylamine method.[109] ν_{max} 3050, 2910, 2850, 1485, 1460, 1250, 1105, 1010, 820 & 730 cm^{-1}., m/e 328, 258, 251, 235, 221, 216, 168, 166, 139, 119, 110 & 108, δ 0.85(3H, dd, J 2 Hz & 7 Hz), 1.26 (6H, d, J 19 Hz), 1.44(6H, d, J 16 Hz), 1.9(1H, m), 6.62(4H, s) & 7.14-7.86 (5H, m), $^{31}P(CDCl_3)$ + 1 p.p.m.

2b. P-r-phenyl-2',2'-trans-3',4',4'-pentamethyl-4,4,5,5-tetrakistrifluoromethyl-1,3,2-dioxaphospholan-2-spiro-1'-phosphetan (200),[58] was prepared from 2,2-trans-3,4,4-pentamethyl-r-1-phenylphosphetan-1-oxide and perfluoropinacol in 36% yield, m.p. 94-95°C, ν_{max} 1435, 1280-1200(b), 1140, 1100, 950, 880, 765, 745 & 705 cm^{-1}., δ 0.72(3H, dd, J 1.5 Hz & 7 Hz), 1.35(6H, d, J 19 Hz), 1.4(6H, d, J 17 Hz) & 7.17-8.17(5H, m),

$^{31}P(CDCl_3)$ -3.3 p.p.m.

2c. P-r-Phenyl-2',2'-trans-3',4',4',4,4,5,5-nonamethyl-1,3,2-dioxaphospholan-2-spiro-1'-phosphetan (199), was prepared as a white crystalline solid that was unstable at room temperature, from 2,2-trans-3,4,4-pentamethyl-r-1-phenylphosphetan-1-oxide and pinacol in 34% yield, ν_{max} 2910, 2850, 1460, 1385, 1375, 1365, 1155, 1105(sharp), 970, 910 & 700 cm^{-1}., m/e no molecular ion (336), 321, 266, 251, 236, 221 & 166, δ 0.6-1.8[28H structure including 0.65(s), 1.55(d, J 11 Hz), 1.16(s) & 1.38(d, J 9 Hz)] & 7.2-8.1 (5H, m), $^{31}P(CDCl_3)$ +25 p.p.m.

2d. 5,6-Dimethoxy-P-r-phenyl-2',2'-trans-3',4',4'-pentamethyl-1,3,2-benzodioxaphosphole-2-spiro-1'-phosphetan (201), was prepared from 2,2-trans-3,4,4-pentamethyl-r-1-phenylphosphetan-1-oxide and 4,5-dimethoxycatechol in 63% yield, m.p. 93.5-94.5°C., ν_{max} 2910, 2850, 1490, 1370, 1220, 1195, 1165 & 885 cm^{-1}., m/e 338, 318, 303, 276, 261, 236, 221 & 198, δ 0.8-1.13(4H, dd, J 7 Hz & 2 Hz), 1.22(6H, d, J 14 Hz), 1.48(6H, d, J 11 Hz), 3.69(6H, s), 6.49(2H, s) & 7.2-7.8 (5H, m). (The 3'-H was not visible but contributed to the total integral of the methyl region of the spectrum). $^{31}P(CDCl_3)$ -0.1 p.p.m. Found C, 68.0; H, 7.5; P, 8.0%; $C_{22}H_{29}O_4P$ requires C, 68.0; H, 7.5; P, 8.0%.

2e. P-r-Benzyl-2',2'-trans-3',4',4'-pentamethyl-1,3,2-benzodioxaphosphole-2-spiro-1'-phosphetan (204), was prepared from r-1-benzyl-2,2-trans-3,4,4-pentamethylphosphetan-1-oxide and catechol in 51% yield, m.p. 139-141°C. The spectral data and melting point of this compound were identical with a sample prepared by the N-chlorodi-isopropylamine method.[109] ν_{max} 3060, 1460, 1360, 1240, 1100, 890, 865, 815, 765, 730 & 680 cm^{-1}., δ 0.82(3H, dd, J 2 Hz & 7 Hz), 1.30(6H, d, J 16 Hz), 1.35(6H, d, J 18 Hz), 3.28(2H, d, J 7 Hz), 6.34(4H, s) & 6.82(5H, s), $^{31}P(CDCl_3)$ + 3 p.p.m.

2f. 4,6-Di-t-butyl-P,P,P-triphenyl-1,3,2-benzodioxaphosphole (116), was prepared from triphenylphosphine oxide and 3,5-di-t-butylcatechol in 92% yield, m.p. 146-147°C. This compound was identified by comparison of its spectral data with a sample prepared by the N-chlorodi-isopropylamine method,[109] (see experiment 1b).

2g. P,P,P-Triphenyl-4,4,5,5-tetrakistrifluoromethyl-1,3,2-dioxaphospholan (117), was prepared from triphenylphosphine oxide and perfluoropinacol in 71% yield, m.p. 103(decomp.). The spectral data and melting point of this compound were consistent with the data given by Ramirez et al.[22,161]

2h. P-Methyl-P,P-diphenyl-4,4,5,5,-tetrakistrifluoromethyl-1,3,2--dioxaphospholan (174), was prepared from methyldiphenylphosphine oxide and perfluoropinacol in 51% yield, m.p. 95.5°C (decomp.), ν_{max} 3060, 1480, 1440, 1435, 1350-1200(b), 1160(b), 1110, 1000, 960, 890, 810 & 750 cm^{-1}., m/e 532, 517, 513, 463, 455, 317, 200 & 185, δ 2.5(3H, d, J 11 Hz) & 7.35-7.95(10H, m), $^{31}P(CDCl_3)$ + 11.4 p.p.m. Found C, 43.1; H, 2.4; P, 6.05%, $C_{19}H_{13}F_{12}O_2P$ requires C, 42.9; H, 2.5; P, 5.8%.

2i. 3',4'-Dimethyl-2-phenylspiro[1,3,2-benzodioxaphosphole-2,1'-phosphol--3'-ene] (151), was prepared from 3,4-dimethyl-1-phenylphosphol-3-ene-1--oxide (143) and catechol in 80% yield, m.p. 122-123°C. This compound was identified by comparison of its spectral data with a sample prepared by the N-chlorodi-isopropylamine method (see experiment 1l).

2j. 2,2,3,3-Tetrakistrifluoromethyl-7,8-dimethyl-5-phenyl-1,4-dioxa-5--phospha($5P^V$) spiro[4,4]non-7-ene (153), was prepared from 3,4-dimethyl--1-phenylphosphol-3-ene-1-oxide (143) and perfluoropinacol in 85% yield. This compound was identified by comparison of its spectral data with a sample prepared by the N-chlorodi-isopropylamine method, (see experiment 1k).

2k. 2,2,3,3-Tetrakistrifluoromethyl-5,7,8-trimethyl-1,4-dioxa-5-phospha-($5P^V$)spiro[4,4]non-7-ene (180), was prepared from 1,3,4-trimethylphosphol-3-ene-1-oxide (178) and perfluoropinacol in 69% yield, $b_{0.2}$ 105°C, m.p. 44-45°C, ν_{max} 1440, 1400, 1320-1150(b), 1110, 1070, 980, 960, 910, 875, 740 & 710 cm^{-1}., m/e 460, 441, 416, 319, 294, 277 & 129, δ 1.7(6H, s), 1.74(3H, d, J 11 Hz), 2.33(2H, d, J 14 Hz) & 2.6(2H, d, J 19 Hz), ^{31}P ($CDCl_3$) -14.0 p.p.m., ^{19}F(CH_2Cl_2) + 4.8 p.p.m., Δν 22Hz, Tc(ether-light petroleum) -125±1°C. Found C, 33.9; H, 2.9; P, 7.0%, $C_{13}H_{13}F_{12}O_2P$ requires C, 33.9; H, 2.9; P, 6.7%.

2l. 2,2,3,3-Tetrakistrifluoromethyl-5-ethyl-7,8-dimethyl-1,4-dioxa-5-phospha($5P^V$)spiro[4,4]non-7-ene (181), was prepared as an oil from 1-ethyl-3,4-dimethylphosphol-3-ene-1-oxide (179) and perfluoropinacol in 66% yield, $b_{0.3}$ 110-115°C, ν_{max}(Film) 2980, 2950, 2860, 1445, 1405, 1385, 1300-1200(b), 1160, 1110, 990, 880, 745 & 710 cm^{-1}., m/e 474, 455, 445, 405, 392, 308, 289, 197, 157 & 142, δ 0.97(3H, dt, J_{PH} 22 Hz, J_{HH} 8 Hz), 1.53(6H, s) & 1.6-3.0(6H, m), ^{31}P($CDCl_3$) -19.1 p.p.m., ^{19}F(ether-light petroleum) + 5.4 p.p.m., No Tc above -148°C in liquid propene-ether. Found C, 35.6; H, 3.4; P, 6.75%, $C_{14}H_{15}F_{12}O_2P$ requires C, 35.5; H, 3.2; P, 6.5%.

2m. 4,6-Di-t-butyl-P-methyl-P,P-diphenyl-1,3,2-benzodioxaphosphole. When methyldiphenylphosphine oxide and 3,5-di-t-butylcatechol were used in this phosphorane synthesis an unstable oil was produced which had ^{31}P($CDCl_3$) + 24 p.p.m.

3. Attempted preparation of Phosphoranes by using trimethylsilyl trifluoromethanesulphonate (195).

Trimethylsilyl trifluoromethanesulphonate (5 mmol) in 5 cm^3 of dichloromethane was added to 2,2-trans-3,4,4-pentamethyl-r-1-phenylphosphetan-1-oxide (5 mmol) in 5 cm^3 of dichloromethane at 0°C. After two

hours the solution had $\delta(CH_2Cl_2)$ 0.33(9H, s), 1.13(3H, dd, J 7 Hz & 2 Hz), 1.28(6H, d, J 22 Hz), 1.33(6H, d, J 19 Hz) & 2.48(1H, quintet, J 6·5 Hz), $^{31}P(CH_2Cl_2)$ -81 p.p.m.

This mixture was cooled to -78°C and a solution of catechol (5 mmol) and di-isopropylamine (5 mmol) in 10 cm^3 of ether was added with rapid stirring. After 30 minutes the mixture was allowed to warm up to room temperature and a further 15 cm^3 of ether was added to precipitate the di-isopropylammonium trifluoromethanesulphonate. Filtration, followed by evaporation, gave a crude mixture which contained the starting phosphetan oxide. This was identified by comparison of the n.m.r. data with the n.m.r. data of an authentic sample, (see experiment 16). No phosphoranes were prepared.

A similar reaction was carried out with 2,2-cis-3,4,4-pentamethyl--r-1-phenylphosphetan-1-oxide. The intermediate had δ (CH_2Cl_2) 0.33(9H, s), 1.18(3H, dd, J 6.5 Hz & 2 Hz), 1.45(6H, d, J 21.5 Hz), 1.53(6H, d, J 20 Hz) & 2.2-2.85(1H, m). Treatment of this solution with catechol and di-isopropylamine at -78°C gave a mixture of compounds containing the starting phosphetan oxide which was identified by comparison of the n.m.r. data with that of an authentic sample, (see experiment 17).

4. Preparation of 5,6-dimethoxy-P-r-phenyl-2',2'-trans-3',4',4'--pentamethyl-1,3,2-benzodioxaphosphole-2-spiro-1'-phosphetan (201).

1.2 g of 2,2-trans-3,4,4-pentamethyl-r-1-phenylphosphetan in 15 cm^3 of dichloromethane, was added slowly to 0.48 g of 4,5-dimethoxy-ortho-benzoquinone in 15 cm^3 of dichloromethane and the mixture was set aside for 48 hours. Evaporation of the solvent gave the crude phosphorane which was purified by chromatography on a short alumina column (Type H alumina-ether), and was crystallised from light petroleum to give 1.3 g (65%) m.p. 94°C, mixed m.p. 91-92°C. The spectral data were identical with the data for the same compound prepared by the trifluoromethanesulphonic

anhydride method, (see experiment 2d).

5. Preparation of 4,5,6,7-tetrachloro-2-ethoxy-4',4',5',5'-tetramethyl--1,3,2-benzodioxaphosphole-2-spiro-2'-[1,3,2-dioxaphospholan] (299).

1.23 g (5 mmol) of tetrachloro-ortho-benzoquinone in 20 cm^3 of ether was added slowly to 0.92 g (5 mmol) of 2-chloro-4,4,5,5-tetramethyl-1,3,2--dioxaphospholan in 20 cm^3 of ether and was allowed to stand at room temperature until the colour of the quinone had almost completely disappeared. The solution was then cooled to 0^oC and a mixture of 0.23 g (5 mmol) of ethanol and 0.4 g (5 mmol) of pyridine in 40 cm^3 of ether was added slowly with stirring. A heavy precipitate of pyridinium chloride formed rapidly and this was set aside overnight. Filtration, followed by evaporation of the solvent gave the crude product which gave 1.6 g (73%) of white crystals m.p. 144-145^oC from ethyl acetate-light petroleum. This compound was identified as phosphorane 299 by comparison of its spectral data with the data of an authentic sample.[42]

6. Preparation of 2,2,3,3-tetrakistrifluoromethyl-5-phenyl-1,4,6-trioxa--5-phospha(5P^V)spiro[4,4]nonane (257).

1 cm^3 of liquefied hexafluoroacetone was allowed to distill slowly into a stirred solution of 0.5 g of 2-phenyl-1,2-oxaphospholan (256) in 15 cm^3 of ether at -78^oC. This was set aside and allowed to warm up to room temperature slowly, overnight. Evaporation of the solvent gave the crude phosphorane which was crystallised from light petroleum to give 0.7 g (47%) of phosphorane 257, m.p. 90-91^oC, ν_{max} 2980, 2910, 1490, 1445, 1350-1170(b), 1100, 1060, 970, 880, 760, 720 & 710(b) cm^{-1}., m/e 498, 479, 457, 440, 429, 421, 332, 313, 116 & 147, δ 1.3-2.2 (2H, m), 2.3-2.9(2H, m), 3.5-4.4(2H, m), 7.3-7.6(3H, m) & 7.8-8.3(2H, m), $^{31}P(CDCl_3)$ +3.8 p.p.m., $^{19}F(C_6H_6)$ + 3.4 p.p.m. (multiplet). Found C, 36.1; H, 2.4;

P, 6.4%, $C_{15}H_{11}F_{12}O_3P$ requires C, 36.2; H, 2.2; P, 6.6%.

7. Preparation of 4,4,5,5-tetrakistrifluoromethyl-P-[2 trimethylsiloxyethyl]-P,P-diphenyl-1,3,2-dioxaphospholan (308).

1 cm^3 of liquefied hexafluoroacetone was allowed to distill slowly into a solution of 1 g of 2-trimethylsiloxyethyldiphenylphosphine (310), in 25 cm^3 of ether at -78°C. This was allowed to warm up to room temperature slowly and stand overnight. Evaporation of the solvent gave 2.3 g of a heavy oil that was miscible with light petroleum in all proportions. ν_{max}(Film) 3060, 2960, 1490, 1440, 1370, 1320-1070(b), 1000, 960, 880, 840 750, 720 & 695 cm^{-1}., δ (CCl_4) 0.04(9H, s), 2.79(2H, dt, J_{PH} 8 Hz, J_{HH} 7 Hz), 3.80(2H, dt, J_{PH} 12 Hz, J_{HH} 7 Hz) & 7.2-7.8(10H, m), ^{31}P($CDCl_3$) +16.8 p.p.m., ^{19}F(C_6H_6) +4.5 p.p.m. (singlet).

8. Preparation of Phosphoranes from Methylthiophosphetanium salts.

8a. P-r-Phenyl-2',2'-trans-3',4',4'-pentamethyl-1,3,2-benzodioxaphosphole-2-spiro-1'-phosphetan (190).

A mixture of 0.55 g (5 mmol) of calechol and 0.51 g (5 mmol) of di-isopropylamine in 20 cm^3 of ether was added to a stirred solution of 2.06 g (5 mmol) of 1-methylthio-2,2,-trans-3,4,4-pentamethyl-r-1-phenylphosphetanium hexafluorophosphate (215), in 10 cm^3 of dichloromethane at -78°C. After 10 minutes at -78°C a further 10 cm^3 of ether was added and the mixture was allowed to warm up to room temperature. Filtration, followed by evaporation and extraction with light petroleum gave 1.1 g (60%) of phosphorane 190. The spectral data for this compound were identical with the data for an authentic sample (see experiment 2a).

8b. P-r-Phenyl-2',2'-cis-3',4',4'-pentamethyl-1,3,2-benzodioxaphosphole-2-spiro-1'-phosphetan (217).

This compound was prepared in a similar way to the trans-3'-analogue from 1-methylthio-2,2-cis-3,4,4-pentamethyl-r-1-phenylphosphetanium hexafluorophosphate (216) in 73% yield. δ 0.84(3H, dd, J 2Hz & 4 Hz), 1.2(6H, d, J 18 Hz), 1.4(6H, d, J 15 Hz), 2.03(1H, m), 6.5(4H, s) & 7.0-7.7(5H, m), $^{31}P(CH_2Cl_2)$ -6 p.p.m. This compound was identified by comparison of its spectral data with the data of an authentic sample prepared by the N-chlorodi-isopropylamine method.[42,109]

8c. Fourier-Transform n.m.r. studies on the reactions described in Experiments 8a and 8b.

0.13 g (1.2 mmol) of catechol and 0.12 g (1.2 mmol) of di-isopropylamine in 0.5 cm^3 of dichloromethane were added to a solution of 0.5 g (1.2 mmol) of 1-methylthio-2,2-trans-3,4,4-pentamethyl-r-1-phenylphosphetanium hexafluorophosphate (215) in 1.5 cm^3 of $CH_2Cl_2/CDCl_3$ in a 10 mm.n.m.r. tube at 0°C. The Fourier-Transform ^{31}P n.m.r. spectrum of this mixture after two minutes showed the only phosphorane formed was P-r-phenyl-2',2'-trans-3',4',4'-pentamethyl-1,3,2-benzodioxaphosphole-2-spiro-1'-phosphetan (190), δ + 0.4 p.p.m. Small quantities of phosphetan oxides were also present.

A similar reaction using the cis-3-analogue gave only the cis-3'-phosphorane δ -6.25 p.p.m.

9. Preparation of 3,4-Dimethyl-1-phenylphosphol-3-ene-1-oxide (143).

The method for preparing this phospholene oxide that is described by MacCormack[164] gave a mixture of the phosphol-2-ene and phospol-3-ene-1-oxides in the ratio of 40:60 (by n.m.r. integrals) respectively.

The pure phosphol-3-ene-1-oxide (143) was prepared by the hydrolysis of 2,2,3,3,7,8-hexamethyl-5-phenyl-1,4-dioxa-5-phospha($5P^V$)spiro[4,4]-non-7-ene (146). This phosphorane (146), was prepared by mixing 22.4 g (0.1 mol) of 4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaphospholan (270) with 16.4 g (0.2 mol) of 2,3-dimethylbuta-1,3-diene (142) and a trace of quinol (0.1 g), under dry nitrogen, and allowing the mixture to stand at room temperature in a dark cupboard for five days. Evaporation of the excess diene gave the crude product in quantitative yield.[53]

The crude adduct was refluxed with 50 cm^3 of 1% sodium hydroxide solution for five hours after which it was cooled and extracted with dichloromethane. The solution was dried with $MgSO_4$, filtered, evaporated and distilled giving pinacol hydrate $b_{0.3}$ 41°C (~1 g) and phosphol-3-ene-1-oxide (143), $b_{0.3}$ 151-158°C (12.8 g, 66% yield), δ 1.78(6H, s), 2.77(4H, d, J 12 Hz) & 7.4-8.0(5H, m), $^{31}P(CDCl_3$-Fourier-Transform) -52.64 p.p.m.

10. Preparation of 3,4-dimethyl-1-phenylphosphol-3-ene (147) by reduction of the corresponding phospholene oxide (143).

10.3 g (50 mmol) of 3,4-dimethyl-1-phenylphosphol-3-ene-1-oxide (143) were mixed with 20 cm^3 of MS1107 silicone fluid and slowly heated to 170°C over a period of 90 minutes. This temperature was maintained for two hours. Distillation of the product from the resulting foam gave 9.5 g (97% yield) of the phospholene (147), $b_{0.3}$ 86-90°C,[211] δ 1.68 (6H, s), 2.2-3.3(4H, m) & 7.05-7.65(5H, m).

11. Preparation of 1-Bromo-3,4-dimethylphosphol-3-ene (148).[166]

17.3 g (0.21 mol) of 2,3-dimethylbuta-1,3-diene (142) was added dropwise, with mechanical stirring, over a period of two hours to a solution of 4.6 g (0.15 mol) of white phosphorus in 20.3 g (0.075 mol) of phosphorus tribromide at room temperature. After approximately thirty minutes the reaction mixture warmed up to 30-40°C and remained at this temperature until the addition of the diene was complete. When the reaction was over and the temperature had fallen to room temperature, the thick orange liquid was distilled using a short Vigreux column b_{15} 94-99°C, to give 21.4 g (52% yield based on diene) of a pale yellow liquid, δ 1.7(6H, s) & 2.93 (4H, d, J 20 Hz), $^{31}P(CDCl_3)$ -104 p.p.m.

12. Preparation of 1-Dimethylamino-3,4-dimethylphosphol-3-ene (149).

9.5 g (0.21 mol) of dimethylamine in 50 cm^3 of ether was added slowly to a stirred solution of 19.3 g (0.1 mol) of 1-bromo-3,4-dimethyl--phosphol-3-ene (148) in 350 cm^3 of ether at -10°C (ice-salt), and was set aside overnight. Filtration, followed by evaporation and distillation gave 10.1 g (64%) of aminophospholene 149, b_{26} 78-80°C, δ 1.77(6H, s), 2.43(6H, d, J 10 Hz) & 2.45(4H, d, J 9 Hz).

13. Preparation of 1-Phenoxy-3,4-dimethylphosphol-3-ene (150).

9.6 g (50 mmol) of 1-bromo-3,4-dimethylphosphol-3-ene (148) in 50 cm^3 of ether was added slowly to a stirred solution of 4.7 g (50 mmol) of phenol and 5.1 g (50 mmol) of triethylamine in 200 cm^3 of ether at -10°C (ice-salt). This was stirred for thirty minutes at room temperature and then refluxed for two hours. Filtration, followed by evaporation and distillation gave 6.6 g (64%) of the phenoxyphospholene 150, $b_{0.7}$ 112-118°C, δ1.73(6H, s), 2.7(4H, m) & 6.95-7.47 (5H, m).

14. Preparation of 1,3,4-Trimethylphosphol-3-ene-1-oxide (178).

9.6 g (50 mmol) of 1-bromo-3,4-dimethylphosphol-3-ene (148) in 50 cm^3 of ether was added slowly to a stirred solution of 1.6 g (50 mmol) of methanol and 5.1 g (50 mmol) of triethylamine in 200 cm^3 of ether at -10°C (ice-salt), and then the mixture was stirred at room temperature for three hours. Without isolating the methoxyphospholene, 10 g (70.4 mmol) of iodomethane was added to the reaction mixture and set aside overnight. Filtration, followed by evaporation and distillation gave 3.3 g (46%) of the methylphospholene oxide (178), $b_{0.3}$ 155°C, ν_{max} (Film) 2980, 2900, 2875, 1440, 1400, 1295, 1230, 1170, 1110 & 845 cm^{-1}., δ 1.66 (3H, d, J 15 Hz), 1.72 (6H, s), 2.52(2H, d, J 8 Hz) & 2.57 (2H, d, J 14 Hz), $^{31}P(CDCl_3)$ -57.4 p.p.m.

15. Preparation of 1-Ethyl-3,4-dimethylphosphol-3-ene-1-oxide (179).

This compound was prepared in 14% yield by the method described for the P-methyl analogue (see experiment 14). $b_{0.3}$ 160°C, ν_{max}(Film) 2980, 2900, 2875, 1440, 1400, 1380, 1240, 1220, 1180, 1030, 840, 795 & 760 cm^{-1}., δ 1.2(3H, dt, J_{PH} 17 Hz, J_{HH} 7 Hz), 1.71(6H, s), 1.93 (2H, quintet, J 7 Hz) & 2.47(4H, d, J 10 Hz), $^{31}P(CDCl_3)$ -61.3 p.p.m.

16. Preparation of 2,2-Trans-3,4,4-pentamethyl-r-1-phenylphosphetan-1-oxide (188).

This compound was prepared by the method of Hawes & Trippett[8] in good yields, m.p. 125-126°C, δ 1.05(3H, dd, J 7 Hz & 1.5 Hz), 1.12(6H, d, J 19 Hz), 1.43(6H, d, J 16 Hz), 1.9-2.3(1H, m), 7.45-7.7(3H, m) & 7.83-8.2(2H, m), $^{31}P(CDCl_3)$ -53 p.p.m.

17. Preparation of 2,2-Cis-3,4,4-pentamethyl-r-1-phenylphosphetan-1--oxide (189).

This compound was prepared by the method of Corfield[178] in good yields, m.p. 116-117°C, δ1.03(3H, d, J 7 Hz), 1.23(6H, d, J 19 Hz), 1.42(6H, d, J 17 Hz), 1.9-2.8(1H, m) & 7.4-8.0(5H, m), $^{31}P(CDCl_3)$ -55.5 p.p.m.

18. Preparation of 2,2-Trans-3,4,4-pentamethyl-r-1-phenylphosphetan-1--oxide (188) by the isomerisation of a cis-trans mixture of phosphetan oxides.

20 g of a mixture of phosphetan oxides 188 and 189 (cis-trans mixture) was refluxed with 5 g of trifluoromethanesulphonic anhydride (167) in 50 cm^3 of benzene for one hour. The cool solution was then washed with 20 cm^3 of 10% sodium hydroxide solution followed by 20 cm^3 of water and the organic layer was dried with $MgSO_4$. The solution was filtered and the solvent was evaporated giving the crude product which was recrystallised from light petroleum giving 17 g (85%) of the trans--phosphetan oxide 188, m.p. 120-122°C. The n.m.r. data were consistent with the data for an authentic sample (see experiment 16).

19. Trichlorosilane reduction of Phosphetan Oxides.

Pentamethylphenylphosphetan oxides 188 and 189 were reduced stereospecifically to the corresponding phosphetans by the method of Corfield.[178] The phosphetans were used without isolation from the benzene solvent in which the reductions were carried out or the benzene was evaporated and the phosphetans were used without further purification.

20. Preparation of 2,2-Trans-3,4,4-pentamethyl-r-1-phenylphosphetan-1--sulphide.

10 g of 2,2-trans-3,4,4-pentamethyl-r-1-phenylphosphetan-1-oxide (188) was reduced to the corresponding phosphetan with trichlorosilane following the method of Corfield.[178] A trace (~0.05 g) of anhydrous aluminium chloride was added to the crude phosphetan solution and 1.4 g of sulphur was added slowly in small quantities. After the addition of the sulphur was complete the mixture was refluxed for one hour. The benzene was evaporated and the crude phosphetan sulphide was purified by chromatography on basic alumina using light petroleum and then ether as solvents. 9.1 g (82%) of the trans-phosphetan sulphide was formed, m.p. 101-103°C,[178] δ 1.03(3H, dd, J 7 Hz & 1.5 Hz), 1.13(6H, d, J 19 Hz), 2.45(6H, d, J 20 Hz), 2.4-2.9(1H, m), 7.5-7.75(3H, m) & 8.15-8.6 (2H, m), $^{31}P(CDCl_3)$ -81 p.p.m.

21. Preparation of 2,2-Cis-3,4,4-pentamethyl-r-1-phenylphosphetan-1--sulphide.

This compound was prepared in the same way as the trans-3 analogue (see experiment 20), in 65% yield, m.p. 92-93°C,[178] δ 0.97(3H, dd, J 7 Hz & 1.5 Hz), 1.37(6H, d, J 18 Hz), 1.43(6H, d, J 20 Hz), 2.2-2.7 (1H, m) & 7.4-7.9(5H, m), $^{31}P(CDCl_3)$ -84.7 p.p.m.

22. Preparation of 1-Methylthio-2,2-trans-3,4,4-pentamethyl-r-1--phenylphosphetanium hexafluorophosphate (215).

3.7 g (18 mmol) of trimethyloxonium hexafluorophosphate and 4.53 g (18 mmol) of 2,2-trans-3,4,4-pentamethyl-r-1-phenylphosphetan-1-sulphide were mixed with 10 cm^3 of dichloromethane at room temperature and allowed to stir overnight. The phosphetanium salt was precipitated by slowly

pouring the dichloromethane solution into 200 cm^3 of rapidly stirred ether, in a dry box. This was filtered off, washed with ether and pumped dry. This product was pure by n.m.r. but a sample was purified further by recrystallisation from dry acetone-ethyl acetate, m.p. 139-140°C. 7.1 g (96%) of phosphetanium salt 215 was formed. ν_{max} 1445, 1170, 1110, 1005, 975, 845, 750 & 695 cm^{-1}., δ (d^6 acetone-TMS external) 0.97 (3H, dd, J 7 Hz & 1 Hz), 1.37(6H, d, J 22 Hz), 1.4(6H, d, J 21 Hz), 1.9(3H, d, J 13 Hz), 2.33-2.93 (1H, m) & 7.35-7.93(5H, m), ^{31}P(d^6 acetone) -82.3 p.p.m., Fourier-Transform ^{31}P($CDCl_3$-CH_2Cl_2) -82.7 p.p.m.(s) & +144.4 p.p.m. (heptet, J_{PF} 29.4 Hz). Found C, 43.7; H, 5.8; P, 14.7%, $C_{15}H_{24}F_6P_2S$ requires C, 43.7; H, 5.9; P, 15.0%.

23. Preparation of 1-Methylthio-2,2-cis-3,4,4-pentamethyl-r-1-phenyl--phosphetanium hexafluorophosphate (216).

This compound was prepared in the same way as the trans-3-analogue (see experiment 22), in 70% yield, m.p. 129-129.5°C, ν_{max} 1445, 1175, 1115, 1005, 845, 760, 730 & 700 cm^{-1}., δ (d^6 acetone-TMS external) 0.73(3H, dd, J 7Hz & 1 Hz), 1.27(6H, d, J 22 Hz), 1.3(6H, d, J 23 Hz), 1.9-(3H, d, J 13 Hz), 2.33-2.95 (1H, m) & 7.33-7.9(5H, m), ^{31}P(d^6 acetone) -82.2 p.p.m., Fourier-Transform ^{31}P($CDCl_3$-CH_2Cl_2) - 82.7 p.p.m.(s) & +144.4 p.p.m. (heptet, J_{PF} 29.4 Hz). Found C, 43.7; H, 5.85; P, 14.9; $C_{15}H_{24}F_6P_2S$ requires C, 43.7; H, 5.9; P, 15.0%.

24. Preparation of 1-Ethoxy-2,2-trans-3,4,4-pentamethyl-r-1-phenyl--phosphetanium hexachloroantimonate (214).[178,179]

This compound was prepared by an analogous method to trans--methylthiophosphetanium salt 215 (see experiment 22), by using triethyloxonium hexachloroantimonate and 2,2-trans-3,4,4-pentamethyl-

-r-1-phenylphosphetan-1-oxide (188), $\delta(CH_2Cl_2)$ 1.25(3H, t, J 7 Hz), 1.27(3H, dd, J 7 Hz & 1 Hz), 1.73(6H, d, J 21 Hz), 1.8(6H, d, J 19 Hz), 2.5-3.27(3H, m) & 7.8-8.5(5H, m). $^{31}P(CH_2Cl_2)$ -93 p.p.m.

25. Preparation of 4,4,5,5-Tetramethyl-2-phenyl-1,3,2-dioxaphospholan (270).

This compound was prepared in 54% yield by the method of White,[53] $b_{0.3}$ 90-94°C,[53,212], m.p. 90-100°C,[53,212] δ 1.25(6H, s), 1.4(6H, s) & 6.6-7.2(5H, m).

26. Preparation of 2-Chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholan.

This compound was prepared in high yields by the method of Arbuzov,[213] $b_{2.0}$ 61-64°C.

27. Preparation of 2-Methoxy-4,4,5,5-tetramethyl-1,3,2-dioxaphospholan (279).[213]

18.25 g (0.1 mol) of 2-chloro-4,4,5,5-tetramethyl-1,3,2--dioxaphospholan in 50 cm^3 of ether was added to a stirred solution of 3.2 g (0.1 mol) of methanol and 8 g (0.1 mol) of pyridine in 200 cm^3 of ether at -10°C, (ice-salt), and was set aside overnight. Filtration, followed by evaporation and distillation gave 9.3 g (53%) of P--methoxydioxaphospholan 279, $b_{44.0}$ 95-98°C, δ 1.23(6H, s), 1.37(6H, s) & 3.53(3H, d, J 13 Hz).

28. Preparation of 2-Chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholan--2-oxide (292).

Dry oxygen was passed into a solution of 1 g of 2-chloro-4,4,5,5--tetramethyl-1,3,2-dioxaphospholan in 20 cm^3 of benzene until the exothermic

reaction had ceased. Evaporation of the solvent gave a quantitative yield of chlorodioxaphospholan oxide 292 as a white crystalline solid m.p. 63-69°C, ν_{max} 1405, 1305, 1270, 1150, 1135, 1020, 960, 935 & 810 cm^{-1}., m/e 200, 198, 187, 185, 158, 156, 142, 140, 119, 117 & 116, $\delta(CCl_4)$ 1.33(s), $^{31}P(CCl_4)$ -12.6 p.p.m.

29. Reaction of 2-Chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholan-2--oxide (292) with Methanol in the presence of Pyridine.

A solution of 0.16 g (5 mmol) of methanol and 0.4 g (5 mmol) of pyridine in 5 cm^3 of CCl_4 was added to a stirred solution of 1 g (5 mmol) of 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholan-2-oxide (292) in 25 cm^3 of CCl_4 at 0°C and stirred for 45 minutes. A sample was removed and filtered into an n.m.r. tube. The n.m.r. spectrum of this sample showed that only 45% of the reagents had reacted. After stirring the remainder of the mixture at room temperature overnight, the pyridinium chloride was filtered off, the solvent evaporated and the product, 2-methoxy-4,4,5,5-tetramethyl-1,3,2-dioxaphospholan-2-oxide (285), was recrystallised from light petroleum, m.p. 98-99°C, ν_{max} 1405, 1285, 1275, 1150, 1055, 1020, 970, 900, 835, 805 & 780 cm^{-1}., m/e 194, 179, 152, 136, 121, 113 & 82. δ 1.37(6H, s), 1.42(6H, s) & 3.79(3H, d, J 11 Hz), $^{31}P(C_6H_6)$ -13 p.p.m.

30. Preparation of 2:3'-methylbut-2'enyl-4,4,5,5-tetramethyl-1,3,2--dioxaphospholan-2-oxide (281).

1.78 g (10 mmol) of 2-methoxy-4,4,5,5-tetramethyl-1,3,2--dioxaphospholan (279) and 1.49 g (10 mmol) of 1-bromo-3-methylbut-2-ene (280) were mixed together and heated between 90 and 110°C for fifteen minutes until no more bromomethane distilled out. The crude product

was distilled and further purified by passing it down a short alumina column with ether to give 1.7g (69%) of a very hygroscopic white solid. Similar yields were obtained when the reaction was carried out on larger scales. $b_{0.3}$ 150°C, ν_{max} 1670, 1470, 1400, 1265, 1150, 1015, 960, 930, 885, 820, 795 & 745 cm^{-1}., m/e 232, 217, 190, 163, 150 & 82, $\delta(CCl_4/TMS)$ 1.28(6H, s), 1.42(6H, s), 1.63-1.86(6H, m), 2.55(2H, dd, J 21 Hz & 8 Hz) & 4.9-5.4(1H, m), $^{31}P(CCl_4)$ -40.4 p.p.m., (CCl_4-CDCl_3) -39.1 p.p.m.

31. Preparation of Dimethyl allylphosphonate (302).[214]

15 cm^3 of trimethyl phosphite and 15 cm^3 (excess) of freshly distilled allyl bromide were heated together at 80°C with 0.5 g of anhydrous aluminium chloride for twelve hours. Distillation gave 7.7g (95%) of dimethyl allylphosphonate b_{10} 60-65°C,[214] ν_{max}(Film) 3080, 2960, 2860, 1645, 1465, 1435, 1260(b), 1185, 1040, 930, 860, 805 & 735 cm^{-1}., $\delta(CCl_4-TMS)$ 2.57(2H, dd, J 15.5 Hz & 7 Hz), 3.64(6H, d, J 11 Hz) & 4.85-6.05(3H, m), $^{31}P(CCl_4)$ -27.3 p.p.m.

32. Preparation of Dimethyl 3-methylbut-2-enylphosphonate (303).

15 cm^3 of trimethyl phosphite and 15 cm^3 (excess) of 2-chloro-2--methylbut-3-ene (293) were heated together at 120°C for 24 hours during which time approximately 1g of anhydrous aluminium chloride was added in several small portions. 10 cm^3 of water was added to destroy any complexes and the mixture was extracted with dichloromethane and dried over $MgSO_4$. Evaporation and distillation gave 9.75g (46%) of allylphosphonate 303 $b_{0.3}$ 120°C, ν_{max}(Film) 2960, 2920, 2860, 1670, 1455, 1380, 1260(b), 1185, 1000(b), 875 & 815, $\delta(CCl_4-TMS)$ 1.66(3H, d, J 5 Hz), 1.78(3H, d, J 6 Hz), 2.52(2H, dd, J 19 Hz & 8 Hz), 3.69(6H, d, J 11 Hz) & 4.9-5.4(1H, m), $^{31}P(CCl_4)$ -30.0 p.p.m.

33. Preparation of 2,4,4,5,5-Pentamethyl-1,3,2-dioxaphospholan-2--oxide (172).

An Arbuzov rearrangement of 2-methoxy-4,4,5,5-tetramethyl-1,3,2--dioxaphospholan (279) was carried out by refluxing it with excess iodomethane in benzene. Evaporation of the solvent and distillation gave 68% of dioxaphospholan oxide 172, $b_{1.0}$ 115-120°C, ν_{max}(Film) 2980, 2930, 1460, 1390, 1370, 1310, 1260(b), 1140, 1005, 960, 860 & 755 cm^{-1}., δ 1.23(6H, s), 1.43(6H, s) & 1.55(3H, d, J 16 Hz), $^{31}P(CDCl_3)$ -41.6 p.p.m.

34. Preparation of Methylphosphonic dichloride.

7.8g (0.1 mol) of dimethylsulphoxide was added to 11.7g (0.1 mol) of methylphosphonous dichloride in 20 cm^3 of dichloromethane at -78°C. This was allowed to warm up to room temperature slowly and set aside overnight. The solvent and dimethylsulphide were evaporated and the product distilled to give 10.4 g (78%) of methylphosphonic dichloride, b_{25} 66-68°C, δ 3.07(d, J 12 Hz), $^{31}P(CDCl_3)$ -45 p.p.m.

35. Preparation of 2-Phenyl-1,3,2-benzodioxaphosphole-2-oxide (171).

This compound was prepared in 73% yield by a modification of the method of Berlin et al.[215] where ether was used as the solvent and two equivalents of pyridine were added to remove the HCl. $b_{0.8}$ 160-162°C, δ 7.07(4H, s) & 7.23-8.05(5H, m), $^{31}P(CDCl_3)$ -36.3 p.p.m.

36. Preparation of 2-Methyl-1,3,2-benzodioxaphosphole-2-oxide (171).

9g (67.6 mmol) of methylphosphonic dichloride in 20 cm^3 of ether was added slowly to a stirred solution of 7.5g (68 mmol) of catechol and

13.7g (135.3 mmol) of triethylamine in 200 cm^3 of ether at 0°C and was then set aside overnight. Filtration, followed by evaporation and distillation gave 6g (54%) of benzodioxaphosphole 171, $b_{0.3}$ 80°C, ν_{max} 2920, 1595, 1495, 1313, 1200(b), 1100, 825 & 750 cm^{-1}., δ 1.87 (3H, d, J 18 Hz) & 6.93(4H, s), $^{31}P(CDCl_3)$ -49.5 p.p.m.

37. Preparation of 2-Methyl-1,3,2-benzodioxaphosphole-2-sulphide (211).

This compound was prepared by the addition of sulphur to 2-methyl--1,3,2-benzodioxaphosphole which was prepared in 32% yield by the method of Weiber and Otto,[216] b_{11} 40°C, δ 1.18(3H, d, J 9 Hz) & 7.05(4H, s).

1g of sulphur was refluxed with 4.8g of 2-methyl-1,3,2-benzodioxaphosphole in 50 cm^3 of benzene in the presence of a trace (0.05g) of anhydrous aluminium chloride. After four hours the solvent was evaporated and the product distilled to give 4.3g (80%) of benzodioxaphosphole 211, $b_{0.3}$ 80°C, δ 2.17(3H, d, J 14.5 Hz) & 6.92(4H, s), $^{31}P(CDCl_3)$ -118 p.p.m.

38. Preparation of 2-Phenoxy-4-methyl-1,3,2-benzodioxaphosphole (273).

A solution of 6.5g (3.34 mmol) of phenylphosphorodichloridite in 50 cm^3 of ether was added slowly to a stirred solution of 4.13g (3.34 mmol) of 3-methylcatechol and 6.7g (6.67 mmol) of triethylamine in 150 cm^3 of ether at 0°C, and was set aside overnight. Filtration, followed by evaporation and distillation gave 3.5g (40%) of benzodioxaphosphole 237, $b_{0.3}$ 95-100°C, δ 2.26(3H, s) & 6.62-7.35(8H, s).

39. Preparation of Methyl diphenylphosphinite.

This compound was prepared by the method of Arbuzov[217] in 69% yield, $b_{1.0}$ 110-115°C, δ 3.46(3H, d, J 15 Hz) & 6.95-7.43(10H, m), $^{31}P(CDCl_3)$ -114 p.p.m.

40. Preparation of Methyldiphenylphosphine oxide.[219]

This compound was prepared by refluxing 6.5g of methyl diphenylphosphinite with 5g (excess) of iodomethane in 20 cm^3 of benzene for 16 hours. Evaporation of the solvent gave the crude product which was recrystallised from light petroleum to give 5.7g (88%) of methyldiphenylphosphine oxide m.p. 109-110°C, δ 2.01(3H, d, J 13 Hz) & 7.43-8.07 (10H, m), $^{31}P(CDCl_3)$ -31.1 p.p.m.

41. Preparation of Dimethyl phenylphosphonite (254).

This compound was prepared by the method of Arbuzov[218] in 73% yield, b_{15} 89-90°C, δ 3.60(6H, d, J 11 Hz) & 7.5-8.15(5H, m), $^{31}P(CDCl_3)$ -149 p.p.m.

42. Preparation of Diethyl phenylphosphonite (251).

This compound was prepared by the method of Arbuzov[218] in 75% yield, $b_{0.3}$ 72-78°C, δ 1.23(6H, t, J 7 Hz), 3.82(4H, dt, J 7 Hz & 8 Hz) & 7.22-7.76(5H, m).

43. Preparation of 2-Ethoxy-1,2-oxaphospholan-2-oxide (170).

This compound was prepared by the method of Garner,[220] but the reaction mixture had to be heated to a higher temperature than stated (180-200°C for four hours) and the yield was smaller (3%), $b_{1.0}$ 110-115°C, δ 1.27(3H, t, J 7 Hz), 1.5-2.5(4H, m) & 3.72-4.25(4H, m), $^{31}P(CDCl_3)$ -50.3 p.p.m.

Under the conditions given by Garner,[220] diethyl 3-bromopropylphosphonate can be obtained in 30% yield, $b_{0.9}$ 111-112°C, δ 1.27 (6H, t, J 7 Hz), 1.5-2.67(4H, m), 3.34(2H, t, J 5.5 Hz) & 3.92(4H, dt, J 7 Hz & 8 Hz). This can be converted to 2-ethoxy-1,2-oxaphospholan-2-oxide (170) in 10% yield by heating it between 180 and 200°C for four hours.

44. Preparation of 2-Phenyl-1,2-oxaphospholan-2-oxide (169).

25g (0.126 mol) of diethyl phenylphosphonite (251) and 20.2g (0.1 mol) of 1,3-dibromopropane were heated together between 120 and 190°C for four hours. When bromoethane ceased to distill out of the reaction mixture the crude product was distilled to give 4.9g (30%) of oxaphospholan oxide 169, $b_{0.3}$ 150-152°C, ν_{max}(Film) 3070, 2980, 1445, 1220, 1125, 1025, 980, 900, 810, 760 & 710 cm^{-1}., m/e 182, 141, 124, 105 & 77, δ 1.80-2.77(4H, m), 4.1-4.9(2H, m) & 7.33-8.13(5H, m).

45. Preparation of 3-Hydroxypropylphenylphosphine (253).

Method i). From diethyl phenylphosphonite (251) and 1,3-dibromopropane.

These compounds were heated together as described in experiment 44 but the crude product was used without purification. 10g of this crude product was dissolved in 50 cm^3 of T.H.F. and added slowly to 2.5g of lithium aluminium hydride in 200 cm^3 of ether. This was stirred mechanically overnight and then 5 cm^3 of water was added carefully. This was refluxed for one hour and then the mixture was dried with $MgSO_4$. Filtration followed by evaporation and distillation gave 1.3g (14%) of 3-hydroxypropylphenylphosphine $b_{0.3}$ 118-128°C,[182] δ1.43-2.07(4H, m), 3.3(1H, s), 3.57(2H, t, J 6 Hz), 4.17(1H, d, J_{PH} 210 Hz) & 7.15-8.90(5H, s). In a subsequent preparation on a larger scale the yield was improved to 28%.

Method ii). From dimethyl phenylphosphonite (254) and acrylic acid.

7.2g (0.1 mol) of acrylic acid was slowly added to a solution of 17g (0.1 mol) of dimethyl phenylphosphonite (254) in 20 cm^3 of ether at 0^oC and was allowed to stir for two days at room temperature. Distillation gave 15g (62%) of methyl 3-(methoxy, phenylphosphinyl)propionate (255),[221] $b_{0.3}$ 158-162°C, ν_{max}(Film) 3060, 2960, 1740, 1440, 1230, 1120, 1040, 895, 795 & 700 cm^{-1}., δ 1.93-2.97(4H, m), 2.58(3H, s), 3.62(3H, d, J 9 Hz) & 7.4-7.97(5H, m), $^{31}P(CDCl_3)$ -44.3 p.p.m.

15g of propionate 255 in 50 cm^3 of ether was added slowly to 3g of lithium aluminium hydride in 100 cm^3 of ether at 0^oC and allowed to stir at room temperature overnight. Water (10 cm^3) was added carefully and stirred for one hour. The solution was dried with $MgSO_4$, filtered, evaporated and distilled to give 2.7g (29%) of 3-hydroxypropylphenylphosphine (253) $b_{0.3}$ 118-120°C, (see experiment 45, method i, for n.m.r. data).

46. Preparation of 2-Phenyl-1,2-oxaphospholan (256).

2.7g (16 mmol) of 3-hydroxypropylphenylphosphine (253) in 20 cm^3 of ether and 2.2g (16 mmol) of N-chlorodi-isopropylamine in 20 cm^3 of ether were added simultaneously over a period of one hour, to 50 cm^3 of ether at -78°C, with stirring. When addition was complete the mixture was allowed to warm up slowly and stirred at room temperature for one hour. Filtration, followed by evaporation and distillation gave 0.5g (20%) of 2-phenyl-1,2-oxaphospholan (256), $b_{0.3}$ 110-120°C,[181] ν_{max}(Film) 3060, 3040, 2960, 2870, 1430, 1410, 1015, 950, 885, 850, 740 & 690 cm^{-1}., δ 1.5-2.57(4H, m), 3.77-4.46(2H, m) & 7.16-7.67(5H, m), $^{31}P(CDCl_3)$ -110.4 p.p.m.

47. Preparation of 2-Phenoxy-1,3,2-dioxaphosphepane (165).

This compound was prepared in 75% yield by the method of Guimaraes and Roberts,[222] $b_{0.5}$ 200-210°C, m/e 212, 140, 119 & 94, δ 1.6-2.1 (4H, m), 3.7-4.6(4H, m) & 7.37(5H, s). Treatment of this compound with excess hexafluoroacetone in ether at -78°C gave a heavy oil, ν_{max}(Film) 3060, 2960, 1605, 1505, 1360-880(b), 780, 730 & 700 cm^{-1}., $^{19}F(CH_2Cl_2)$ 6.7 p.p.m.(s) also other signals between 6.7 & 6.9 p.p.m. The ^1H n.m.r. spectrum was similar to the starting material but there were twice as many aromatic protons as there should have been.

48. Chlorination of Allylphosphonates. General method.

The allylphosphonate (281, 302 or 303) was dissolved in CCl_4 (2-10% solutions by weight), and dry chlorine was passed in at 0°C until a yellow colour persisted. The solution was then purged with dry nitrogen until the colour was discharged.

48a. From dimethyl allylphosphonate (302, 1.5g in 15 cm^3 of CCl_4), 32% yield of dimethyl 2,3-dichloropropylphosphonate (304) was formed $b_{1.5}$ 120-130°C, ν_{max}(Film) 2960, 2860, 1460, 1255(b), 1185, 1040(b), 855, 820 & 785 cm^{-1}., m/e 222, 220, 187, 185, 149, 147, 145, 110, 79 & 75, δ 2.47(2H, dt, J 19 Hz & 6.5 Hz), 3.78(6H, d, J 11 Hz), 3.94(2H, d, J 6 Hz), & 4.15-4.83(1H, m), $^{31}P(CDCl_3)$ -27.4 p.p.m. An involatile oil (0.85g) was also formed.

48b. From dimethyl 3-methylbut-2-enylphosphonate (303), a mixture of six compounds was obtained (g.l.c. 200°C, 3% OV17 column). Mass spectra were obtained by g.l.c.-mass spectroscopy. Samples were obtained for n.m.r. by prep. g.l.c. (195°C, 10% OV17 column). Yields are expressed in terms of the percentage of the total area under the gas chromatogram,

and the products are listed in the order in which they appeared in the gas chromatrogram.

i & ii) (305) 65%, identical mass spectra were obtained for both of these compounds. m/e 200, 198, 185, 183, 163 & 136, ν_{max}(Film) 2980, 2960, 2860, 1465, 1380, 1270(b), 1035(b), 960, 920, 880, 845 & 825 cm^{-1}., δ (CCl_4-TMS), 3 singlets (total 3H) at 1.43, 1.5 & 1.87, 2.1-2.65(1.5H, m), 3.75(3H, d, J 10 Hz) & 4.67-5.4(1H, m), $^{31}P(CCl_4)$ -24 p.p.m.

iii) 26%, m/e 215, 213, 211, 178, 173, 110 & 109, δ (CCl_4-TMS) 1.65(3H, s), 1.78(3H, s), 1.9-2.0(2H, m), 3.8(6H, d, J 10.5 Hz) & 3.95-4.5(1H, m).

This data suggests that this compound could be dimethyl 2,3-dichloro--3-methylbutylphosphonate (306).

iv) 6.5%, m/e 213, 211, 199, 197, 169, 167, 161 & 109. Insufficient compound for n.m.r.

v & vi) 2.5% identical mass spectra were obtained for each of these compounds. m/e 248, 246, 213, 211, 173, 172, 171, 146, 144 & 109. Insufficient compound for n.m.r.

48c. From 2:3'-methylbut-2'-enyl-4,4,5,5-tetramethyl-1,3,2-dioxaphospholan--2-oxide (281, 1.6g in 30 cm^3 of CCl_4), 0.7g of dimethylamine in 20 cm^3 of CCl_4 was added to the chlorinated compound at 0°C with stirring. A thick white precipitate formed rapidly which was filtered off after thirty minutes and the solvent evaporated. An oil remained which appeared to contain 2-dimethylamino-4,4,5,5-tetramethyl-1,3,2-dioxaphospholan-2-oxide (284). Distillation gave an impure sample of this compound, $b_{0.05}$ 80°C, ν_{max}(Film) 2980, 2930, 1460, 1395, 1265, 1260, 1255, 1140, 1010, 965, 940 & 810 cm^{-1}., m/e 207, 192, 179, 163, 139 & 125, δ (C_6H_6) 0.97(6H, s), 1.26(6H, s) & 2.48(6H, d, J 10 Hz), $^{31}P(C_6H_6)$ -20.3 p.p.m.

In a similar way a solution of 0.4g (5.06 mmol) of pyridine and 0.16g (5 mmol) of methanol in 5 cm^3 of dichloromethane was added to a chlorinated solution of 1.16g (5 mmol) of allyldioxaphospholan oxide 281

in 40 cm^3 of CCl_4 at 0°C. After one hour the solution was filtered and the crude n.m.r. showed the presence of 2-methoxy-4,4,5,5-tetramethyl--1,3,2-dioxaphospholan-2-oxide (285). This was obtained in a pure state by crystallisation from light petroleum and sublimation (0.3 mm Hg, 65°C) to give 2.9g (29%) of the pure dioxaphospholan oxide 285, m.p. and mixed m.p. 98-99°C. This had identical spectral data with an authentic sample, (see experiment 29). Longer reaction time did not improve the yield of this reaction.

48d. Reaction of 2:3'-Methylbut-2'-enyl-4,4,5,5-tetramethyl-1,3,2--dioxaphospholan-2-oxide (281), with benzenesulphenyl chloride.

0.125g (0.865 mmol) of benzenesulphenyl chloride in 5 cm^3 of benzene was added to a stirred solution of 0.2g (0.862 mmol) of dioxaphospholan oxide 281, in 5 cm^3 of benzene which was cooled in ice. The orange colour of the benzenesulphenyl chloride discharged instantly. Evaporation of the solvent gave a colourless oil which had the following data. ν_{max}(Film) 3060, 2980, 2940, 1585, 1480, 1440, 1400, 1385, 1375, 1270(b), 1140, 1010, 960, 930, 880, 790 & 760 cm^{-1}., m/e 378, 376, 341, 299, 257, 232, 217, 150, 149, 121, 119 & 117, δ (CCl_4-TMS) 1.23(6H, s), 1.47(6H, s), 1.6(6H, s), 2.07-3.23(2H, m), 3.53-4.03(1H, m) & 7.13-7.8 (5H, m), $^{31}P(CCl_4)$ -31 p.p.m. This data suggests that the product was 2:2'-chloro-3'-phenylthio-3'-methylbutyl-4,4,5,5-tetramethyl-1,3,2--dioxaphospholan-2-oxide (301).

49. Thermolysis of P-Methyl-P,P-diphenyl-4,4,5,5-tetrakistrifluoromethyl--1,3,2-dioxaphospholan (174).

2.0g of this phosphorane were heated at 170°C for five minutes and the volatile materials were collected in dichloromethane at -78°C. A colourless oil remained which was hexafluoro-2-propyl diphenylphosphinate (176),[223] ν_{max} 3060, 2950, 1600, 1445, 1385, 1240(b), 1200, 1135, 870,

840 & 735 cm^{-1}., δ 5.54(1H, heptet, J 6 Hz) & 7.37-8.07(10H, m).

The volatile material was 1,1-bistrifluoromethylethene (175),[223] ν_{max} (CH_2Cl_2) 1670, 1420, 1385, 1250-1160(b), 1090 & 995 cm^{-1}., δ ($CDCl_3$-CH_2Cl_2) 6.42 singlet.

50. Thermolysis of 2,2,3,3-Tetrakistrifluoromethyl-5-phenyl-1,4,6--trioxa-5-phospha(5P^V)spiro[4,4]nonane (257).

0.2g of this phosphorane were heated at 140°C for thirty minutes. 0.2g of a colourless oil remained that was 4,4-bistrifluoromethylbut-3--enyl hexafluoro-2-propyl phenylphosphonate (258), ν_{max}(Film) 3060, 2950, 1685, 1600, 1445, 1400, 1385, 1280-1200(b), 1160(b), 1110, 980, 875, 745 & 685 cm^{-1}., m/e 498, 479, 457, 429, 349, 334, 332, 319, 306, 291, 271 & 251, δ 2.63-3.15(2H, m), 4.37(2H, dd, J 6 Hz & 7 Hz), 5.4(1H, heptet, J 6 Hz), 6.9(1H, dt, J 7 Hz & 1 Hz) & 7.3-8.1(5H, m), ^{31}P(bromonaphthalene) -110 p.p.m., ^{19}F(bromonaphthalene) -4.5 p.p.m. (3F, quartet, J 7 Hz), +1.5 p.p.m. (3F, quartet, J 7 Hz) & +10.65 p.p.m. (6F, d, J 6 Hz).

This thermolysis was also carried out by heating a solution of the phosphorane in bromonaphthalene at 130°C in an n.m.r. tube.

51. Thermolysis of 3',4'-Dimethyl-2-phenylspiro[1,3,2-benzodioxaphosphole--2,1'-phosphol-3'-ene] (151).

This compound was stable below 260°C. When it was heated at 260°C for two hours some 2,3-dimethylbuta-1,3-diene (142) distilled out and was identified by its ^1H n.m.r. spectrum and by g.l.c. comparison with an authentic sample, (3% OV17 column at 40°C). The residue contained the starting phosphorane and 2-phenyl-1,3,2-benzodioxaphosphole (154) which was identified by comparison of its spectra with the spectra of an authentic sample that was prepared by the method of Wieber & Hoos[224] in 30% yield, $b_{0.8}$ 136-140°C.

52. Thermolysis of P,P,P-Trimethoxy-1,3,2-benzodioxaphosphole (127).

0.5g of this phosphorane were heated at 200°C for three hours. The crude product had spectral data that were identical with the data for an authentic sample of dimethyl 2-methoxyphenyl phosphate (138), (see experiment 56). Comparisons were also made using thin layer chromatography (alumina-ether).

53. Thermolysis of P,P,P-Triethoxy-1,3,2-benzodioxaphosphole (128).

0.5g of this phosphorane were heated at 200°C for three hours. The product, diethyl 2-ethoxyphenyl phosphate (139), was purified by thick layer chromatography, using basic alumina-ether. ν_{max}(Film) 2980, 1500, 1260(b), 1195, 1110, 1030(b), 950(b), 795 & 740 cm^{-1}., m/e 274, 259, 190, 172, 155 & 137, δ 1.23-1.57(9H, m), 4.02-4.63(6H, m) & 6.9-7.6(4H, m). The 6H multiplet decouples to two quartets of relative intensity 2:1. $^{31}P(CDCl_3)$ +6.1 p.p.m.

54. Reaction of P,P,P-Trimethoxy-1,3,2-benzodioxaphosphole (127), with triethyl phosphite.

3g (12.93 mmol) of phosphorane 127 and 5g (23.7 mmol) of triethyl phosphite were heated together under reflux for five hours (oil bath temperature, 200°C). The excess triethyl phosphite was distilled off and the residue separated by thick layer chromatography on basic alumina with ether. The product contained diethyl 2-ethoxyphenyl phosphate (139) which was identified by comparison of its spectral data with the data for a sample prepared by the direct thermolysis of P,P,P-triethoxy-1,3,2--benzodioxaphosphole (128, see experiment 53). A further comparison was made using thin layer chromatography (R_f=0.44 on basic alumina-ether).

55. Reaction of P,P,P-Triethoxy-1,3,2-benzodioxaphosphole (127), with trimethyl phosphite.

2g (8.85 mmol) of phosphorane 127 and 6g (48.4 mmol) of trimethyl phosphite were heated together under reflux for four hours (oil bath temperature 200°C). Excess trimethyl phosphite was distilled off and chromatography on UGl alumina with ether gave dimethyl 2-methoxyphenyl phosphate (138) which was identified by comparison of its spectral data with the data for an authentic sample, (see experiment 56).

56. Preparation of Dimethyl 2-methoxyphenyl phosphate (138).

A solution of 6.2g (50 mmol) of 2-methoxyphenol (guaiacol) in 20 cm^3 of ether was added to 6.9g of phosphorus trichloride at 0°C and stirred at room temperature for three days. Evaporation and distillation gave 4.5g (39%) of 2-methoxyphenylphosphorodichloridite, b_{25} 132-138°C, δ 3.78(3H, s) & 6.75-7.4(4H, m).

1.3g (40.6 mmol) of methanol in 10 cm^3 of ether was added slowly to a stirred solution of 4.3g (20 mmol) of 2-methoxyphenylphosphorodichloridite and 4g (40 mmol) of triethylamine in 200 cm^3 of ether at 0°C, and was set aside overnight. Filtration, followed by evaporation and distillation gave 2.95g (72%) of dimethyl 2-methoxyphenyl phosphite, $b_{0.5}$ 85-92°C, δ 3.66(6H, d, J 15 Hz), 3.73(3H, s) & 6.8-7.25(4H, m), $^{31}P(CDCl_3)$ -140.2 p.p.m.

1.08g (5 mmol) of dimethyl 2-methoxyphenyl phosphite in 5 cm^3 of dichloromethane was added to a solution of 2.0g (11 mmol) of 3-chloroperbenzoic acid in 50 cm^3 of dichloromethane at 0°C and was allowed to stir overnight. The solution was evaporated down to 10 cm^3 and most of the insoluble 3-chlorobenzoic acid was filted off. Further purification was achieved by chromatography on a short basic alumina column (UGl alumina-ether) and finally distillation gave 0.65g (56%) of dimethyl

2-methoxyphenyl phosphate (138), $b_{0.5}$ 145°C, ν_{max}(Film) 3040, 2980, 2875, 1610, 1510, 1465, 1300, 1270, 1185, 1050, 955, 860, 815 & 760 cm^{-1}., m/e 232, 217, 203, 201, 199, 186, 156, 138 & 124. δ 3.8(3H, s), 3.84 (6H, d, J 12 Hz) & 6.8-7.45(4H, m), $^{31}P(CDCl_3)$ +3.7 p.p.m.

57. Reaction of P,P,P-Trialkoxy-1,3,2-benzodioxaphospholes with triphenylphosphine or tri-p-tolylphosphine.

1g (3.65 mmol) of P,P,P-triethoxy-1,3,2-benzodioxaphosphole (128) and 1.2g (4.6 mmol) of triphenylphosphine were heated together between 160 and 180°C for three hours. A white oil was formed which crystallised on washing with light petroleum. The petrol soluble part contained triethyl phosphate (g.l.c., 3% OV17 column at 105°C). The crystalline part was recrystallised from methanol-water, m.p. 236-237°C, ν_{max} 1490, 1440, 1245, 1210, 1115, 875, 820 & 725 cm^{-1}., δ 6.63(2H, s), 7.45-8.05 (3H, m), $^{31}P(CH_2Cl_2)$ -24.2 p.p.m. A structure has not been assigned to this compound.

The same reaction was carried out with 1.5g (6.46 mmol) of P,P,P-trimethoxy-1,3,2-benzodioxaphosphole (127) and 3g (11.45 mmol) of triphenylphosphine. The products were trimethyl phosphate (g.l.c., 3% OV17 column at 100°C) and the same unidentified crystalline product.

1g (3.65 mmol) of P,P,P-triethoxy-1,3,2-benzodioxaphosphole (128) and 2g (6.85 mmol) of tri-p-tolylphosphine were heated together at 180°C for five hours. The product was washed with petrol and the residue was crystallised from ethanol to give 0.55g of a white crystalline solid m.p. approximately 200°C (large range). The $^{31}P(CH_2Cl_2)$ n.m.r. spectrum showed two compounds were present at -22.1 & +10.25 p.p.m. δ 2.37(9H, s), 6.57(1.4H, s) & 7.05-7.55(12H, m), ν_{max} 3040, 1610, 1500, 1390, 1260, 1225, 1125, 1025, 885, 825, 755 & 735 cm^{-1}., This data suggests that two or more compounds are present and are probably the starting phosphine and its oxide based on the ^{31}P n.m.r. data.

58. Preparation of Tri-p-tolylphosphine.

This compound was prepared in 30% yield by the method of Mann and Chaplin,[225] m.p. 146°C, δ 2.33(3H, s) & 7.1-7.4(4H, m).

59. Attempted alkylation of 4,4,5,5-tetramethyl-2-phenyl-1,3,2--dioxaphospholan (270).

Attempts to alkylate dioxaphospholan 270 using trimethyloxonium hexafluorophosphate in dichloromethane, resulted in the isolation of 2-hydroxy-1,1,2-trimethylpropyl methylphenylphosphinate (272), ν_{max} 3340, 3060, 1445, 1305, 1210, 1180, 1160, 1120, 980, 895 & 790 cm^{-1}., m/e 256, 241, 198, 197, 157 & 156. δ 1.21(3H, s), 1.37(6H, s), 1.47(3H, s), 1.72(3H, d, J 15 Hz) & 7.3-8.1(5H, m), $^{31}P(CDCl_3)$ -39.4 p.p.m.

60. Attempted isomerisation of 3,4-Dimethyl-1-phenylphosphol-2-ene (144) to the phosphol-3-ene (143).

4.12g (20 mmol) of a mixture of 3,4-dimethyl-1-phenylphosphol-2--ene (144, 40%) and the corresponding phosphol-3-ene (143, 60%) in 20 cm^3 of ether was added to a solution of lithium di-isopropylamide, previously prepared from 2.5g (24.7 mmol) of di-isopropylamine and 13.5 cm^3 of 1.5M n-butyl-lithium solution, in 50 cm^3 of ether at 0°C and stirred for forty minutes. The red solution was quenched with 1 cm^3 of water, dried over Na_2SO_4, filtered and evaporated. Distillation gave 3.6g (88%) of a mixture of phospholenes 143 (68%) and 144 (32%), $b_{0.3}$ 160°C. The isomer ratio was determined by n.m.r. spectroscopy.

The reaction was repeated but the lithio-complex was allowed to stand for two hours before work-up. The isomer ratio in this experiment was 84% of phospholene 143 and 16% of 144. Longer reaction times gave the same isomer ratio.

61. Preparation of Diphenylphosphine.

This compound was prepared in up to 91% yield by the method of Kuchen and Buchwald,[226] $b_{0.5}$ 112-118°C.

62. Preparation of 2-Trimethylsiloxyethyldiphenylphosphine (307).

A solution of sodium diphenylphosphide was prepared by adding 8g of diphenylphosphine in 100 cm^3 of T.H.F. to 2g of sodium wire and refluxing for two hours. Excess sodium wire was removed and destroyed. Approximately 3g (excess) of ethylene oxide were added at 0°C followed by 4.7g of chlorotrimethylsilane in 5cm^3 of ether. This was refluxed for thirty minutes, filtered and evaporated. The crude product was distilled to give 9.6g (74%) of phosphine 307, $b_{0.3}$ 160°C, ν_{max}(Film) 3060, 2950, 2880, 1590, 1480, 1430, 1170(b), 1120, 1040, 840 & 690 cm^{-1}, m/e 302, 287, 272, 230, 213, 212, 199, 187 & 134, δ -0.06(9H, s), 2.29(2H, t, J 7 Hz), 3.64(2H, dt, J 8Hz & 7 Hz) & 7.0-7.5(10H, m), $^{31}P(CDCl_3)$ +29.5 p.p.m.

63. Preparation of 2-Trimethylsiloxy-2-phenylethyldiphenylphosphine (307).

This was prepared by the method described in experiment 62 using styrene oxide. This compound was impure and could not be distilled. It was characterised as its phosphonium iodide (310, see experiment 66).

64. Preparation of 2-Trimethylsiloxybutyldiphenylphosphine (307).

This was prepared by the method described in experiment 62 using but-1-ene oxide. This compound was impure and could not be distilled, δ -0.2(9H, s), 0.75(3H, t, J 7 Hz), 1.46(2H, m), 2.04(2H, d, J 6·5 Hz), 3.45(1H, m) & 6.7-7.4(10H, m).

65. Preparation of 2-Trimethylsiloxyethylmethyldiphenylphosphonium iodide (310).

1 cm^3 of iodomethane and 1g of 2-trimethylsiloxyethyldiphenylphosphine (307) were mixed in 20 cm^3 of deoxygenated benzene and stirred overnight. The product was filtered off and washed with benzene. 1.2g (80%) of crude phosphonium iodide 310 was collected. δ -0.08(9H, s), 2.83(3H, d, J 15 Hz), 3.73(2H, dt, J 6 Hz & 13 Hz), 4.3(2H, t, J 6 Hz) & 7.5-8.3 (10H, m), $^{31}P(CDCl_3)$ -30 p.p.m.

Attempts to recrystallise this compound from acetone-ethyl acetate resulted in the isolation of 2-hydroxyethylmethyldiphenylphosphonium iodide (320), m.p. 181-182°C, ν_{max} 3360, 1440, 1120, 1115, 1070, 910, 750, 730 & 690 cm^{-1}., δ (CF_3CO_2H-TMS) 2.67(3H, d, J 13.5 Hz), 3.4 (2H, dt, J 13 Hz & 6 Hz), 4.28(2H, dt, J 18 Hz & 6 Hz) & 7.65-8.05(10H, m), $^{31}P(CF_3CO_2H)$ -23.6 p.p.m. This compound was also compared with an authentic sample prepared by the method of Issleib,[227] mixed m.p. 181-182°C.

66. Preparation of 2-Trimethylsiloxy-2-phenylethylmethyldiphenylphosphonium iodide (310).

This compound was prepared by the method described in experiment 65 using 2-trimethylsiloxy-2-phenylethyldiphenylphosphine (307). The crude phosphonium salt 310, was formed as an amorphous powder in 79% yield, ν_{max} 3010, 1440, 1250, 1070, 995, 935, 875, 840, 750 & 680 cm^{-1}., δ -0.33(9H, s), 3.85(3H, d, J 14 Hz), 3.7(2H, m) & 5.35(1H, dt, J 6.5 Hz & 7 Hz). The aromatic region contained far too many aromatic protons. Attempts to recrystallise this phosphonium salt from $CHCl_3$-ethyl acetate, resulted in the isolation of 2-hydroxy-2-phenylethylmethyldiphenylphosphonium iodide (320), m.p. 181-182°C, ν_{max} 3270, 1430, 1120, 1055, 895, 740 & 684 cm^{-1}., δ (CF_3CO_2H) 2.01(3H, d, J 13 Hz), 3.15(2H, m), 4.8(1H, dt, J

6 Hz & 8 Hz) & 6.9-7.4(15 H, m).

67. Preparation of 2-Trimethylsiloxybutylmethyldiphenylphosphonium iodide (310).

This compound was prepared by the method described in experiment 65 using 2-trimethylsiloxybutyldiphenylphosphine (307). The crude phosphonium salt (310) was formed as an amorphous powder in 59% yield, ν_{max} 3060, 1440, 1110, 920, 900, 735 & 680 cm^{-1}., δ -0.03(9H, s), 0.8(3H, t, J 7 Hz), 1.73(2H, m), 2.83(3H, d, J 14 Hz), 3.6(1H, m) & 7.5-8.0(10H, m).

Attempts to recrystallise this phosphonium salt from $CHCl_3$-ethyl acetate resulted in the isolation of 2-hydroxybutylmethyldiphenylphosphonium iodide (320), m.p. 135°C, ν_{max} 3320, 1430, 1110, 900, 735 & 680 cm^{-1}., δ 0.83(3H, t, J 6.5 Hz), 1.8(2H, m), 2.86(3H, d, J 14 Hz), 3.96(1H, m) & 7.5-8.0(10H, m).

68. Reactions of 2-Trimethylsiloxy-2-phenylethylmethyldiphenylphosphonium iodide (310), with phenyl-lithium.

3 cm^3 of 1.303 M phenyl-lithium solution in ether was added slowly to a stirred suspension of 2g of 2-trimethylsiloxy-2-phenylethylmethyldiphenylphosphonium iodide (310) in 35 cm^3 of ether at 0°C and was set aside at room temperature overnight. A fine yellow powder was filtered off and washed with ether. This could not be recrystallised. The crude product had δ2.98(3H, d, J 13 Hz) & 7.2-8.3 (large multiplet), $^{31}P(CDCl_3)$ -18.1 p.p.m. A solution of this compound in acetone gave a dense yellow precipitate with aqueous silver nitrate. This precipitate was insoluble in ammonium hydroxide solution. This data suggests that the product was methyldiphenylstyrylphosphonium iodide (312).

A suspension of 0.6g (13 mmol) of the product from the above experiment, in 30 cm^3 of ether was treated with 1 cm^3 of 1.303M phenyl-lithium solution at 0°C and stirred for one hour. When it had completely dissolved, 0.24g (13 mmol) of benzophenone in 5 cm^3 of ether was added and the reaction allowed to warm up to room temperature. When the colour had discharged the organic layer was washed with 5 cm^3 of dilute HCl followed by water, and dried over $MgSO_4$. Chromatography (light petroleum-ether on 'Type H' alumina) gave 1,1-diphenylethene as the major product which had identical spectral data and R_f values (ether - basic alumina) with an authentic sample.

69. N-Chlorodi-isopropylamine was prepared in high yields by the method of Block and Kompa.[228]

70. Trifluoromethanesulphonic anhydride (167) was prepared by the method of Burdon et al.[229] with the exception that only half of the recommended quantity of phosphorus pentoxide was used. The anhydride was prepared in 73% yield and unchanged trifluoromethanesulphonic acid was recovered by distillation from the phosphorus pentoxide under reduced pressure.

71. Perfluoropinacol was prepared in high yields by the method of Gambaryan et al.[230]

72. 2,3-Dimethylbuta-1,3-diene (142), was prepared from pinacol by the method described by Vogel.[231] Traces of pinacolone were removed by storing the diene over fused $CaCl_2$ at -40°C for a few days before the diene was used.

73. Triethyloxonium hexachloroantimonate was prepared in high yields by the method of Meerwein et al.[232]

74. 1-Bromo-3-methylbut-2-ene (280) was prepared by the method of Karrer et al.[233] This method, however, produces a small amount of the isomer 2-bromo-2-methylbut-3-ene which cannot be separated by distillation.

75. Preparation of 1-Chloro-3-methylbut-2-ene (297) and 2-Chloro-2-methylbut-3-ene (293).

Dry HCl was passed into 102g (1.5 mol) of freshly distilled 2-methylbuta-1,3-diene (isoprene), at -10°C until the weight had increased by 53.25g. Loss of diene was prevented by using a -78°C condenser. After 3½ hours the reaction was comolete and solid anhydrous potassium carbonate was added to remove any unreacted HCl. After one hour the clear liquid was filtered off and distilled to give 73.4g (47%) of 2-chloro-2-methylbut-3-ene (293), b_{100} 35°C, δ(neat-TMS external) 1.87(6H, s), 5.0(1H, d, J 10 Hz), 5.18(1H, d, J 15 Hz) & 6.08(1H, dd, J 10 Hz & 15 Hz), and 25.8g (17%) of 1-chloro-3-methylbut-2-ene (297), b_{100} 50-54°C, δ 1.73(6H, s), 4.01(2H, d, J 7.5 Fz) & 5.4(1H, t, J 7.5 Hz). By the same method Jones and Chorley[234] only obtained 19% yield of the higher boiling isomer and none of the lower boiling isomer.

76. Preparation of 1-Trimethylsiloxybutane.

5.5g (50 mmol) of chlorotrimethylsilane in 30 cm^3 of ether was added slowly to a stirred solution of 4.0g (50 mmol) of pyridine and 3.7g (50 mmol) of butan-1-ol in 60 cm^3 of ether at 0°C, and allowing it to stir overnight at room temperature. Filtration, followed by evaporation and distillation gave 5.4g (73%) of 1-Trimethylsiloxybutane, b_{760} 122-123°C,[235]

$\delta(CH_2Cl_2)$ 0.06(9H, s), 0.72-1.65(7H, m) & 3.13-3.73(2H, m).

77. Experiment to investigate the hydrolysis of 1-Trimethylsiloxybutane in the presence of phosphonium iodides.

Three solutions were prepared:

i) 0.5g of 1-trimethylsiloxybutane in 23 cm^3 of acetone.

ii) 0.5g of the silylether and 0.14g of methyltriphenylphosphonium iodide in 23 cm^3 of acetone.

iii) 0.5g of the silylether and 1.4g of the phosphonium iodide in 23 cm^3 of acetone.

It was assumed that the acetone was sufficiently wet to hydrolyse the silylether. The solutions were monitored by g.l.c. (10% OV17 column at 46°C). After three hours no hydrolysis had occurred. After 48 hours there was a small amount of hydrolysis in each of the solutions, i.e. approximately the same amount of butan-1-ol was present in each solution by g.l.c.

78. Preparation of Benzenesulphenyl chloride.

Dry chlorine was passed into a solution of 10g of thiophenol in 50 cm^3 of CCl_4 at room temperature until an intense red colour persisted. Evaporation followed by distillation gave 12.1g (93%) of benzenesulphenyl chloride b_{10} 88-89°C.

79. Diethyl azodicarboxylate (D.A.D.) was made in 53% yield by the method described in Organic Synthesis.[236]

80. Separation of cis- and trans-Cyclohexane-1,4-diols.

These isomers were separated as diacetates by the method described by Olberg et al.[237]

81. Preparation of 4-Hydroxybutyl ethyl carbonate (338).

0.54g (5 mmol) of ethyl chloroformate in 10 cm^3 of ether was added to a stirred solution of 0.45g (5 mmol) of butane-1,4-diol and 0.51g (5 mmol) of triethylamine in 200 cm^3 of ether at 0^oC. After two hours the solution was filtered, evaporated and purified by chromatography (silica M.F.C. - ether). δ 1.23(3H, t, J 7 Hz), 1.53-1.9(4H, m), 3.47 (2H, t, J 6 Hz), 3.71(1H, s) & 3.87-4.23(4H, m). Attempts to distill this compound resulted in the formation of ethanol and T.H.F.[238]

82. Preparation of Heterocyclic compounds from diols and related compounds by using Diethyl azodicarboxylate (D.A.D.). General method a).

Triphenylphosphine (5 mmol) and the diol (5 mmol) were dissolved in ether (20 cm^3) and D.A.D. (5 mmol) in ether (5 cm^3) was added at 0^oC. When the colour had discharged the precipitate of diethyl hydrazodicarboxylate was filtered off and the solution was distilled, collecting any volatile material in a -78^oC trap. Compounds were characterised and yields were calculated by gas chromatography. By this method the following heterocyclic compounds were prepared:

a) Ethylene oxide from ethane-1,2-diol in high yields but the product also contained some acetaldehyde.

b) Styrene oxide from 1-phenylethane-1,2-diol, 73%.

c) Butene-1,2-oxide from butane-1,2-diol, 90%.

d) Ethylene sulphide from 2-mercaptoethanol, 54%.

e) T.H.F. from butane-1,4-diol, 55%.

The solvent was changed, in some cases, to CH_2Cl_2, $CHCl_3$ or benzene with little effect on the reaction.

General method b).

This method was very similar to method a, with the exception that trisdimethylaminophosphine was used in place of triphenylphosphine. By this method the following compounds were prepared:

a) Ethylene sulphide from 2-mercaptoethanol, 80%.

b) T.H.F. from butane-1,4-diol, 29%.

The crude reaction product from the reaction of diethyl azodicarboxylate and butane-1,4-diol in the presence of trisdimethylaminophosphine contained the unchanged phosphine, δ 2.5(d, J 8.5 Hz), $^{31}P(CDCl_3)$ -117 p.p.m., trisdimethylaminophosphine oxide, δ 2.63(d, J 10 Hz), $^{31}P(CDCl_3)$ -41.3 p.p.m., and another phosphorus compound, δ 2.77(d, J 10 Hz), $^{31}P(CDCl_3)$ -41.7 p.p.m., were present. 4-Hydroxybutyl ethyl carbonate was also present and identified by thin layer chromatography comparison with an authentic sample (see experiment 81), R_f=0.74, 5% methanol-ether on silica gel, R_f=0.51, ether-basic alumina.

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S. ANTCZAK Ph.D. THESIS 1977

The Synthesis and Reactions of Some Pentacoordinate Phosphorus Compounds.

by

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ABSTRACT.

The synthesis and reactions of phosphoranes are reviewed, and the mechanisms of ligand permutational isomerisms of phosphoranes are discussed in terms of Berry pseudorotations (B.P.Rs.) and Turnstile rotations (T.Rs.). The factors effecting the activation energies for these pseudorotations are discussed.

The synthesis and thermal reactions of phosphoranes prepared from acyclic trivalent phosphorus compounds and from 3,4--dimethylphosphol-3-enes by using N-chlorodo-isopropylamine is described. A short investigation into the preparation of phosphoranes that contain seven-membered rings suggested that these compounds are inherently unstable.

The synthesis of phosphoranes from cyclic and acyclic phosphine oxides and from phosphetan oxides by using trifluoromethanesulphonic anhydride, is described. Cis-trans isomerisations in 2,2,3,4,4,--pentamethylphenylphosphetan ditriflate are discussed in terms of pseudorotations of intermediate phosphoranes.

The dynamic n.m.r. spectra of certain phosphoranes were recorded and, in some cases, the difference in relative apicophilicities of phenyl, methyl and methoxyl groups were determined.

The preparation of phosphoranes from alkoxyphosphetanium salts resulted in Arbuzov reactions whereas the preparation of phosphoranes from alkylthiophosphetanium salts is described and the stereospecific nature of this reaction is discussed in terms of the mechanisms of substitutions in pentacoordinate phosphorus compounds. The preparation and thermal rearrangement of 2,2,3,3,-tetrakistrifluoromethyl-5-phenyl-1,4,6-trioxa-5-phospha($5P^{V}$)spiro[4,4]nonane, i.e. the first example of spirophosphorane containing a 1,2--oxaphospholan ring, is described. Pseudorotations of this phosphorane are discussed.

The preparation of cyclic phosphoranes, containing 1,2--oxaphospholan rings, from epoxides and ylids is discussed and attempts to adapt this reaction to spirophosphorane synthesis is described. The preparation of chlorophosphoranes by the halogenation of allenylphosphonic dichlorides is discussed and attempts to adapt this reaction to allylphosphonates are described. In some cases this reaction lead to carbon-phosphorus bond fission.

Condensation reactions using diethyl azodicarboxylate (D.A.D.) and triphenylphosphine are discussed and the use of these reagents to prepare heterocyclic compounds from diols and related compounds is described.

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