THE SYNTHESIS AND PSEUDOROTATIONS OF SPIROPHOSPHORANES

by

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A Thesis presented
for the degree of
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in the Faculty of Science
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Finally, I would like to thank my wife for her support and encouragement at all stages of this work; and the Science Research Council for a maintenance grant.

TO HILARY

STATEMENT

The accompanying thesis submitted for the degree of Doctor of Philosophy entitled "The Synthesis and Pseudo-rotations of Spirophosphoranes" is based on work conducted by the author in the Department of Chemistry of the University of Leicester, 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 John Brierley.

John Brierley.

August, 1978.

CONTENTS

SUMMARY

A review of phosphorane chemistry is presented. From a range of spirophosphoranes the relative apicophilicity of sulphur and oxygen containing ligands was determined. The conclusion reached was that the relative apicophilicities of ethylthio, ethoxy and trimethylsiloxy were similar.

The N-chlorodi-isopropylamine method for the preparation of spirophosphoranes was developed, enabling the preparation of various unsymmetrical phosphoranes, from which the relative apicophilicities of phenoxy and phenylthio groups were determined. The preparation of spirophosphoranes from phosphetans was shown to go with retention of configuration at phosphorus. The interconversion of the cis and trans spirophosphoranes prepared from phenyl and benzylphosphetans was followed kinetically, and from this study the phenyl group was shown to be more apicophilic than the benzyl group.

Cyclic and acyclic phosphites were reacted with acrylic acid. In the case of cyclic phosphites spirophosphoranes were prepared from which the relative apicophilicity of the phenyl group was determined. A series of spirophosphoranes was prepared containing a 4,4,5,5-tetramethyl-1,3,2-dioxaphospholan ring. On thermolysis these were found to give 2,3-dimethyl-butadiene as the major component and some t-butyl methyl ketone.

From a series of hexafluorobiacetyl and tetrachloro-o-benzoquinone adducts the relative apicophilicities of chlorine, cyanide, isocyanate and isothiocyanate were determined. It was shown that the cyanide was more apicophilic than chlorine, whilst the isocyanate and isothiocyanate were found to have a similar apicophilicity to chlorine.

The first pentaco-ordinate phosphorane containing an azide ligand was prepared by direct substitution of a chlorospirophosphorane. From this spirophosphorane the relative apicophilicity of the azide group was determined; it was found to be slightly more apicophilic than the phenoxy group. By a similar procedure a spirophosphorane containing a cyanide ligand was prepared.

Parts of this work have been described in the following publications:

The Apicophilicity of the Ethylthio-group in Trigonal Bipyramidal Phosphoranes

By J. Brierley, S. Trippett* and M. W. White,

J. C. S. Perkin I, 1977, 273.

Synthesis of Phosphoranes by using N-chlorodi-isopropylamine

By S. Antczak, S. A. Bone, J. Brierley and S. Trippett,*

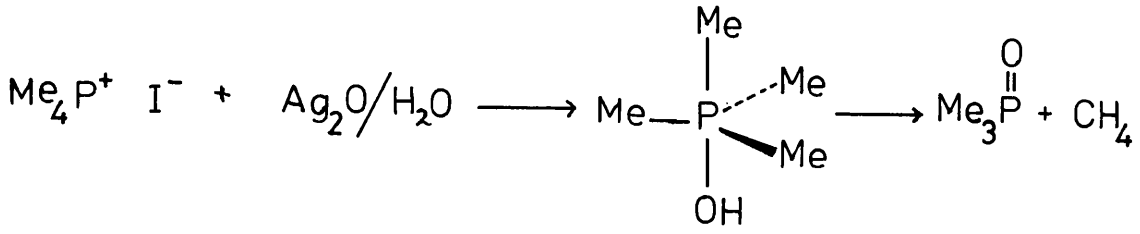
J. C. S. Perkin I, 1977, 278.

1 PHOSPHORANES

1.1 INTRODUCTION

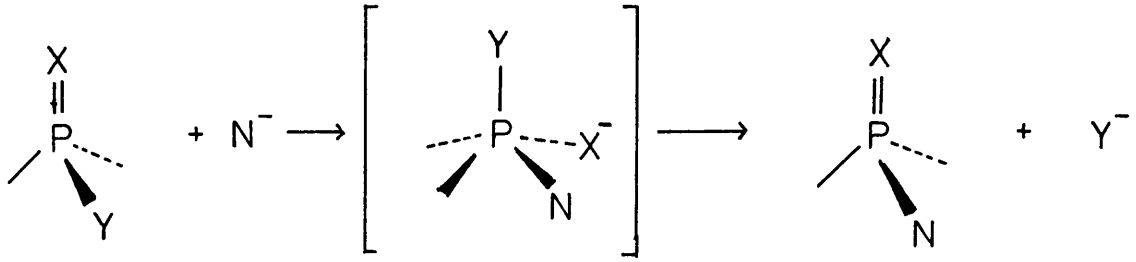
Throughout this thesis the term 'phosphorane' is used to describe a phosphorus atom with five covalently bonded ligands attached to it.

The first reported phosphorane was an intermediate (2) proposed by Ingold[1] in 1929, in the reaction of tetramethylphosphonium iodide (1) with moist silver oxide. On heating methane gas and trimethylphosphine oxide (3) are formed.



(1) (2) (3)

In contrast to the analogous ammonium series where discrete Me_4N^+ and OH^- ions exist, Ingold proposed that the intermediate (2) existed as a pentacovalent compound, i.e. with a covalent phosphorus - oxygen bond. Although none of these phosphorane intermediates has been isolated, many papers have been published [2-12] concerning the intermediacy of pentacovalent phosphoranes in nucleophilic attack at a tetracoordinated phosphorus compound.



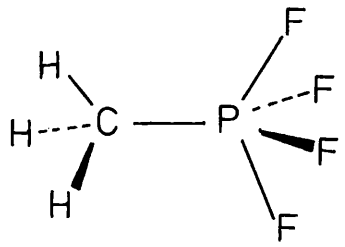
(4)

The evidence for intermediates of the type (4) is therefore indirect, but there is another type of phosphorane which is reasonably stable, may be isolated and fully characterised. It is generally assumed that the structure and properties of these stable phosphoranes are applicable to the intermediate type of phosphorane (4).

1.2 THE STRUCTURE OF PHOSPHORANES

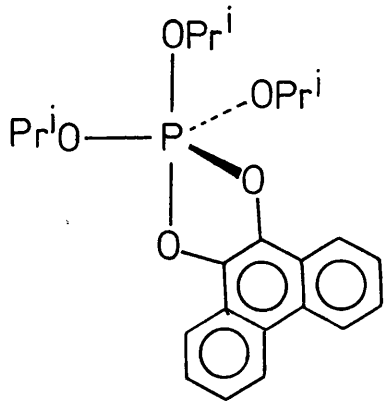
Acyclic phosphoranes with five identical ligands attached to the phosphorus atom have been shown to have trigonal bipyramidal geometry. These data have been derived from X-ray diffraction studies of pentaphenylphosphorane[13] and pentaphenoxyphosphorane[14], and electron diffraction[15], infrared, and Raman studies[16, 17] of pentafluorophosphorane. Pentachlorophosphorane has also been shown to be trigonal bipyramidal by an electron diffraction study[18].

In the phosphorane (5) electron diffraction studies[19] have shown the molecule to be definitely trigonal bipyramidal with only a small amount of distortion, the four fluorine atoms being bent away from the methyl group.



(5)

The incorporation of different ligands or small rings into the phosphoranes (6)[20], (7)[21], (8)[22], and (9)[23] has been shown from X-ray diffraction studies to result in only small distortions from perfect trigonal bipyramidal geometry.



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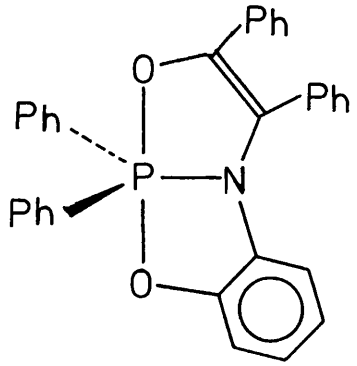

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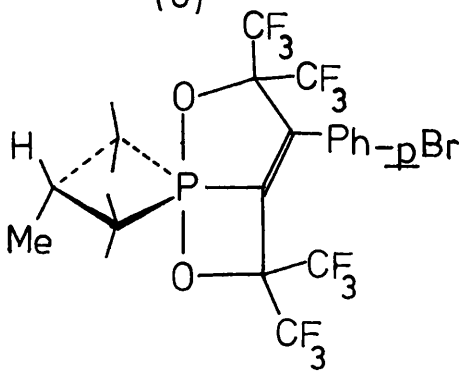

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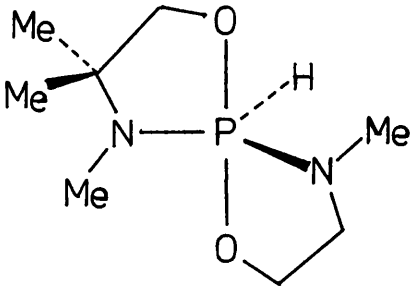
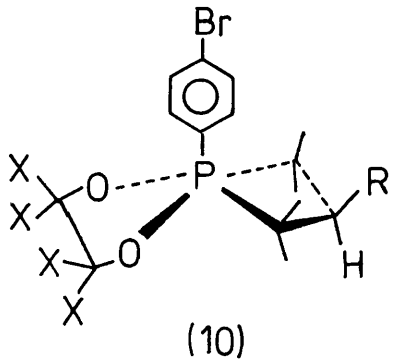


(9)

However not all the distortions are small. X-ray diffraction studies of the spirophosphoranes (10)[24] and (11)[25] have shown them to be much closer to a square pyramidal configuration, with the four ring atoms taking the basal positions and the fluorine or _p_-bromophenyl group the apical position.



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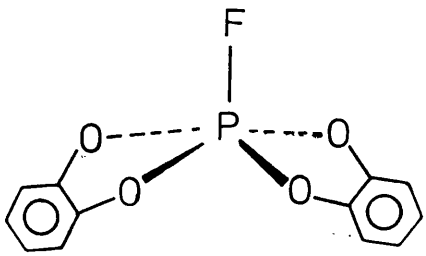


(11)

X = CF_3 R = H or _cis_ Me

Previously the ^{19}F n.m.r. spectral data of the spirophosphorane (11)[26] had been interpreted in terms of the fluorine atom occupying an equatorial position in a trigonal bipyramid. Holmes[27] has shown that the n.m.r. spectral data of (11), and other spirocyclic oxyphosphoranes, are consistant with the square pyramidal structures known to exist by X-ray diffraction studies.

Reduced ring strain and enhanced electronic balance are cited as important factors stabilizing a square pyramidal conformation for spirophosphoranes containing highly electronegative atoms directly attached to phosphorus.

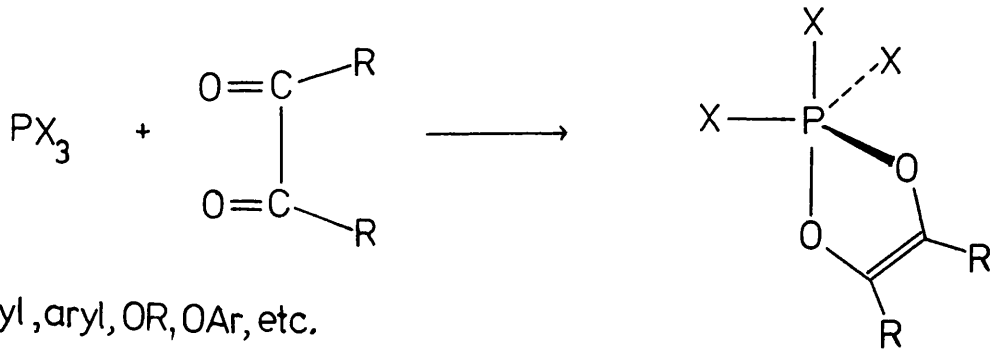
Generally speaking phosphoranes whether containing one, two or no rings are essentially trigonal bipyramidal and will be treated as such in any following discussions. The reasons for this assumption will become clear in the following chapters.

1.3 THE SYNTHESIS OF CYCLIC PHOSPHORANES

Early work on the synthesis of cyclic phosphoranes made use of the reaction of tervalent phosphorus compounds with α-diketones of the aliphatic, alicyclic and aromatic series[28-31] to give 1,3,2-dioxaphospholens.

Cyclic phosphoranes such as (12) are fairly reactive compounds and readily react with another molecule of the α-diketone to give a 1,3,2-dioxaphospholan ring system. (14)[29]

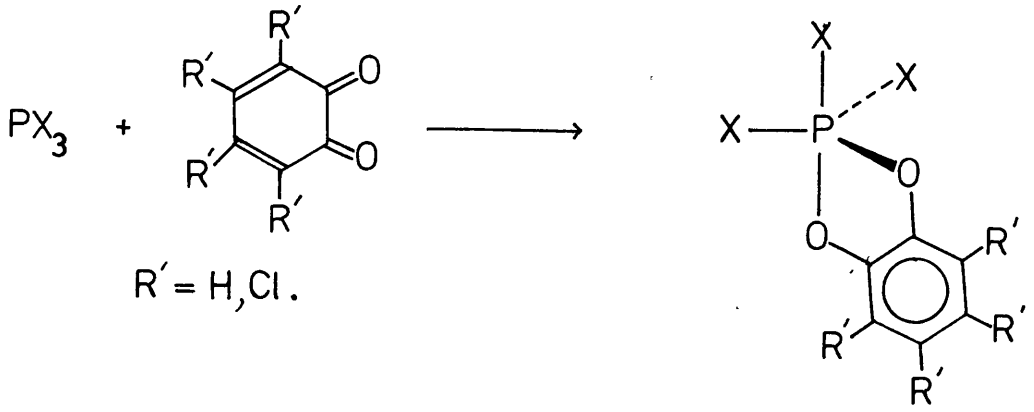
This reaction is believed to go *via* the intermediate (13) which involves ring opening and then an attack of the stabilized negative charge on the carbonyl of the second molecule of biacetyl. That similar molecules undergo ring opening can be shown in the adduct (15) made from trisdimethylaminophosphine and benzil.[32]



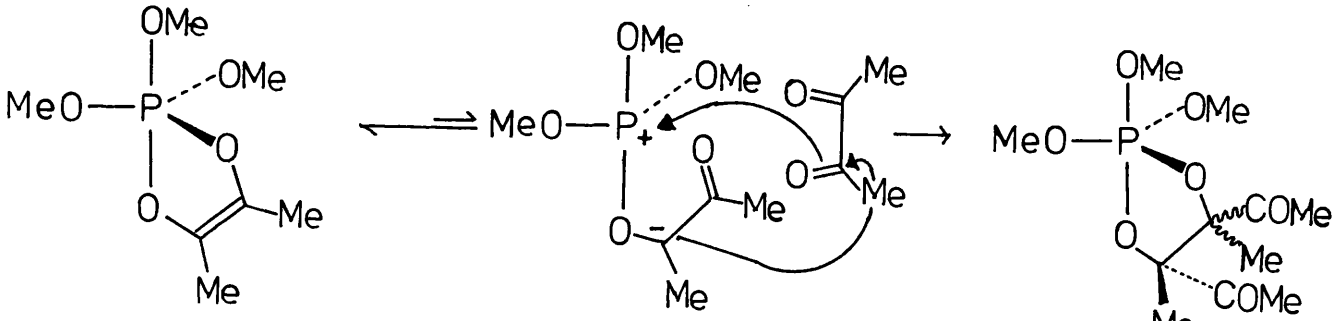
X = alkyl, aryl, OR, OAr, etc.

R = H, CH_3, CF_3, Ph.

(12)



R′ = H, Cl.



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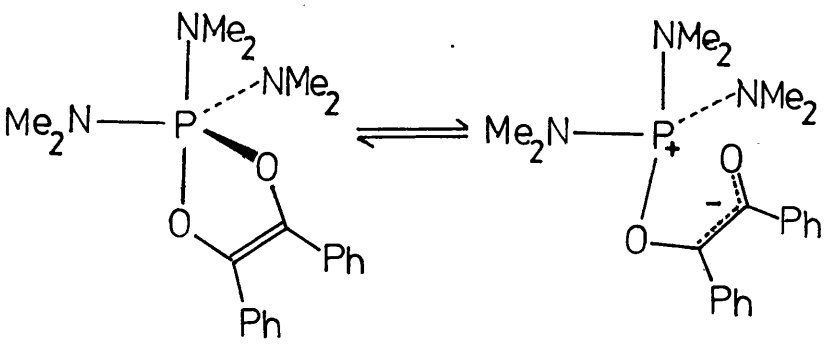
(14)



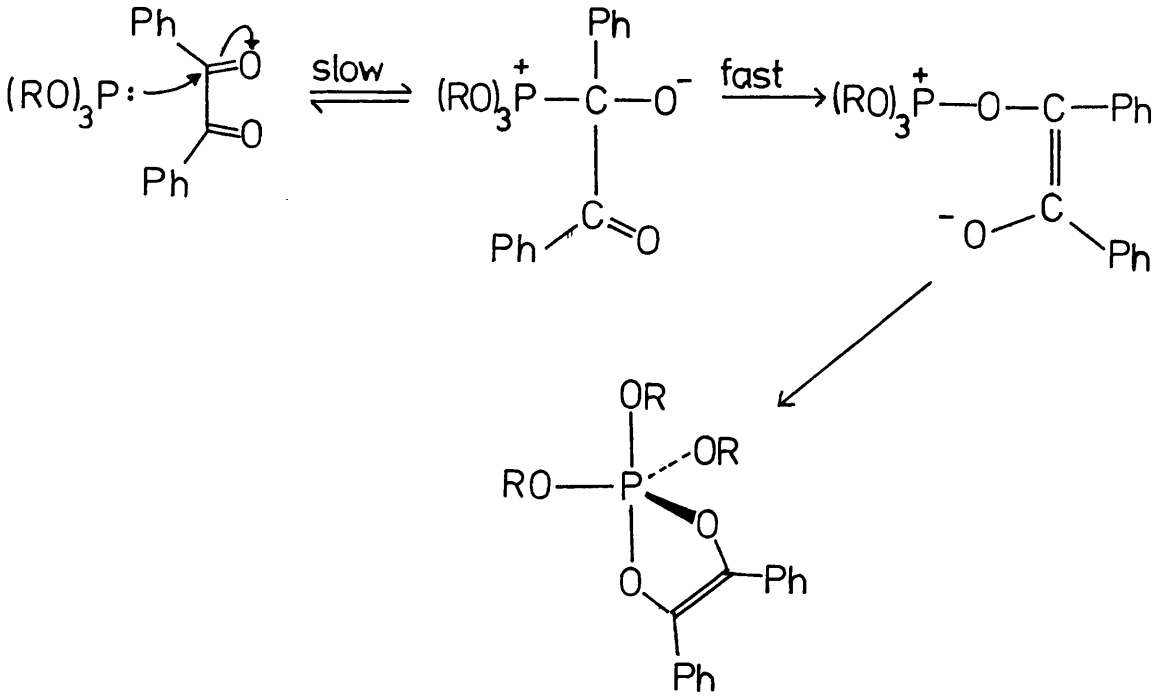
(15)

(16)

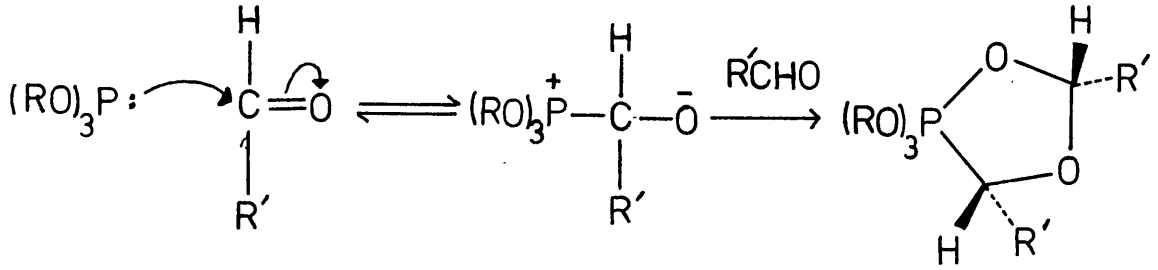
In solution this adduct (15) exists in two forms. The presence of the dipolar form (16) was deduced from the fact that the ^{31}P n.m.r. spectrum was dependant on solvent polarity, moving to low field as the solvent polarity was increased. Adduct (15) should have a positive ^{31}P n.m.r. chemical shift relative to 85% H_3PO_4, whilst that of (16) should be negative. This gives the ^{31}P n.m.r. chemical shift observed as a weighted average of the two forms (15) and (16). Only one signal is ever observed so we can see that the equilibrium (15) $\rightleftharpoons$ (16) is fast on the n.m.r. time scale.

Ramirez[33] has attempted to explain this result as being due to the lower electronegativity of nitrogen compared to oxygen and partly due to the fact that dimethylamino groups are more bulky than alkoxy groups.

The following mechanism has been proposed[34] on the basis of a kinetic study of the reactions of trialkyl phosphites with benzil.

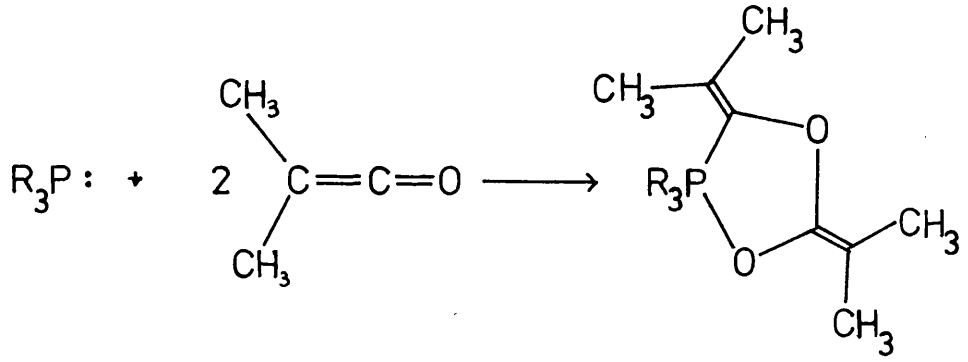


Phosphites undergo reaction with two moles of aliphatic aldehydes, under mild conditions, to give diastereomeric 1,4,2-dioxaphospholans (17)[35].



(17)

Similar 1,4,2-dioxaphospholans (18) are also formed from tervalent phosphorus compounds and dimethylketene[36].

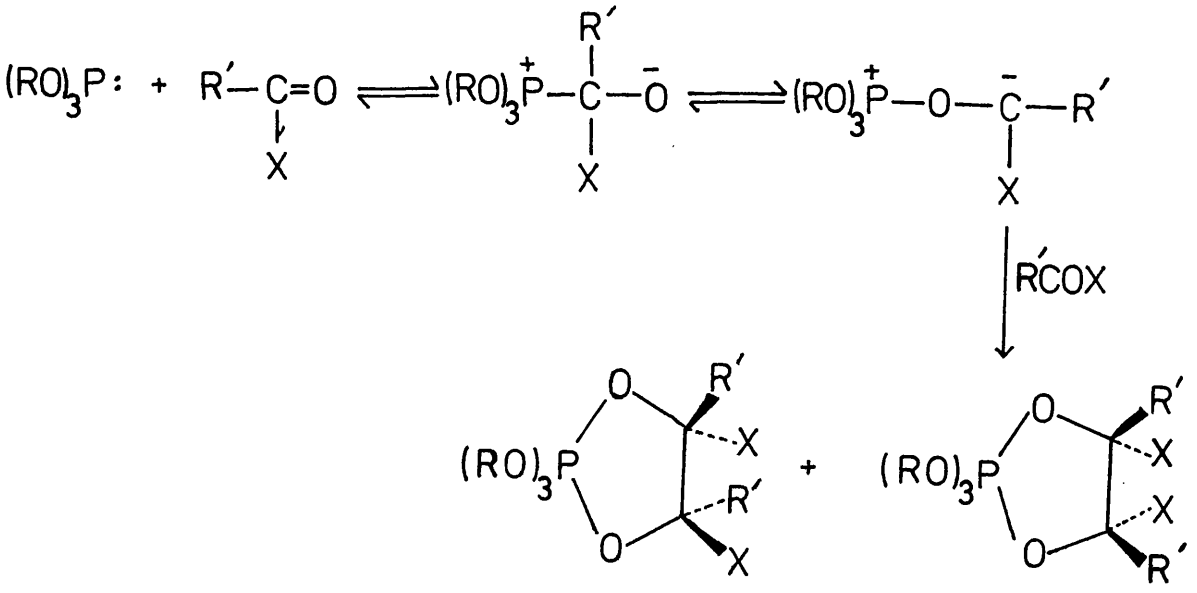


(18)

If aromatic aldehydes, or ketones activated by electron withdrawing groups, e.g. $(CF_3)_2C{=}O$, PhCOCN, are used then the product of reaction with a tervalent phosphorus compound is a 1,3,2-dioxaphospholan ring. (19), (20).[37-41]

Ramirez[33,42] has found that the initial 2 : 1 adduct formed from trimethyl phosphite and pentafluorobenzaldehyde, at 0°, was a 1,4,2-dioxaphospholan, which on heating to 80° isomerised to the 1,3,2-dioxaphospholan. The spirophosphorane (22) has been isolated from reaction of

hexafluoroacetone and the thiophosphinite (21).[43,44]



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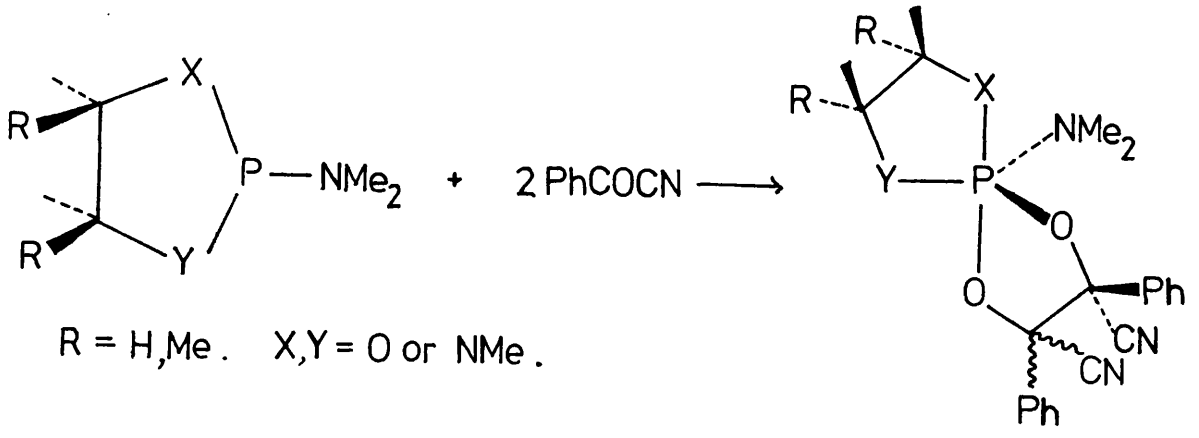

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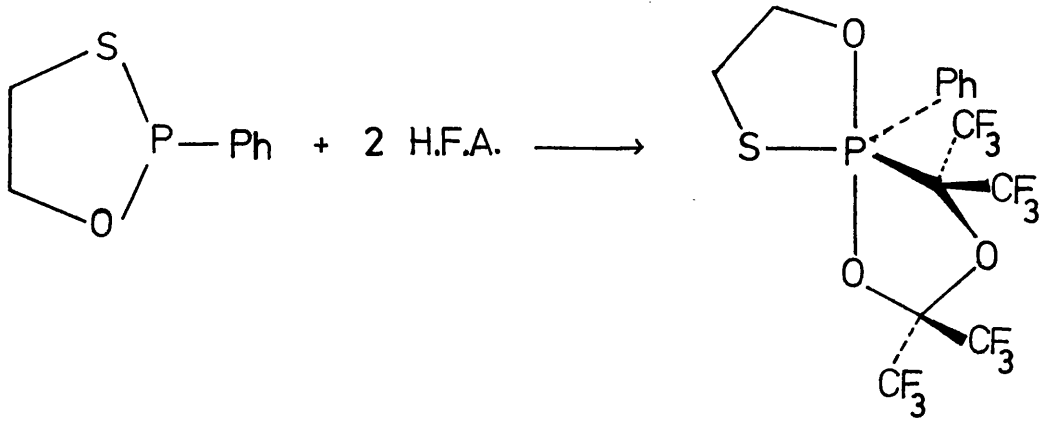
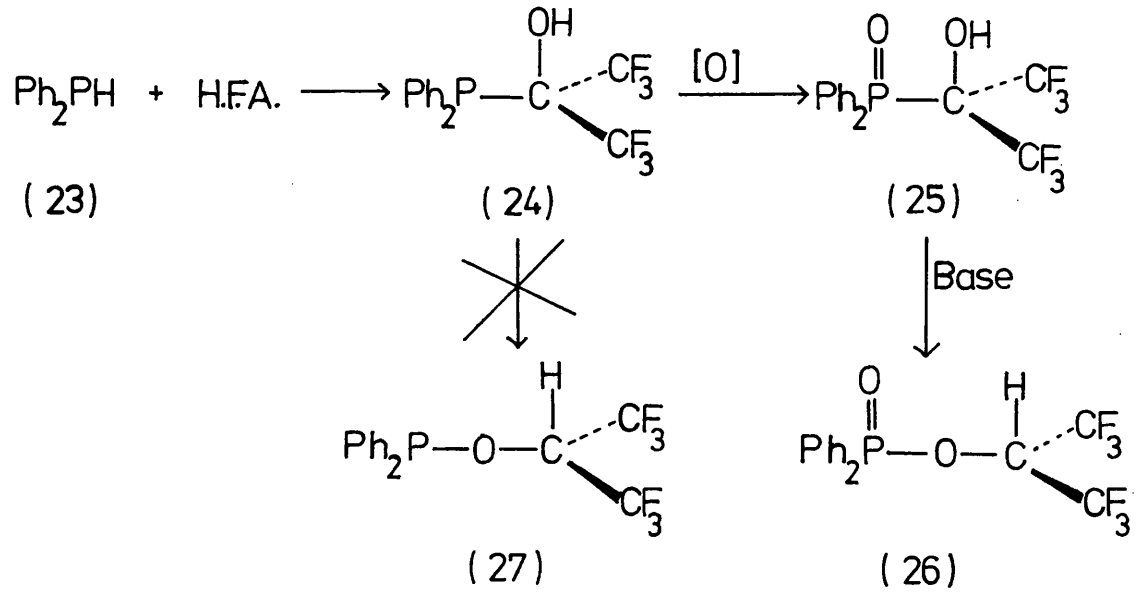


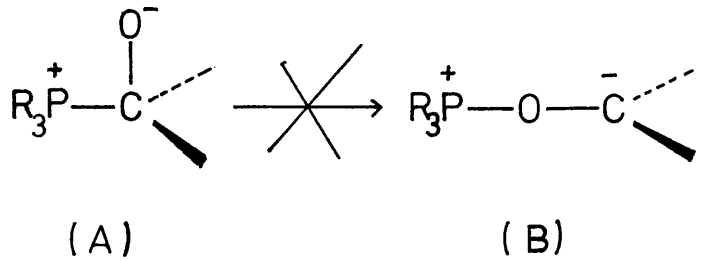
(21) (22)

This type of adduct shows no tendency to isomerise to a 1,3,2-dioxaphospholan system, which indicates that 1,4,2-dioxaphospholans are not intermediates in the formation of 1,3,2-dioxaphospholans from H.F.A. and tervalent phosphorus compounds.

Work carried out by Janzen and Vaidya[45] on the reaction between hexafluoroacetone and diphenylphosphine (23), showed that the initial product was the phosphorus alcohol (24). This phosphorus alcohol was very susceptible to oxidation and readily gave (25), which on treatment with base rearranged to (26).

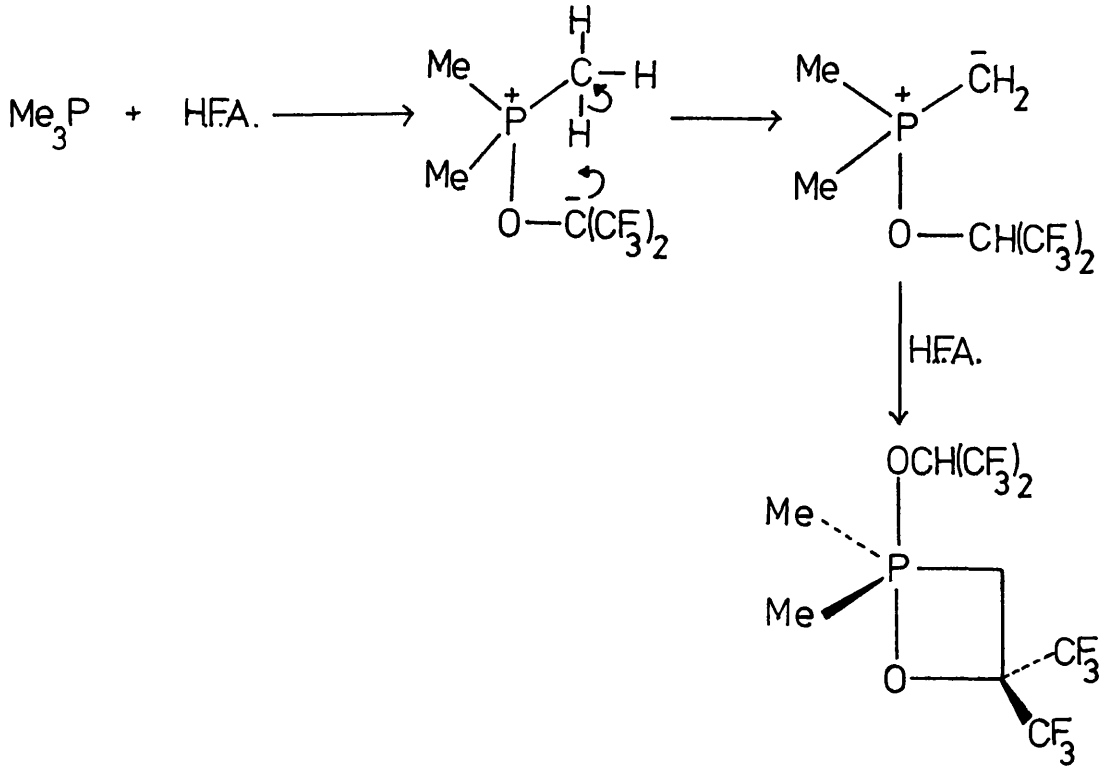


They also found that the intermediate (24) was stable and showed no tendency to isomerise to (27). This could be taken as indirect evidence that the following isomerisation (A)⇌(B) will not occur.



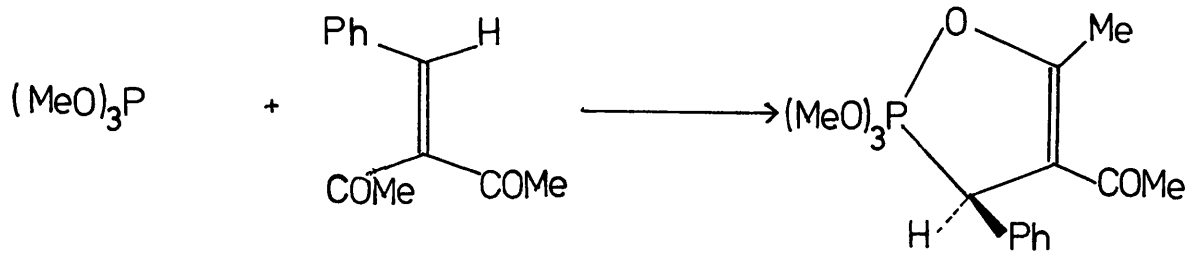
However this assumption is not strictly valid as isomerisation of the charged betaine (A) is likely to be easier than for the unchanged phosphorus alcohol (24). So although it appears that the initial attack occurs at the carbon of the carbonyl group followed by rearrangement as in (A) ⇌ (B), we cannot rule out the possibility of direct attack on oxygen in certain cases.

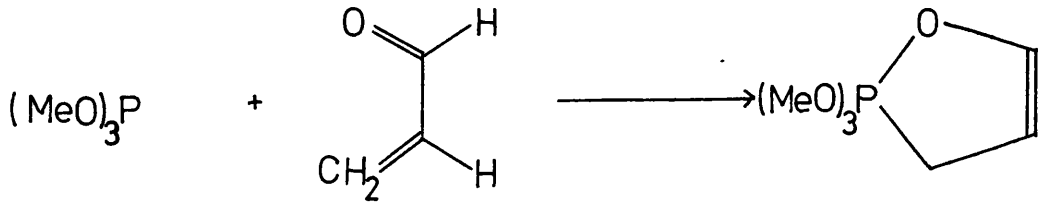
If the tervalent phosphorus compound contains a fairly mobile hydrogen atom in the ∝- position, then the possibility of migration occurs when the phosphine reacts with H.F.A.[46]

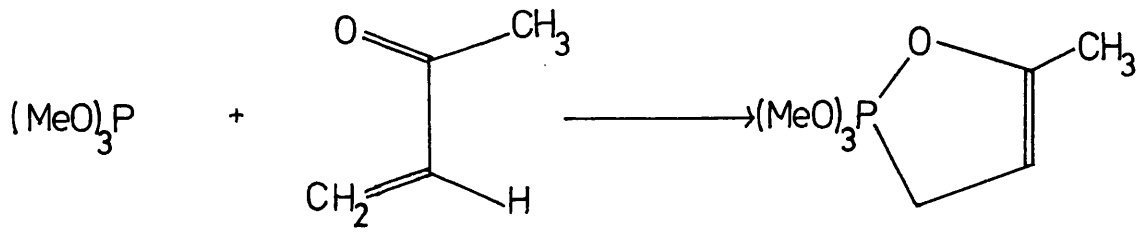


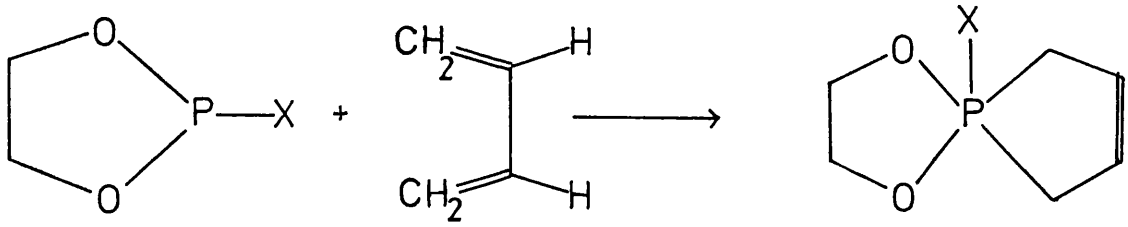
Stable phosphoranes have been prepared from tervalent phosphorus compounds and a wide range of 1,3 - unsaturated compounds e.g. benzylideneacetylacetone[47,48], acrolein[49,50], methyl vinyl ketone[51] and butadienes[52,53].

Reactions between trivalent phosphorus compounds and trans, trans hexa-2,4-diene(29) go by a concerted six electron disrotatory process[54] and are therefore stereospecific, e.g. give the phospholene ring (30) with the methyl groups cis to one another.

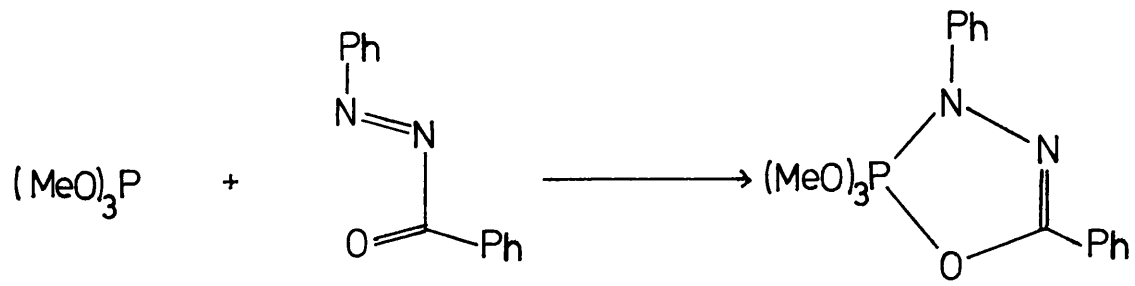


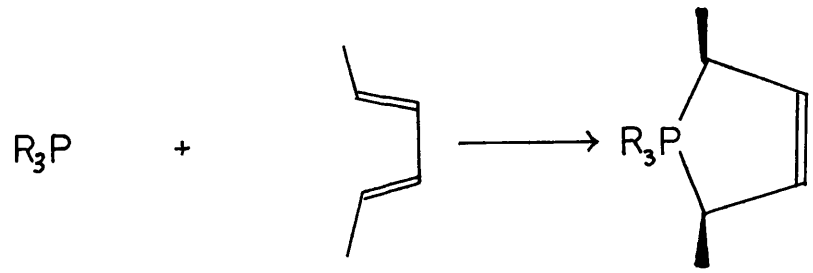






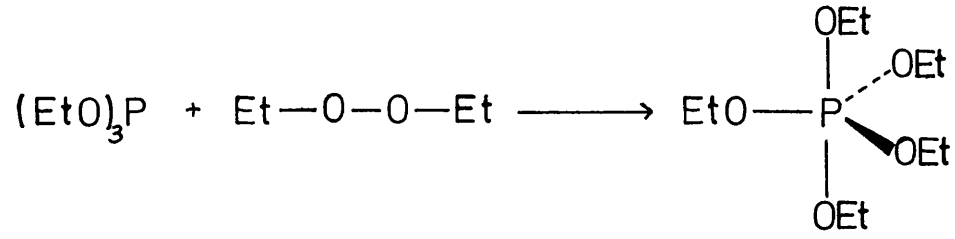
X = F, OMe, NMe, Me, Ph.





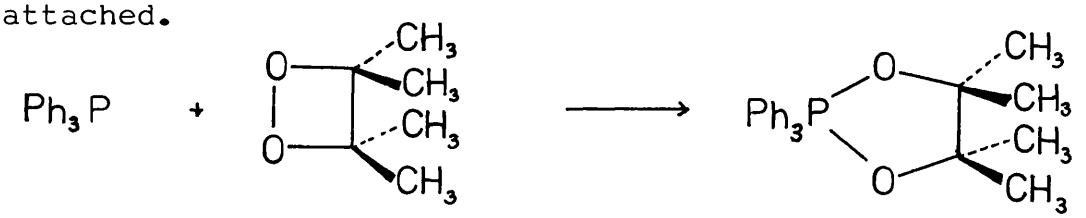
(29) (30)

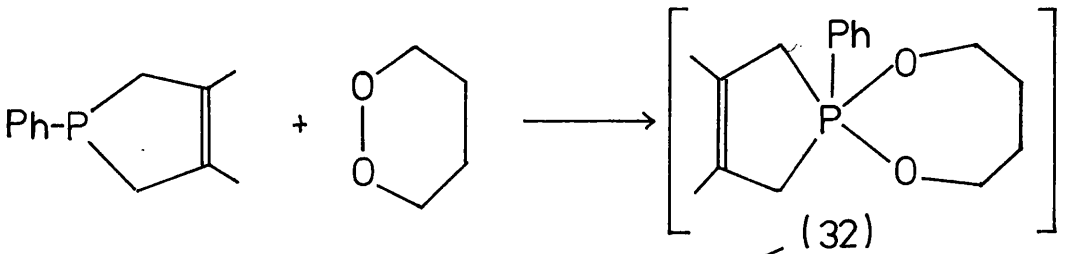
In 1964, Denney and Relles[55] prepared pentaethoxyphosphorane (31) from triethyl phosphite and diethyl peroxide.



(31)

By this method many oxyphosphoranes have been prepared and by varying the peroxide[56,57] other groups have been attached.





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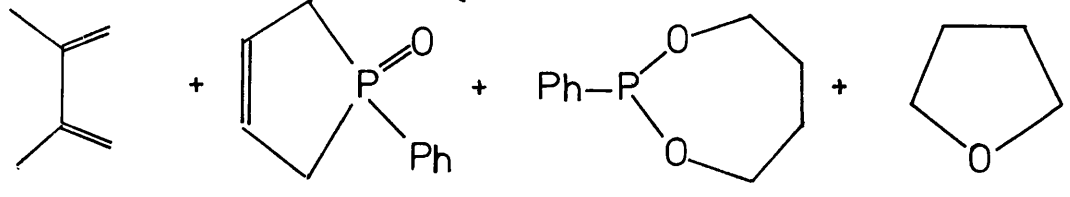
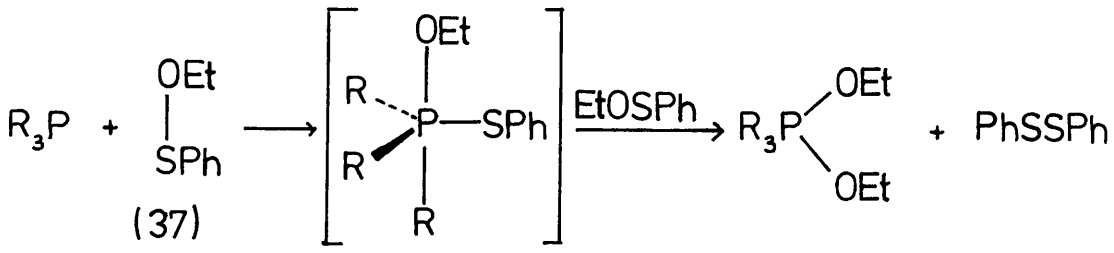


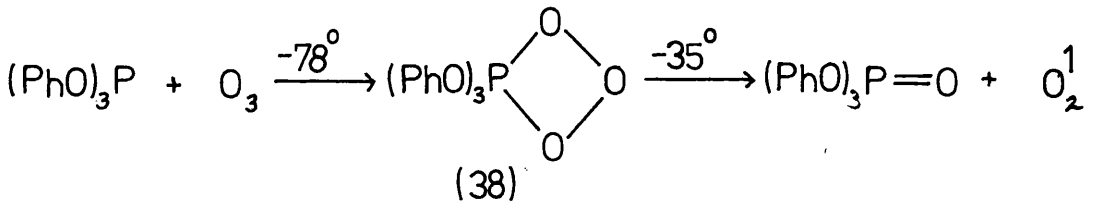
(33) (34) (35) (36)

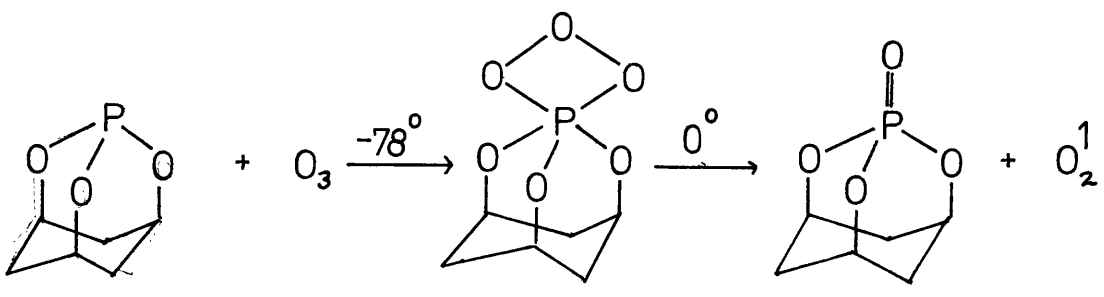
Presumably the products (33) - (36) are from an initial adduct (32) which then falls apart.

A general fault of these peroxide reactions is that they are very slow, which can lead to various side reactions and a subsequent lowering of yield. The use of ethyl benzenesulphenate (37)[58] greatly speeds up the reaction; however the diphenyl disulphide formed is difficult to remove.



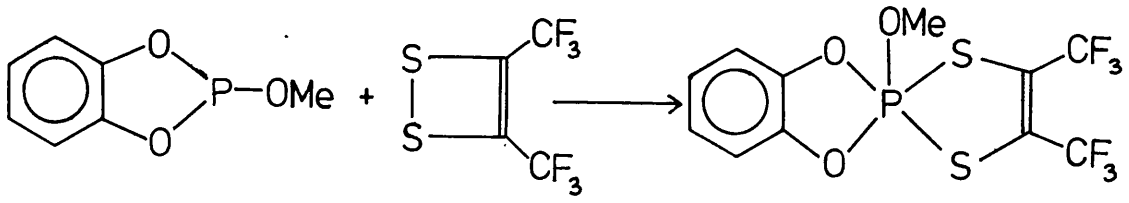
Phosphites react with ozone[59,60] at low temperatures to give phosphoranes (38) and (39). On raising the temperature these decompose to give the phosphates and singlet oxygen.





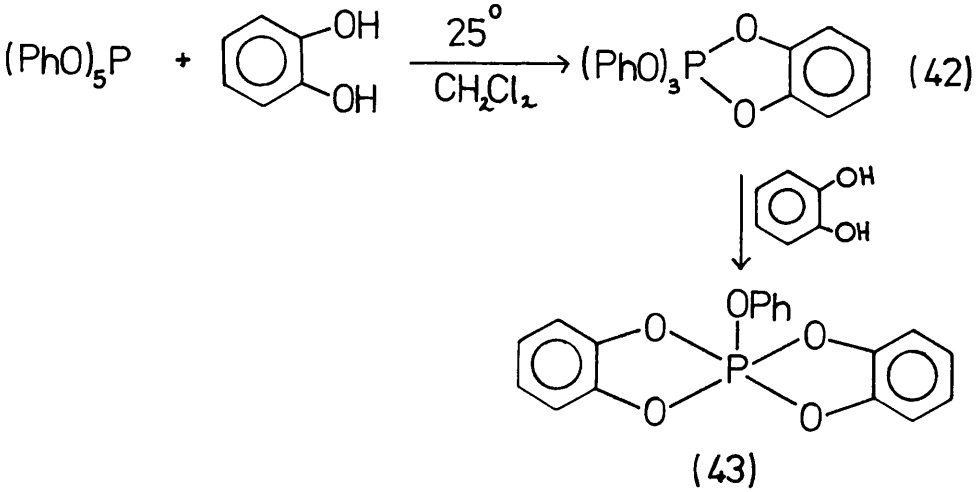
(39)

A preparation of spirophosphoranes containing two P-S bonds is facilitated by the use of bis-3,4-trifluoromethyldithieten (40), which forms fairly stable adducts (41) with cyclic phosphites.[61]



(40) (41)

If pentaphenoxyphosphorane is reacted with one mole of catechol, in methylene chloride, at 25°C the catechol displaces two molecules of phenol to give the cyclic phosphorane, (42). This molecule will then react with another mole of catechol to give the spirophosphorane (43).[62]

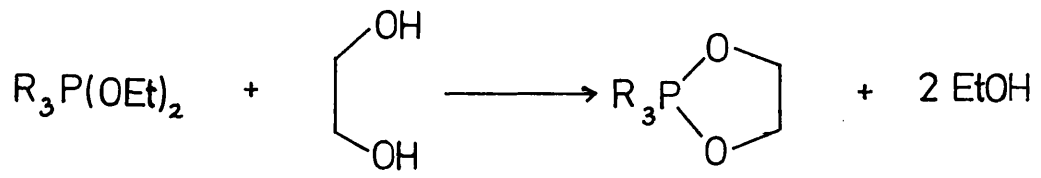


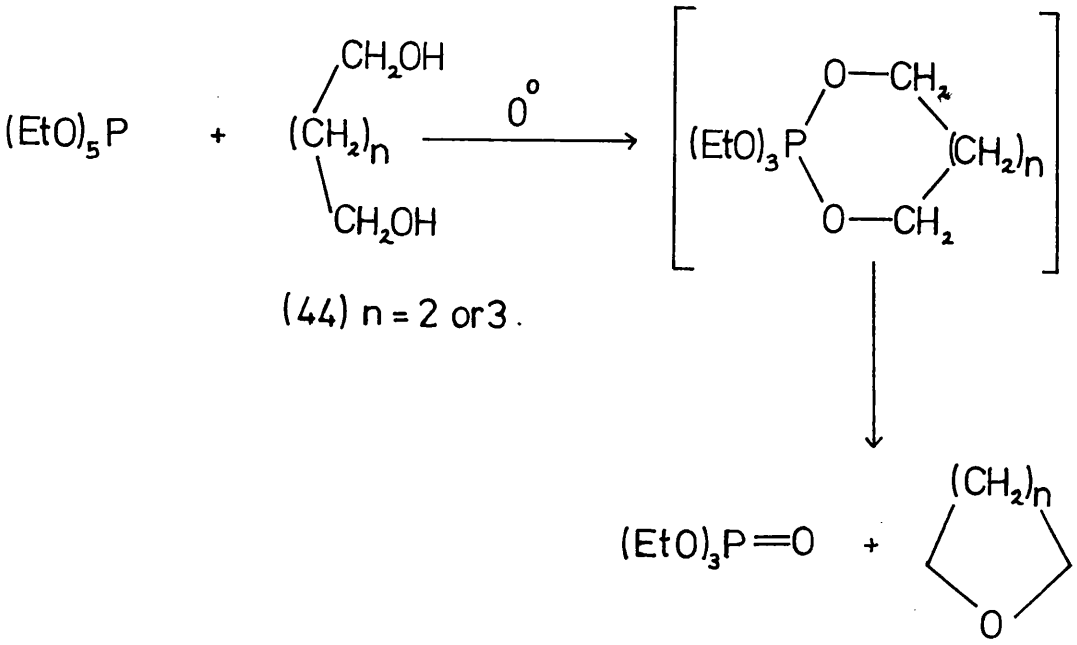
(43)

Denney[63,64] later showed that certain diols react with acyclic oxyphosphoranes to give cyclic and spirophosphoranes.

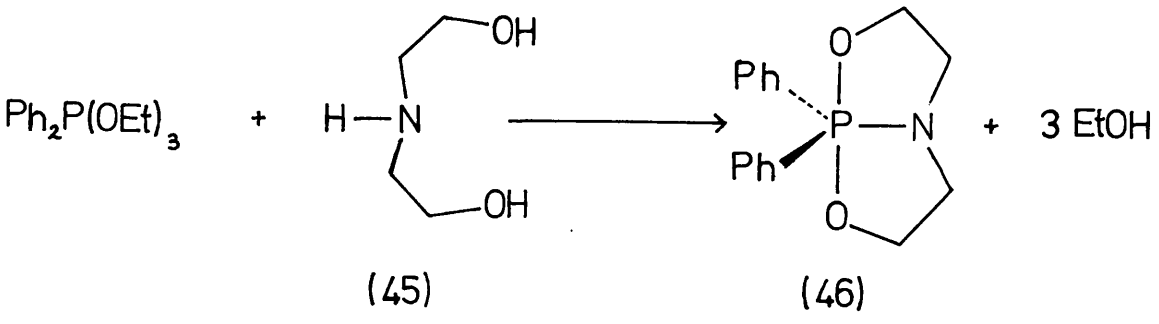
With pentaethoxyphosphorane the exchange reaction to form cyclic oxyphosphoranes only works smoothly with 1,2- and 1,3-diols, since 1,4-butane diol (44, n=2) and 1,5-

pentane diol (44, n=3) give T.H.F. and tetrahydropyran respectively.

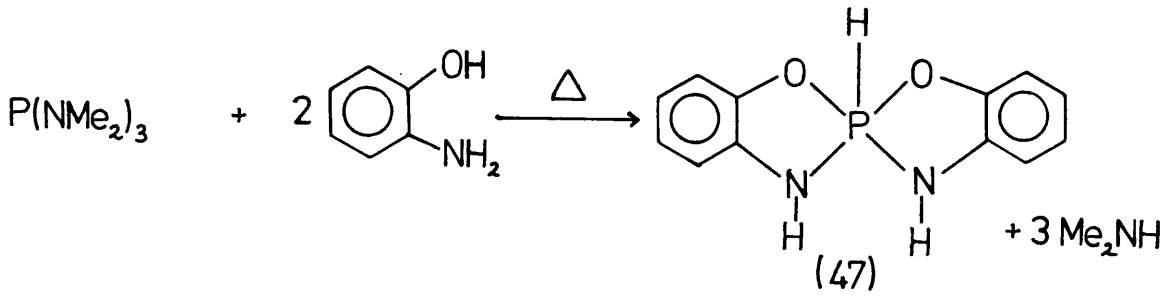




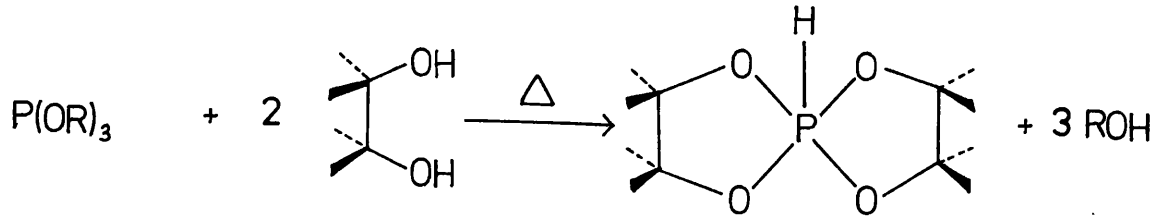
Denney has extended this exchange reaction by preparing bicyclicphosphorane (46) using the aminodiol (45).



Sanchez et al[66,67] have developed a useful method for the preparation of spirophosphoranes (47) and (48) containing a P-H bond, from reaction of diols and aminoalcohols with either trisdimethylaminophosphine or trialkyl phosphites.

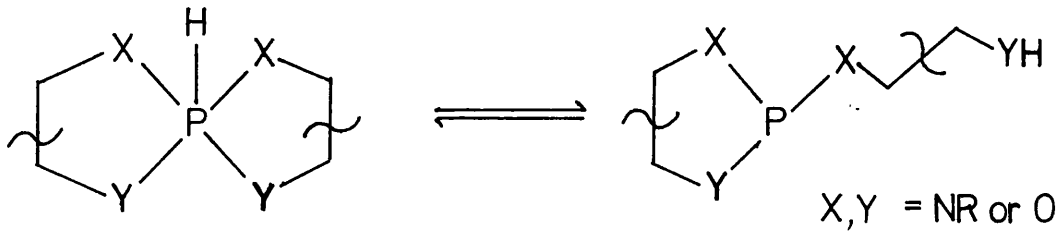


(47)



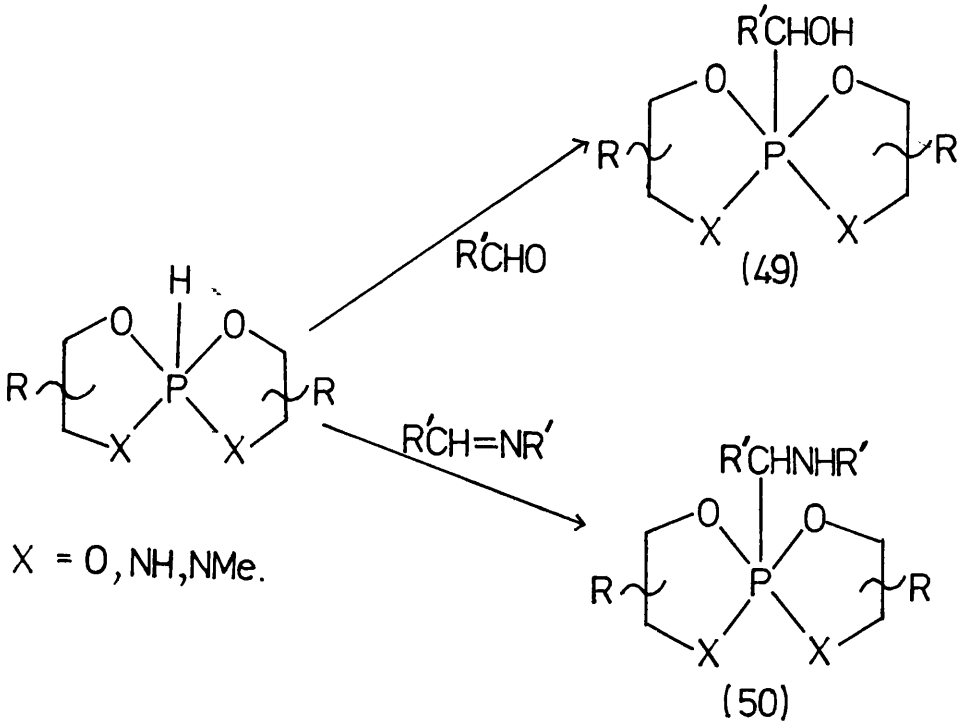
(48)

Similar reactions involving cyclicphosphites[68] and cyclic phosphoramidites[69] have also been used to prepare a wide range of spirophosphoranes containing a P-H bond. A tautomeric phosphite ⇋ spirophosphorane equilibrium is characteristic of spirophosphoranes with a P-H bond derived from glycols or amino alcohols.

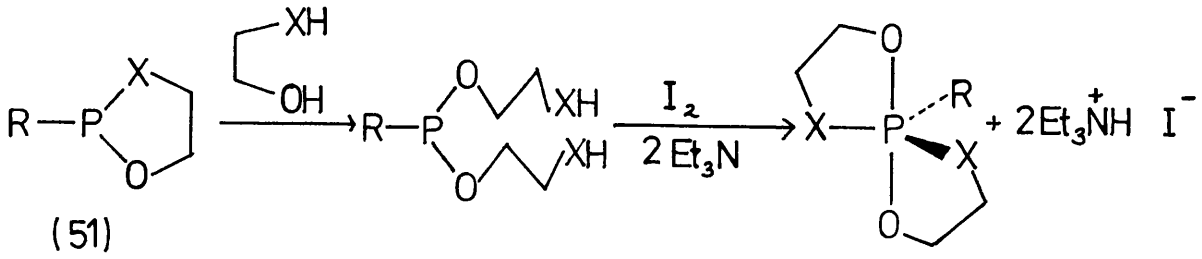


The equilibrium position depends on the temperature and the nature of the substituent in the ring and on the nitrogen atom. When X = Y = O the equilibrium at room temperature is almost completely displaced towards the spirophosphorane.[68] The form with a P^V atom is more

characteristic of unsaturated or aromatic systems than of saturated rings or rings with alkyl substituents. In asymmetric spirophosphoranes the less substituted ring is opened preferentially.[79] These P-H spirophosphoranes will react with aldehydes[70] and imines[71] to give the new systems (49) and (50).



If a cyclic phosphonite (51) is treated with one mole of a 1,2- aminoalcohol or diol followed by one mole of iodine in the presence of two moles of triethylamine, then spirophosphoranes (52) are formed in high yields.[72]

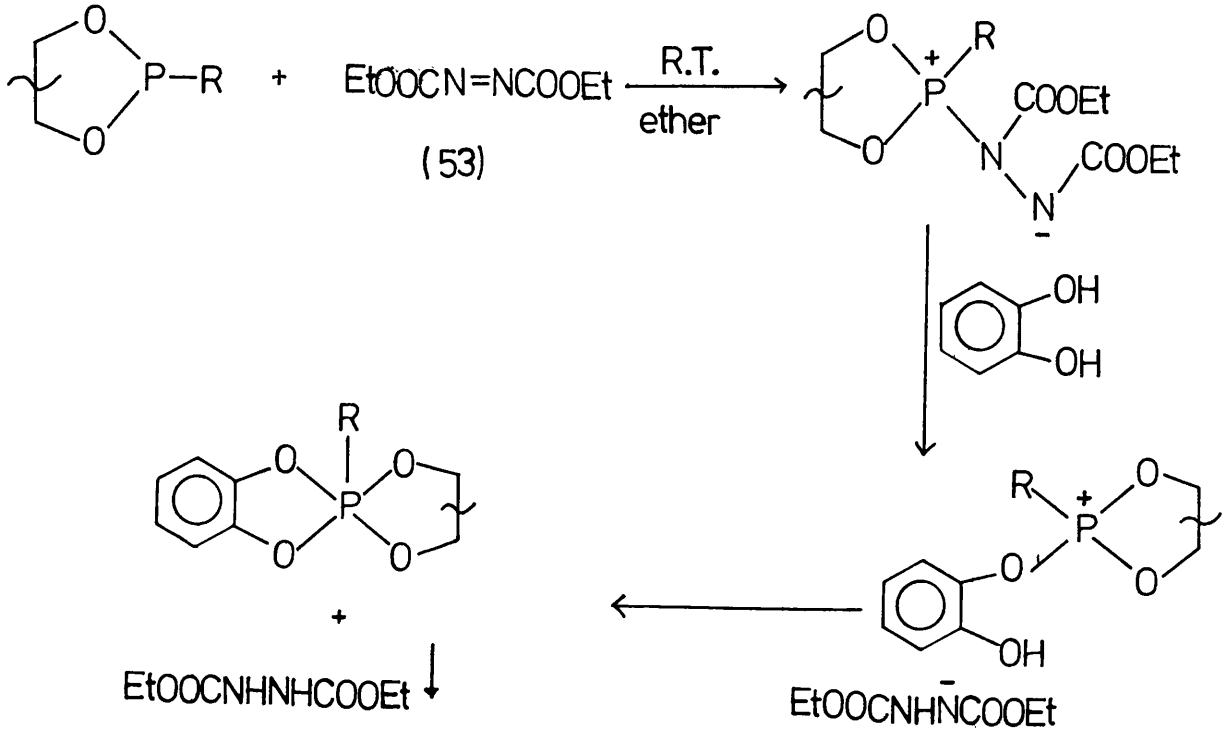


(51)

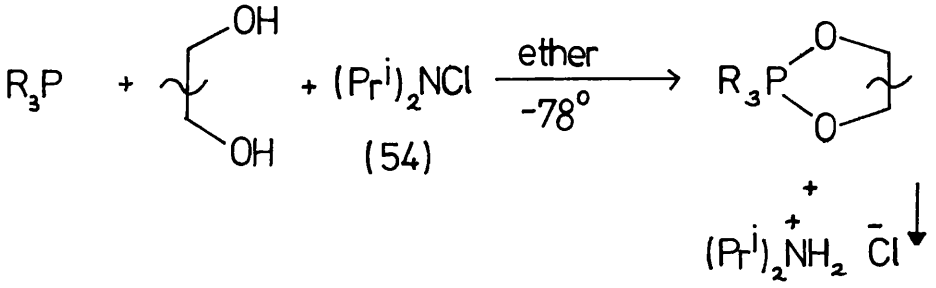
R = Ph, Me.
X = O, NH.

(52)

Recently two very useful methods for the preparations of spirophosphoranes have been published by Bone and Trippett.[73,74] The first method involves the condensation of a tervalent phosphorus compound with a 1,2- or 1,3- diol (except perfluoropinacol) using diethyl azodicarboxylate.(53)



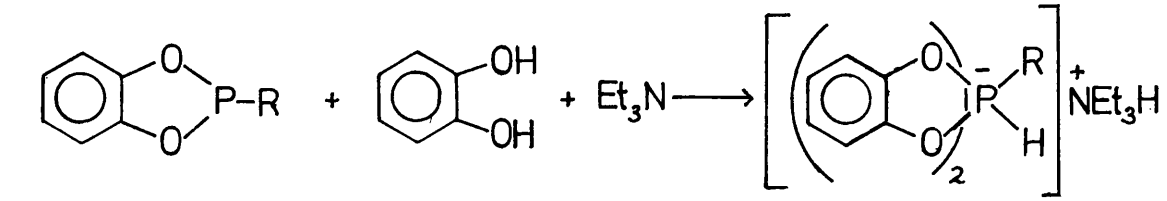
The second method involves N-chlorodi-isopropylamine (54), which reacts with tervalent phosphorus compounds in the presence of a wide range of diols according to the equation.



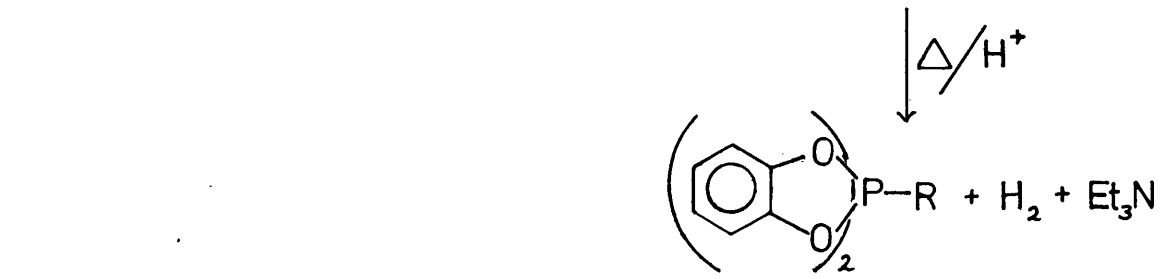
This method can be used for acyclic and cyclic phosphorus compounds with various diols and catechols.[75] Recent work has shown that certain 1,2-amino alcohols and o-amino-

phenols will also undergo this reaction.[76]

The reactions of cyclic trivalent phosphorus compounds with 1,2-glycols and 1,2-aminoalcohols leading to the formation of spirophosphoranes, takes place in acid or neutral conditions.[66-69] In the presence of amines, ammonium salts (55) with a hexaco-ordinate phosphorus atom are formed, from which spirophosphoranes can be obtained by treatment with acid or on heating.[77,78]

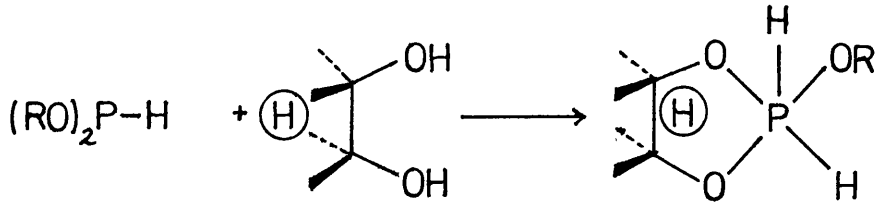


(55)

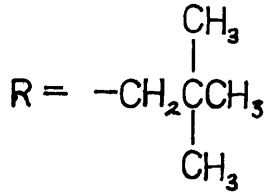


(56)

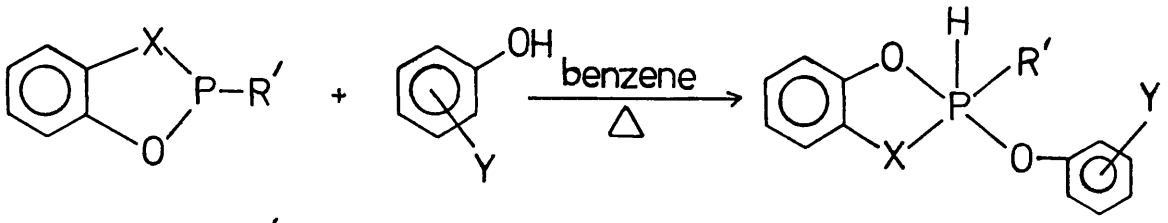
Recently Stec[80] has isolated stable phosphoranes (56) and (57) which have been shown to contain two P-H bonds.



(57)

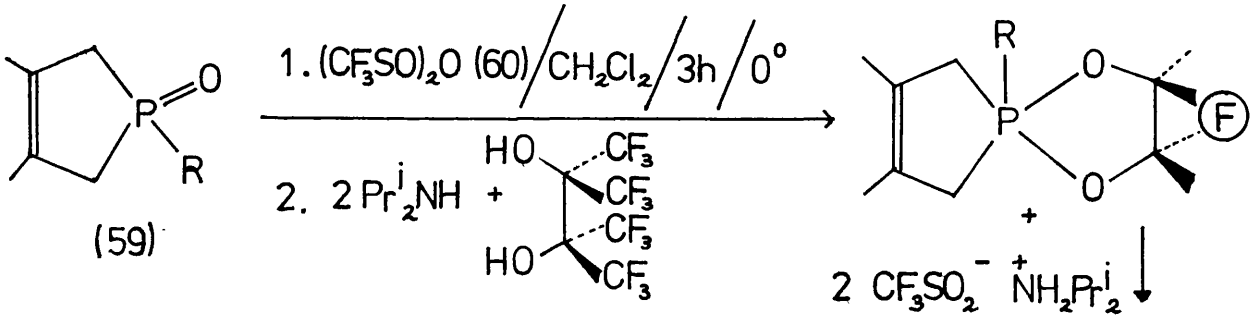


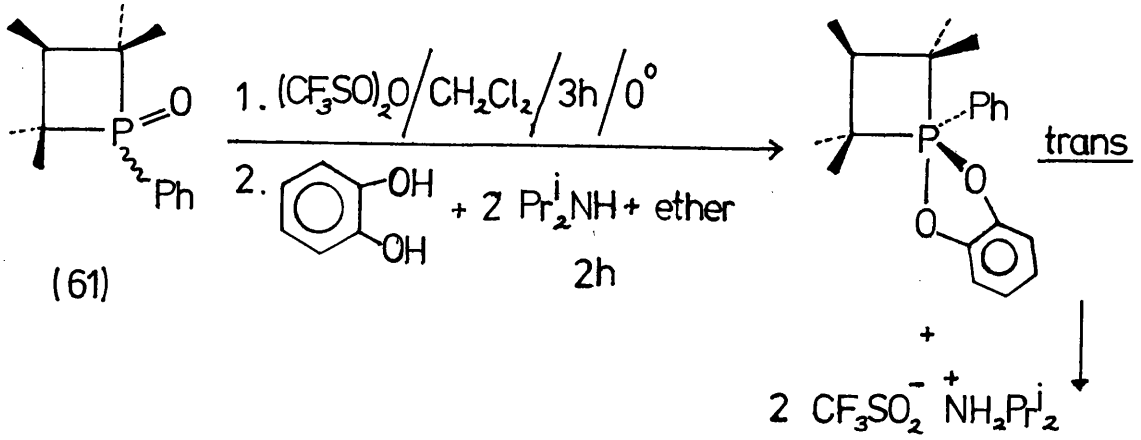
Stable phosphoranes (58) have also been prepared from phenols and cyclic phosphorus compounds on refluxing in benzene.[81]



X = O, NH . R′ = Me, Et, Ph. (58)
Y = H, o-NH_2, o-OH.

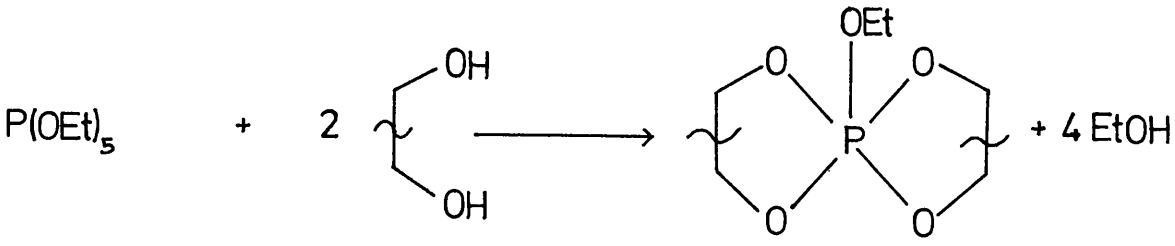
Antczak[82] has shown that phosphoranes can be prepared directly from phosphine oxides using trifluoromethane sulphonic anhydride (60), diol and two moles of base. Acyclic phosphines and phospholen oxides (59) react very quickly, whereas phosphetan oxides (61) take up to 3 hours. The yields are usually good (30-90%) depending on the starting material. The reaction will not go if there is another oxygen atom attached to the phosphorus atom.





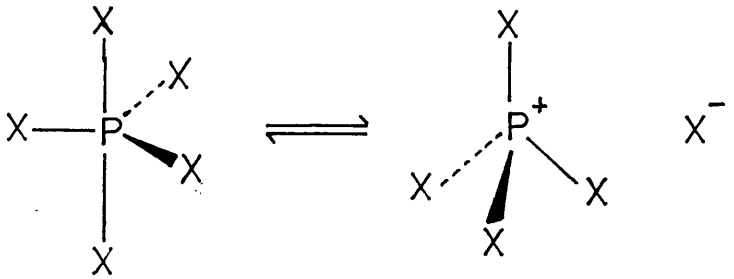
1.4 THE STABILITY OF PHOSPHORANES

There is a lot of evidence[62,63] that suggests that phosphoranes incorporating four or five membered rings are more stable than acyclic phosphoranes.



This type of exchange reaction indicates that the thermodynamic stability of spiro and cyclic phosphorane systems is greater than that of acyclic oxyphosphoranes.

Numerous X-ray diffraction studies[83-85] indicate that there exists considerable crowding in a trigonal bipyramidal oxyphosphorane. Ramirez[33] suggests that this crowding can be reduced when the phosphorus is part of a small membered ring. As a result of this crowding in the oxyphosphorane there will be a tendency to ease this by dissociation into ions, the tetrahedral geometry of the phosphonium salt (63) being less crowded.



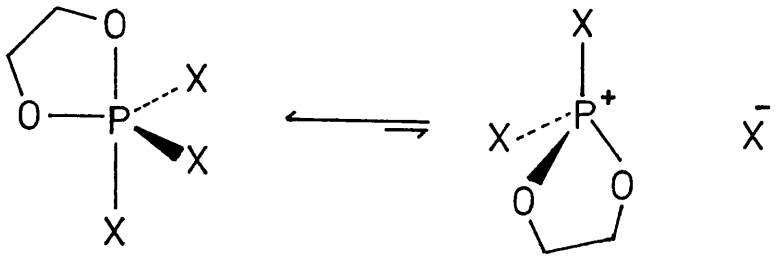
(62) (63)

The incorporation of a small membered ring into (62) will have a two-fold effect on the above equilibrium.

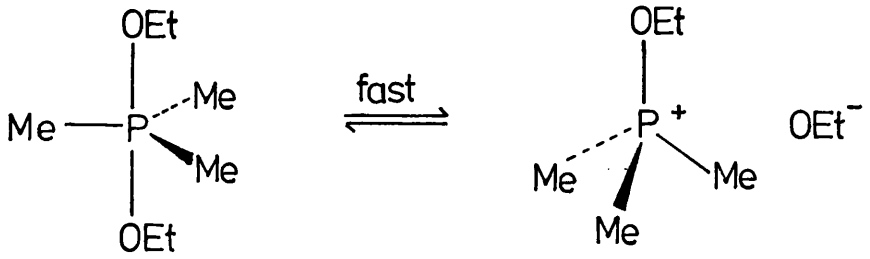
a) according to Ramirez[33] there will be a reduction in steric crowding,

b) in going from the trigonal bipyramidal structure of (62) to the tetrahedral geometry of (63), there would be an

increase in ring strain, which would have the effect of shifting the equilibrium position to the left.

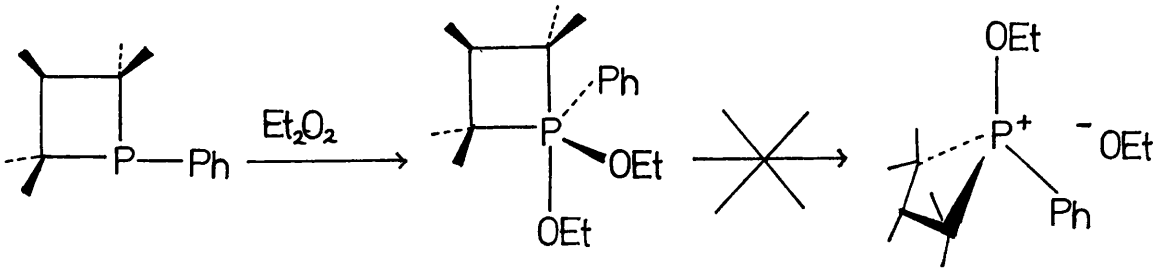


Denney[86] has shown that in the phosphorane (64), prepared from trimethylphosphine and diethyl peroxide, there was no observable P-H coupling for the methylene groups of the ethoxy ligands. This must be due to a rapid exchange via (65).



(64) (65)

Compound (64) could best be described as a phosphonium ethoxide. However if the starting phosphine is one containing a small membered ring (66), then a stable phosphorane (67) is produced. There is no ionization to (68) due to the increase in ring strain which would be required to go from trigonal bipyramidal to tetrahedral geometry.

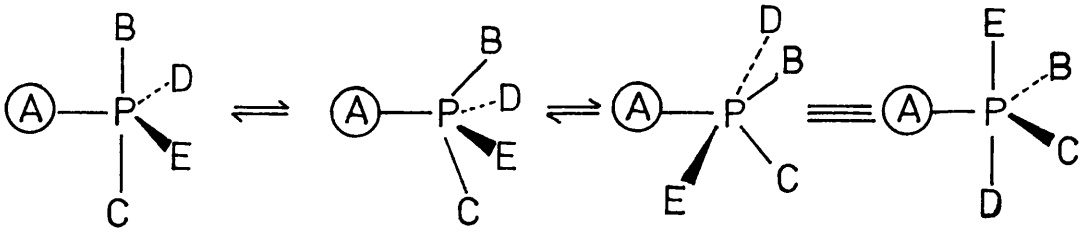


(66) (67) (68)

2 LIGAND PERMUTATIONAL ISOMERISM IN PHOSPHORANES

2.1 BERRY PSEUDOROTATION

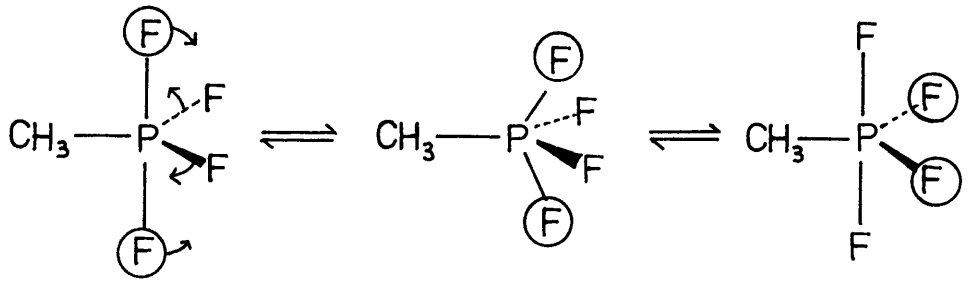
Pentafluorophosphorane has been shown to be trigonal bipyramidal by electron diffraction[15] and Raman studies,[16,17], however only one type of fluorine atom is observed in the ^{19}F n.m.r. spectrum over the temperature range $-197^{o} \rightarrow +60^{o}C$.[87] Berry[88] suggested that the n.m.r. result might be explained in terms of a rapid interchange of fluorine atoms, on the n.m.r. time-scale making all the fluorine atoms equivalent. The name he gave to this process was pseudorotation, and it can be illustrated as follows.



(69) (70) (71) (72)

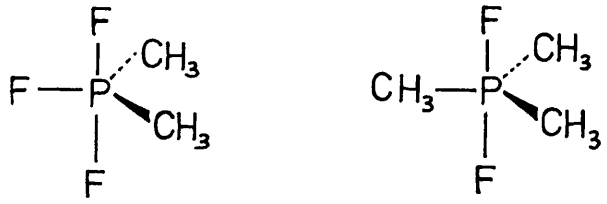
Using A as a pivot towards the two remaining equatorial positions (69) the two apical ligands move in the direction shown. In (70) an intermediate or transition state is reached, which has a square pyramidal geometry. Ligands D and E move apart from 120^{o} to 180^{o}, whilst the angle between B and C has moved from 180^{o} to 120^{o} (71). From (72) the two new apical positions are occupied by D and E, whilst B and C now occupy equatorial positions. Another series of pseudorotations, this time using B or C as the pivot, will make all the positions A to E equivalent. This feature of apical and equatorial exchange is a pairwise mechanism is known as Berry pseudorotation.

In a subsequent series of investigations, Muetterties and Schmutzler[89-93] examined and interpreted the n.m.r. spectra of a large number of alkylfluorophosphoranes in terms of Berry pseudorotation. For example CH_3PF_4(73) shows only one kind of fluorine atom from $-120^{o} \rightarrow +100^{o}C$.



(73) (74) (75)

If we take the methyl group as the pivot then in one Berry pseudorotation we can make all the fluorine atoms equivalent (73)⇌(75). In $(CH_3)_2PF_3$(76) there is only one type of methyl group in the ^1H n.m.r. but two different kinds



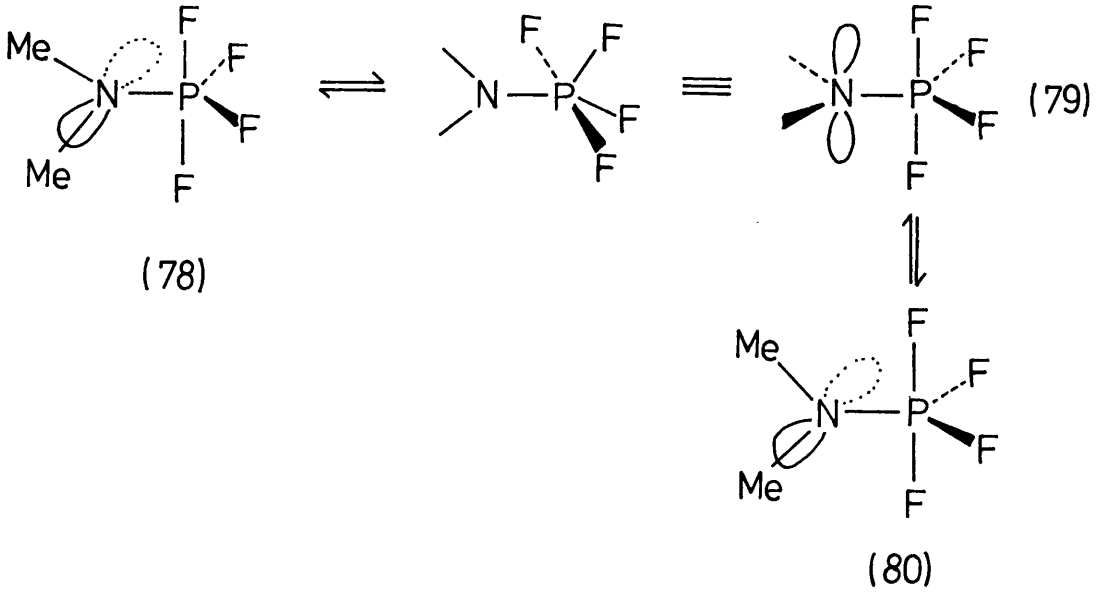
(76) (77)

of fluorine atom in the ^{19}F n.m.r., in the ratio of 2:1. This can be explained if both methyl groups occupy two equatorial positions in a trigonal bipyramid (see Chapter 3), $(CH_3)_3PF_2$(77) shows only one type of methyl group and one type of fluorine atom, with a similar chemical shift to the fluorine atoms assigned the apical positions in (76). The structures of (73), (76) and (77) have been verified by electron diffraction measurements.[15,19]

2.2 ALTERNATIVES TO BERRY PSEUDOROTATION

Muetterties[94] put forward several alternative mechanisms to explain the equivalence of the fluorine atoms in PF_5. However he eliminated them on the basis of Whitesides and Mitchells experiment[95], in which they looked at the temperature dependent ^{31}P n.m.r. spectrum of Me_2N-PF_4(78). In order to achieve equivalence of the fluorine atoms in this molecule, rotation about the P-N bond must be rapid. This is independent

of the exact nature of the nitrogen co-ordination geometry, whether it is planar or pyramidal.



(78) (79) (80)

If the N-methyl groups are in (78) and a Berry pseudorotation then occurs, structure (79) is obtained in which the N-methyl groups are parallel to the equatorial fluorine atoms. The only way to get equivalence would be to do a 90° rotation around the P-N bond to give (80). From theoretical calculations and experimental work Hoffmann et al[96,97] have shown that the phosphorane (79) is of a higher energy than (78), due to the lone pair of electrons of the nitrogen atom not being in the equatorial plane, which is the favoured position. This leads to a barrier to rotation around a P-N bond, which they found to be approximately 9 kcal mol^{-1}. Thus to get equivalence of the fluorine atoms an energy barrier of at least 9 kcal mol^{-1} must be overcome.

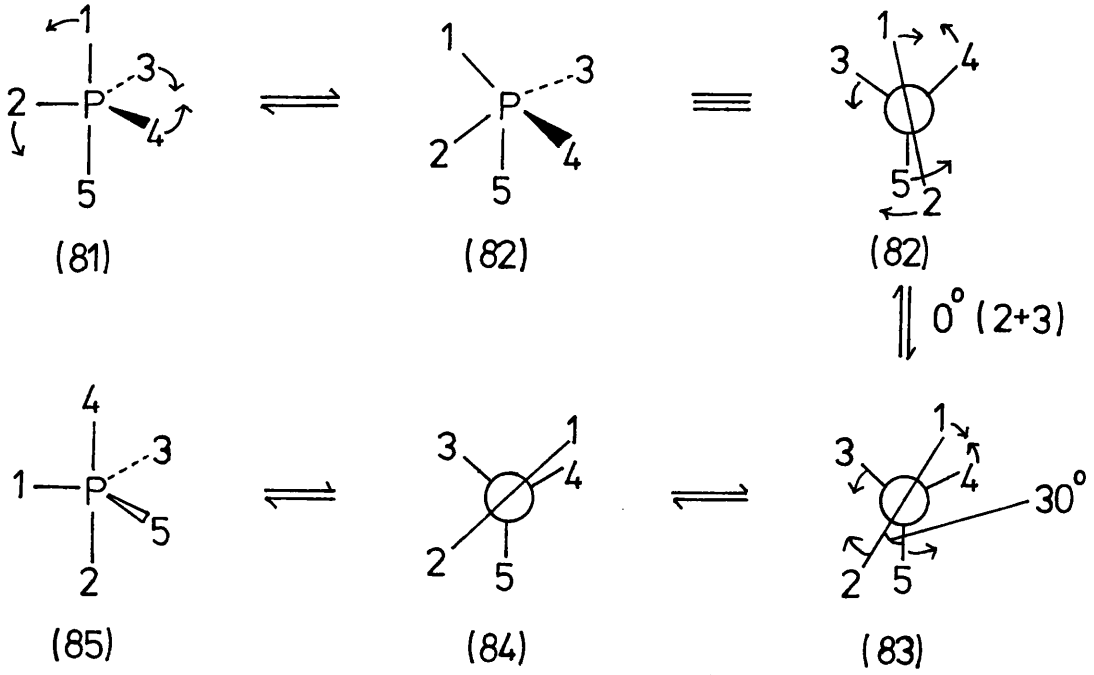
Whitesides and Mitchell found that on cooling Me_2NPF_4(78) down to -100°C the ^{31}P n.m.r. spectrum showed a triplet of triplets, which would be expected for a rigid trigonal bipyramid, with the NMe_2 group equatorial. On raising the temperature to 50°C the ^{31}P n.m.r. spectrum changed to a regular quintet, which can only be accounted for by four equivalent fluorine atoms. Using a full line shape analysis of the ^{31}P n.m.r. spectrum

over the temperature range $-100^{\circ} \longrightarrow -50^{\circ}C$, Whitesides and Mitchell concluded that the equivalence of the four fluorine atoms was taking place by simultaneous interchange of the two apical with the two equatorial fluorine atoms. Of the mechanisms considered by Muetterties only the Berry pseudorotation process was consistant with such an observation.

2.3 TURNSTILE ROTATION

As an alternative to Berry pseudorotation, Ramirez, Ugi et al,[98-102] proposed a mechanism which they termed Turnstile Rotation. This process is characterised by a rotation of one apical and one equatorial ligand against the other three ligands. The result of such a 60° rotation was to form a new phosphorane in which the pair of apical ligands were exchanged for one pair of equatorial ligands. The overall process exchanges ligands in a pairwise manner, in agreement with the experiment of Whitesides and Mitchell.

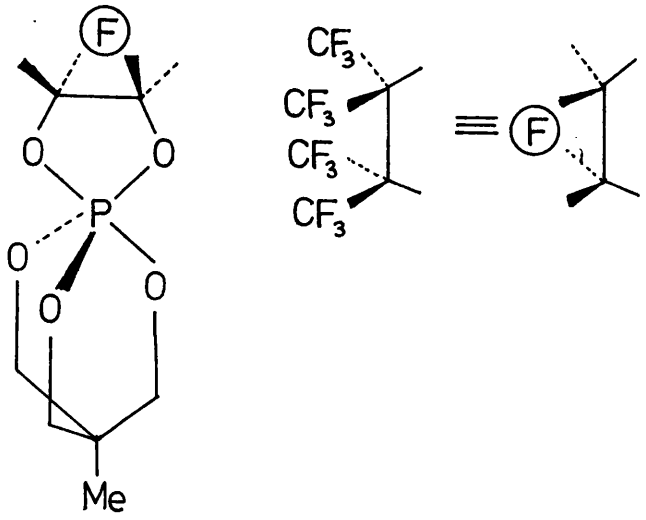
The actual process can be illustrated as follows.



Firstly, ligands 1 and 2 move down by about 9^{o} in the plane of the paper, these ligands are referred to as 'the pair'. Ligands 3 and 4 now move together until they are 90^{o} to each other; the ligands 3, 4 and 5 are referred to as 'the trio'. As a result of this bending, the intermediate phosphorane (82) is formed, the name given to it is a 0^{o} (2+3), but in fact this intermediate is never actually formed because whilst 1 and 2 and 3 and 4 are bending, there is an internal rotation of the pair against the trio of 30^{o}, 18^{o} by the pair and 12^{o} in the opposite direction by the trio. This internal rotation of the hypothetical intermediate (82) gives rise to the intermediate (83), which is known as a 30^{o} (2+3).

If the rotations are continued for another 30^{o}, intermediate (84) is formed, which is a 0^{o} (2+3), (the names being derived from the smallest dihedral angle between ligands in the Newman projection). Synchronous to this last rotation, there is a bending back to a trigonal bipyramid (85). This process is known as a $(TR)^{1}$ and gives the same result as a Berry pseudorotation using ligand 3 as the pivot.

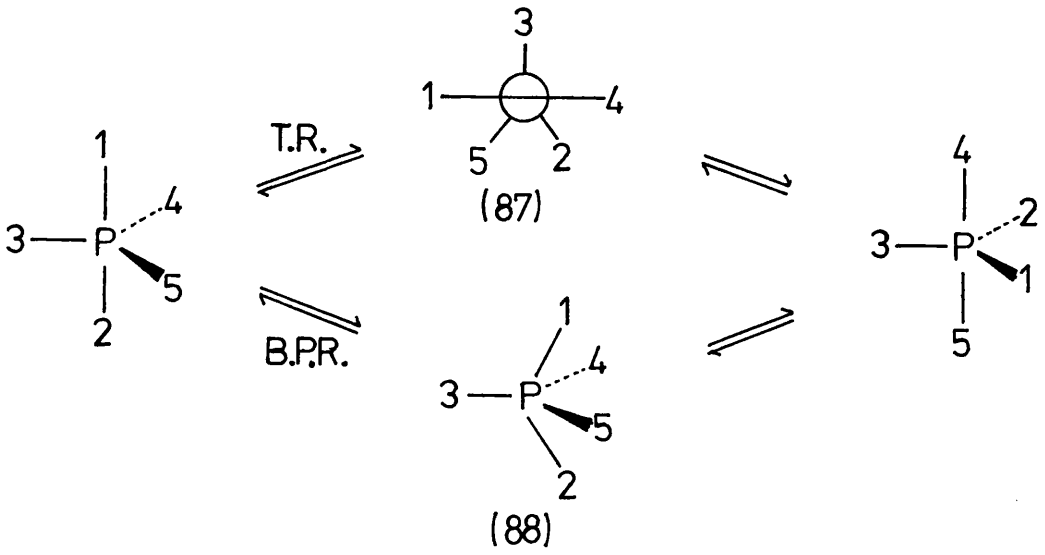
Numerous theoretical calculations based on symmetrical phosphoranes of the type PX_5, suggest that the Berry pseudorotation process is of lower energy than the Turnstile rotation mechanism.[96, 103] In highly strained systems this may not be the case and Ramirez[101] has argued that the rapid ligand exchange which the caged spirophosphorane (86) undergoes, is just such a case. The rapid ligand isomerism could be explained by the Turnstile rotation mechanism in terms of a process rotating the five membered ring against the cage system. It was suggested that the equivalent exchange by the Berry pseudorotation process had a prohibitively high energy barrier, due to the high degree of ring strain involved in the square pyramidal intermediate, although no strong evidence was put forward



(86)

to back-up this hypothesis.

If a comparison of the geometries and energies of the intermediates from Turnstile (87) and Berry mechanisms (88) are made, they are found to be very similar, so that any differences are likely to be very small.



(87)

(88)

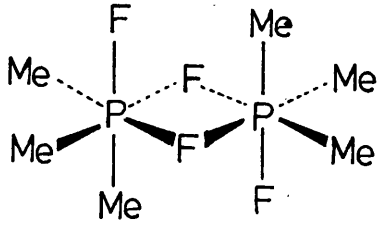
In the absence of more conclusive evidence to the contrary, ligand permutational isomerism will be considered to proceed via the Berry pseudorotation mechanism, in future discussions of d.n.m.r. data presented in this thesis.

2.4 IRREGULAR PROCESSES

The ligand permutational isomerisation processes already discussed have all been unimolecular and involve no bond breakage or formation i.e. regular processes. Ligand permutational isomerism can take place via an irregular process which may be bimolecular or involve the formation of new bonds or bond breakage.

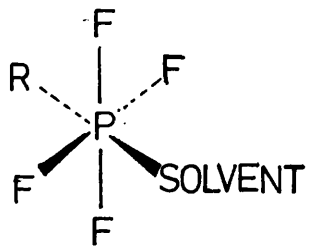
There is a lot of evidence to suggest that irregular processes are quite common in certain systems. Moreland and Doak[104] have shown that the ligand permutational isomerisation of Ph_2PF_3 in Teflon n.m.r. tubes is an intramolecular process with first order kinetics. However if Pyrex n.m.r. tubes are used then the process becomes intermolecular. This intermolecular process is thought to be due to impurities in the pyrex tubes. Such processes make d.n.m.r. data on fluorophosphoranes open to question.

Another irregular process involving fluorophosphoranes was brought to light by Cowley[105], who observed second order kinetics and large negative entropies of activation for the ligand permutational isomerisation of Me_2PF_3 and Me_3PF_2. The postulation was the formation of a dimeric intermediate (89) that led to equivalence of the fluorine atoms.



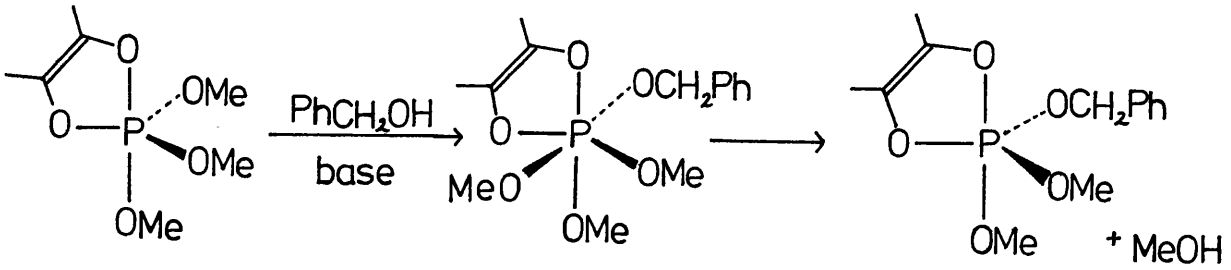
(89)

Other analogous mechanisms involve the co-ordination of a solvent molecule to the fluorophosphorane[106] to give the hexaco-ordinate intermediate (90). Indeed there are many examples in the literature[107] of stable hexaco-ordinate phosphorus



(90)

compounds. Ramirez et al[12] have posulated their intermediacy (91) in base-catalysed exchange reactions at pentaco-ordinate phosphorus. Hence there is always the possibility that a trace

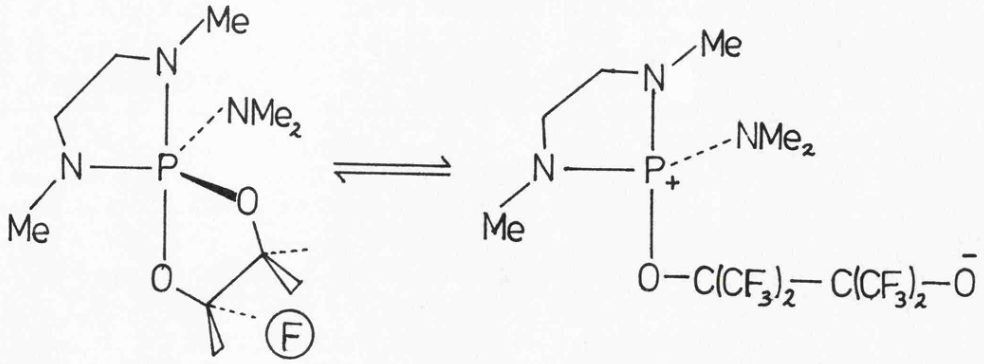


(91)

of nucleophilic impurity may bring about an irregular process, the impurity either being supplied by the solvent or the phosphorane itself.

A common cause of irregular processes in phosphoranes is that of ionization (92)$\rightleftharpoons$(93)[108] usually involving ring opening. Such ring opening processes can take place without ionization[109], if the phosphorane is one containing a P-H bond, (94)$\rightleftharpoons$(95).

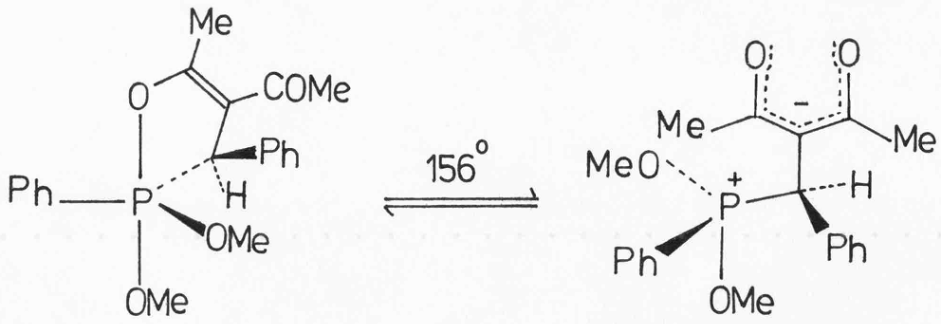
If such processes become rapid, i.e. on heating, then this will bring about equivalence. Hence when dealing with data on ligand permutational isomerism, originating from d.n.m.r. experiments, the possibility of an irregular process operating via a ring opened species cannot be overlooked. Experimentally, a good way of detecting such a mechanism is to check if the ^{31}p n.m.r. chemical shift is dependant on solvent polarity. If marked changes occur then it is likely that ring opening is occurring. The loss of phosphorus coupling[86] is another indication that rapid ionization is occurring.



(92) (93)

(94) (95)

At high temperature (156°) the aliphatic methyl groups of (96) become equivalent[47,110], although the two methoxyl groups do not. This almost certainly results from the thermal opening and closing of the five membered ring via the zwitterion (97).



(96) (97)

3 THE ARRANGEMENT OF LIGANDS IN PHOSPHORANES

3.1 THE APICOPHILICITY OF LIGANDS

Hoffmann's[96] molecular orbital calculations showed there are three factors which contribute to a ligand's preference for the apical positions in a trigonal bipyramidal phosphorane.

(i) electronegativity

(ii) π donation

(iii) π acceptance

This preference for the apical position has been encompassed by the term 'apicophilicity'.[101]

There have been many attempts at predicting the relative apicophilicities of various ligands using n.m.r. studies of fluorophosphoranes[89,93] and cyclic oxyphosphoranes.[47,48,51,111]

From kinetic studies[5,112] of cyclic and acyclic phosphate, phosphonate and phosphinite esters, 'preference rules' were obtained.

These empirical rules state that when the phosphorus is part of a small (four or five)-membered ring, the ring prefers to span an apical-equatorial position in a trigonal bipyramid and that electronegative groups prefer the apical positions.

X-ray diffraction studies[23,83,108] have shown the apical-equatorial preference for small rings, but other factors apart from electronegativity have been shown to affect apicophilicity values.

The preference for the apical position of electronegative atoms or groups can be explained by the accumulation of negative charge at the apical positions. This accumulation of negative charge was indicated from molecular orbital calculations on PH_5[96], though the same effect has also been found for other phosphoranes.[101,113,114]

π DONATION AND π ACCEPTANCE

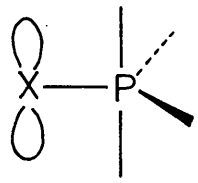
Hoffmann[96] went on to consider the interaction of π orbitals of a substituent in both the apical and equatorial positions. π interactions between ligand donor orbitals and phosphorus were considered in terms of destabilising interactions between the phosphorane framework and the ligand π system, and stabilising interactions between the ligand π system and tne phosphorus d orbitals.

Hoffmann et al[96] concluded that the phosphorus d orbitals participated only to a small extent and had only a small effect in determining the ligand arrangement around phosphorus. The small part played by the phosphorus d orbitals in Hoffmann's calculations differs from that in those of other workers.[99,100,101,102] From the amount of overlap between molecular orbitals it was concluded that the greatest interaction occurred in the apical position for both π acceptors and π donors. Therefore π donors having a destabilising effect will prefer the equatorial position, where interaction is less. π acceptors having a stabilising effect will prefer the apical position where interaction is greater. So the preference of a ligand for a particular position in a trigonal bipyramid is determined mainly by the interaction of the ligand π systems with the framework σ orbitals.

Although there is no preferential orientation of the π orbital in an apical position, an equatorial π acceptor will prefer to have its acceptor orbital perpendicular to the equatorial plane (98), whereas a π donor will prefer to have its donor orbital in the equatorial plane (99).

STERIC FACTORS

In the case of steric interactions, the apical position having three ligands at 90^{o} may be considered to be the more



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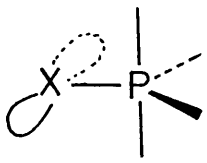
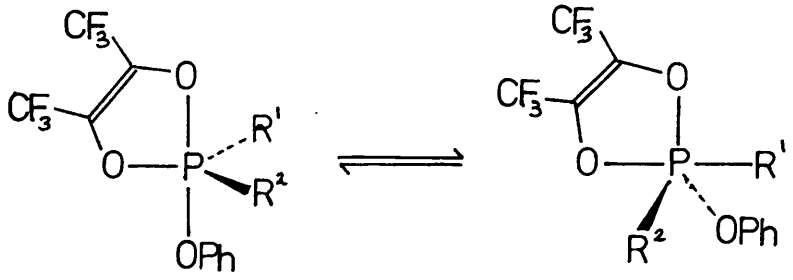


(99)

hindered position, the equatorial position having only two. This will be offset to some extent by the fact that the apical bond is longer and therefore steric interactions will be smaller.

Whittle[108] found that steric effects in a trigonal bipyramid are relatively small unless there are at least two bulky groups attached directly to phosphorus. This information was obtained from a series of hexafluoro-biacetyl adducts (100).



(100) (101)

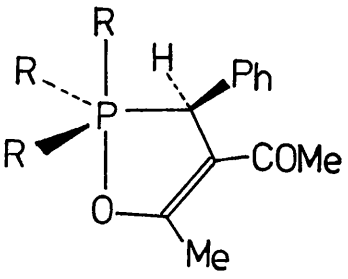
The pseudorotation (100) $\rightleftharpoons$ (101) can be slowed on the n.m.r. time-scale and from this information the free energy of activation can be calculated (see section 3.4).

RESULTS

R^1 = Me	R^2 = Me	$G^{\#}$ = 10.0 kcal. mol^{-1}
R^1 = Me	R^2 = Bu^t	$G^{\#}$ = 11.1 kcal. mol^{-1}
R^1 = Bu^t	R^2 = Bu^t	$G^{\#}$ = 14.6 kcal. mol^{-1}

Gorenstein[111] found another type of steric hindrance to pseudorotation when bulky substituents are present on the α

carbon atom. He found that the barriers to pseudorotation in the benzylideneacetylacetone adducts (102) were a lot greater than in the corresponding methyleneacetylacetone adducts (103).



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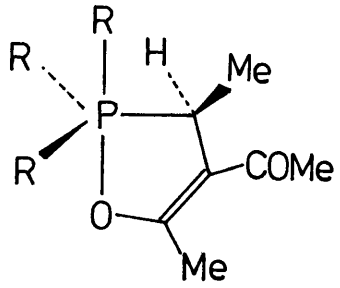
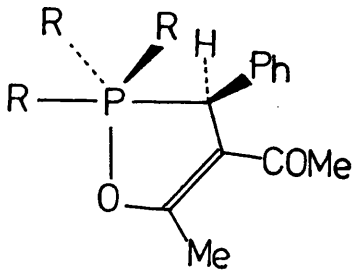


(103)

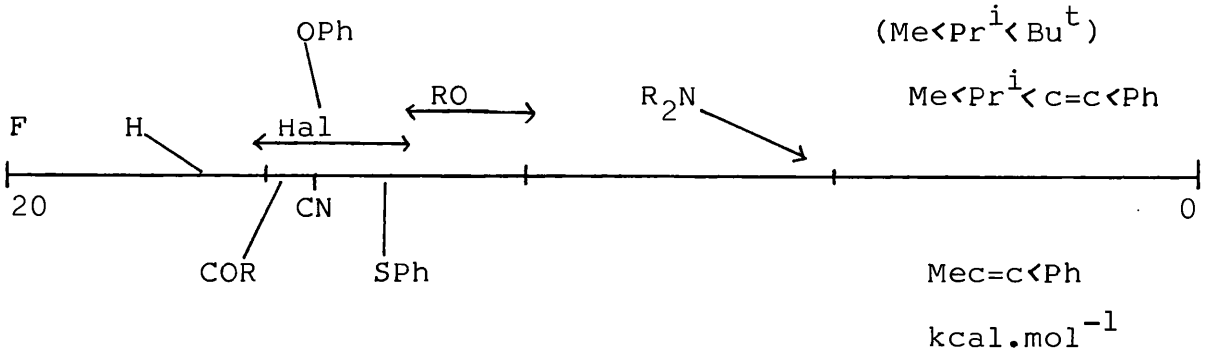
The steric hindrance in (102) arises from the eclipsing of the phenyl group and an equatorial R group when the ring carbon atom is in an apical position (104).



(104)

From a series of d.n.m.r. studies, a scale of relative apicophilicities[121] has been proposed. This information was obtained from the variation in $\Delta G^{\#}$ values of a series of spirophosphoranes bearing differing ligands, the change in ligand bringing about a difference in the free energy of activation for the Berry pseudorotation processes available.

Scale of Relative Apicophilicities



From the scale above it can be seen that the relative apicophilicity of a group is determined primarily by its electronegativity. However when π acceptor or donor orbitals are present on the ligand corrections have to be made. This is also truewhen steric effects become important, as steric effects are known to reverse small differences in apicophilicities.[121]

3.2 RING STRAIN IN FIVE-MEMBERED CYCLIC PHOSPHORANES

Hoffmann et al[96] predicted the preferred orientation of π donors bearing a single π system. They concluded that in the apical position a π orbital of a substituent encountered a six-fold barrier to rotation and nence there would be little preferential orientation of the π orbital. However if the ligand occupies an equatorial site, the interaction was strongest when the π orbital was parallel to tne apical bond, i.e. the interaction (105) is stronger than interaction (106).

(105) (106)

Hoffmann concluded that as these π donor orbital will prefer to lie in the equatorial plane (106) where interaction

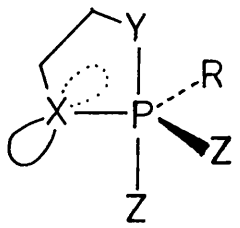
is less.

π acceptors stabilise the molecule, therefore the π acceptor orbital will prefer to lie parallel to the apical bonds (105) where interaction is stronger.

This preferred orientation of a substituent with a single π donor orbital will lead to a barrier to rotation around the sigma bond to phosphorus, as the orbital rotates from (106) to the unfavourable apical plane (105). Heteroatoms bonded to pnosphorus have been shown to be sp^2 hybridised by X-ray difrraction studies,[23,83,108] and as such act as single π systems.

Barriers to rotation have been determined experimentally for P-N[90,95,97,115-117] and P-S[118] bonds as the temperature is lowered. The slowing down of rotation around a P-O bond has never been observed experimentally; however it has been shown to be less than 8 kcal.mol^{-1}.[119]

From a d.n.m.r. study of a range of stable spirophosphoranes Trippett et al[120] obtained data on the energies required to move various five membered rings from favoured apical-equatorial to diequatorial positions. They found that the energy required to move five-membered rings, containing heteroatoms bonded to phosphorus, to an equatorial-equatorial position is greater than is needed in the case of a phospholan ring. The energy required depends not only on the heteroatom which moves from an apical to the equatorial position, but also on the nature of the atom which remains equatorial.



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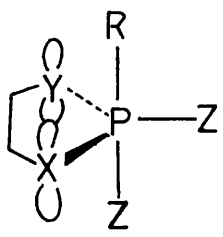


(108)

The difference in energy between (107) and (108) is made up of three factors.

(i) the difference in apicophilicity between R and Y when the lone pair on the equatorial heteroatom Y is constrained to an apical plane.

(ii) the strain involved in going from a 90^{o} bond angle at phosphorus to one of 120^{o}.

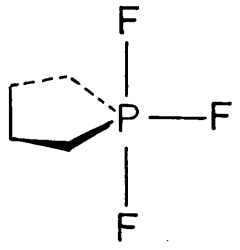
(iii) the energy required to rotate the lone-pair on X from the equatorial to an apical plane.

Therefore

$$E^{108} - E^{107} = S + R^{X} + \Delta A(Y-R) + R^{Y}$$

The strain factor (S) was determined to be 8 $kcal.mol^{-1}$ for a phospholan ring and 10 $kcal.mol^{-1}$ for a phospholen ring system.

The strain factor for the phospholan ring is consistant with the value obtained by Muetterties et al[89] from the pseudorotation of (109).



(109)

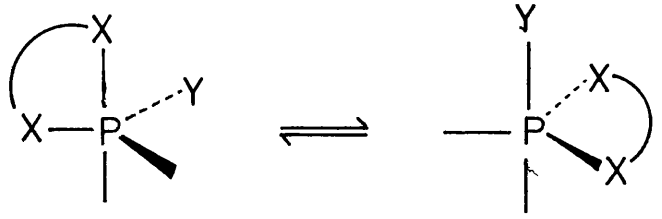
With information on the barriers to rotation around the sigma bonds between various heteroatoms and phosphorus, differences in apicophilicites and ring strain, it has proved possible to calculate approximate $\Delta G^{\#}$ values for the pseudorotation processes of a large number of phosphoranes containing five-membered rings.[120]

3.3 USES OF APICOPHILICITY VALUES

A thorough knowledge of relative apicophilicity values, in theory, would provide a way of predicting the most energetically

favoured arrangement of ligands in an acyclic phosphorane.

In dealing with cyclic phosphoranes one must also take into account ring strain. Small rings will prefer to span the apical-equatorial position in a trigonal bipyramid, but this arrangement may sometimes conflict with apicophilicity considerations.



(110) (111)

If Y is more apicophilic than X, then on apicophilicity arguments, structure (111) would be the low energy phosphorane, but from ring strain considerations (110) would appear to have the lowest energy. So that the preferred arrangement of ligands in a cyclic phosphorane is dependent upon the balance of relative apicophilicites and ring strain.

The main use of apicophilicity values and ring strain data is in the field of nucleophilic substitution at tetracoordinated phosphorus. Before predictions of any sort can be made, the following assumptions have been made by workers in this field.[5,8]

(i) The intermediates in nucleophilic substitution are trigonal bipyramidal phosphoranes.

(ii) The nucleophile enters the apical position of a trigonal bipyramid and the leaving group departs from an apical position.

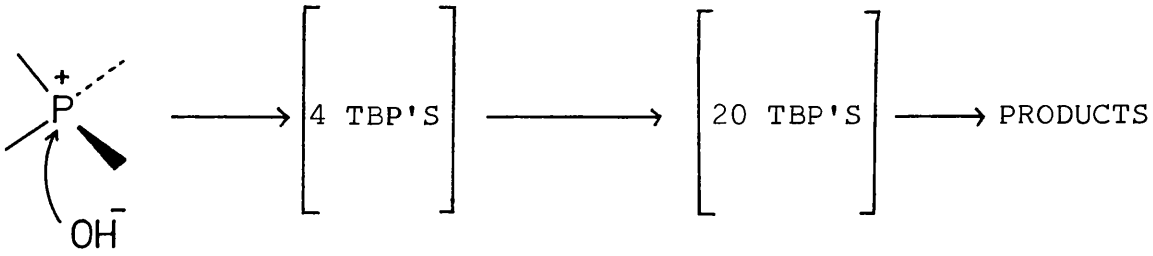
(iii) Phosphorane formation is under thermodynamic and not kinetic control, i.e. the most stable phosphorane is formed fastest. The presence of bulky ligands on the phosphorus might invalidate this assumption by determining the direction of attack, not by apicophilicity considerations, but by the

by the ease of approach of the incoming nucleophile.[122]

(iv) Nucleophilic attack occurs at the faces of the tetrahedron and this will result in the formation of four possible trigonal bipyramids.

(v) These initial trigonal bipyramids may be sufficiently long-lived to undergo pseudorotation processes to give up to twenty phosphoranes.[2-12]

(vi) Any of these intermediate phosphoranes may be capable of decomposing to form products, therefore there is the possibility of a wide range of stereochemistry in the products.



The formation of products will most likely be derived from the most stable phosphorane, i.e. relative leaving group abilities will not affect tne reaction pathway. Usually this will be the case, as the most apicophilic group is usually the best leaving group. However there are a few exceptions; fluorine is more apicophilic than chlorine but it is a poorer leaving group. In this case the reaction pathway might be altered by leaving group ability.

A full apicophilicity scale coupled with ring strain values would provide knowledge on the relative stabilities of the phosphorane intermediates, and hence enable prediction of what the reaction pathway is most likely to be.

3.4. DETERMINATION OF APICOPHILICITY VALUES

There are three general methods in the literature for the determination or ligand apicophilicity.

a) Berry pseudorotation rates are dependent upon the energy difference between tne interconverting phosphoranes. Systems have been designed to enable the Berry pseudorotation rate to be monitored by d.n.m.r. spectroscopy.[123-127] If the energy difference between the interconverting phosphoranes is quite high (>26 kcal mol^{-1}) then a conventional kinetic determination of the rate of conversion is possible.[128,129]

Therefore from a knowledge of the Berry pseudorotation rate, the energy difference between tne phosphoranes can be determined and hence information on apicophilicities can be obtained. The apicophilicity values derived from kinetic measurements will differ slightly from the true thermodynamic values (see 3.6).

b) If the stereochemical course of nucleophilic substitution at tetraco-ordinated phosphorus can be predicted by leaving group abilities and apicophilicity considerations, then Debruin[130] reasoned that the reverse must also be true. A semi-quantitative apicophilicity scale has been built up from the stereochemistry and reaction pathways of various substituents.

c) A limited apicophilicity scale has been determined[131] by studying the ground state arrangements of ligands in certain asymmetrically substituted phosphoranes. This was accomplished by cooling the sample until all pseudorotations were slow on the n.m.r. time-scale. Analysis of the n.m.r. spectrum of the 'frozen' molecule can determine the arrangement of the ligands.[89,93,131-133] The apicophilicity scale derived by this method is not particularly useful for obtaining quantitative data.

The apicophilicity values described in this thesis were determined by evaluation of Berry pseudorotation rates using d.n.m.r. spectroscopy or standard kinetic measurements (see Chapter 5.3). In the case of d.n.m.r. spectroscopy the rate

data were obtained by measurement of the coalescence temperature (T^c) of signals of equal intensity. Free energies of activation ($\Delta G^{\#}$) were derived from the coalescence temperature and the maximum frequency separation ($\Delta\nu$) of the signals below coalescence using the Eyring equation.[134]

$$k_1 = \frac{kT}{h} e^{\frac{-\Delta G^{\#}}{RT^c}}$$

k = Boltzmann's constant
T^c = Coalescence temperature
h = Planck's constant
R = Gas constant

Where the rate of pseudorotation k_1 at the coalescence temperature is given by the Gutowsky-Holm equation.[135]

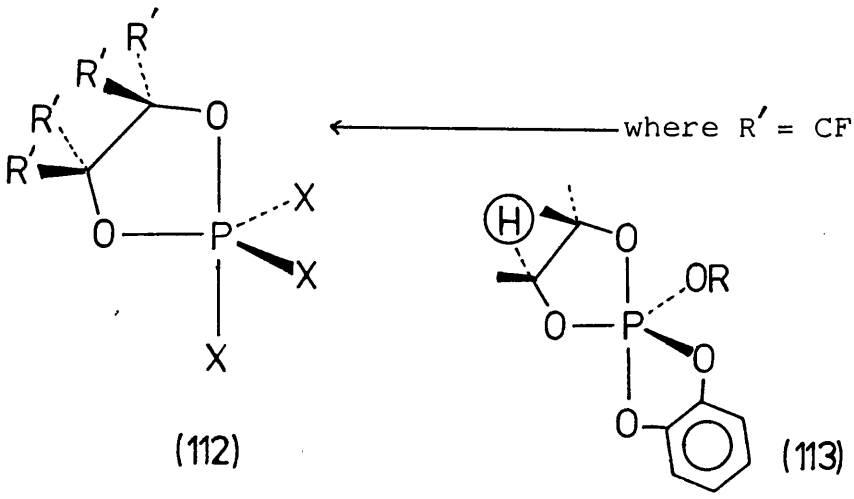
$$k_1 = \frac{\pi\Delta\nu}{\sqrt{2}}$$

The values of $\Delta G^{\#}$ calculated in this way at different temperatures can only be compared if the entropies of activation ($\Delta S^{\#}$) are zero. Gorenstein[111] and Wolf[128] have concluded that the values of $\Delta S^{\#}$ are very small and to the first approximation may be regarded as zero.

3.5 APPLICATION OF D.N.M.R. IN DETERMINING APICOPHILICITY VALUES

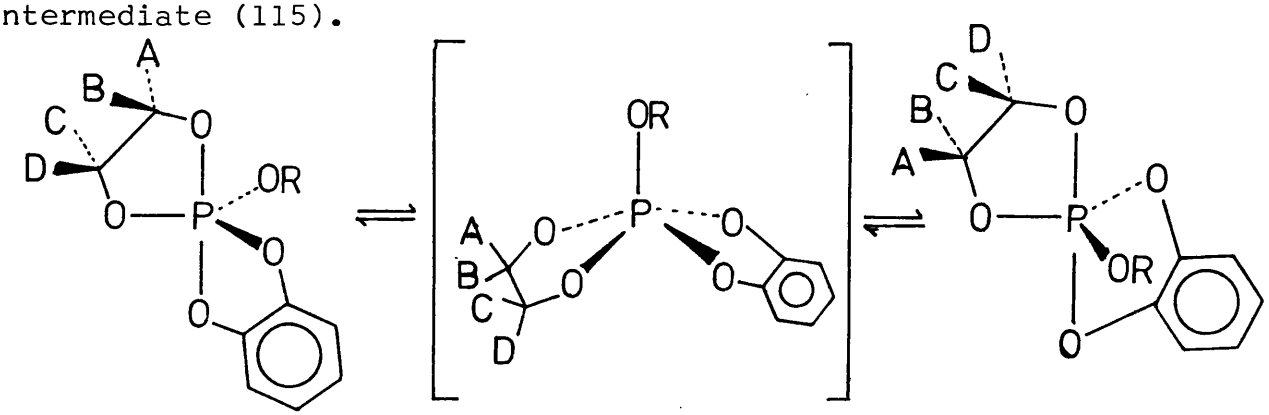
In order to monitor a process by n.m.r. the molecule must contain suitable groups that are clearly visible in the n.m.r. spectrum of the molecule. The apicophilicity data described in this thesis have been obtained from the following systems.

A. This system makes use of a five-membered 1,3,2-dioxaphospholan ring with four identical groups on the two carbon atoms of the ring (112), these groups can be readily monitored by n.m.r.



(112) (113)

Using the spirophosphorane (113) as an example, with the methyl groups labelled A-D. (114), a possible pseudorotation is that of (114) to (116), via the square based pyramidal intermediate (115).

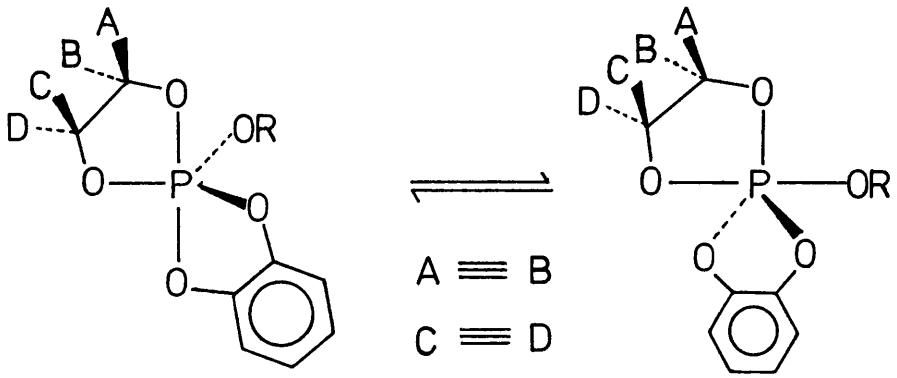


(114) (115) (116)

$A \equiv C$ and $B \equiv D$

This intermediate contains a plane of symmetry, which makes A equivalent to C and B equivalent to D. The spirophosphoranes (114) and (116) are of equal energy and are known as topomeric species. This pseudorotation process cannot become slow on the n.m.r. time-scale, being a very low energy process; as a result of this topomeric pseudorotation the methyl signals in (114) appear as two equal intensity singlets in the ^{1}Hn.m.r. spectrum at room temperature.

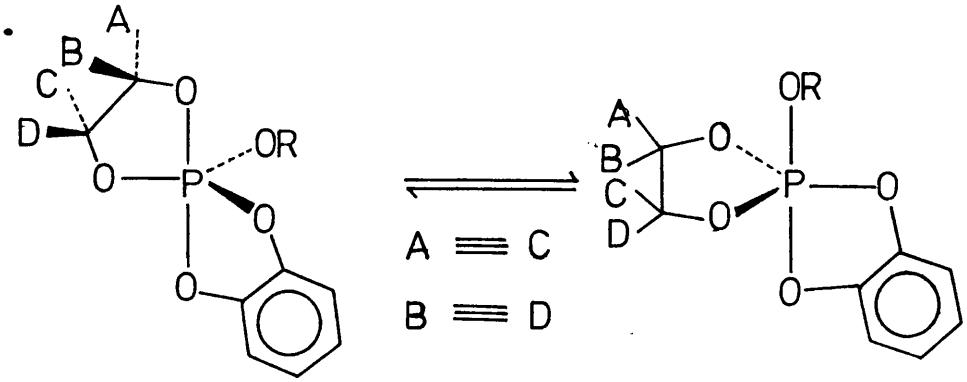
A second pseudorotation involves putting the catechol ring into a diequatorial position (114) $\rightleftharpoons$ (117), and the -OR group apical.



(114) (117)

In (117) there is a new plane of symmetry which makes A equivalent with B and C equivalent with D. Unlike the last pseudorotation this will be of a high energy because the catechol ring is in an unfavourable diequatorial position and the -OR group has moved to the apical position. This pseudorotation will be slow on the n.m.r. time-scale at room temperature, but will become fast when the temperature is raised. When this pseudorotation is fast on the n.m.r. time-scale, all the methyl groups A-D will become equivalent in the n.m.r. spectrum. This will be observed as a gradual broadening of the methyl signals as the temperature is raised, until they coalesce to a single broad peak (the coalescence temperature T^c). Further heating will cause the peak to sharpen.

There is a third possible pseudorotation which involves putting the pinacol ring in a diequatorial position, (114)⇌(118).

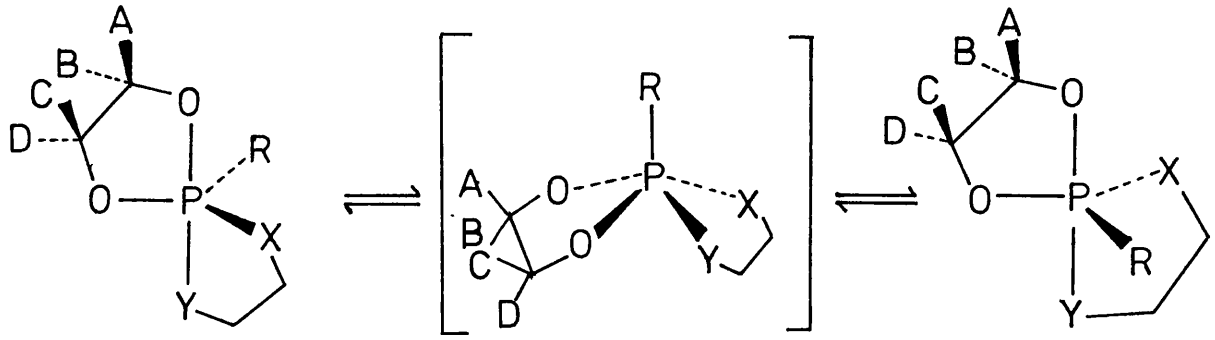


(114) (118)

This pseudorotation has the same effect as the low energy topomeric pseudorotation (114)⇌(116), and makes A equivalent to C and B equivalent to D. The only way complete

equivalence of the methyl signals can occur is if the catechol ring is forced to occupy a diequatorial position with the -OR group moving to an apical position. The energy associated with such a pseudorotation has been shown by Bone[44] to be ca 20 kcal. mol^{-1}.

B. If the catechol ring is replaced by a second ring which is not symmetrical (119), then the low energy topomeric pseudorotation (119)$\rightleftharpoons$(121) will not make any of the methyl groups equivalent.

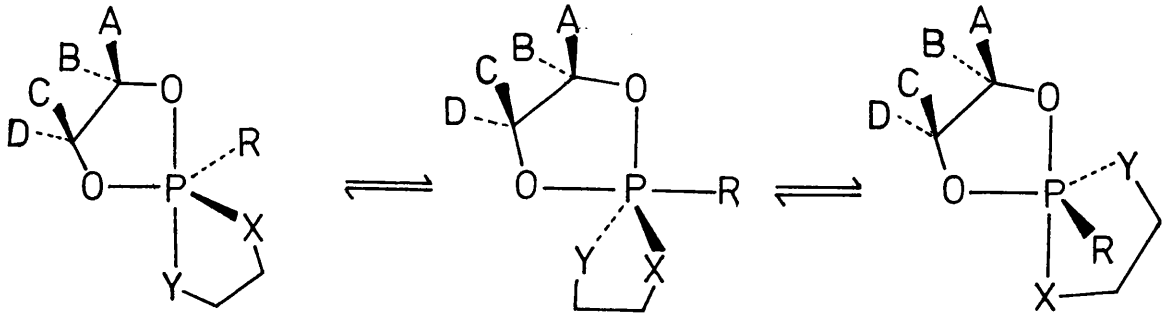


(119) (120) (121)

Due to the lack of a plane of symmetry in (120), the ^1H n.m.r. spectrum at room temperature will show four equal intensity signals for the four methyl groups A-D.

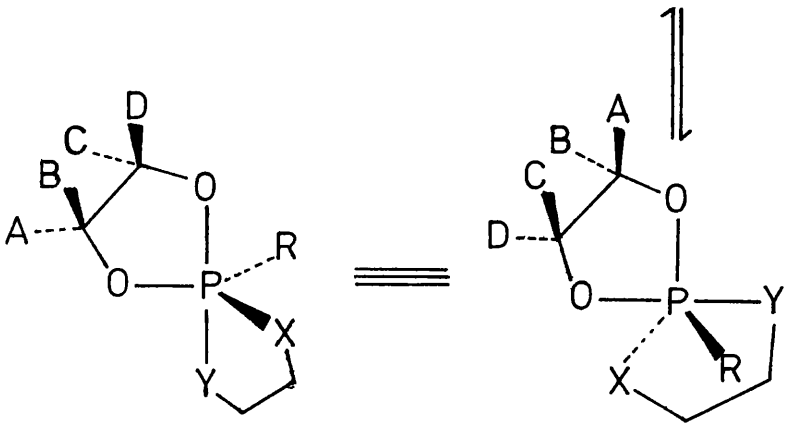
Partial equivalence of the methyl groups can occur by a multistep pseudorotation pathway which has the unsymmetrical ring in a diequatorial position and the R group apical.

The high energy intermediates (120) and (121) are dependant to a large extent on the nature of X and Y. If for instance X = N and Y = O, the intermediate (120) is of high energy due to ring strain, the spirophosphorane (121) is also of high energy because it contains a nitrogen group in the apical position, so a third pseudorotation takes place to give (122). The overall result is that A has become equivalent



(119) (120) (121)

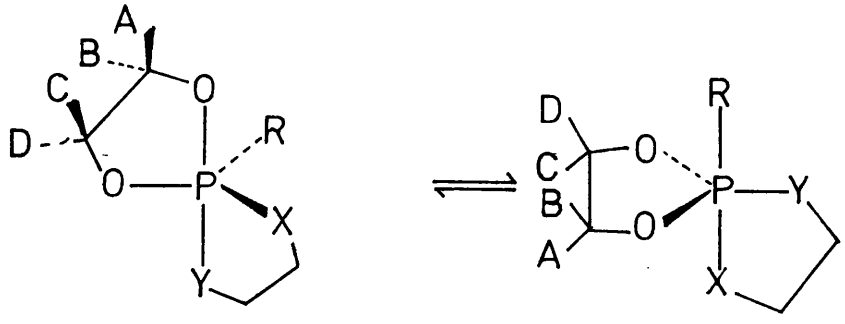
SCHEME A



(122) (122)

to D and C equivalent to B. When the pseudorotation processes (119) ⇌ (122) become fast on the n.m.r. time-scale as the temperature is increased, the four methyl signals coalesce to two signals.

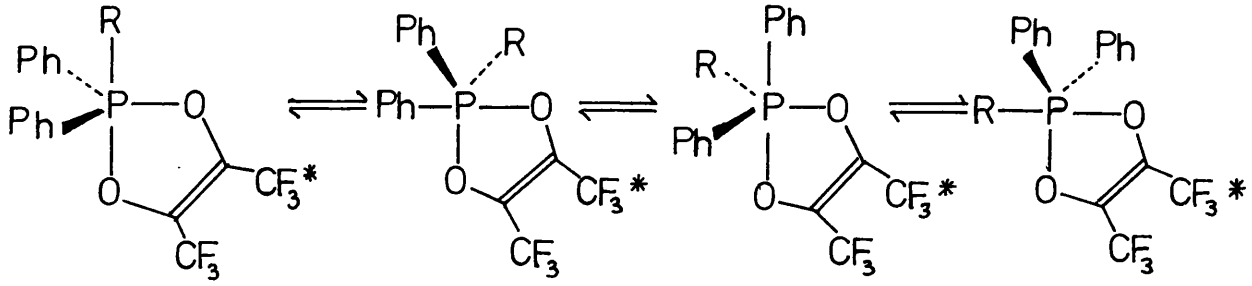
An alternative pseudorotation involves the high energy intermediate (123) in which the pinacol ring is in a diequatorial position.



(119) (123)

The intermediate (123) has a plane of symmetry in the plane of the paper which makes A and C equivalent and B and D equivalent. If the pseudorotations in scheme A and the one above (119)$\rightleftharpoons$(123) become fast on the n.m.r. time-scale, complete equivalence of the four methyl groups will be observed. Hence the theoretical possibility that in a molecule of this type two coalescences may occur, the four signals going to two as one ring goes out diequatorial, then two signals coalescing to one as both rings go out diequatorial.

C. In the perfluorobiacetyl adducts (124) equilibration of the two CF_3 groups is achieved only via the topomers (125) and (126).



(124) (125) (126) (127)

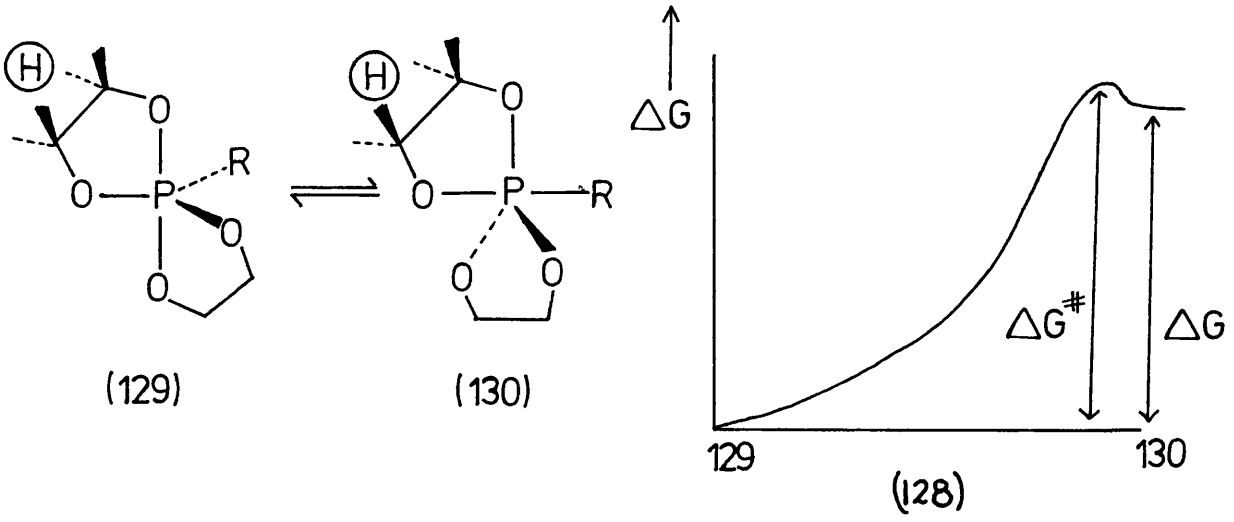
If R is more apicophilic than phenyl then the most stable conformation of the phosphorane is (124). The adducts (125) and (126) are high energy trigonal bipyramids and as the sample is cooled, the equilibrium process via these species will eventually become slow on the n.m.r. time-scale. When this happens the single absorption of the CF_3 groups will split out into two quartets of equal intensity and from the coalescence temperature the relative apicophilicities of the R and phenyl groups can be determined. The free energy of activation for a particular R group will overestimate the difference in apicophilicity between R and phenyl. However pseudorotations between topomers are thought to be very low-energy processes[143]

and high-energy trigonal bipyramids are usually regarded as transition states rather than intermediates, (see Section 3.6).

3.6 ACCURACY AND LIMITATION OF THE D.N.M.R. METHOD FOR THE DETERMINATION OF LIGAND APICOPHILICY VALUES

a) Accuracy

The accuracy of the d.n.m.r. method for the determination of $\Delta G^{\#}$ will depend on various factors. The Gutowsky-Holm equation has been shown[136] to be almost as accurate as a complete line shape analysis. This holds only for systems where coalescence is of signals of equal intensity; in practice even deviations from equality lead to only small errors. The sources of error lie not in the equation itself, but in the determination of the coalescence temperature (T^c) and the maximum frequency separation ($\Delta\nu$). The total error in measuring T^c is of the order of $\pm$ 0.3 kcal.mol^{-1}. The maximum frequency separation is usually obtained accurately, however problems do arise when the coalescence temperature is near the lower limit of the n.m.r. spectrometer. This source of error is very small however, an inaccuracy of 50% will lead to an error of only $\pm$ 0.2 kcal.mol^{-1} in the final answer.



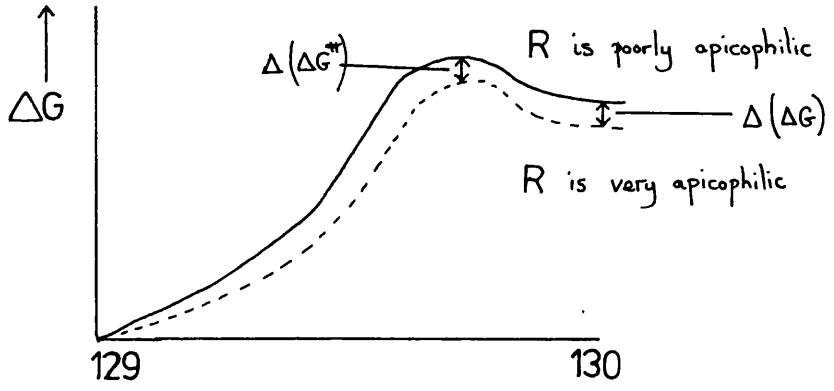
(129) (130) (128)

If we consider the reaction co-ordinate (128) of the pseudorotation pathway (129)$\rightleftharpoons$(130), the Gutowsky-Holm equation measures $\Delta G^{\#}$, the free energy of activation, whereas

the true difference in energy between (129) and (130) is given by ΔG; hence $\Delta G^{\#}$ is an overestimate of ΔG. However the spirophosphorane (130) is a high energy species (due to the diequatorial five membered ring) and according to Hammonds Postulate, the product will closely resemble the transition state. The $\Delta G^{\#}$ for a topomeric Berry pseudorotation is no greater than 4 kcal. mol^{-1} [143], therefore the over-estimation in (128) is unlikely to be more and will probably be less, than this value. Thus it seems reasonable to assume that the difference between ΔG and $\Delta G^{\#}$ will be small.

In determining the relative apicophilicity of two groups, small errors can arise if these groups have a large difference in apicophilicity. The reaction co-ordinate (131) is for two phosphoranes (130), where one R group is very apicophilic and the other phosphorane has a poorly apicophilic R group.

(131)



From Hammonds Postulate the phosphorane (130) with a poorly apicophilic R group will more closely resemble the transition state, than the phosphorane with the very apicophilic R group. Hence the measured $\Delta(\Delta G^{\#})$ is smaller than the actual difference in energy between the two phosphoranes, $\Delta(\Delta G)$. Unless extremes of apicophilicity are encountered such differences are likely to be small. In order to build up a quantitative apicophilicity scale, $\Delta(\Delta G)$ must be regarded as equal to $\Delta(\Delta G^{\#})$, which is true for comparison of groups with reasonably similiar apicophilicities.

b.) Limitations

In interpreting d.n.m.r. results, care must be taken that the changes observed in the n.m.r. are due to the speeding up or slowing down of a pseudorotation and not to some other process.

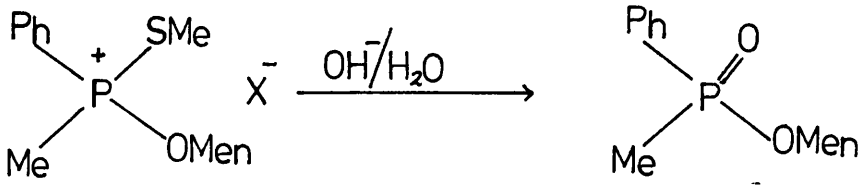
For instance coalescence may be caused by the groups under investigation becoming accidently magnetically equivalent. It is possible to eliminate this source of error by studying the line widths of the signals as they approach coalescence there should be a decrease in height of the signal and a corresponding increase in line width. In an accidental equivalence there should be no variation in peak heights or line widths.

Other possibilities for the misinterpretation of d.n.m.r. data come from the irregular processes outlined in chapter 1 page 29 , in which ionic species were detected from their ^{31}p n.m.r. chemical shifts being dependent on solvent polarity. Ramirez[12,42] showed that a marked difference in the ^{31}p n.m.r. chemical shift with change of solvent polarity was indicative of ionic species being present in solution.

4 RELATIVE APICOPHILICITY OF SULPHUR AND OXYGEN LIGANDS

4.1 RELATIVE APICOPHILICITY OF ETHYLTHIO- AND ETHOXY GROUPS IN TRIGONAL BIPYRAMIDAL PHOSPHORANES

Evidence on the relative apicophilicity of sulphur ligands is available from data on the hydrolysis of tetraco-ordinated phosphorus compounds.[137] For example alkaline hydrolysis of the optically active phosphonium salt (132) gives the phosphinate (133) with retention of configuration at phosphorus. Using the

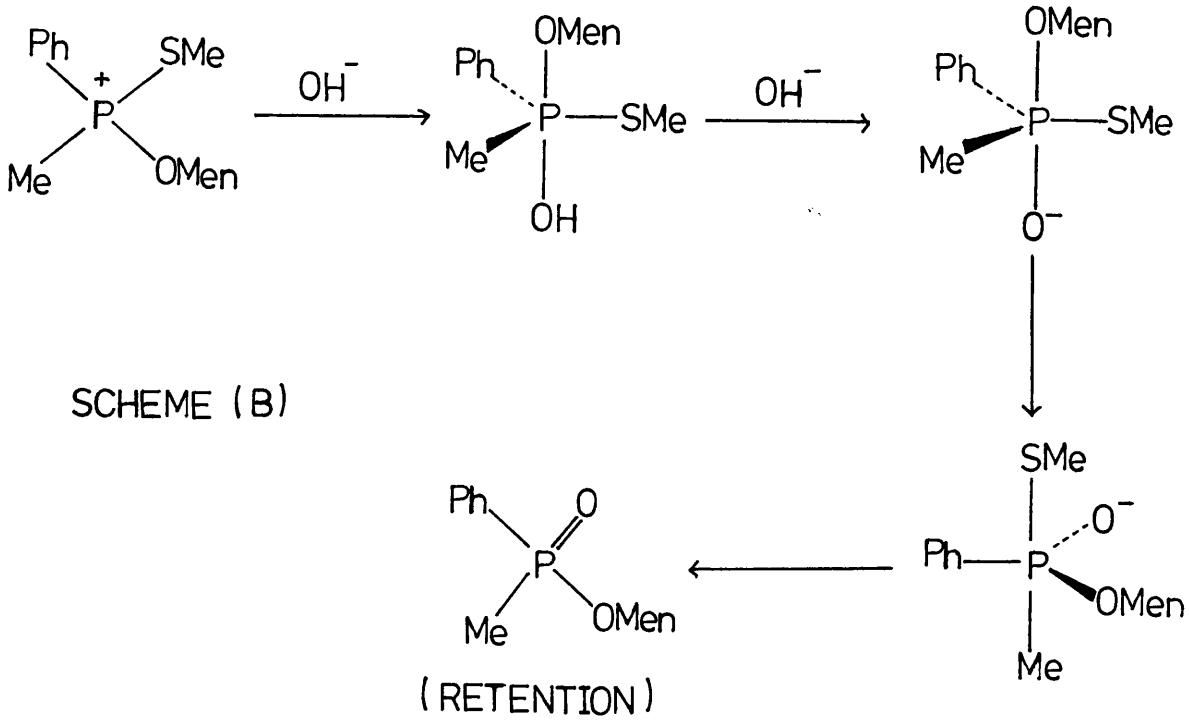


Men = (−)menthyl

(132) (133)

assumptions previously outlined in chapter 3, there are two possible intermediates from (132) formed by attack of the hydroxyl ion.

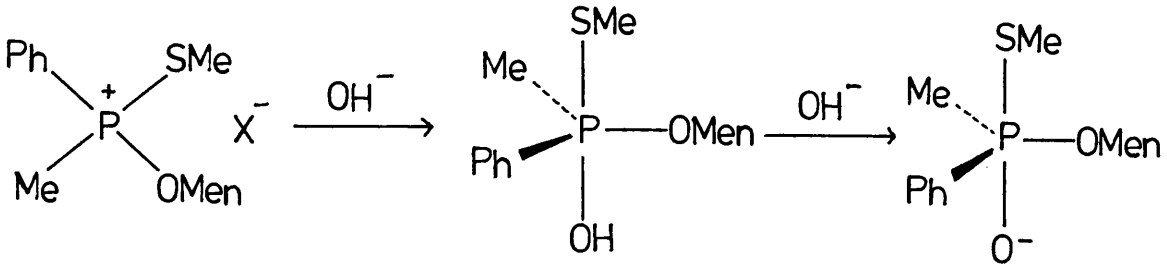
(i) Attack opposite O-menthyl -



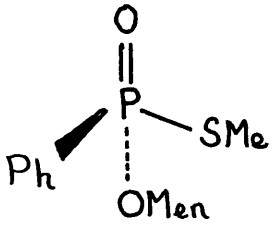
SCHEME (B)

(RETENTION)

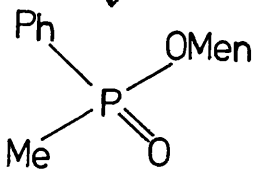
(ii) Attack opposite - SMe



SCHEME (C)



(132a)



(INVERSION)

Scheme (B) leads to retention whilst scheme (C) leads to inversion; experimentally the result is RETENTION. This means that the trigonal bipyramid with O- menthyl apical is more stable than with the -SMe group apical, i.e. O-menthyl is more apicophilic than -SMe in this system.

Methanolysis of (132a) is found to go with INVERSION at phosphorus, which by a similar arguement is explained by the -SMe group being more apicophilic than O-Menthyl.

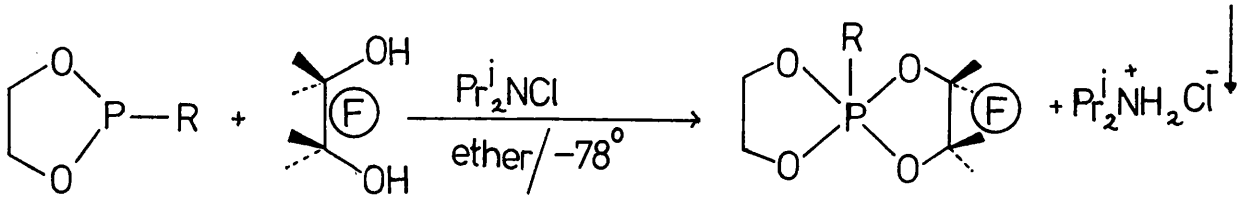
Clearly further information on the relative apicophilicity of sulphur and oxygen substituents would be helpful in trying to explain the unusual results sometimes observed in nucleophilic substitution at phosphorus bearing both alkoxy and alkylthio groups.[138] Debruin[139] has shown that the kinetic apicophilicities of alkoxy and alkylthio groups are similar, based on the hydrolysis of alkoxy (alkylthio-) phosphetanium salts.

Trippett et al[140] from a study of the variable temperature n.m.r. spectra of the pseudorotation processes available to

a number of spirophosphoranes having a phenoxy or phenylthio group attached to phosphorus, have shown that the relative apicophilicities of phenoxy and phenylthio groups are similar, the balance varying according to the other groups attached to phosphorus.

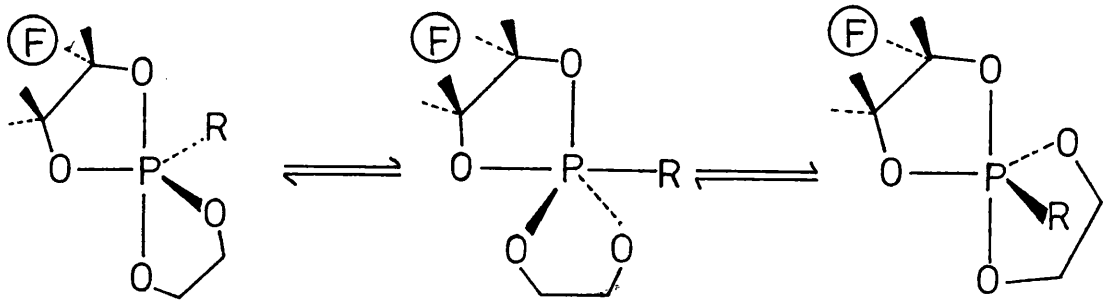
A variable temperature n.m.r. study of spirophosphoranes bearing ethoxy or ethylthio groups was considered to be of more direct relevance to the relative apicophilicity of sulphur and oxygen ligands. The systems needed for such a study had previously been difficult to synthesis by the more traditional methods. White[141] attempted to prepare spirophosphoranes bearing ethoxy and ethylthio groups, in order to obtain information on their relative apicophilicities. The limited systems that were available to him at the time gave no information, either because of thermal instability or because their n.m.r. spectra did not show the expected multiplicity in any of the solvents investigated. Attempts were made to alleviate this problem using the shift reagent tris(dipivaloylmethanato) europium III, ($Eu(dpm)_3$), but they gave inconclusive results.[141,142] However with the development of the N-chlorodi-isopropylamine method by Bone,[74] a ready route was available to give pure spirophosphoranes, bearing ethoxy and ethylthio groups, in good yields.

The system first looked at was the spirophosphorane (135,R = OEt), obtained from the reaction of 2 -ethoxy- 1,3,2-dioxaphospholan (134, R = OEt) with perfluoropinacol in the presence of N-chlorodi-isopropylamine.



(134) (135)

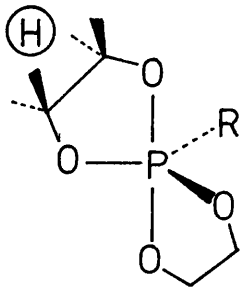
At room temperature the ^{19}F n.m.r. spectrum of (135, R = OEt) in 1-bromonaphthalene showed two signals of equal intensity, which underwent a reversible coalescence at $116 \pm 2^{o}C$. The free energy of activation ($\Delta G^{\#}$) associated with this coalescence is $\underline{20.1 \pm 0.2\ kcal.mol^{-1}}$. This corresponds to the pseudorotation process, (136) $\rightleftharpoons$ (138), which involves the high energy intermediate (137, R = OEt) in which the ethoxy group is in an apical position with the ethylene glycol ring in a diequatorial position.



(136) (137) (138)

The ^{19}F n.m.r. spectrum of the corresponding ethylthio spirophosphorane (136, R = SEt) also showed two signals of equal intensity in 1- bromonaphthalene. These underwent a reversible coalescence at $121 \pm 2^{o}C$, with an associated $\Delta G^{\#}$ value of $\underline{19.1 \pm 0.2\ kcal.mol^{-1}}$. In this system (136) $\rightleftharpoons$ (138), the ethylthio-group is more apicophilic than ethoxy by about 1 $kcal.mol^{-1}$.

To check the validity of this result other systems were considered.

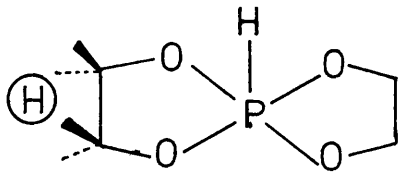


R = -SEt and -OEt

(139)

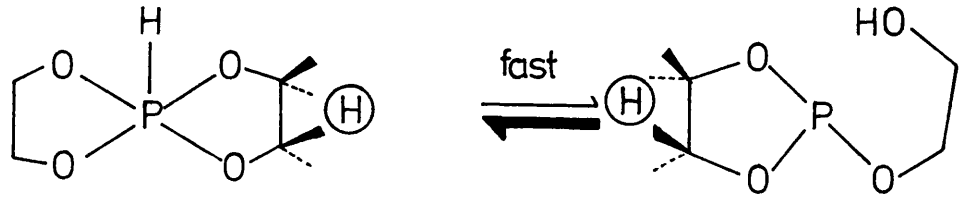
The attempted synthesis of the spirophosphorane (139, R = OEt) by the N-chlorodi-isopropylamine method resulted in the

total loss of the ethoxy group on addition of pinacol and N-chlorodi-isopropylamine to the dioxaphospholan (134, R = OEt). The compound obtained was found from spectral data to be the spirophosphorane (140). The ^1H n.m.r. spectrum showed the large



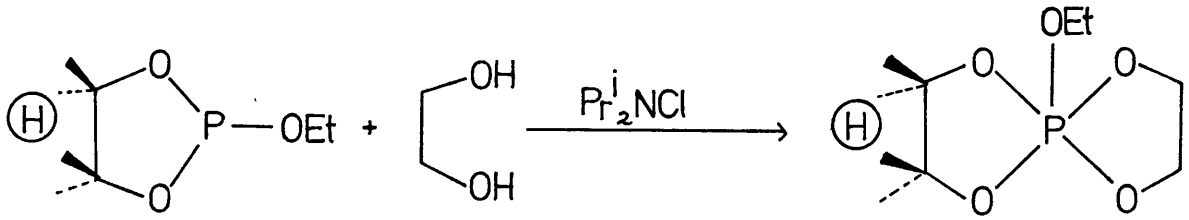
(140)

P-H coupling constant associated with such compounds. The ν_{max} showed evidence of a strong -OH absorption, although no trace of the hydroxyl group was detected in the ^1H n.m.r.; this is consistant with the fast ring-opening (141) $\rightleftharpoons$ (142) found in this type of molecule[68,79].



(141) (142)

The spirophosphorane (144) could be prepared in 76% yield using ethylene glycol as the diol and 2-ethoxy- 4,4,5,5, -tetramethyl-1,3,2-dioxaphospholan (143).

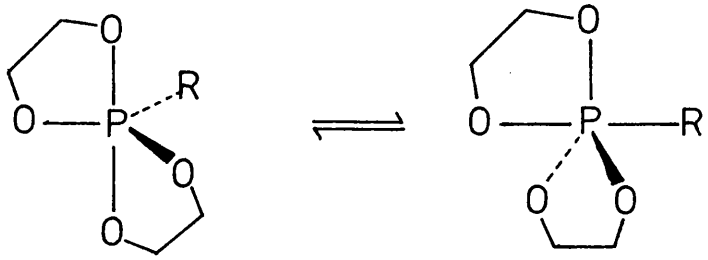


(143) (144)

The ^1H n.m.r. of the adduct (144) in 1- bromonaphthalene showed the pinacol methyls as two equal intensity signals. On heating these coalesced at 92 ± 2^{o}, corresponding to a $\Delta G^{\#}$ value of $\underline{19.4 \pm 0.2 \text{ kcal.mol}^{-1}}$. On preparing the ethylthio analogue of (144), from ethylene glycol and the corresponding

trivalent phosphorus compound, the pinacol methyls were found to be a sharp singlet in all solvents tried at R.T. This must be a case of accidental equivalence of the methyl signals and not a coalescence brought about by putting the ethylthio group apical and the ethylene glycol ring diequatorial. Such a process would not become rapid on the n.m.r. time-scale at room temperature, as the $\Delta G^{\#}$ value for such a system would be expected to be ca 18 kcal.mol^{-1}.[120]

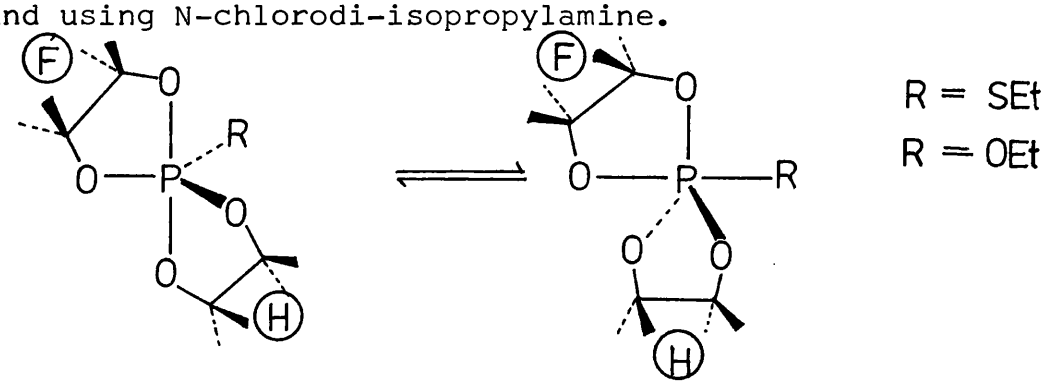
The energy barrier for the pseudorotation process (145 $\rightleftharpoons$ 146, R = OEt) had already been determined[75], the ^{1}H n.m.r. spectrum of the ring protons in (145, R = OEt) simplifying to a doublet at 125° in 1- bromonapthalene.



(145) (146)

The spirophosphorane (145, R = SEt) was prepared by the N-chlorodi-isopropylamine method in order to get a direct comparison of the ethylthio and ethoxy groups. Unfortunately the ring protons of (145, R = SEt) were found to a doublet in all solvents tried; the pattern observed by Denney[63] for the ethoxy adduct was not observed.

Another system looked at was (147) prepared from perfluoropinacol and the corresponding trivalent phosphorus compound using N-chlorodi-isopropylamine.

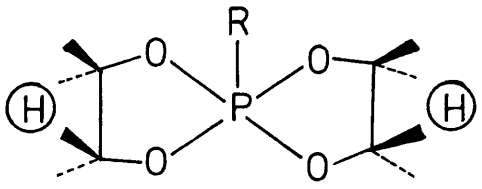


(147) (148)

R = SEt
R = OEt

The ^{19}F n.m.r. spectrum of the spirophosphorane (147, R = OEt) was found to be a singlet in all solvents tried. A similar result was recorded by Bone[44] for the adduct (147, R = OPh). The ^{19}F n.m.r. spectrum of the ethylthio analogue of (147) however did contain two multiplets of equal intensity. Unfortunately they did not coalesce up to 180° (the upper-limit of the n.m.r. machine). This result corresponds to a $\Delta G^{\#} > \underline{22\ kcal.mol^{-1}}$ for the pseudorotation process (147)$\rightleftharpoons$(148), R = SEt. Obviously the placing of a pinacol ring into a diequatorial position is of much greater energy than for the ethylene glycol ring ($\Delta G^{\#}$ 19.1 ± 0.2 $kcal.mol^{-1}$).

The spirophosphoranes (149; R = SEt, OEt) were also prepared by the N-chlorodi-isopropylamine method.



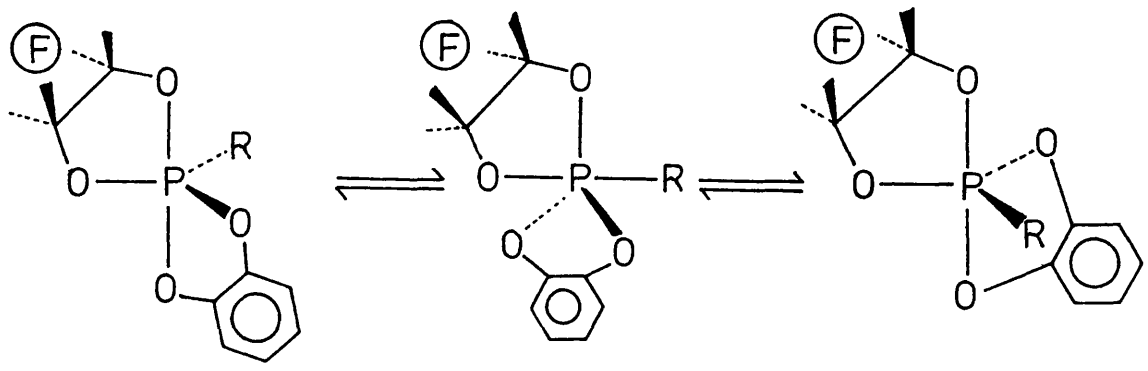
R = SEt, OEt.

(149)

The adduct (149, R = OEt) decomposed before coalescence in 1- bromonaphthalene. The ethylthio analogue (149, R = SEt) did show two equal intensity signals for the ring methyl groups in CCl_3Br but this too decomposed before coalescence.

In an attempt to obtain another result on the relative apicophilicities of the ethoxy and ethlthio groups the systems (150, R = OEt, SEt) were prepared using perfluoropinacol as the diol and the appropiately 2- substituted - 1,3,2-benzodio-oxaphosphole in the presence of N-chlorodi-isopropylamine.

The ^{19}F n.m.r. spectrum of the compound (150, R = OEt) at R.T. showed two equal intensity signals which reversibly coalesced at 180± 2° in 1- bromonaphthalene. This corresponds to the pseudorotation (150)$\rightleftharpoons$(152) becoming fast on the n.m.r. time-scale, with an associated $\Delta G^{\#}$ of $\underline{22.1 \pm 0.2\ kcal.mol^{-1}}$. The



(150) (151) (152)

similar spectrum of the ethylthio anologue (150, R = SEt) also underwent a reversible coalescence at 163± 3° in the same solvent, which corresponds to a $\Delta G^{\#}$ for the same process, (150)⇌(152), of 21.4±0.2 kcal.mol^{-1}. In this system the ethylthio group is again shown to be more apicophilic than ethoxy by about 1 kcal.mol^{-1}.

A summary of the d.n.m.r. data obtained for the spirophosphoranes prepared by N-chlorodi-isopropylamine is shown in Table 1.

TABLE 1

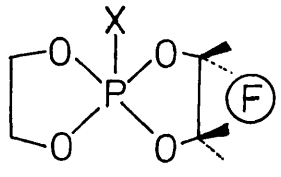
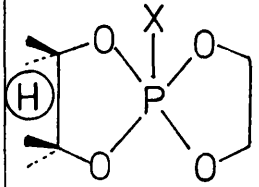
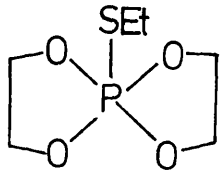
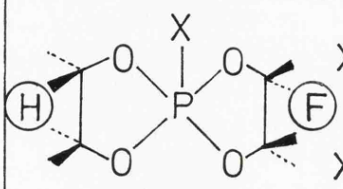
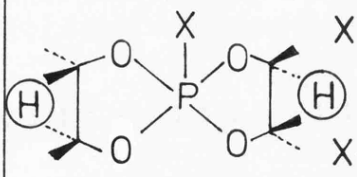
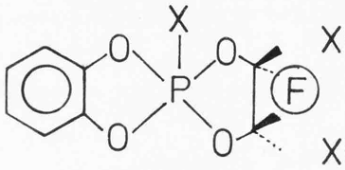
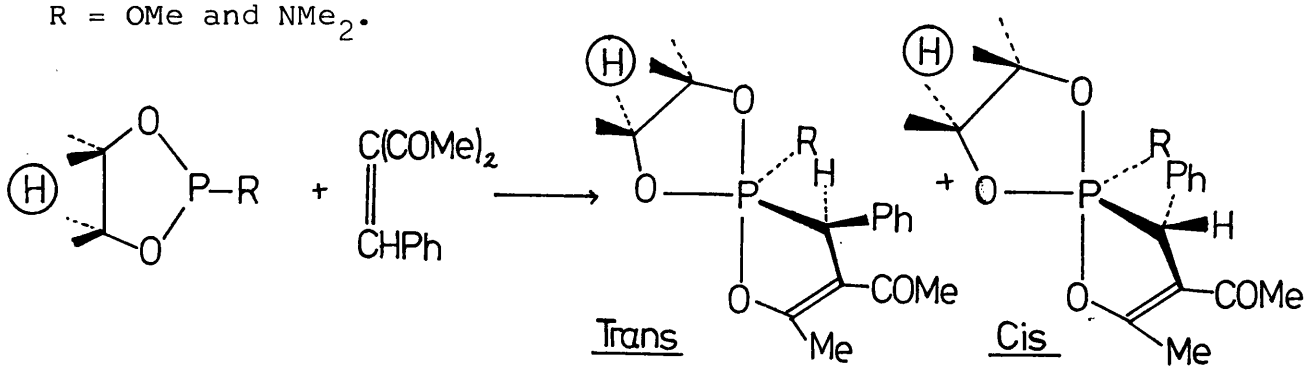
Compound[a]	Yield (%)	^{31}P (ppm)[b]	D.n.m.r. Results[c]
 X = OEt	68	+28·8	$\Delta\nu$ 21[d], T[c] 116±2[e], $\Delta G^{\#}$ 20·1±0·2[f].
X = SEt	78	+2·5	$\Delta\nu$ 104, T[c] 121±2, $\Delta G^{\#}$ 19·1±0·2.
 X = OEt	76	+34·9	$\Delta\nu$ 8, T[c] 92±2, $\Delta G^{\#}$ 19·4±0·2.
X = SEt	78	+10·5	singlet for the pinacol methyls in all solvents tried.
	57	+7·3	ring protons doublet in all solvents tried.

TABLE 1 (continued)

Compound[a]	Yield (%)	^{31}P(p.p.m.)[b]	D.n.m.r. Results[c]
 X=OEt	81	+37·1	^{19}F n.m.r. singlet in all solvents tried.
X=SEt	80	+7·2	$\Delta\nu$ 137[d], T[c] >180[e], $\Delta G^{\#}$ >22[f].
 X=OEt	82	+42·4	$\Delta\nu$ 5, decomposition before coalescence.
X=SEt	85	+23·0	$\Delta\nu$ 4·5[g], decomposition before coalescence.
 X=OEt	85	+30·7	$\Delta\nu$ 98, T[c] 180 ± 2, $\Delta G^{\#}$ 22·1±0·2.
X=SEt	82	+1·0	$\Delta\nu$ 76, T[c] 163±2, $\Delta G^{\#}$ 21·4±0·2.

a) In each case the right-hand ring as drawn was derived from the 1,2-diol.
b) In $CDCl_3$ to the high-field of external 85% H_3PO_4.
c) On 100 MH_3 machine using 1-bromonaphthalene as solvent.
d) In H_3.
e) °C.
f) k.cal.mol^{-1}.
g) CCl_3Br

To see if the results obtained from the spirophosphoranes (135, R = OEt) and (150, R = OEt, SEt) were applicable to other systems, the adducts from suitably substituted 1,3,2-dioxaphospholans (153, R = OEt) and 3-benzylidenepentane -2,4-dione (154) were prepared. This reaction has been shown to give mixtures of isomeric spirophosphoranes from which the major <u>trans</u> isomers (155) can be readily obtained in a pure crystalline form for R = OMe and NMe_2.



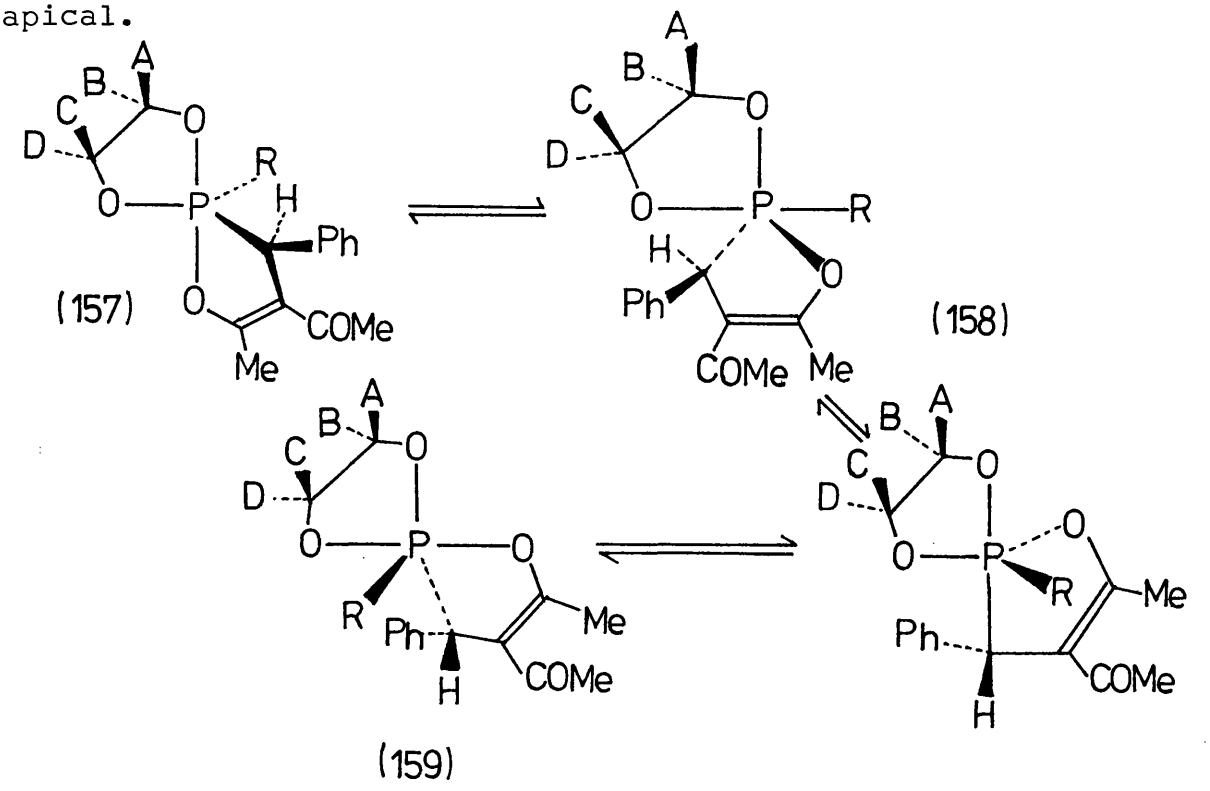
(153) (154) (155) (156)

White[141] has previously prepared a series of the <u>trans</u> spirophosphoranes (155, R = OMe, OBu^t, OPh and NMe_2). The spirophosphorane (155, R = OEt) was now prepared in almost quantitative yield and was obtained as the pure <u>trans</u> isomer on recrystallisation from ethyl acetate -light petroleum. At room temperature, in chlorobenzene solution, the methyl groups of the dioxaphospholan ring gave rise to four widely spaced signals in the 100 MHz ^1H n.m.r. spectrum, characteristic of the <u>trans</u> isomer.[144]

On heating the two inner signals coalesced and at a higher temperature the two outer signals eventually coalesced. Both coalescences were found to correspond to the same free energy of activation ($\Delta G^{\#}$), the two different coalescence points being due to the large difference in frequency between the coalescing signals.

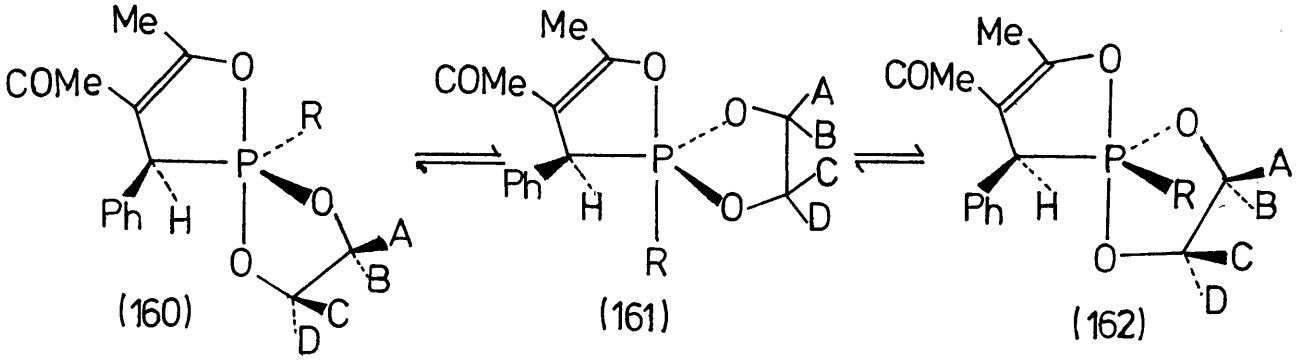
Equivalence of the pairs of methyl groups occurs when the pseudorotations (157) $\rightleftharpoons$ (159) become rapid on the n.m.r.

time-scale. This involves the high-energy spirophosphorane (158) in which the oxaphospholen ring is diequatorial and the R group apical.



Any change in the free energy of activation for the process (157)⇌(159) will depend on the relative apicophilicity of the various R groups.

Pseudorotations which involve placing the dioxaphospholan ring diequatorially, (160)⇌(162), cannot lead to equivalence of any of the methyl groups, but the process will give equilibration of the <u>cis</u> and <u>trans</u> isomers. In fact such processes are



observed to take place in the variable temperature experiments, but they are very slow in the temperature range studied, as would be expected from calculation[120] and previous experimental data on the energies involved in placing a pinacol ring in a

diequatorial position and the R group (OEt or SEt) in an apical position, (see page 57).

On preparing the ethylthio analogue (157, R = SEt) this adduct was obtained predominantly as the trans isomer but on recrystallisation from light petroleum the pure cis isomer was obtained. The d.n.m.r. work was carried out on the trans isomer so that comparisons with the ethoxy-spirophosphorane (157, R = OEt) would be more reliable.

The results obtained from the variable temperature n.m.r. work on the 3-benzylidene pentane-2,4-dione adducts (157, R = OEt, SEt) are summarised in Table 2.

TABLE 2

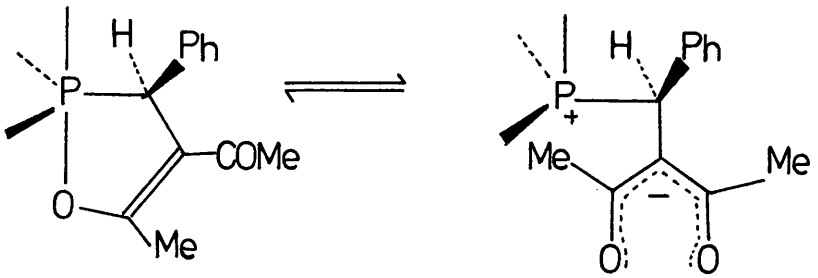
	INNER PAIR OF METHYL SIGNALS[c]			OUTER PAIR OF METHYL SIGNALS		
R group	$\Delta\nu(H_z)$	$T^c(^oC)$[a]	$\Delta G^{\#}$(kcal.mol^{-1})[b]	$\Delta\nu$	T^c	$\Delta G^{\#}$
OEt	14	80	18.3	108	100	18.0
SEt	35	85	18.0	112	100	17.9

a) $\pm 3^o$ b) ± 0.2 kcal.mol^{-1} c) all spectra taken on a 100 MH_z machine in chlorobenzene

The $\Delta G^{\#}$ valves obtained from the inner and outer pairs of methyl signals are in reasonably good agreement, as expected. The results show that in this system the apicophilicity of ethylthio and ethoxy are very similar.

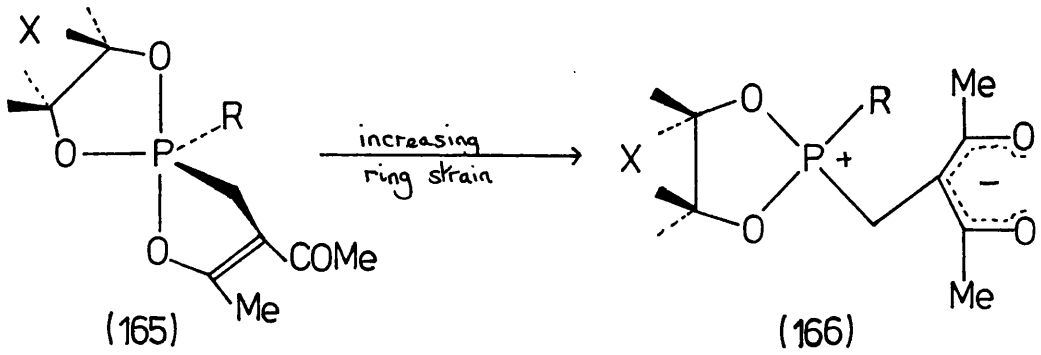
Gorenstein and Westheimer[51,111] have shown that in 3-benzylidenepentane-2,4-dione adducts there is an 'irregular' process, having a free energy of activation in the region of 21 kcal.mol^{-1}, which is due to the ring-opening process (163)$\rightleftharpoons$(164). This was based on ^1H n.m.r. evidence which showed equivalence of the phospholen methyl signals as the process became rapid on the n.m.r. time-scale.

This ring-opening step would be expected to have an even



(163) (164)

higher energy barrier in a spirophosphorane system, e.g. (157, R = OEt, SEt), due to the increase in ring strain which would be experienced in the dioxaphospholan ring as it went from the trigonal bipyramidal geometry of the spirophosphorane (165) to the tetrahedral geometry of the ring-opened dipolar species (166).



(165) (166)

White[141,145] has also shown that with the spirophosphorane (157, R = NMe_2) there is no coalescence up to 150°, which corresponds to a $\Delta G^{\#}$ of greater than 22 kcal.mol^{-1}. If no ring-opening occurs in (157, R = NMe_2), in which the dimethylamino group would stabilize the formation of a positive charge on phosphorus[33], then it would seem likely that the coalescences observed at lower temperatures for the adducts. (157, R = OEt, SEt) are due to the pseudorotation pathway (157)$\rightleftharpoons$(159) and not to any dissociation of the adducts into dipolar species.

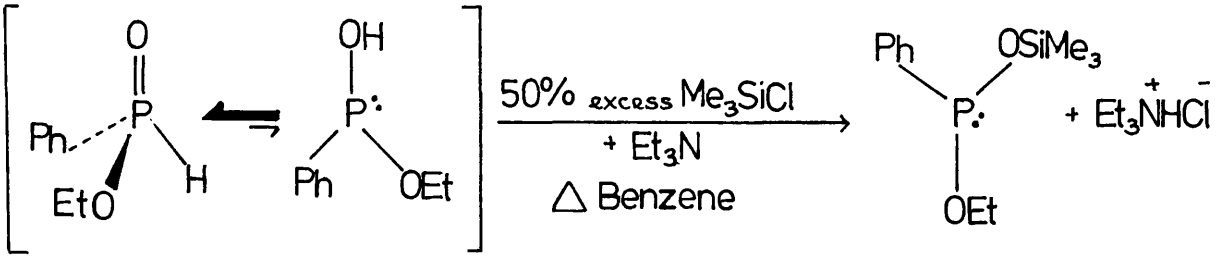
Thus it would seem from the d.n.m.r. data on the pseudorotation processes, (136)$\rightleftharpoons$(138), (150)$\rightleftharpoons$(152) and (157)$\rightleftharpoons$(159) that the relative apicophilicities of the ethylthio and ethoxy groups are very similar, with the balance perhaps slightly in favour of the ethylthio group being just

more apicophilic than the ethoxy group.

This result is rather surprising in view of the lower electronegativity of sulphur and also the strong π donor properties of sulphur ligands. There is also evidence, from the high energy barrier to rotation around P-S bonds, to suggest that the π donation of sulphur to phosphorus is very high.[97,118] Both these factors would make sulphur ligands poorly apicophilic on the theories of Hoffmann et al[96]. On the other hand sulphur does have empty 3d orbitals which could act as an acceptor of π electron density from phosphorus, thus putting sulphur in a situation where it would favour the apical position. Obviously these factors must be cancelling each other out to a large extent, leaving the relative apicophilicity of sulphur roughly the same as that of oxygen.

4.2 THE RELATIVE APICOPHILICITY OF THE TRIMETHLSILOXY GROUP ($-OSiMe_3$)

Acyclic phosphites containing the trimethylsiloxy group are readily synthesised from phosphinates (165) on refluxing in benzene with a 50% excess of chlorotrimethylsilane-triethylamine[146,147].

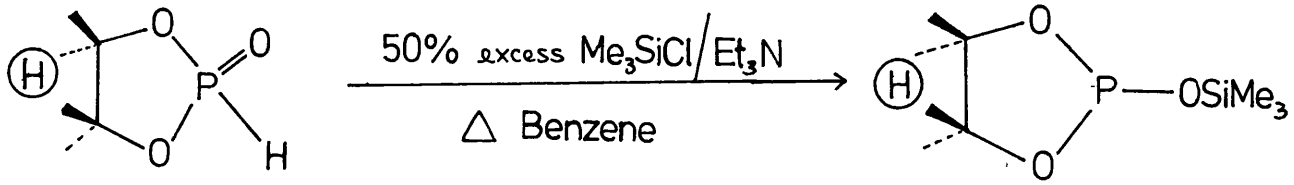


(165) (166)

The large negative ^{31}P n.m.r. chemical shift of (166) relative to external 85% H_3PO_4 is characteristic of a trivalent structure.[147,148]

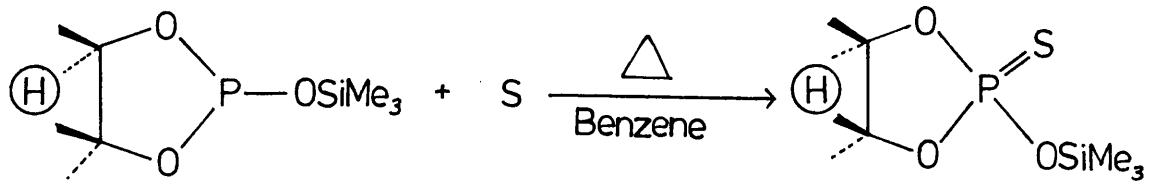
The synthesis of (168) was attempted in order to determine whether the method was applicable to cyclic phosphinates (167) and to prepare spirophosphoranes containing the trimethylsiloxy

group, so that it's relative apicophilicity might be determined by d.n.m.r. studies.



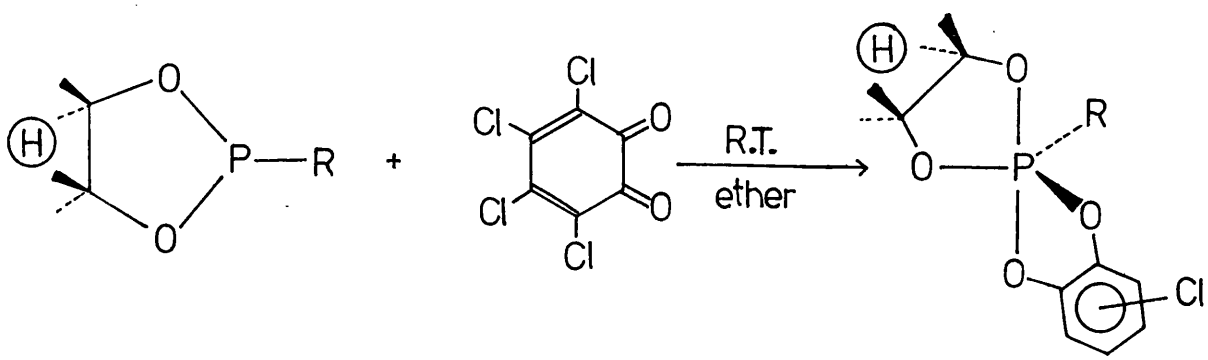
(167) (168)

The 2-trimethylsiloxy -4,4,5,5-tetramethyl-1,3,2-dioxaphospholan (168) was obtained in 70% hield, it's trivalent state was not only shown from the very low ^{31}p n.m.r. chemical shift of -126.9 p.p.m., but it was also fully characterised as the sulphide (169).



(169)

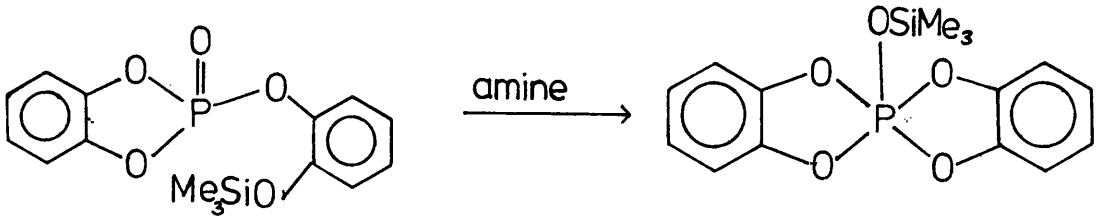
The first system looked at was (170, R = $OSiMe_3$) made from the cyclic phosphite (168) and tetrachloro-o-benzoquinone.



(170)

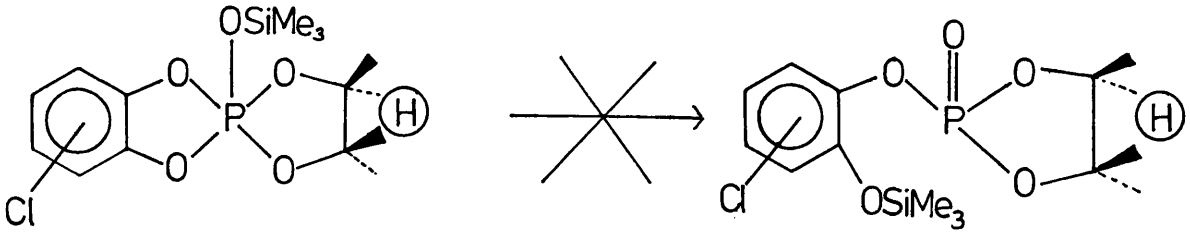
It was hoped that a comparison of the $-OSiMe_3$ group could be made with the series of spirophosphoranes (170, R = OPh, Cl, NMe_2) made by Bone.[44,170] Unfortunately the methyl signals of the dioxaphospholan ring were a singlet in all solvents tried; a similar result was also obtained for the spirophosphorane

(170, R = OEt). The pentaco-ordinate nature of the compound was shown from the high ^{31}P n.m.r. chemical shift of + 35.9 p.p.m., which is typical of a spirophosphorane of this type.[33] Ramirez et al[149] have concluded from their work on the isomerization of (171)⇌(172), that the driving force of the reaction may be provided by the higher stability of the bond $(RO)_4P-O-SiR_3^1$ verses the aryl-O-SiR_3^1 bond.



(171) ^{31}P = -7.3 p.p.m. (172) ^{31}P = +30.5 p.p.m.

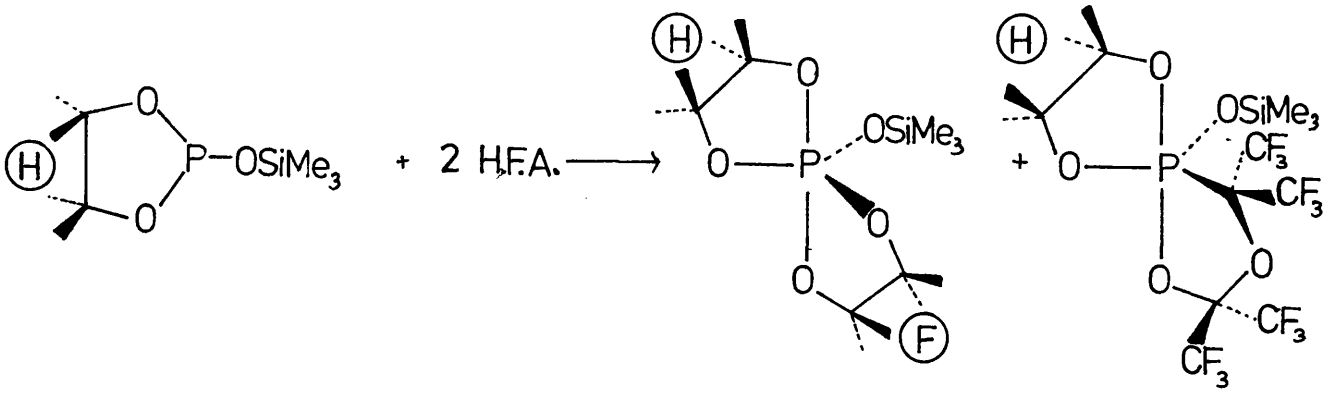
Therefore it would seem unlikely that an irregular process, which involves the transfer of the trimethylsilyl group from the phosphorus oxygen to the aryl oxygen is occurring, (173)⇌(174), and that the singlet for the pinacol methyl signals is due to accidental equivalence.



(173) (174)

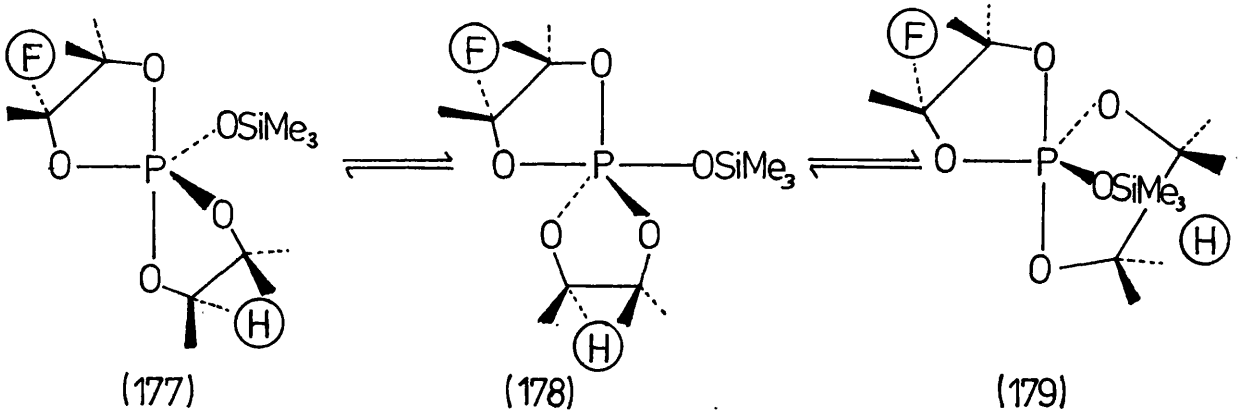
Many attempts were made to synthesis spirophosphoranes from the trimethylsiloxy phosphite (168) and various 1,2-diols using N-chlorodi-isopropylamine, but in no case was any pentaco-ordinate phosphorus compound isolated.

A spirophosphorane containing the trimethylsiloxy group was prepared using hexafluoroacetone and the phosphite (168). However not only was the 1,3,2-dioxaphospholan (175) formed but also the 1,4,2-dioxaphospholan adduct (176).



(175) (176)

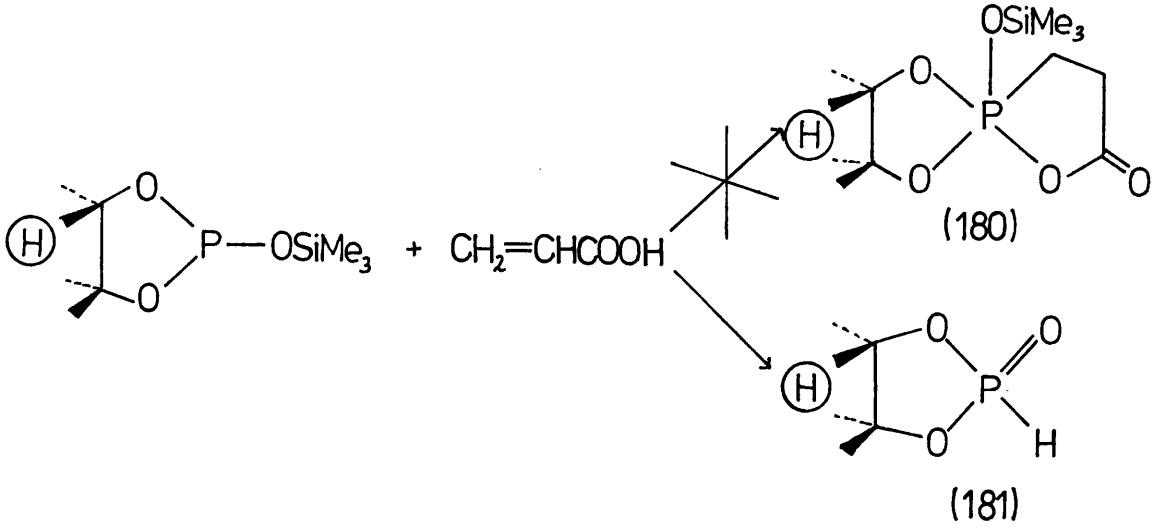
As expected,[44] the adduct (176) showed no tendency to isomerize on heating to give the 1,3,2-dioxaphospholan (175). However the ratio of (175) : (176) was improved from the 50 : 50 reaction mixture by extraction with light petroleum up to the point where an ^{19}F n.m.r. spectrum could be obtained which showed two equal intensity signals at room temperature. In 1-bromonaphthalene these signals underwent a reversible coalescence at 168±2°, corresponding to a $\Delta G^{\#}$ of 22.2±0.2 kcal.mol^{-1}. This coalescence is when the pseudorotation (177) ⇌ (179) has become rapid on the n.m.r. time-scale.



(177) (178) (179)

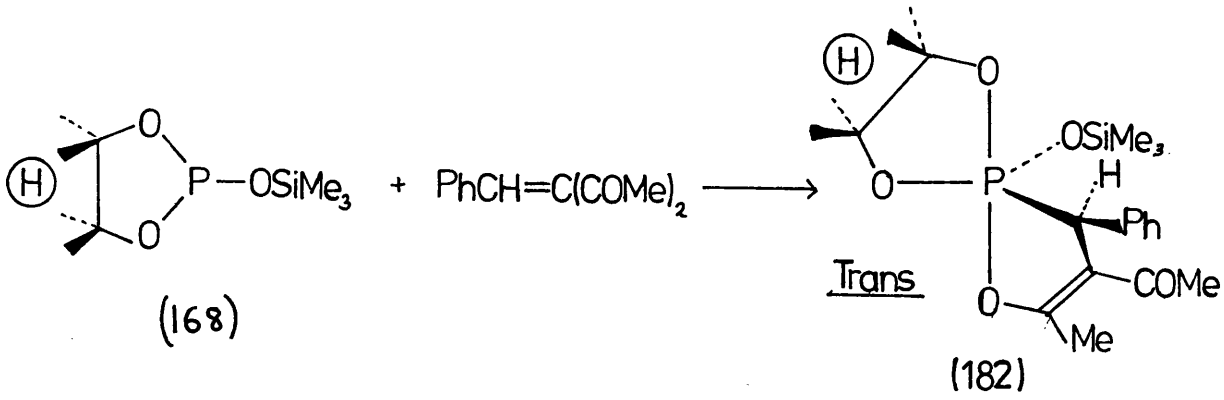
This result shows the trimethylsiloxy group to be slightly more apicophilic than the ethylthio and ethoxy groups and of the same apicophilicity as the thiophenyl group.[43]

The search for another suitable spirophosphorane with which this result could be checked proved difficult. In attempting to make the acrylic acid adduct,[150] (see chapter 6) (180), only the 1,3,2-dioxapholan -2- oxide (181) was isolated in almost quantitative yield.



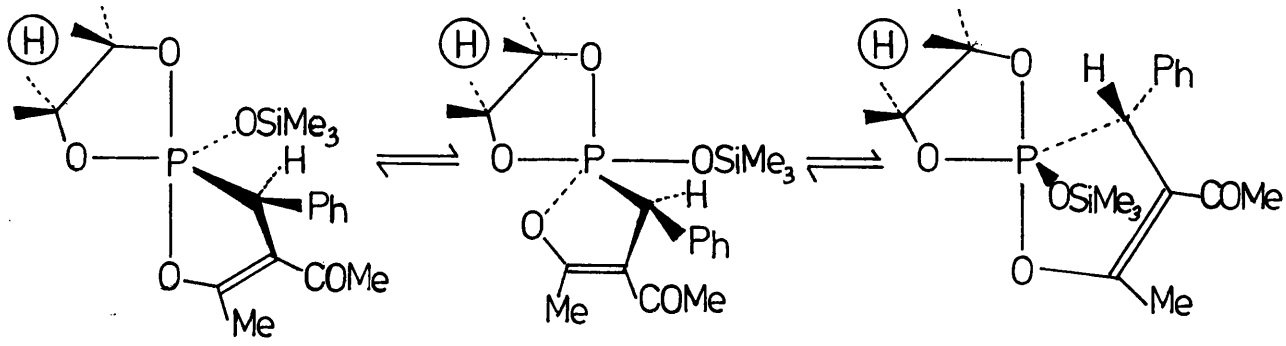
Obviously the mobility of the trimethysilyl group in trivalent phosphorus compounds is greater than in the P^{IV} or P^{V} states.[149] This mobility probably accounts for the failure of the N-chlorodi-isopropylamine reactions in preparing spirophosphoranes.

Fortunately a 3-benzylidenepentane -2,4-dione adduct (182) was prepared from (168) in good yield and crystallised from ethyl acetate - light petroleum as the <u>trans</u> isomer.



This adduct (182) gave the expected four signals for the pinacol ring methyl groups at room temperature in 1-bromonaphthalene.[144] Only the coalescence of the inner methyl signals was obtainable due to the rapid formation of the <u>cis</u> isomer at elevated temperatures, unlike the ethylthio and ethoxy analogues (see section 4.1). The reversible coalescence was at $+70 \pm 5^{\circ}$, $\Delta G^{\#}$ <u>17.9 ± 0.2 kcal.mol</u>$^{-1}$ which corresponds to the pseudorotation

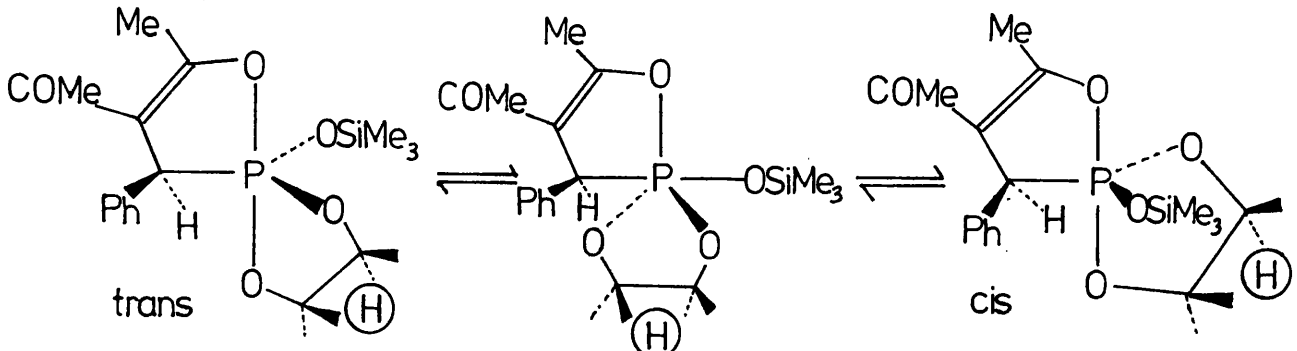
process (183)⇌(185) becoming rapid on the n.m.r. time-scale.



(183) (184) (185)

This result shows the trimethylsiloxy group to be as apicophilic as the ethylthio group in this series of adducts, a result which compares favourably with the one obtained from hexafluoroacetone adduct. (175)

The ease with which trans⇌cis isomerization took place at 70° was surprising in view of experience with previous adducts[145], whose isomerisation was observed to be slow over the temperature range studied. The isomerisation of trans⇌cis, (186)⇌(188), involves the high energy intermediate (187) which has the pinacol ring in a diequatorial position and the trimethylsiloxy group apical. The more apicophilic the group going into the apical position, the lower the energy needed to put the pinacol ring diequatorial. The fact that this isomerisation occurs fairly readily at elevated temperatures backs up the information obtained, that the trimethylsiloxy group is



(186) (187) (188)

quite apicophilic and is about the same as the ethylthio and ethoxy groups.

In accounting for the high apicophilicity value found

for the trimethylsiloxy group, the large size of the ligand, as well as the electronegativity of the oxygen, is likely to be a factor, especially in the crowded 3-benzylidenepentane -2,4-dione adducts (182).

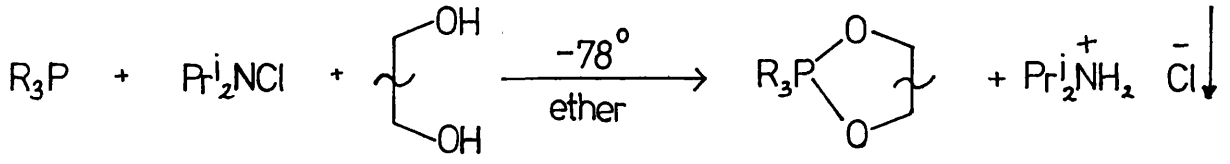
5 SYNTHESIS OF PHOSPHORANES USING N-CHLORODI-ISOPROPYLAMINE

5.1 THE PREPARATION OF UNSYMMETRICAL PHOSPHORANES

Castro[151] has used N-chlorodi-isopropylamine in the synthesis of alkoxy-phosphonium salts according to the following equation.

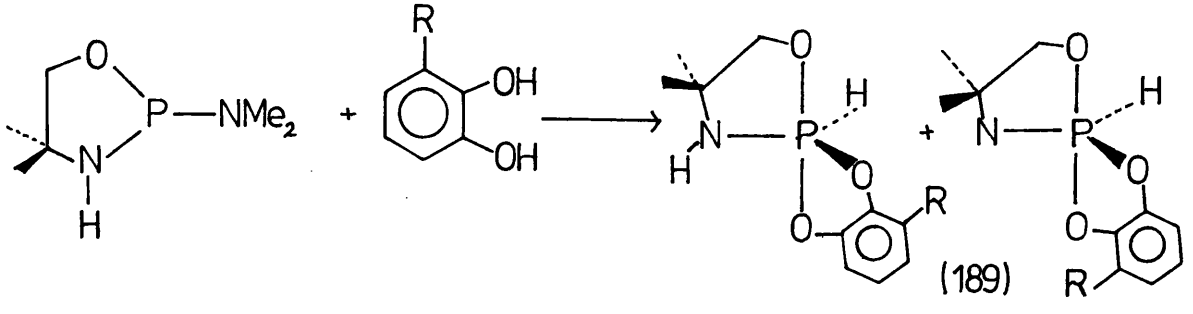
$$(Me_2N)_3P + ClNPr^i_2 + R^1R^2CH(OH) \longrightarrow (Me_2N)_3\overset{+}{P}OCHR^1R^2\ \overset{-}{Cl}$$

Bone[74] found that when N-chlorodi-isopropylamine was added to equimolar quantities of a trivalent phosphorus compound and a 1,2- or 1,3-diol in ether at -78°C a precipitate of di-isopropylamine hydrochloride was formed. Filtration and removal of the solvent gave the phosphorane in good yields.

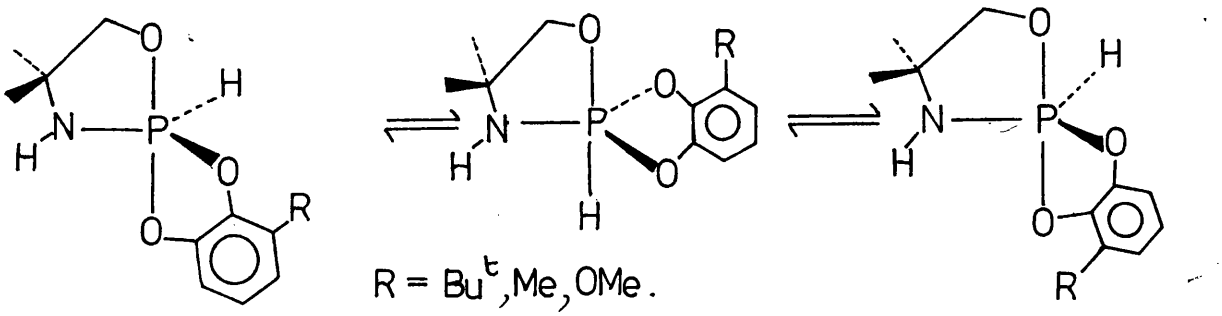


With the development of the N-chlorodi-isopropylamine method for the preparation of spirophosphoranes it now became possible to prepare a wide range of unsymmetrical spirophosphoranes, first looked at by Wolf et al.[152]

They found that the spirophosphorane (189) existed as two isomers at room temperature; this was determined by the presence of two signals for the R groups in the ^1H n.m.r. spectrum. On heating these signals coalesced reversibly,



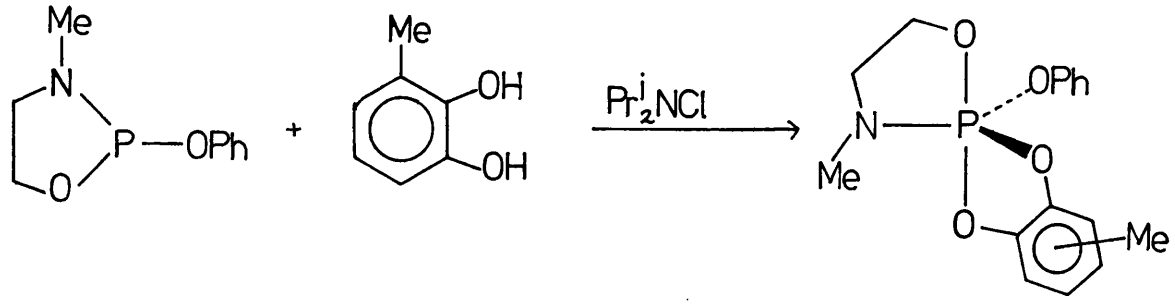
corresponding to the process (190)⇌(192) becoming fast on the n.m.r. time-scale. Equilibration of these isomers takes place *via* the high energy intermediate (191) in which the hydrogen atom is apical and the catechol ring diequatorial. The free energy of activation associated with this process was shown to be about 18 kcal.mol^{-1}. This energy barrier of only



(190) (191) (192)

18 kcal.mol^{-1} for placing the catechol ring diequatorially shows the high apicophilicity value associated with hydrogen.

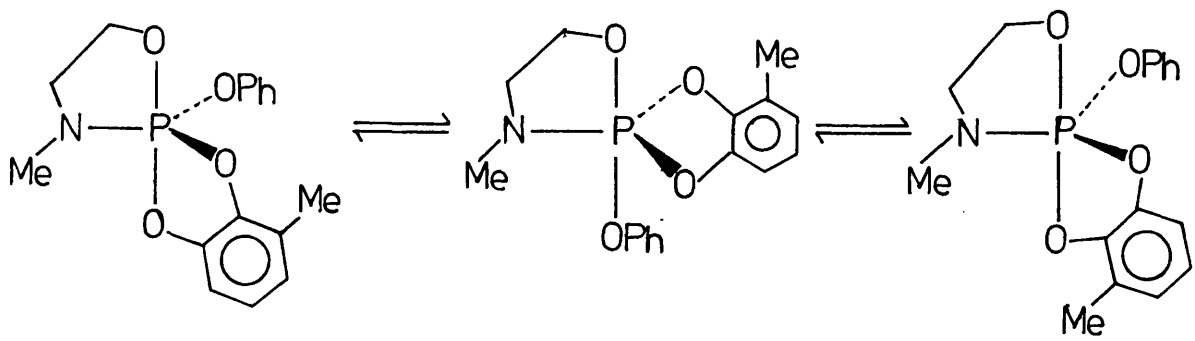
The first system attempted by the N-chlorodi-isopropylamine method was the spirophosphorane (194) made from the 1,3,2-oxazaphospholidine (193) and 3-methylcatechol.



(193) (194)

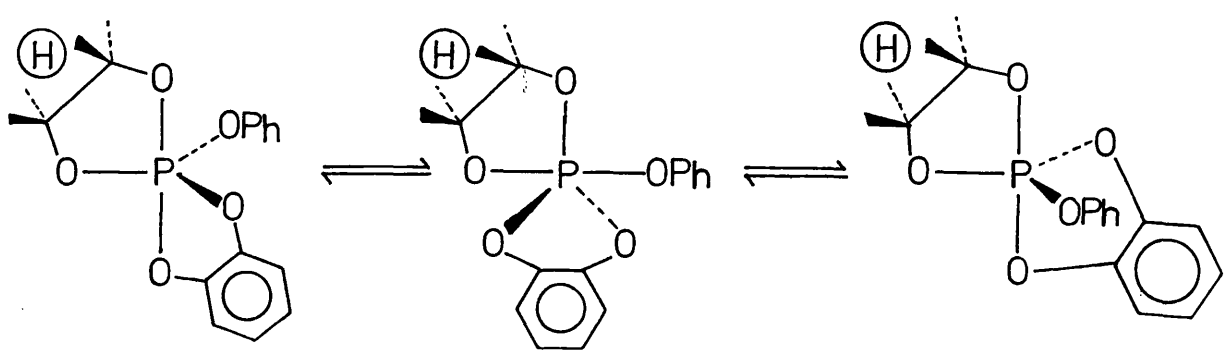
On examining the ^{1}H n.m.r. spectrum it was found that there were two aromatic methyl signals, corresponding to the two isomers (195) and (197), in the ratio of *ca* 1:1 at room temperature.

In 1-bromonaphthalene these two signals coalesced at 127° ± 2°C, corresponding to a $\Delta G^{\#}$ of 20.2 ± 0.2 kcal.mol^{-1}. At this temperature the process (195)⇌(197), which leads to the



(195) (196) (197)

equilibration of the two isomers, had become fast on the n.m.r. time-scale. The value of 20.2 ± 0.2 kcal.mol^{-1} obtained, compares well with that of Bone[44,140], derived from the system (198)⇌(199), of 20.5 kcal.mol^{-1}.



(198) (199)

In order to show the general applicability of these systems in obtaining accurate data on relative apicophilicities, various unsymmetrically substituted catechols were used. In the case of the 4-fluorocatechol adduct excellent agreement was found with the result for the 3-methyl adduct; the d.n.m.r. data are summarised in Table 3.

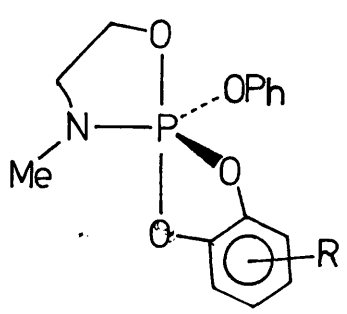
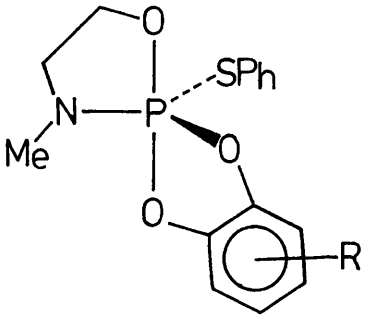


TABLE 3

R	Δν (Hz)	T^c (^oC)[a]	$\Delta G^{\#}$ (kcalmol^{-1})
3-methyl	35	127 ± 2°	20.2 ± 0.2
4-fluoro	300	168 ± 2°	20.3 ± 0.1
4-methyl	only one observable signal in all solvents tried.		

[a]In 1-bromonaphthalene

Replacement of the phenoxy group by other ligands would give information on the apicophilicity of that ligand relative to phenoxy. The first group looked at was the phenylthio group in the spirophosphorane (200).

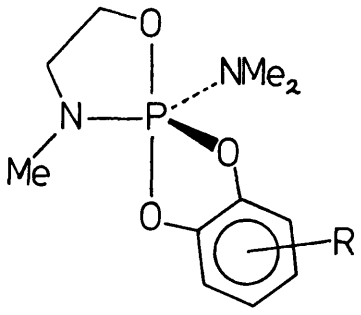


(200)

When R was 3-methyl, two separate signals were observed for the aromatic methyl group in 1-bromonaphthalene. These signals underwent a reversible coalescence at 137 ± 2°, corresponding to a $\Delta G^{\#}$ of 21.7 ± 0.2 kcal.mol^{-1}. This result shows the phenylthio group to be about 1 kcal.mol^{-1} less apicophilic than phenoxy in this system. Bone[44,140] concluded, from a d.n.m.r. study of various spirophosphoranes containing phenoxy and phenylthio groups, that their relative apicophilicities are almost the same, (e.g. $\Delta G^{\#}$ 20.5 and 20.7 kcal.mol^{-1} respectively).

When R was 4-methyl, only one signal was observed in all solvents tried for the aryl methyl group.

The next ligand to be studied was the dimethylamino group, in the spirophosphoranes (201) and (202). Both systems showed



(201) R = 3—methyl

(202) R = 4—methyl

two separate aryl-methyl signals in the ^{1}H n.m.r. spectrum at room temperature. However on heating decomposition occurred before coalescence, in both cases. This result is hardly

surprising in view of the very low apicophilicity of the dimethylamino relative to phenoxy.[153] In fact the spirophosphorane (201) did not decompose until 180°, so we can say that the $\Delta G^{\#}$ value is going to be greater than 24 kcal.mol^{-1} for putting the catechol ring diequatorial and the dimethylamino group apical (c.f. 20.5 kcal.mol^{-1} for phenoxy).

This method of determining relative apicophilicity values has been extended by the use of other unsymmetrical trivalent phosphorus compounds; the results from spirophosphoranes (203) and 204) are summarised in Table 4.

(203) = 3-methyl
(204) = 4-methyl

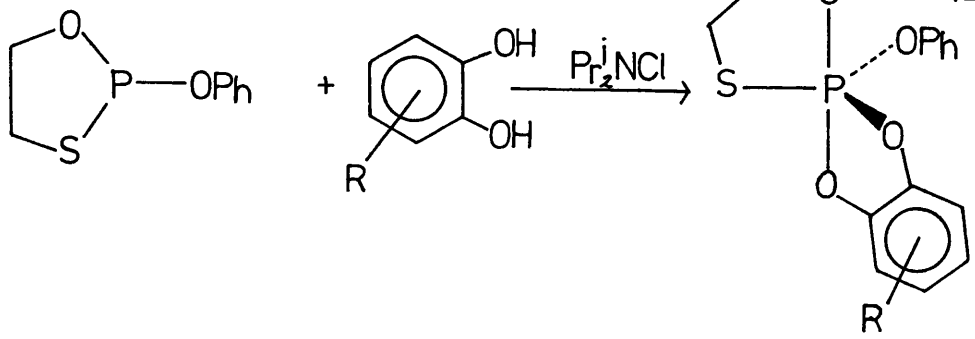
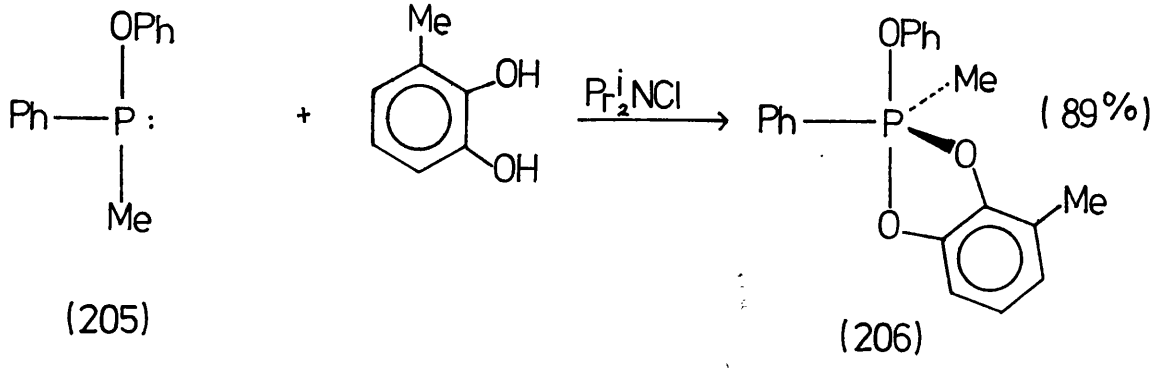


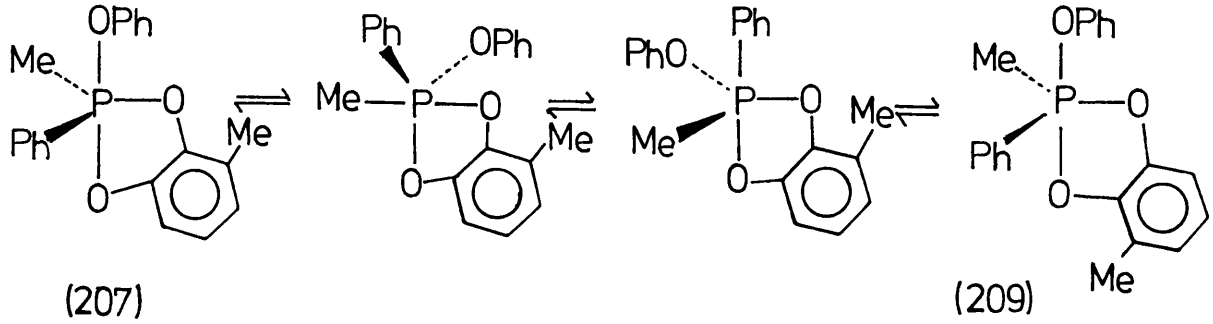
TABLE 4

R	$\Delta\nu$(Hz)	T^c(°C)	$\Delta G^{\#}$(kcal.mol^{-1})
(203) 3-methyl	45.7	112 ± 2°	19.2 ± 0.1
(204) 4-methyl	7.6	82 ± 2°	18.9 ± 0.1

This method is even applicable to acyclic unsymmetrical trivalent phosphorus compounds (205). At room temperature there was only one aryl-methyl signal for (206) in the ^{1}H n.m.r. spectrum.



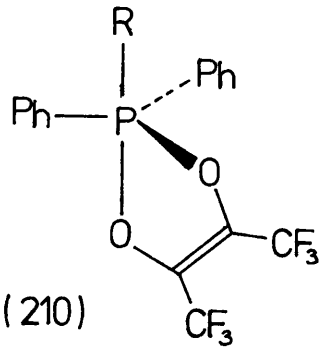
On cooling the sample down to -95°C in CH_2Cl_2, the aryl-methyl group split into two signals of equal intensity; at this temperature the equilibration of the two isomers (207) $\rightleftharpoons$(209), had become slow on the n.m.r. time-scale.



(207) (209)

On raising the temperature the two signals were found to coalesce at -65 ± 2°C, which corresponds to a $\Delta G^{\#}$ of 11.1 ± 0.1 kcal.mol^{-1}.

Dickstein[154] has shown that the relative apicophilicity between phenyl and phenoxy is 12.6 ± 0.1 kcal.mol^{-1}, from a series of hexafluorobiacetyl adducts (210). When slowing down the equilibration of (207) $\rightleftharpoons$(209) on the n.m.r. time-scale we are measuring the apicophilicity of phenoxy relative to methyl, and as methyl has been shown to be 0.5 kcal.mol^{-1} more apicophilic than phenyl[44], this would give a value of 12.0 kcal.mol^{-1} for methyl verses phenoxy in Dickstein's system.

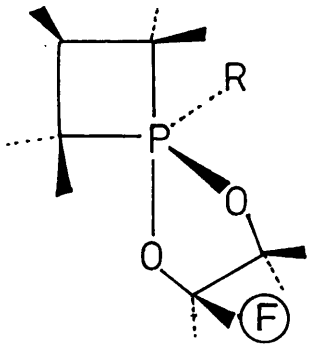


(210)

This discrepancy between observed and calculated values of 1 kcal.mol^{-1} might explain why Dickstein determined the apicophilicities of phenoxy and chlorine to be similar[154], whereas Bone[140] showed chlorine to be more apicophilic than phenoxy by ca 1.5 kcal.mol^{-1}. (For a fuller account see Chapter 7).

5.2 THE STEREOSPECIFICITY OF THE N-CHLORODI-ISOPROPYLAMINE REACTION AND ITS' USE IN PREPARING GEOMETRICAL ISOMERS OF PHENYL AND BENZYL-SPIROPHOSPHETAN CATECHOL ADDUCTS.

Oram and Trippett[124], from their work on the hexafluoroaceton adducts of suitably substituted phosphetans (211), have shown that the phenyl group is very much less apicophilic than methyl or isopropyl.



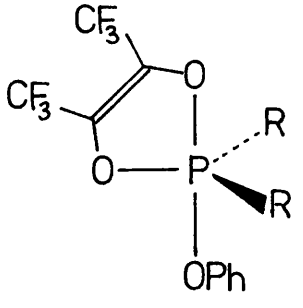
(211)

TABLE 5

R	$\Delta G^{\#}$ kcal.mol^{-1}
Me	16.9
Pr^i	17.8
Ph (cis)	19.6
Ph (trans)	> 22

As can be seen from Table 5 there is a considerable difference in apicophilicity between trans phenyl and cis phenyl, the difference being such that the coalescence temperature for the trans phenyl adduct (211, R = trans Ph) was above the operating conditions of the n.m.r. spectrometer. This result contrasts with the work of Whittle[108] and Bone[44] who found that the apicophilicities of alkyl and phenyl groups were similar.

Whittle obtained his results from the hexafluorobiacetyl adducts (212), R = Ph and Pr^i.

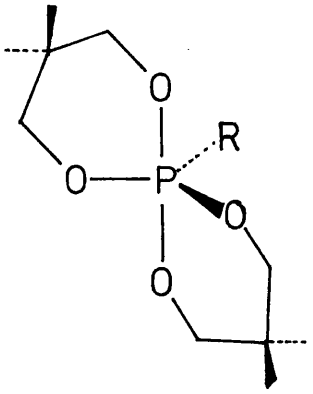


(212)

TABLE 6

R	$\Delta G^{\#}$ kcal.mol^{-1}
Ph	12.6
Pr^i	12.9

Bone prepared the spirophosphoranes (213, R = Ph, Me, $-CH_2Ph$) from the appropriate tervalent phosphonite and neopentyl-glycol using N-chlorodi-isopropylamine. The spirophosphoranes (213, R = Ph and Me) had previously been prepared by Denney's[63] exchange method, though in an impure state.



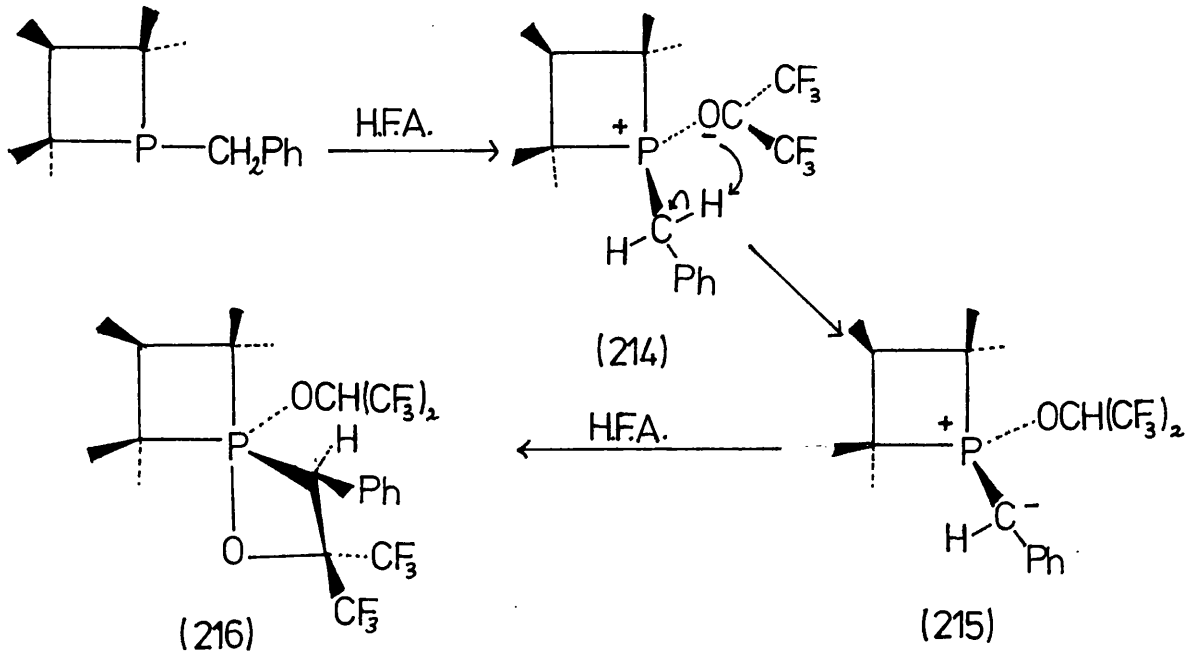
(213)

TABLE 7

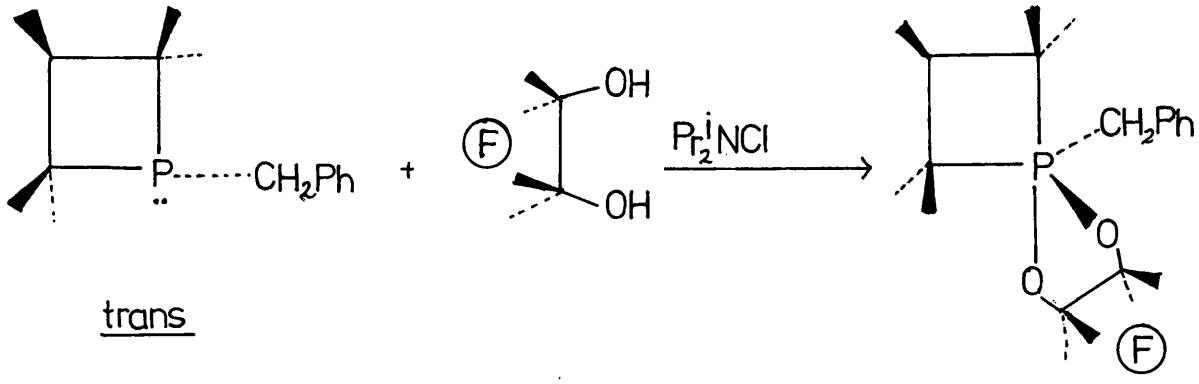
R	$\Delta G^{\#}$ kcal.mol^{-1}
-Ph	13.2
$-CH_3$	12.7
$-CH_2Ph$	12.2

From these results it is clear that the benzyl group is more apicophilic than phenyl by ca 1 kcal.mol^{-1}, but that alkyl groups (methyl and isopropyl) have similar apicophilicities to the phenyl group. Oram's[124] results from the phosphetan-H.F.A. adducts (211) are thus difficult to explain.

Oram was not able to obtain the relative apicophilicity of the benzyl group from his phosphetan - H.F.A. adducts due to the following reaction.



In (214) proton transfer from the benzyl group gives the hexafluoroisopropoxy group in the ylide (215). This ylide can then react with another mole of H.F.A. to give the oxaphosphetan (216). With the advent of the N-chlorodi-isopropylamine method for preparing phosphoranes, it was hoped that this method could be used to prepare the spirophosphorane (218) from trans-benzyl-pentamethylphosphetan (217) and perfluoropinacol.



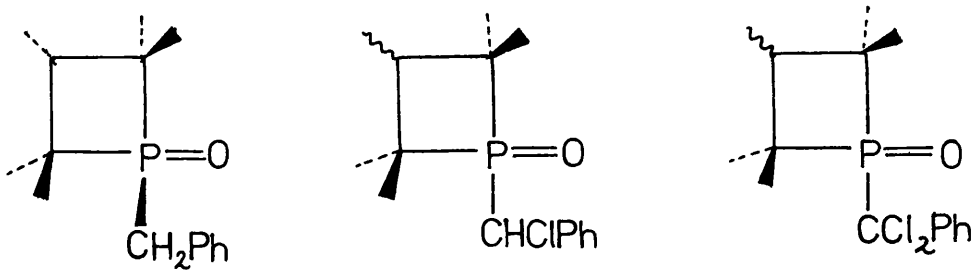
trans

(217)

(218)

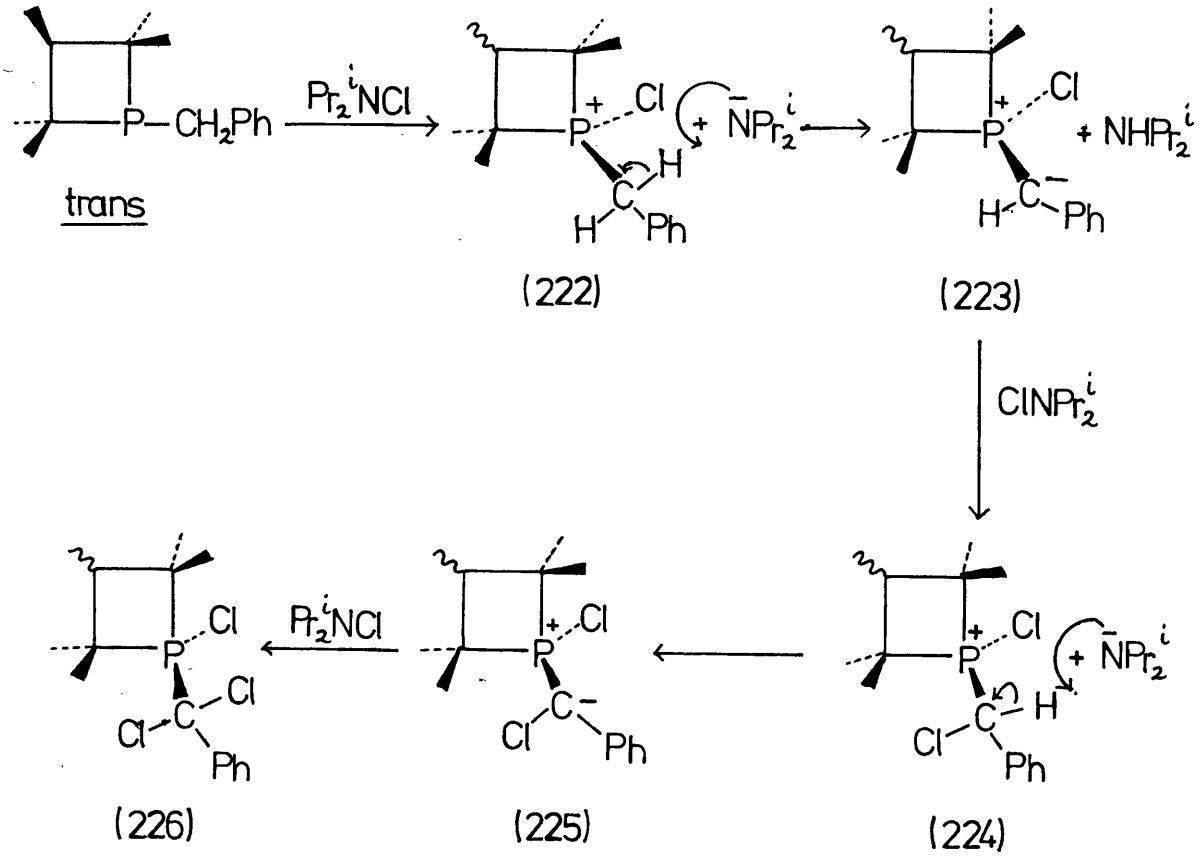
A comparison of benzyl with phenyl in this system would be useful in determining whether the results for the phenyl group were spurious.

When the N-chlorodi-isopropylamine reaction was carried out, the reaction mixture turned pale yellow indicating that something was amiss. Work-up showed that no spirophosphorane had been formed in the reaction. The reaction was carried out again and the products of the reaction separated on an alumina column (40:1) using ether as eluent. From ^{1}H, ^{31}P n.m.r., m^{+}/e and elemental analysis the following three phosphetan oxides were identified.



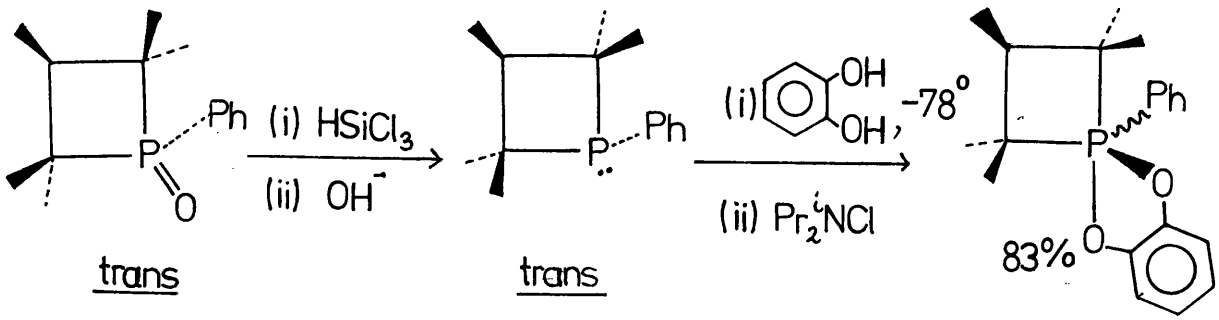
(219) (220) (221)

These phosphetan oxides are thought to originate by the following mechanism.



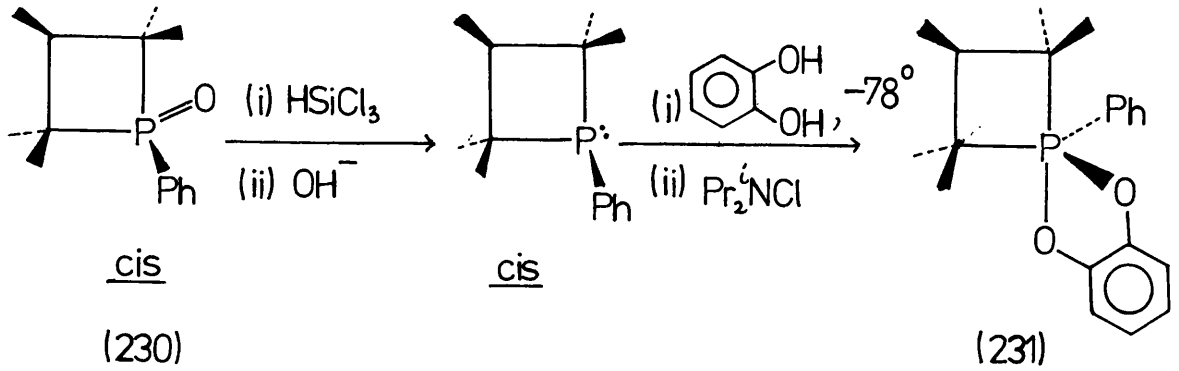
The chlorophosphonium compounds (222), (224) and (226) will hydrolyse during work-up on the column to give the phosphetan oxides (219), (220) and (221) respectively.

The failure of the N-chlorodi-isopropylamine method with trans benzylpentamethylphosphetan (217) was due to its labile hydrogen atom. This problem was overcome by using trans phenylpentamethylphosphetan (227) as the trivalent phosphorus compound and catechol as the diol.



trans (227) trans (228) (229)

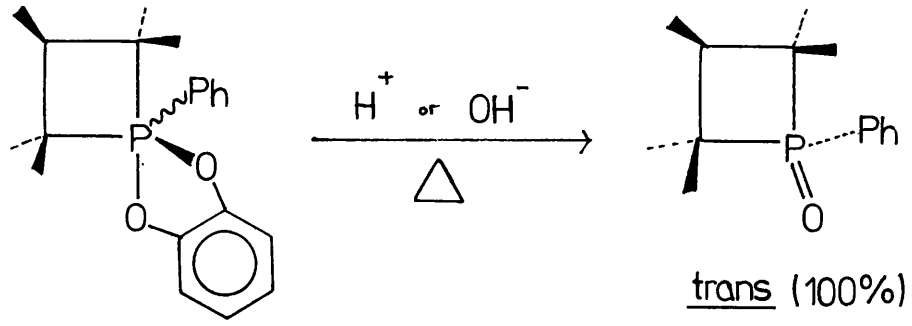
The new spirophosphorane (229) was obtained in excellent yield and it's ^{1}H n.m.r. spectrum in 1-bromonaphthalene indicated the presence of only one isomer. The trans phenylphosphetan oxide (227) had been reduced with retention by the method of Corfield[155]. The spirophosphorane (231) was prepared in a similar manner from the cis phenylphosphetan oxide (230); its ^{1}H and ^{31}p n.m.r., and melting point, were found to differ from those of the phosphorane (229) prepared from the trans phosphetan oxide.



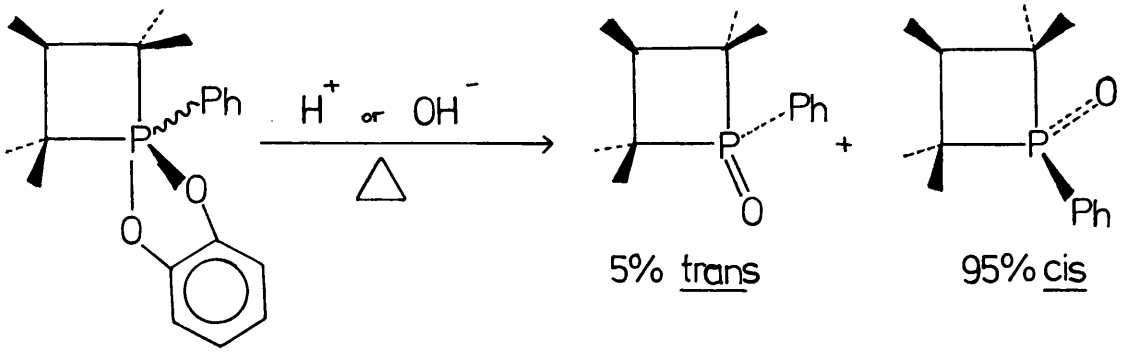
cis (230) cis (231)

The two adducts (229) and (231) were the first examples of spirophosphoranes prepared from phosphines by the N-chlorodiisopropylamine method. Although it was certain that compounds (229) and (231) were two geometrical isomers of the same spirophosphorane, it was not possible to say at this stage whether or not the reaction had given a compound with retention or inversion of configuration at phosphorus. In an attempt to answer this question, alkaline and acid hydrolysis of the spirophosphoranes was tried. Hydrolysis of the phosphorane (229) gave the trans

phenylphosphetan oxide (227) in 100% yield. However the spirophosphorane (231), under the same conditions gave a mixture of 95% cis and 5% trans phenylphosphetan oxides.

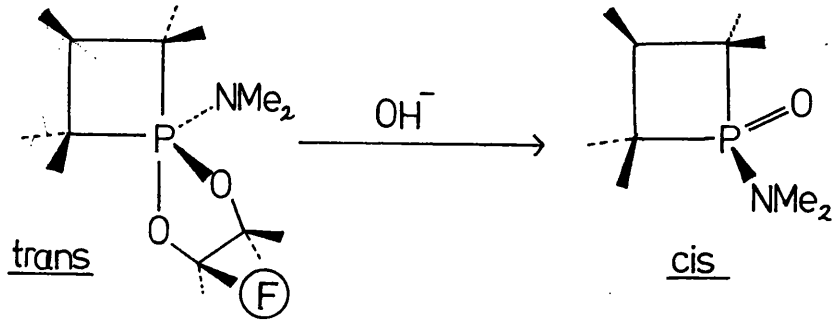


(229)



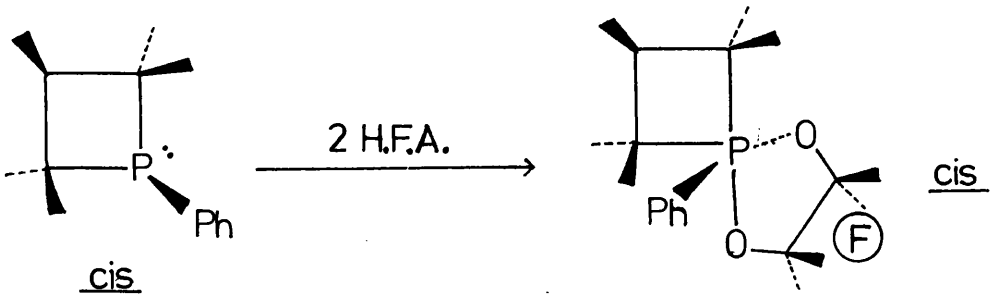
(231)

Hydrolysis reactions of most phosphetan adducts have been found by Whittle[108] to go with retention, although in the case of the dimethylaminophosphetan - H.F.A. adduct (232), inversion was found to take place. The results of the hydrolysis reactions seem to suggest that the N-chlorodi-isopropylamine reaction had gone with retention of configuration.

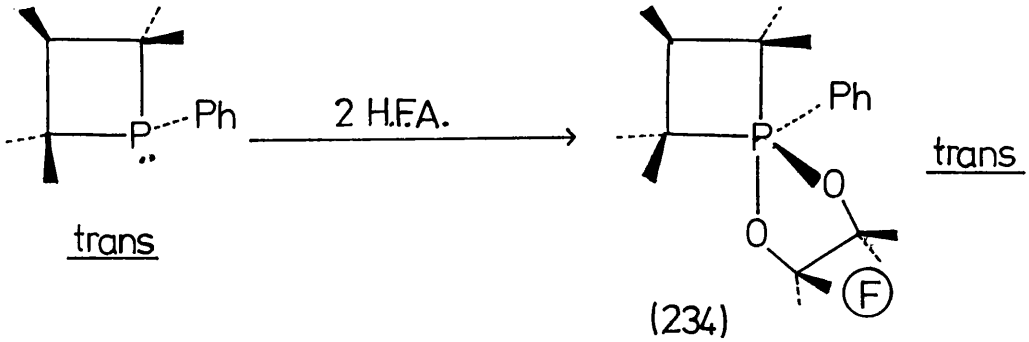


(232)

Oram[124] had prepared the H.F.A. adducts (233) and (234) of both trans and cis pentamethylphenylphosphetan. It was concluded that these H.F.A. reactions had gone with retention based on

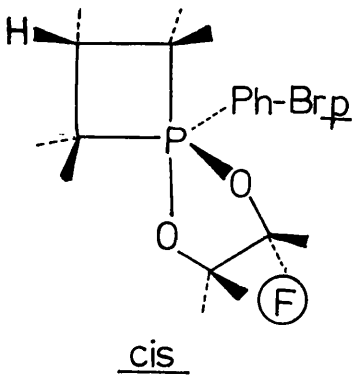


(233)

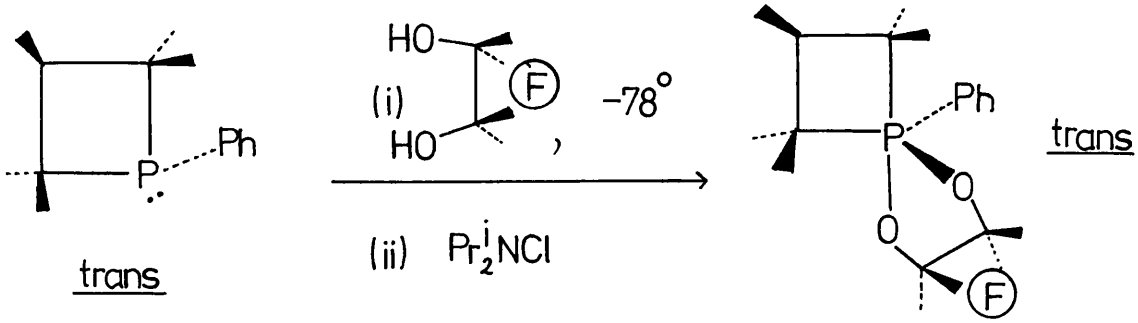


(234)

an X-ray analysis of the H.F.A. adduct (235)[24], prepared from the cis p-bromophenylphosphetan and H.F.A. By preparing either one of the adducts (233) and (234) by the N-chlorodi-isopropylamine method, and comparing its physical properties with those of an authentic sample it was hoped to show that the N-chlorodi-isopropylamine reaction goes with retention or inversion of configuration at phosphorus. The adduct (234) was choosen for its remarkable stability[156] to hydrolysis.

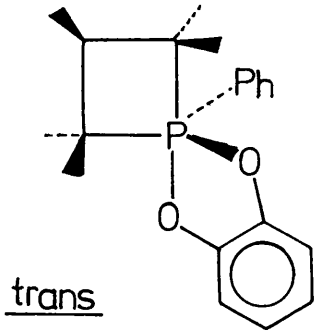


(235)



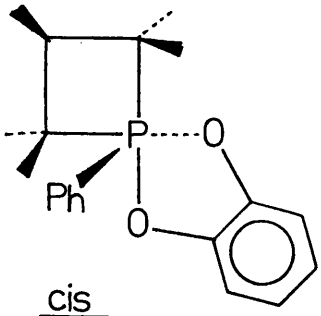
(234)

The physical properties of the adduct (234) prepared by the N-chlorodi-isopropylamine method were found to be identical to those reported by Oram[124] for the adduct prepared from the trans phenylphosphetan and H.F.A. Therefore it was concluded that the N-chlorodi-isopropylamine reaction had indeed gone with retention of configuration at phosphorus. Hence the catechol spirophosphoranes, (229) and (231), were the trans and cis isomers respectively.



trans

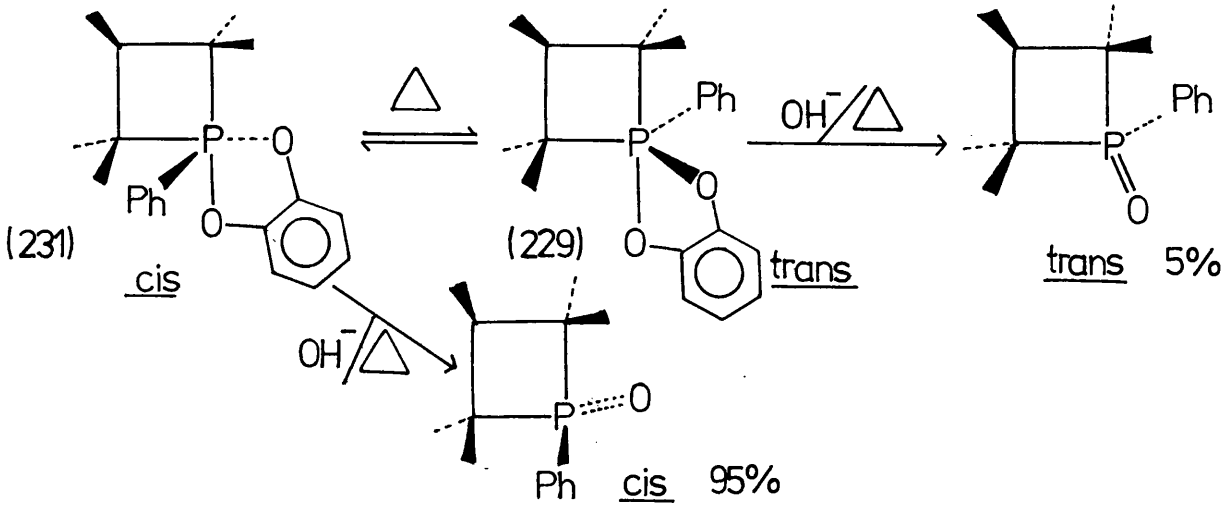
(229)



cis

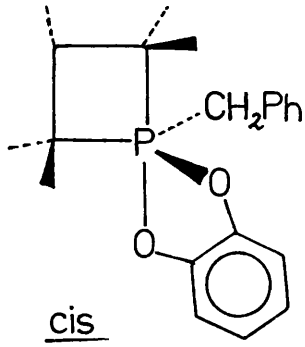
(231)

On heating a sample of the cis phenylspirophosphorane (231) in 1-bromonaphthalene at 100°C for 0.5 h , the appearance of the trans isomer was noted, (as shown by examination of the ^{1}H n.m.r. spectrum and comparing it with an authentic sample). It is this equilibration of the isomers (231)$\rightleftharpoons$(229), which is probably responsible for the small percentage of trans oxide found when the cis spirophosphorane (231) was hydrolysed.



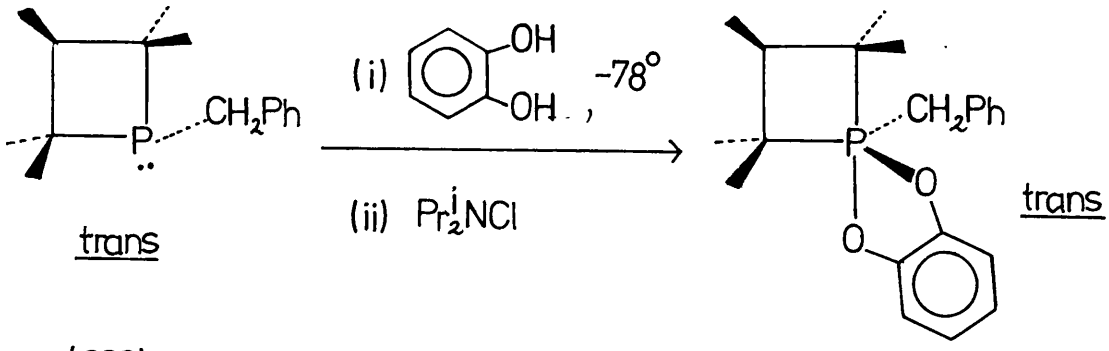
As the equilibration of cis (229) $\rightleftharpoons$ trans (231) was found to be very slow at room temperature, the kinetics of the process could be studied by ^{1}H n.m.r. in 1-bromonaphthalene [129], (see section 5.3).

In order to obtain the relative apicophilicity of phenyl and benzyl groups using this kinetic approach, the preparation of the cis benzylspirophosphetan (232) is necessary.



cis (232)

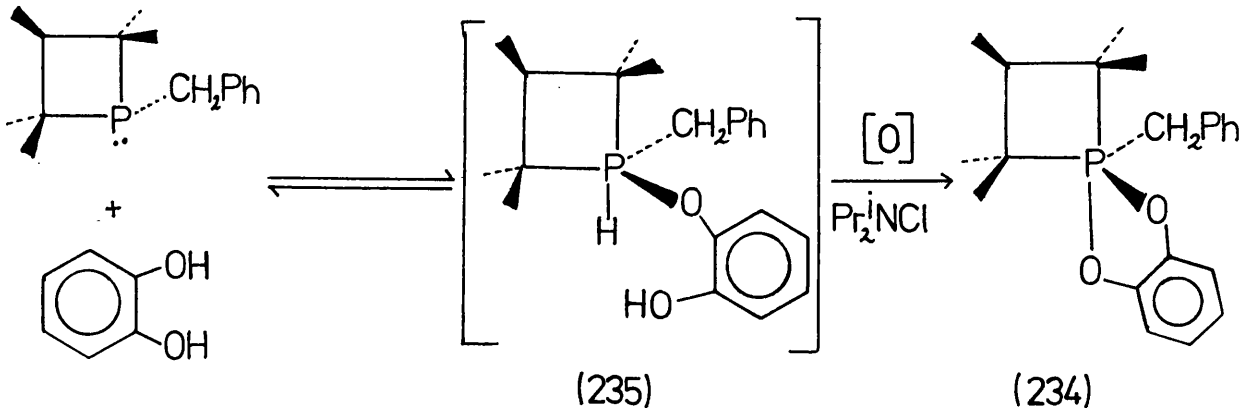
In contrast to the attempted addition of perfluoropinacol by the N-chlorodi-isopropylamine method, the trans benzylphosphetan catechol adduct (234) was made in good yield. No α



trans (233) trans (234)

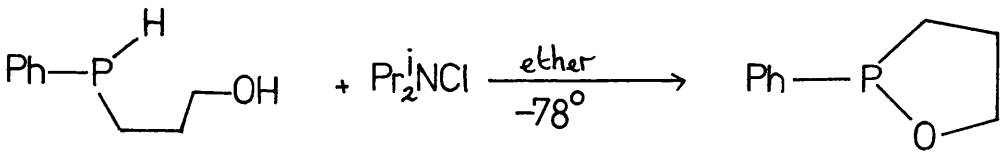
-halogenatedphosphetan oxides (220) and (221) were produced. The only difference between the reaction which gave the spirophosphorane (234) and the one which gave the α-halogenated-phosphetan oxides is the diol used. A way round this problem is to postulate some sort of intermediate compound, formed between catechol (and not perfluoropinacol) and the trans benzylphosphetan (233), which then reacts with N-chlorodi-isopropylamine to give the spirophosphorane (234). The type

of intermediate might even be the phosphorane (235), which is then oxidized by the N-chlorodi-isopropylamine to the spirophosphorane (234).



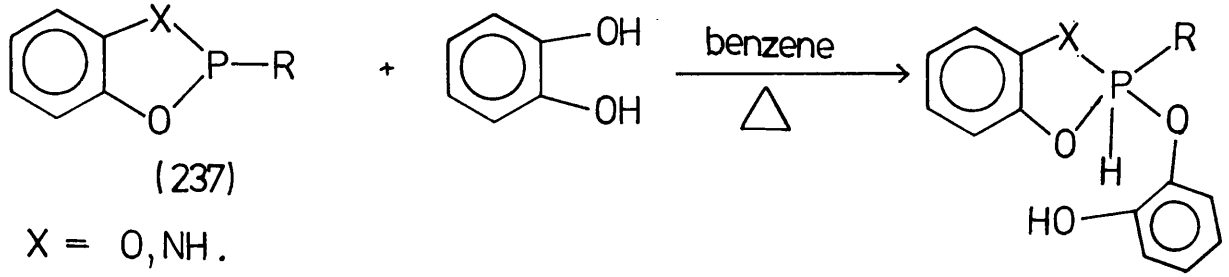
(235) (234)

Antzcak[84] has shown N-chlorodi-isopropylamine to be capable of oxidizing similar compounds (236) under mild conditions. Reaction between tervalent phosphorus compounds



(236) (20%)

and catechol has been observed to give phosphoranes of the type (238)[81]. However such reactions usually need heat, but as the systems employed were 1,3,2-benzodioxaphospholes (237), the more nucleophilic phosphetans might undergo this type of reaction under the mild conditions used in the N-chlorodi-isopropylamine reaction.



(237)

X = O, NH.

R = Me, Et, Ph.

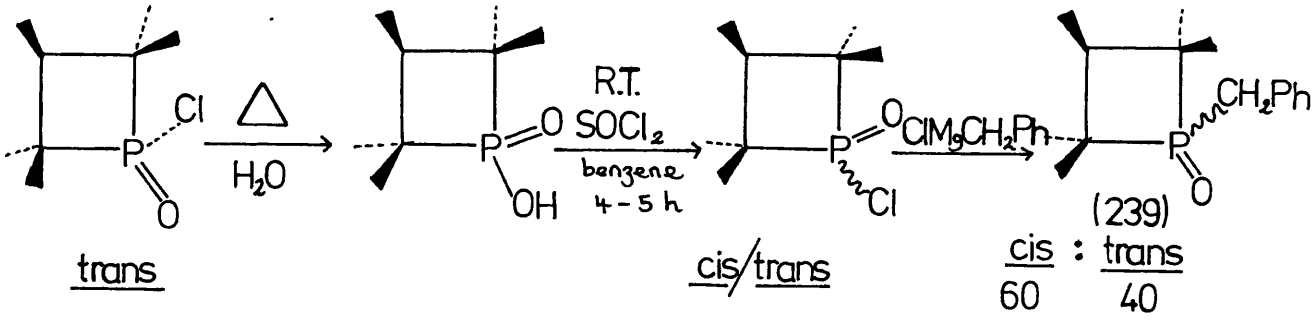
(238)

Kemp[157] has looked at possible reactions of catechols with phenyl phosphetans using F.T. ^{31}P n.m.r., and concluded

that there was no formation of a phosphorane-type intermediate, under mild conditions. This would seem to suggest that no phosphorane intermediate is involved in the N-chlorodi-isopropylamine reaction, although this does not rule out the possibility of some hydrogen-bonded complex formed between catechol and the phosphetan, which then is oxidized by N-chlorodi-isopropylamine to the corresponding spirophosphorane.

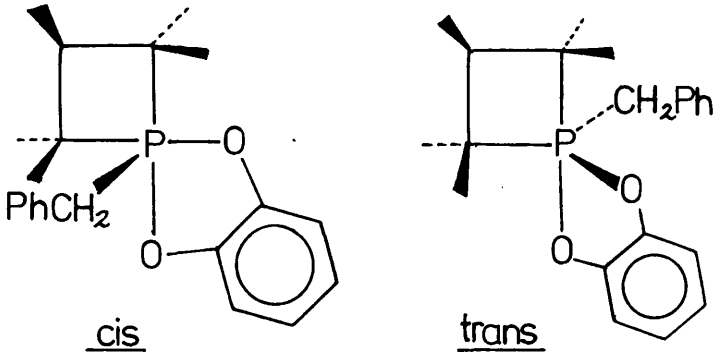
The synthesis of a pure sample of cis benzylphosphetan oxide (239) proved impossible; the best attempt was a cis-trans mixture having a composition of 60% cis and 40% trans (see Scheme D). The isomer ratio was determined by ^{1}H n.m.r., using pyridine as the solvent, the assignments being based on work carried out by Cremer and Gray[158].

SCHEME D



This mixture of oxides (239) on stereospecific reduction and subsequent reaction with catechol and N-chlorodi-isopropylamine at -78°C, gave the spirophosphoranes (240) and (241), which by ^{1}H n.m.r. consisted of two isomers in the ratio of 60:40. It is assumed that the isomer present in the larger amount is the cis phosphorane (240) i.e. the reaction had gone with retention of configuration at phosphorus. The percentage of cis isomer (240) was increased to about 80% by taking advantage of it's greater solubility in cold light petroleum, so that kinetic runs could be more easily followed (see section 5.3).

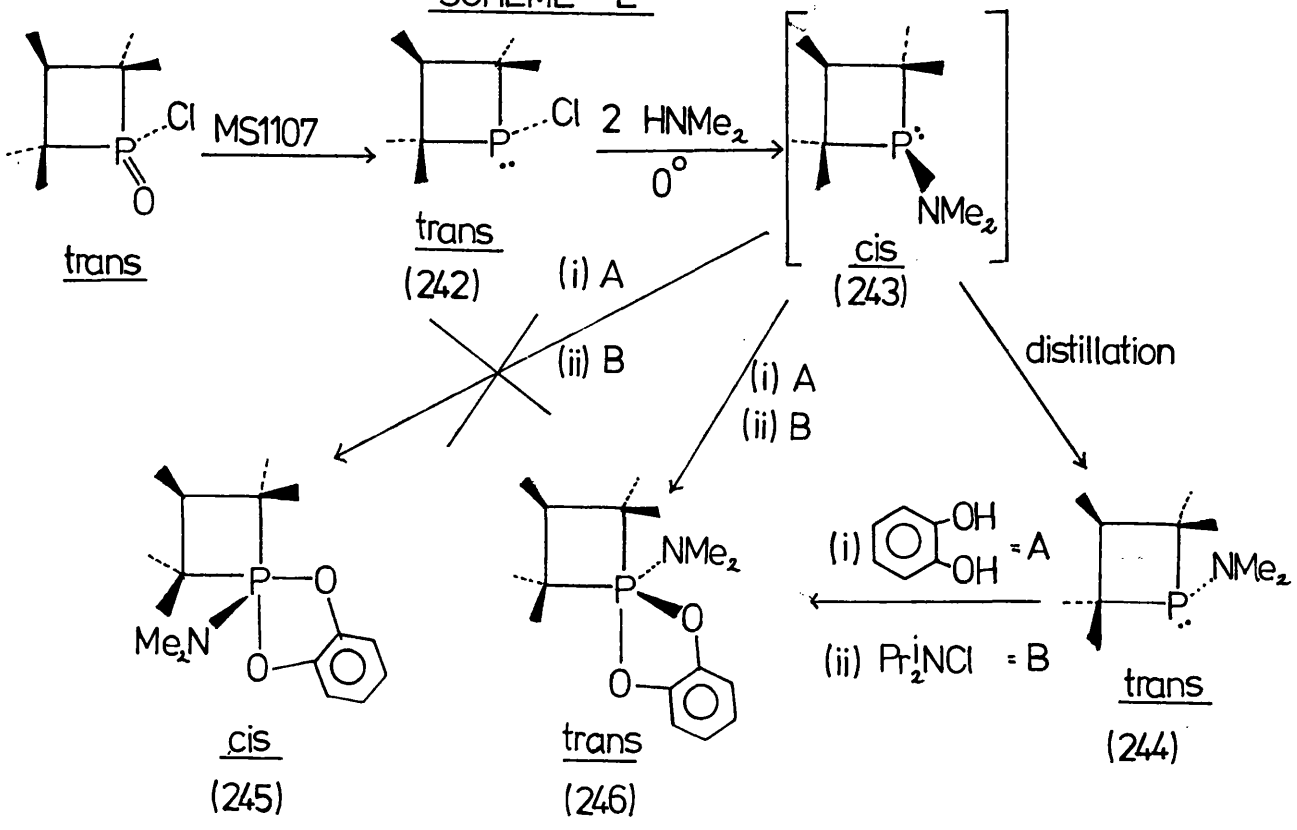
In order to obtain the relative apicophilicity of the dimethylamino group with respect to phenyl and benzyl, the cis



(240) (241)

adduct (245) was desired. Unfortunately only the pure trans isomer (246) was ever obtained (see Scheme E).

SCHEME E

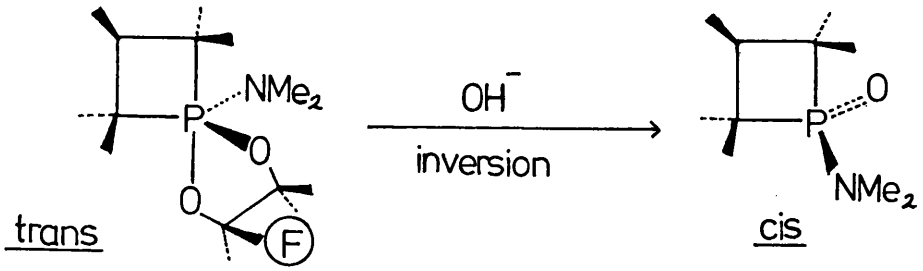


The preparation of the dimethylaminophosphetan (243) had been shown to go with inversion[159]; this cis isomer on distillation then gave the trans isomer (244)[108]. On treating the cis dimethylamino phosphetan (243) with catechol and N-chlorodi-isopropylamine at -78°C, only the trans spirophosphorane (246) was obtained.

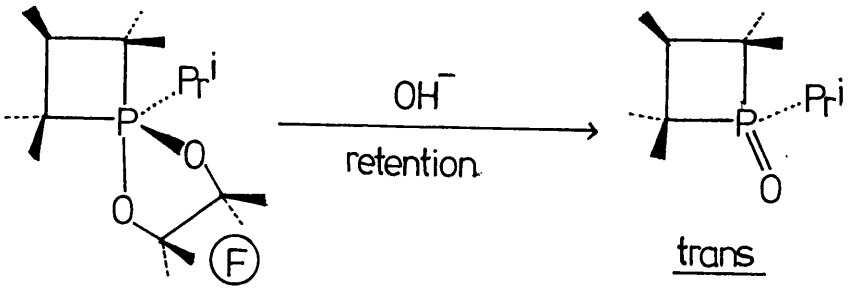
In this case either the N-chlorodi-isopropylamine reaction is not going with retention or the cis spirophosphorane (245) once formed immediately isomerises to the trans isomer (246).

The trans spirophosphorane proved remarkably stable to heat, and only a trace of the presumed cis isomer (245) was formed after heating at 120° for three days. This shows that the cis ⇌ trans equilibrium in this case is far to the side of the trans isomer.

Whittle[108] found that the trans dimethylaminophosphetan - H.F.A. adduct (247) on hydrolysis gave the cis phosphetan oxide (248), in constrast to the usually observed retention of configuration on hydrolysis. Steric considerations were ruled out as a cause of this anomolous behaviour as hydrolysis of the trans isopropylphosphetan (249) adduct went with retention.

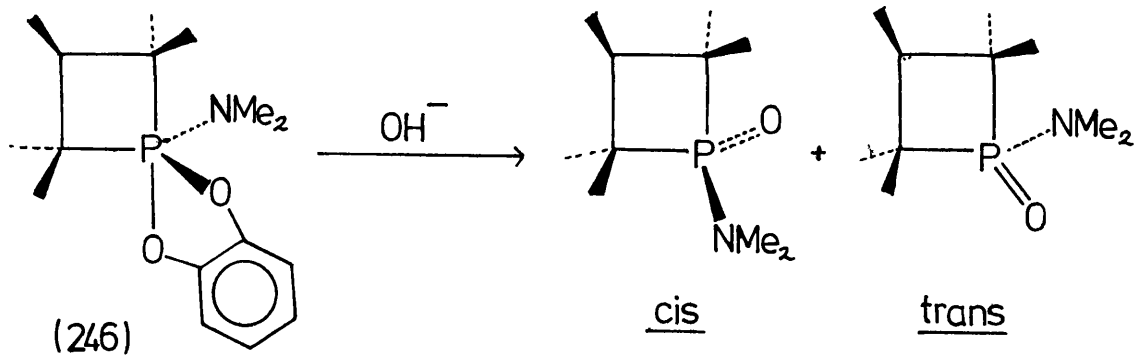


trans (247) cis (248)



trans (249) trans

On hydrolysis of the trans dimethylaminophosphetan catechol adduct (246) both cis and trans oxides were formed, the exact ratio of cis to trans isomers varying with the temperature at which the hydrolysis took place.



(246)

After 24h at room temperature the ratio of trans : cis was 2 : 1 whereas if the hydrolysis was carried out at 60°C for 1h the ratio of trans : cis was 1 : 3.

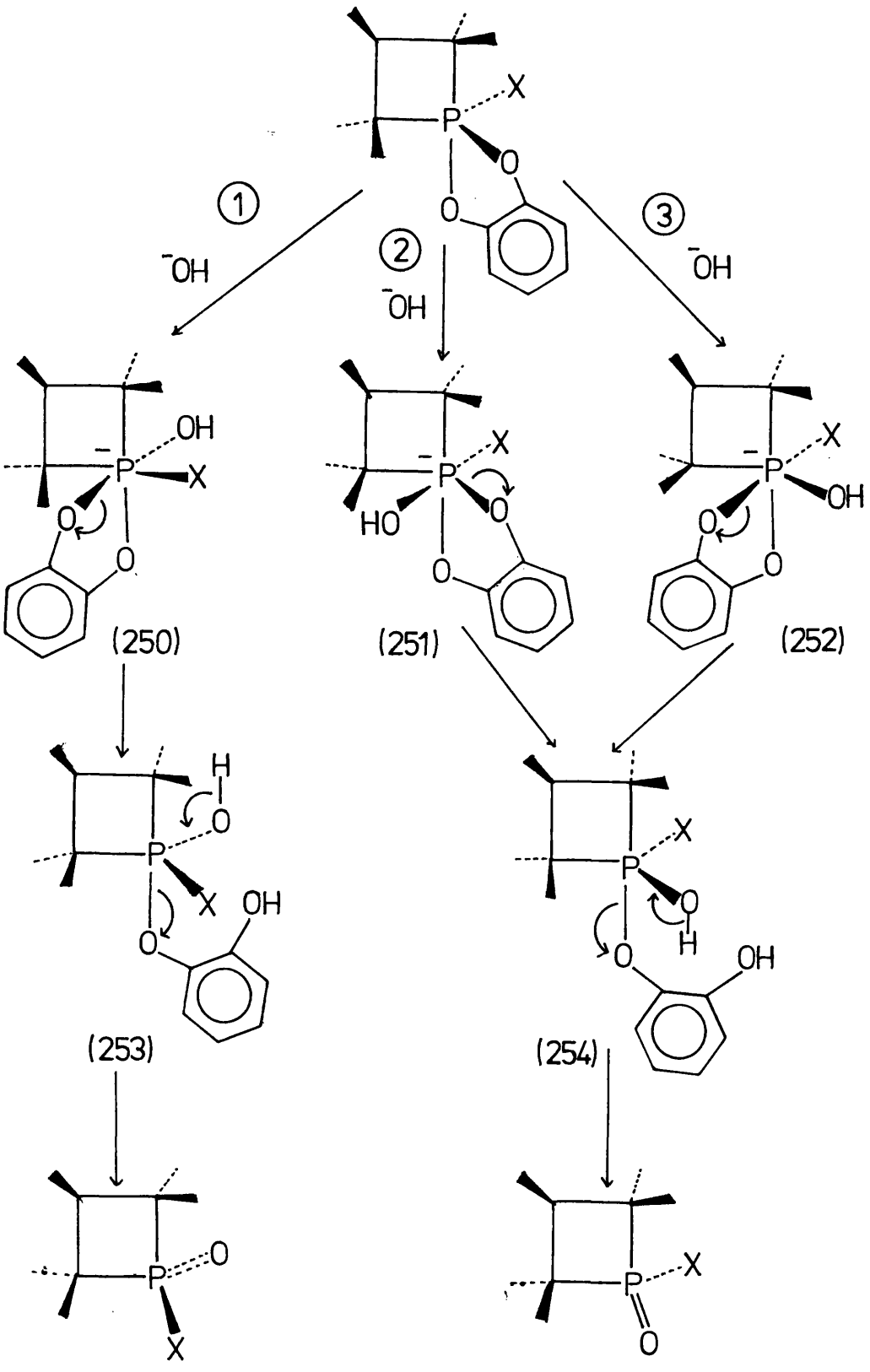
If we consider the possible reaction pathways outlined in scheme F, we can see that attack of the nucleophile can occur opposite any of the equatorial ligands to give three possible hexaco-ordinate species (250) - (252).

It is not clear why the dimethylamino adducts (246) and (247) hydrolyse by different pathways as little is known about the stereoelectronic requirements in hexaco-ordinate phosphorus compounds. A possible explanation of the results is that π - donation from the dimethylamino group plays a part in determining the position of initial nucleophilic attack and this presumably controls the reaction pathway in some way.

5.3 THE RELATIVE APICOPHILICITY OF THE PHENYL AND BENZYL GROUPS BY A KINETIC METHOD

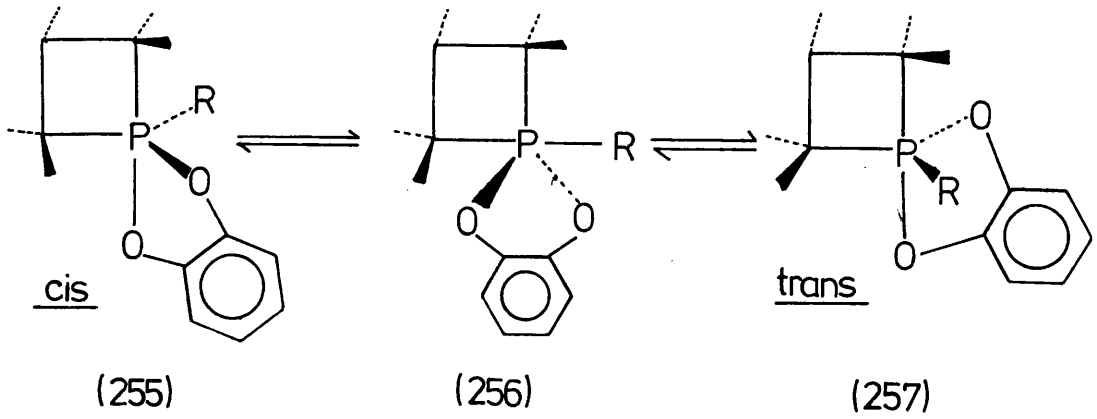
As outlined in sections 3.4 and 3.5 data on the relative apicophilicities of different ligands attached to phosphorus have mainly come from d.n.m.r. studies on suitable phosphoranes. This method is only suitable for a range of $\Delta G^{\#}$ values of about 9 - 22 kcal.mol^{-1}, due to the limited temperature range over which the n.m.r. machine can operate. It is when $\Delta G^{\#}$ values are greater than 24 kcal.mol^{-1} that constant temperature n.m.r. studies become important.

SCHEME F



It was found that cis ⇌ trans isomerisation of suitable spirophosphetans could be followed by monitoring the ^{1}H n.m.r. spectra of the cis compound at a pre-selected constant temperature and at different time intervals, the temperature being such that equilibration was reached in 3-4 h[129]. Integration of the phosphetan methyl signals for each isomer present in the mixture gave the relative amounts of each present at that particular time.

The pseudorotation process which brings about cis ⇌ trans isomerisation is given by (255)⇌(257), involving the high energy intermediate (256) in which the R group is apical and the



(255) (256) (257)

catechol ring diequatorial. If the R group is poorly apicophilic the process is sufficiently slow to be followed kenetically. The rate equation used to obtain the forward and backward rate constants for the isomerisation is outlined below.

For a process cis $\underset{k_r}{\overset{k_f}{\rightleftharpoons}}$ trans.

let the initial concentration of cis isomer = a

and concentration of trans isomer at time t = x

concentration of trans isomer at equilibrium = x_e

Therefore, at time t, concentration of cis isomer = a - x

$$dx/dt = k_f(a - x) - k_r(x) \quad \text{\_\_\_\_\_equation (i).}$$

At equilibrium $dx/dt = 0$

$$\text{hence } k_f(a - x_e) = k_r(x_e) \quad \text{\_\_\_\_\_equation (ii)}$$

$$K = \frac{k_f}{k_r} = \frac{x_e}{a - x_e} \text{ and } k_r = \frac{k_f(a - x_e)}{x_e}$$

Substituting for k_r into equation (i) we obtain.

$$dx/dt = k_f(a-x) - k_f x\frac{(a-x_e)}{x_e}$$

$$= k_f a - k_f x - \frac{k_f xa}{x_e} + \frac{k_f x x_e}{x_e}$$

$$= k_f a - k_f\frac{xa}{x_e} = \frac{k_f x_e a}{x_e} - \frac{k_f xa}{x_e}$$

$$\frac{dx}{dt} = \frac{k_f a}{x_e}(x_e - x)$$

If we integrate this between the limits x = o, t = o

and x = x at t = t.

we obtain $\log_n \frac{x_e}{x_e-x} = k_f\frac{at}{x_e}$ _____ equation (iii)

from equation (ii) $\frac{k_f a}{x_e} = k_f + k_r$

Therefore substituting this into (iii) gives.

$$\log n\left[\frac{x_e}{x_e-x}\right] = (k_f+k_r)t$$

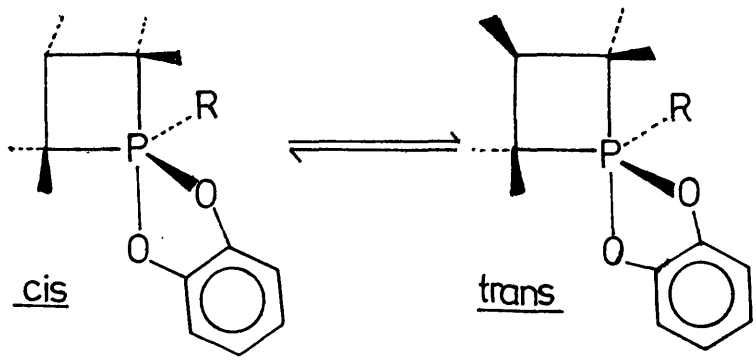
$$= \log_{10}\left[\frac{x_e}{x_e-x}\right] = \frac{(k_f+k_r)t}{2.303}$$

Rearranging this becomes

$$\log_{10}x_e - \log_{10}(x_e-x) = \frac{(k_f+k_r)t}{2.303}$$

Hence a plot of $\log_{10}(x_e-x)$ against time(t) should give a straight line of gradient $-\left[\frac{k_f+k_r}{2.303}\right]$ and intercept $\log_{10}x_e$

From three runs at three different temperatures, three rate constants were obtained. This process was carried out for the spirophosphoranes (258, R = Ph, CH_2Ph) and the activation parameters are summarised in Tables 8 and 9.



(258)

In compiling the tables the following equations were used.

$$\log_{10}\frac{k_2}{k_1} = \frac{E^{\#}}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \quad \text{to give } E^{\#}$$

$$\Delta H^{\#} = E^{\#} - nRT \text{ (in this case n = 1) to give } \Delta H^{\#}$$

$$k = \frac{KTe^{-}}{h}\frac{\Delta G^{\#}}{RT} \quad \text{to give } \Delta G^{\#}$$

$$\Delta G = -RT\log_n K_e \quad \text{to give } \Delta G$$

$$\Delta G = \Delta H - T\Delta S \quad \text{to give } \Delta S$$

TABLE 8

For the spirophosphorane (258, R = Ph)

Temperature ^{o}K	ΔG kcal	k_f sec^{-1}	$E^{\#}$ $kcal.mol^{-1}$	$\Delta H^{\#}$ kcal.	$\Delta G^{\#}$ $kcal.mol^{-1}$	$\Delta S^{\#}$ $kcal.mol^{-1}$
363	-1.4	1.0×10^{-4}	27.4	26.7	27.9	-3×10^{-3}
372	-1.5	2.5×10^{-4}	27.4	26.7	27.8	-2.6×10^{-3}
382	-1.5	7.0×10^{-4}	27.4	26.7	27.9	-3×10^{-3}

Average $\Delta G^{\#}$ = 27.9 $kcal.mol^{-1}$ for cis⟶trans

The $\Delta G^{\#}$ for the reverse equilibration, trans⟶cis was 29.5 $kcal.mol^{-1}$.

TABLE 9

For the spirophosphorane (258, R = CH_2Ph)

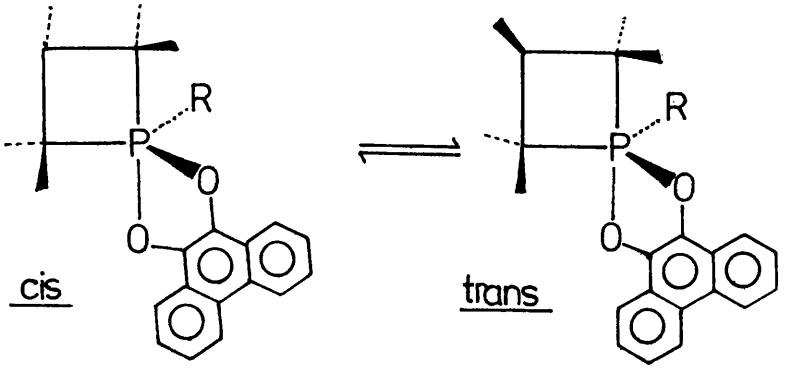
Temperature ^oK	ΔG kcal.	k_f sec^{-1}	$E^{\#}$ $kcal.mol^{-1}$	$\Delta H^{\#}$ kcal.	$\Delta G^{\#}$ $kcal.mol^{-1}$	$\Delta S^{\#}$ $kcal.mol^{-1}$
366	-1.6	$2.0x10^{-5}$	27.5	26.8	29.4	$-7x10^{-3}$
376	-1.6	$5.3x10^{-5}$	27.5	26.8	29.4	$-7x10^{-3}$
386	-1.6	$11.2x10^{-5}$	27.5	26.7	29.5	$-7.1x10^{-3}$

Average $\Delta G^{\#}$ = 29.4 $kcal.mol^{-1}$ for cis ⟶ trans and the $\Delta G^{\#}$ for the reverse equilibration trans ⟶ cis was 31 $kcal.mol^{-1}$.

From these results it is clear that the phenyl group is more apicophilic than the benzyl group in this system by ca 1.5 $kcal.mol^{-1}$. This result contrasts with that of Bone[44] who found the benzyl group to be more apicophilic than the phenyl by ca 1.0 $kcal.mol^{-1}$.

It was not possible to obtain the relative apicophilicity of the dimethylamino group as the spirophosphorane (258, R = NMe_2) could not be prepared. The rate of formation of the cis isomer from the trans could not be followed as it was much too slow. For a pseudorotation process $\Delta S^{\#}$ should be zero. The values found are very small and are within experimental error.

The results obtained for the spirophosphorane (258, R = Ph) are in good agreement with those obtained by Aly[129], on the systems (259) and (260).

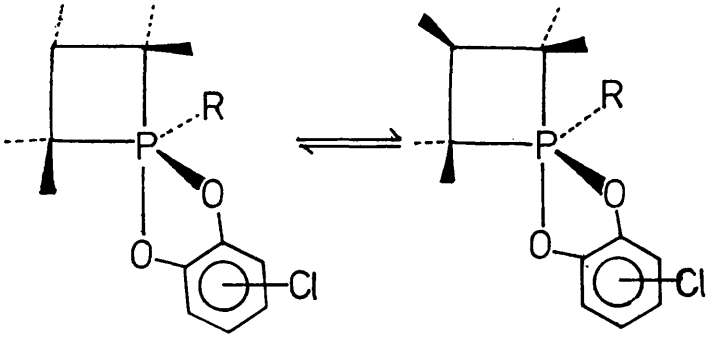


(259)

R = Ph , $\Delta G^{\#}$ = 27·9 kcal.mol^{-1}

R = C≡CPh , $\Delta G^{\#}$ = 29·6 kcal.mol^{-1}

R = C≡CMe , $\Delta G^{\#}$ = 27·1 kcal.mol^{-1}



R = Ph , $\Delta G^{\#}$ = 30·6 kcal.mol^{-1}

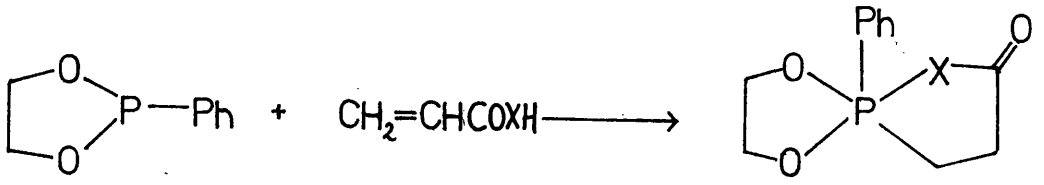
R = C≡CPh, $\Delta G^{\#}$ = 28·7 kcal.mol^{-1}

R = C≡CMe, $\Delta G^{\#}$ = 26·3 kcal.mol^{-1}

6 THE REACTIONS OF PHOSPHITES WITH ACRYLIC ACID

6.1 WITH CYCLIC TRIVALENT PHOSPHORUS COMPOUNDS: THE RELATIVE APICOPHILICITY OF THE PHENYL GROUP

Saegusa et al[150] reported what they considered to be the first pentaco-ordinate phosphorus compounds (262) and (263) obtained from reaction of acrylic acid (or acrylamide) with trivalent phosphorus compounds, in this case 2-phenyl-1,3,2-dioxaphospholan (261).



(261)

(262) X=O

(263) X=NH

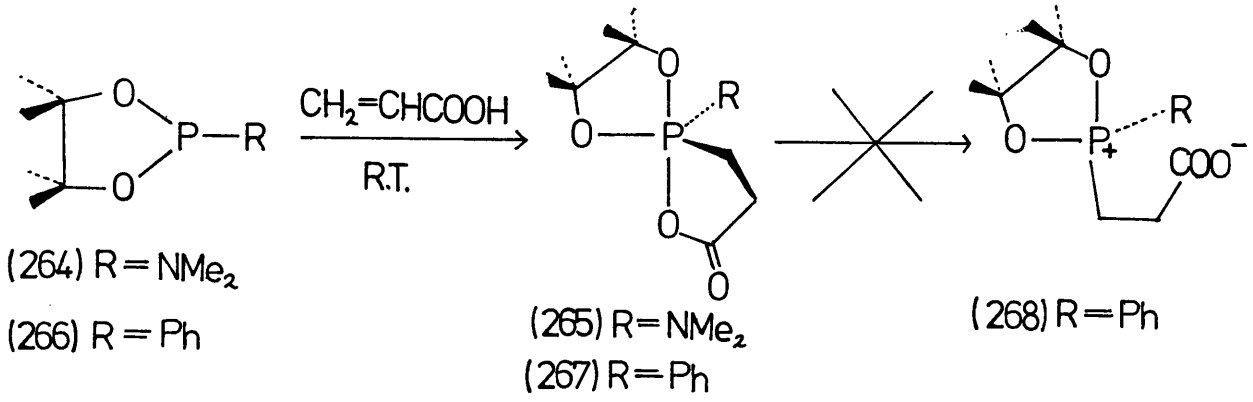
The two spirophosphoranes (262) and (263) were reported as being thermally stable, crystalline and obtainable in high yields. They based their structures on the positive ^{31}P n.m.r. chemical shifts (relative to 85% H_3PO_4) characteristic of phosphoranes and preliminary X-ray data for (262, x = 0) which showed it to be essentially trigonal bipyramidal.

It was hoped to prepare similar phosphoranes for a d.n.m.r. study of poorly apicophilic groups, due to the relatively low energy required (for a five-membered ring) to put the 1,2-oxaphospholan ring diequatorial. Also with the presence of a carbonyl group on the carbon atom next to the oxygen-phosphorus bond, electronic interactions are possible between the carbonyl system and the oxygen p orbitals, which might serve to lower the energy barrier still further.

For a d.n.m.r. study the phosphonite (261) would be of little use, so the 2-dimethylamino-4,4,5,5-tetramethyl-1,3,2,-dioxaphospholan (264) was used.

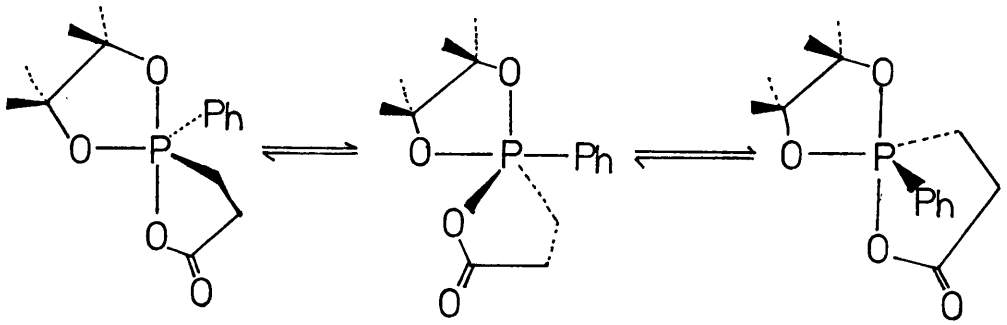
The spirophosphorane (265) was obtained in almost quantatative yield. Its positive ^{31}P n.m.r. chemical shift was indicative of a pentacovalent species. The ^{1}H n.m.r. spectrum in 1-bromonaphthalene at room temperature, showed four separate signals for the pinacol ring methyls as expected. Unfortunately the compound (265) proved to be very thermally unstable, so that d.n.m.r. work proved impossible.

The thermally stable spirophosphorane (267) was obtained from acrylic acid and the phosphonite (266). Its νmax, ^{1}H and ^{31}P n.m.r. values were consistent with it being pentaco-ordinate at room temperature and not a dipolar species (268).



An F.T. ^{13}C n.m.r. spectrum of (267) showed the presence of P - C coupling for the carbon atom bearing the carbonyl group, further evidence for the oxaphospholan ring being intact.

The four methyl signals of (267) coalesced to two on heating at two separate coalescence temperatures. Both coalescences have the same $\Delta G^{\#}$, the difference in T^{C} being due to the large difference in frequency between the coalescing signals. The process speeded up on the n.m.r. time-scale which brings about these coalescences is (269) $\rightleftharpoons$ (271) which involves the high energy intermediate (270), in which the phenyl group is apical and the oxaphospholan ring diequatorial.



(269) (270) (271)

The results obtained are shown in Table 10.

TABLE 10

	$\Delta\nu(H_z)$	$T^c(^oc)$ (a)	$\Delta G^{\#}$ (kcal.mol.$^{-1}$)
1st Coalescence	9	63 ± 3	17.7 ± 0.1
2nd Coalescence	35	77 ± 1	17.5 ± 0.1

(a) in CCl_3Br

When the experimental results are compared to the calculated value[120] of between 20 - 23 kcal.mol^{-1}, we find them to be much lower than expected.

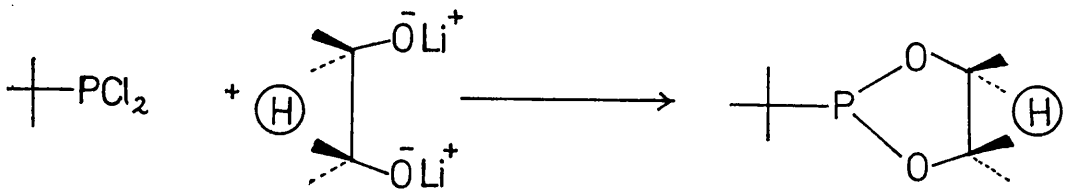
$$\Delta G^{\#}_{obs.} \geqslant \Delta G^{\#}_{calc.} = A(\text{RingO-Ph}) + S_{90-120}(\text{C-O ring}) + \text{RotO}$$

$$= 8 - 12 + 8 + 5$$

$$= \underline{21 - 25 \text{ kcal.mol}^{-1}}$$

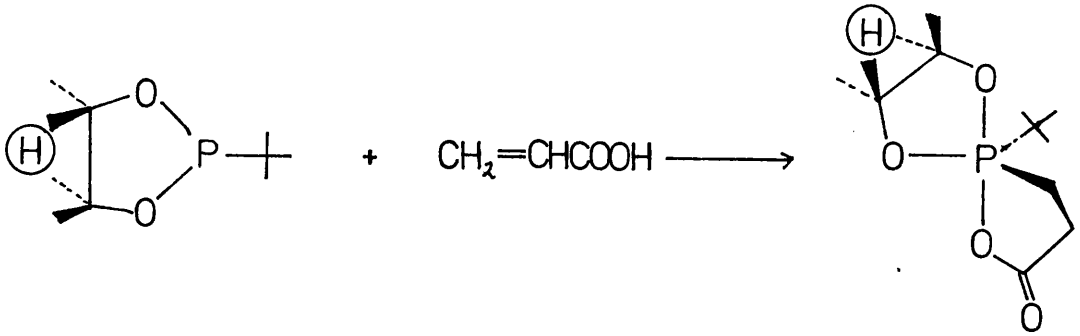
The low result could have three possible causes. Firstly the coalescences observed could be due to an irregular process such as ring-opening (267)⇌(268); such an ionisation would be expected to be reasonably favourable. Secondly the effect of the α - carbonyl group might be considerable, either in reducing the barrier to rotation about the P-O bond or reducing the ring-strain in going from 90° a.e.⟶120° e.e. Thirdly the phenyl group may be more apicophilic than previous measurements suggest, thus lowering the value of 8-12 kcal.mol^{-1} needed in replacing apical ring oxygen by a phenyl group.

If the $\Delta G^{\#}$ value obtained for the phenyl group is valid, then a system exists which would be useful for a comparison of the phenyl group with other poorly apicophilic groups. The first group considered was the t-butyl group. However problems arose in the preparation of the starting phosphonite (272) which could not be prepared from t-butyldichlorophosphine, pinacol and two moles of base in the usual way. The problem was solved by using the dilithium salt of pinacol and t-butyldichlorophosphine which gave the phosphonite (272) in fair yield. The phosphonite



(272)

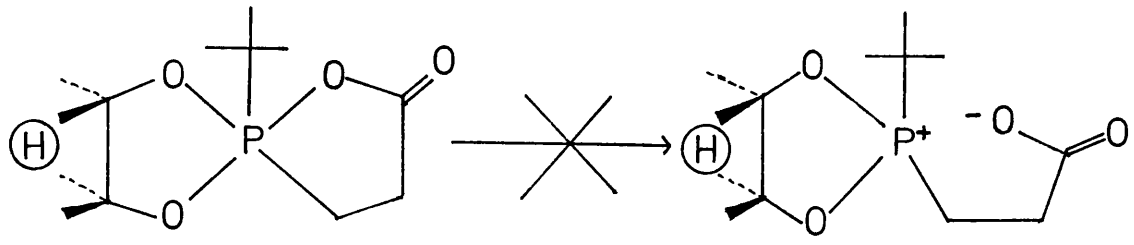
(272) was isolated as a very air sensitive, colourless liquid, the very low ^{31}P n.m.r. chemical shift (relative to 85% H_3PO_4) of -204.1 p.p.m. being characteristic of a trivalent phosphorus compound of this nature[148]. With acrylic acid the phosphonite (272) readily gave the adduct (273) in almost quantitative yield.



(272) (273)

The ^{1}H n.m.r. spectrum of (273) showed the pinacol methyls to be a singlet in all solvents tried, and the ^{31}P n.m.r. chemical shift of -10.5 p.p.m. is not in the normal range of this type of spirophosphorane. The infra-red spectrum showed no trace of any P = O or -OH bands thus ruling out any ring-opening to a

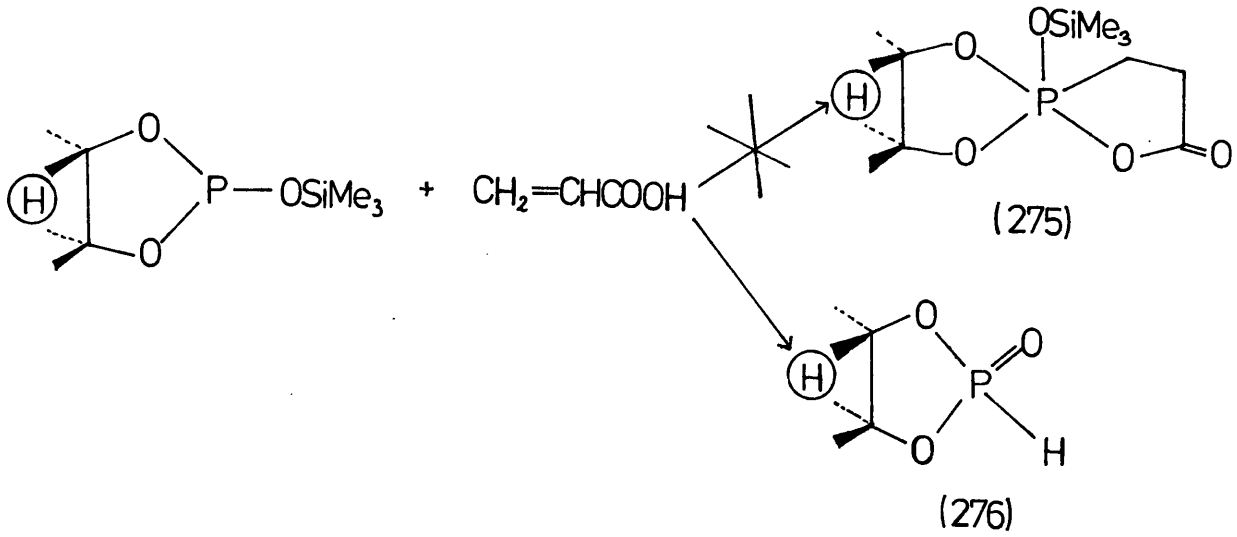
phosphonium-type compound (274). Even if such a process was



(273) (274)

occurring the pinacol methyls should still appear as two signals in the ^{1}H n.m.r. spectrum. The only explanation of the spectral data is that the spirophosphorane (273) was prepared, but the pinacol methyls were accidentally magnetically equivalent.

Acrylic acid was next used in an attempt to prepare the spirophosphorane (275); however all that was isolated was the cyclic phosphinate (276) in 100% yield, (see Section 4.2).



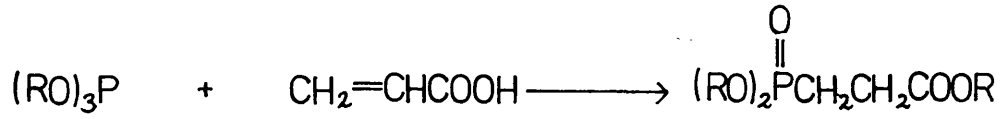
(275)

(276)

Attempts to prepare spirophosphoranes from 2 - ethoxy - 4,4,5,5-tetramethyl - 1,3,2,-dioxapholan and acrylic acid also failed, no phosphoranes were detected in the ^{31}P n.m.r. It would seem from the evidence available that the formation of spirophosphoranes from acrylic acid required the presence of a cyclic phosphorus compound bearing a group not susceptible to 'Arbuzov type' reactions.

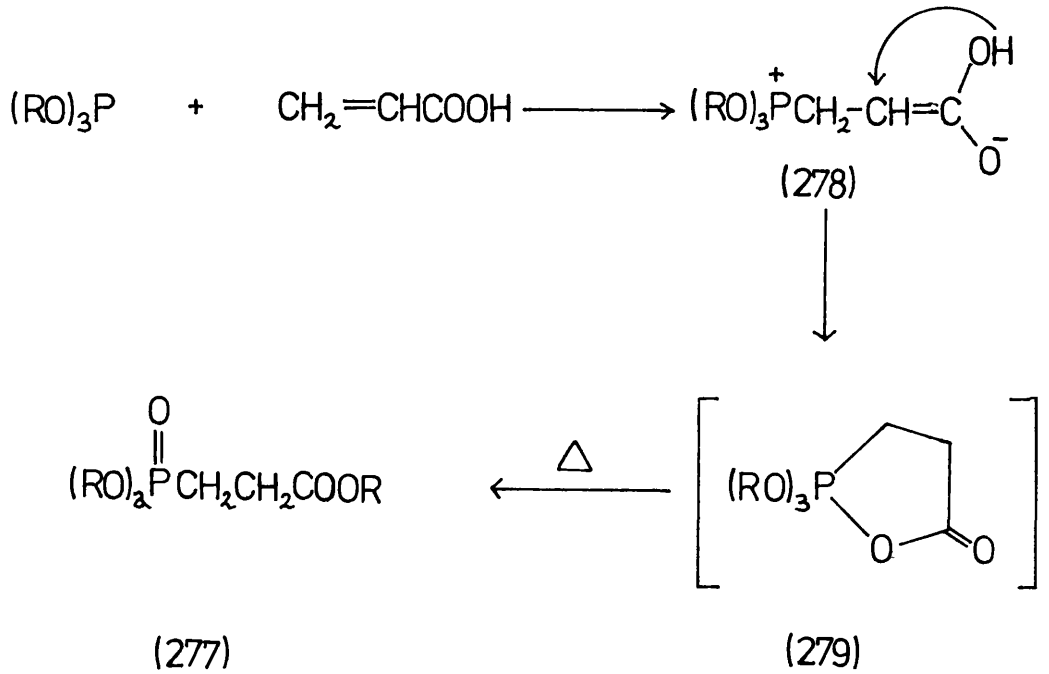
6.2 WITH ACYCLIC TRIVALENT PHOSPHORUS COMPOUNDS

Kukhtin et al[160] carried out many reactions involving acyclic phosphites and acrylic acid, the isolated products of which were not phosphoranes, but the corresponding β - phosphono-carboxylic esters (277). The mechanism put forward involved the



(277)

formation of the cyclic phosphorane (279), which then rearranged on heating. The only evidence for the phosphorane (279) was that



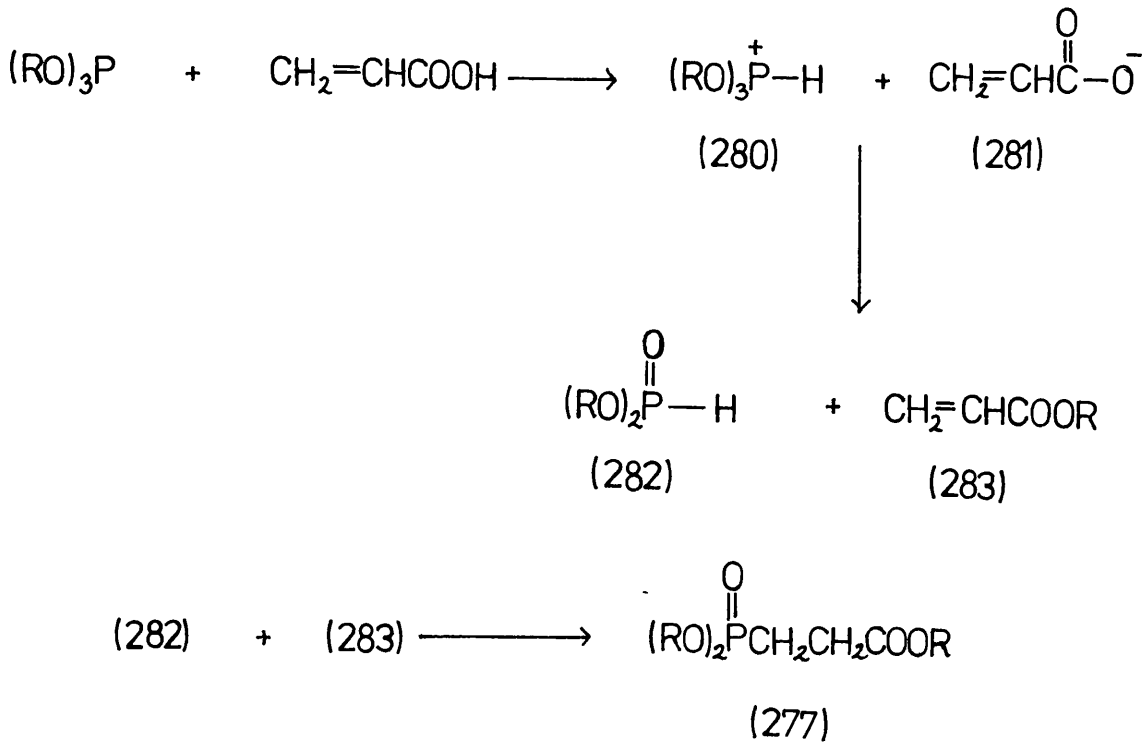
(277) (279)

on addition of methanol or water to the reaction mixture, prior to distillation, an exothermic reaction took place, whereas there was no exothermic reaction with the distillate (277).

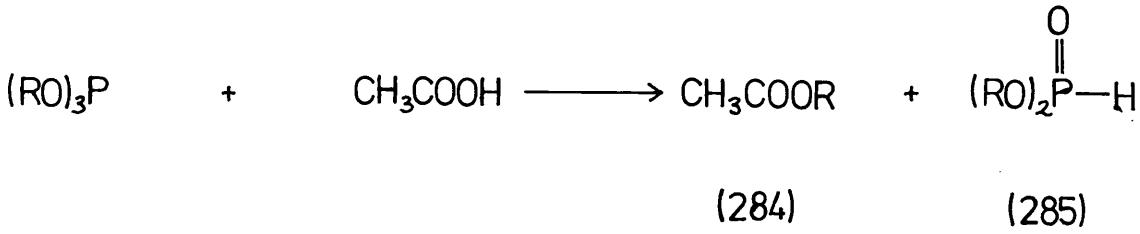
Clearly a re-investigation of this work using modern techniques was necessary. This was indeed carried out by Arbuzov[161] who found no evidence to suggest a cyclic phosphorane intermediate (279) but did find evidence which suggested an alternative mechanism involving initial protonation of the phosphite

to give the species (280) and (281).

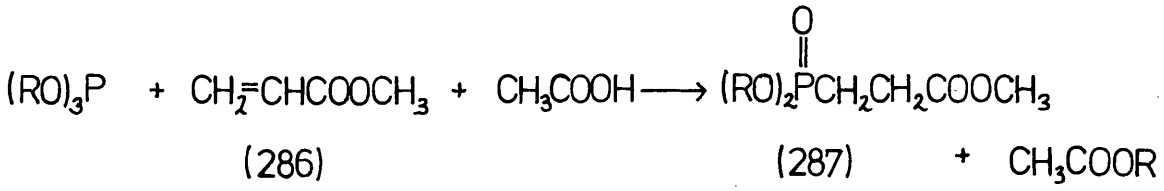
SCHEME G



Their mechanism was based on the observations that carboxylic acids react with trialkyl phosphites to give the corresponding esters (284) and the dialkyl phosphites (285) in good yields[162] and that trialkyl phosphites react with methyl



acrylate (286) in the presence of acetic acid to give the β-phosphonocarboxylic esters (287)[163]. They also found that trialkyl phosphites act as catalysts for the addition of



dialkyl phosphites (288) to the carbon atom of an α,β - unsaturated acid.

$$(RO)_2\overset{O}{\overset{\|}{P}}-H \quad + \quad CH_2{=}CHCOOH \xrightarrow{(R'O)_3P} (RO)_2\overset{O}{\overset{\|}{P}}CH_2CH_2COOH$$

(288)

As further proof of the mechanism outlined in Scheme G , they isolated small amounts of ethyl acrylate (283, R = Et) and diethyl phosphite (282, R = Et) from the reaction between triethyl phosphite and acrylic acid.

When excess protonating agent is used, whether in the form of excess α,β - unsaturated acid or added acetic acid, not only is the β - phosphinate ester (289) produced but also some of the corresponding acid (290).

$$(RO)_3P + \underset{(D)}{CH_2{=}CHCOOH} + CH_3COOH \longrightarrow \underset{(A)}{CH_3COOR} + \underset{(B)}{(RO)_2\overset{O}{\overset{\|}{P}}-H}$$

$$(C) + (B) \longrightarrow \underset{(289)}{(RO)_2\overset{O}{\overset{\|}{P}}CH_2CH_2COOR} + \underset{(C)}{CH_2{=}CHCOOR}$$

$$(B) + (D) \longrightarrow \underset{(290)}{(RO)_2\overset{O}{\overset{\|}{P}}CH_2CH_2COOH}$$

SCHEME H

$$(RO)_3P + CH_2{=}CHCOOH \xrightarrow{slow} (RO)_3\overset{+}{P}-CH_2CH{:}C\begin{matrix}OH\\O^-\end{matrix}$$

$$\downarrow fast$$

$$(RO)_2\overset{O}{\overset{\|}{P}}CH_2CH_2COOR$$

As the results obtained from acyclic phosphites and acrylic acid appear to differ from those obtained with certain cyclic phosphites, a further investigation of these reactions

was undertaken using an F.X. 60 F.T. ^{31}P n.m.r. machine, in order to allow great sensitivity and speed to be employed in the search for ^{31}P n.m.r. signals.

The first system investigated on a preparative scale was the reaction between triethyl phosphite and acrylic acid. The ^{1}H n.m.r. spectrum of the reaction mixture, after leaving

$$(EtO)_3P + CH_2{=}CHCOOH \xrightarrow[0^\circ]{\text{ether}} (EtO)_2\overset{O}{\overset{\|}{P}}CH_2CH_2COOEt$$

(291)

for two days at room temperature, seemed to suggest a 90% conversion into (291), but on reduced pressure distillation only 45% of (291) was actually obtained. The greater yield isolated (previously reported yield = 20%[164]) was probably due to the milder conditions employed, the use of a solvent and lower temperatures. A look at the non-volatile residues showed it to contain roughly 10% of the acid, $(EtO)_2\overset{O}{\overset{\|}{P}}-CH_2-CH_2-COOH$ (292). It would seem from the above results that it is the β - phosphonocarboxylic ester (291) which is thermally unstable and not the proposed cyclic phosphorane intermediate (279).

When this reaction was looked at by F.T. ^{31}P n.m.r. spectroscopy in $CDCl_3$ solution at $0^\circ C$, only slow formation of the ester (291) and the acid (292) was observed. There was no evidence of any other phosphorus compound such as diethyl phosphite. This would seem to suggest a mechanism such as that outlined in Scheme H.

When R was iso-propyl, the same results were obtained except that higher yields of isolated products were recorded.

The discrepancy between initial yield, as judged by the ^{1}H n.m.r. spectrum of the reaction mixture, and the amount of pure distilled material collected would seem to indicate

that the by-products obtained by Arbuzov[161] are not true intermediates, but result from thermal decomposition of the β- phosphonocarboxylic esters (291) at the high temperatures and low pressures involved in distillation.

$(RO)_2\overset{O}{\overset{\|}{P}}-CH_2-CH_2-COOR$

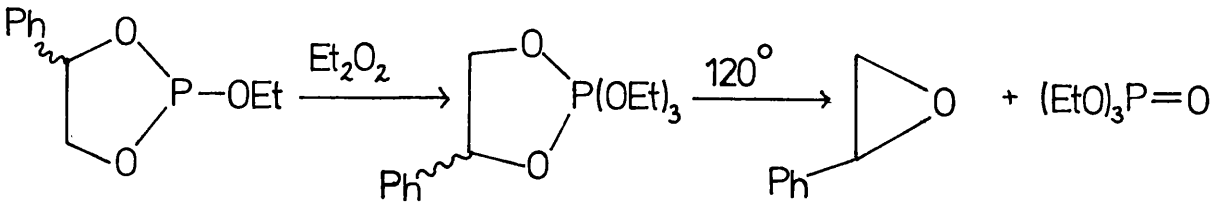
R = Et $b_{0.05}$ 100–110°

R = Pr^i $b_{0.05}$ 105–110°

It would appear that phosphoranes are only formed from acrylic acid and phosphites, if the phosphite is cyclic and contains a group which is not susceptible to 'Arbuzov type' attack. The fact that a ring is necessary is probably another example of the stability conferred on phosphoranes by the presence of two rings.[62,63]

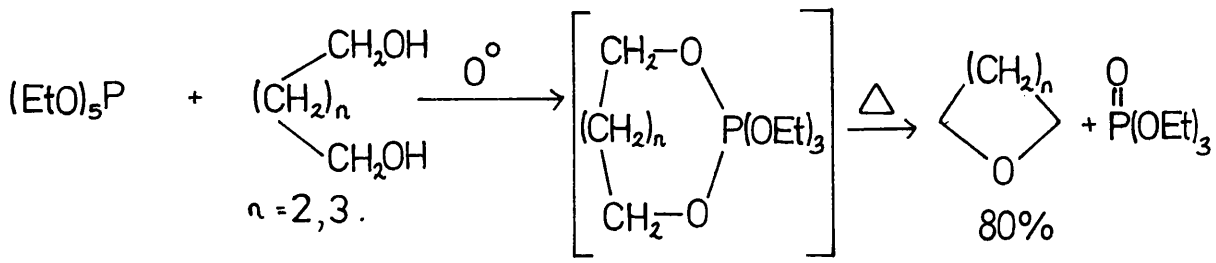
6.3 THERMOLYSIS OF SPIROPHOSPHORANES CONTAINING A PINACOL RING

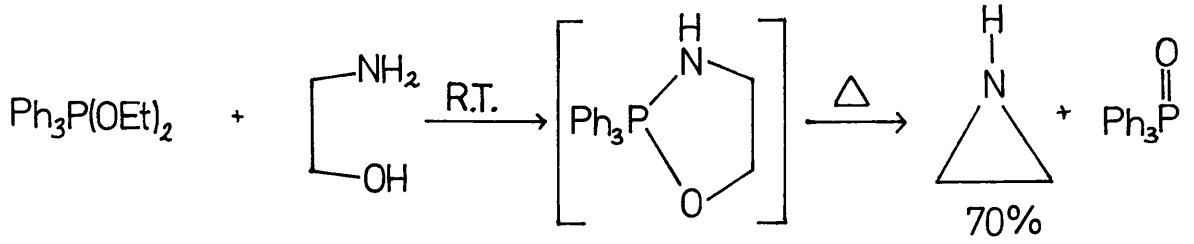
There are many examples in the literature[165] of small-ring heterocycles being obtained from the thermal decomposition of cyclic phosphoranes, e.g.

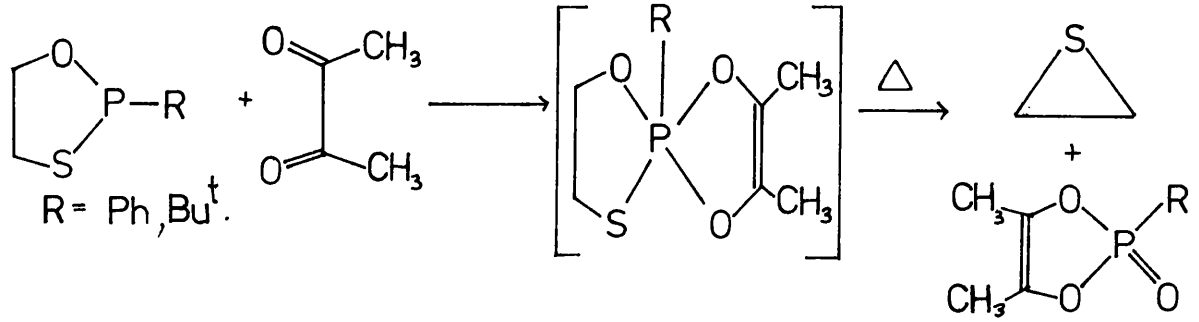


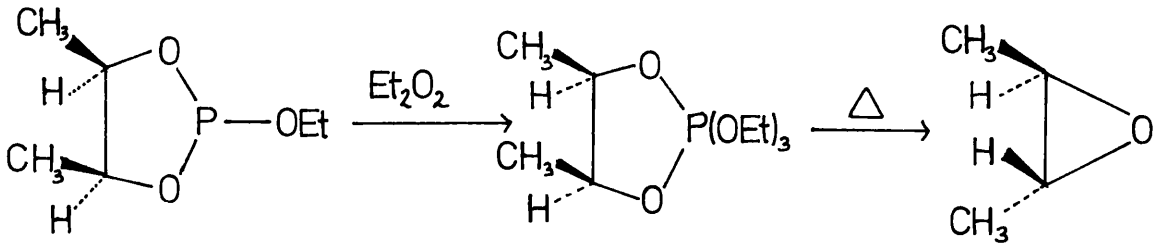
This type of displacement reaction has been utilized as a general method for the synthesis of heterocyclic compounds in very good yields.[63,64,166]

The formation of the epoxides (294) and (295) has been shown to be stereospecific by decomposition of the phosphoranes (292) and (293).

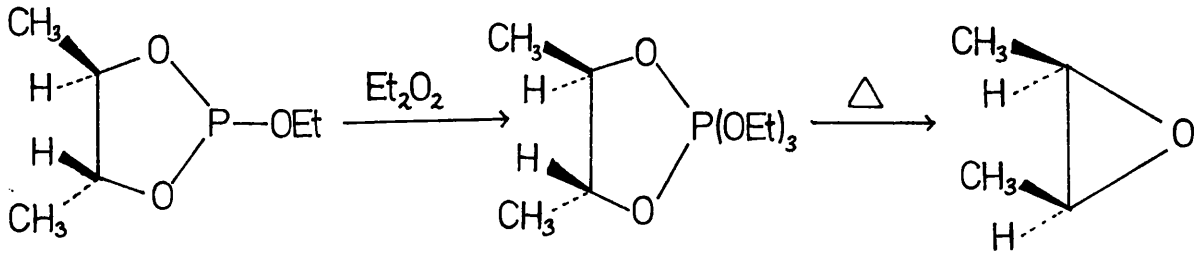






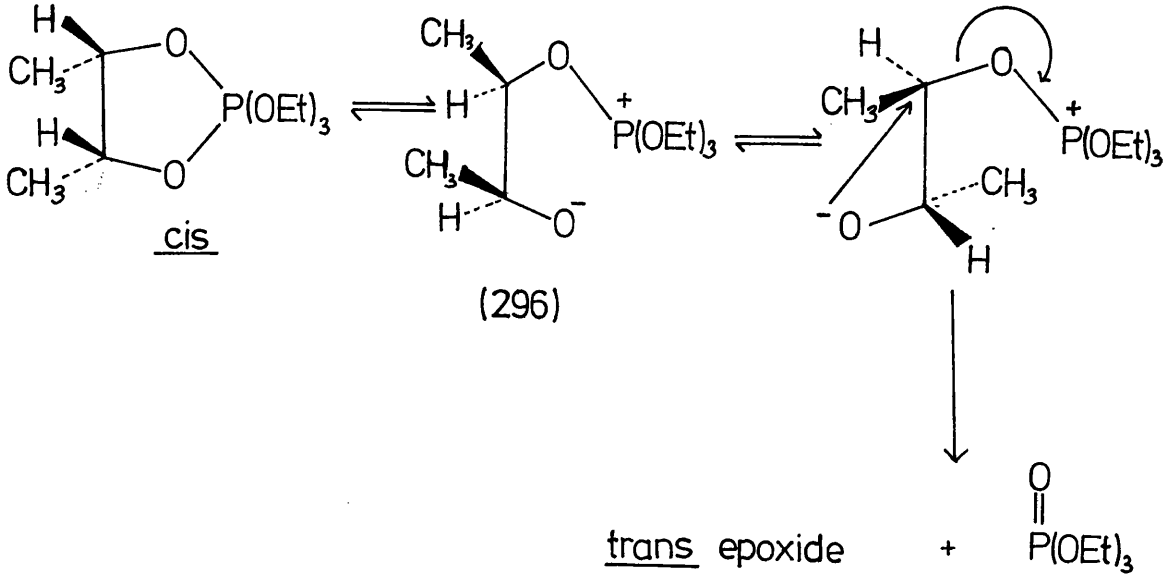


cis (292) trans (294)

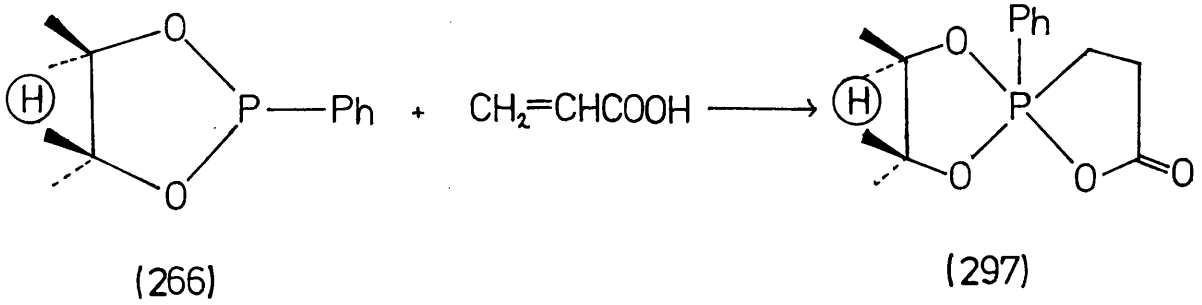


trans (293) cis (295)

The stereospecificity of the reaction must be due to dissociation of the phosphorane into the intermediate (296) followed by rotation about the carbon-carbon bond and back-side attack to displace the phosphate.

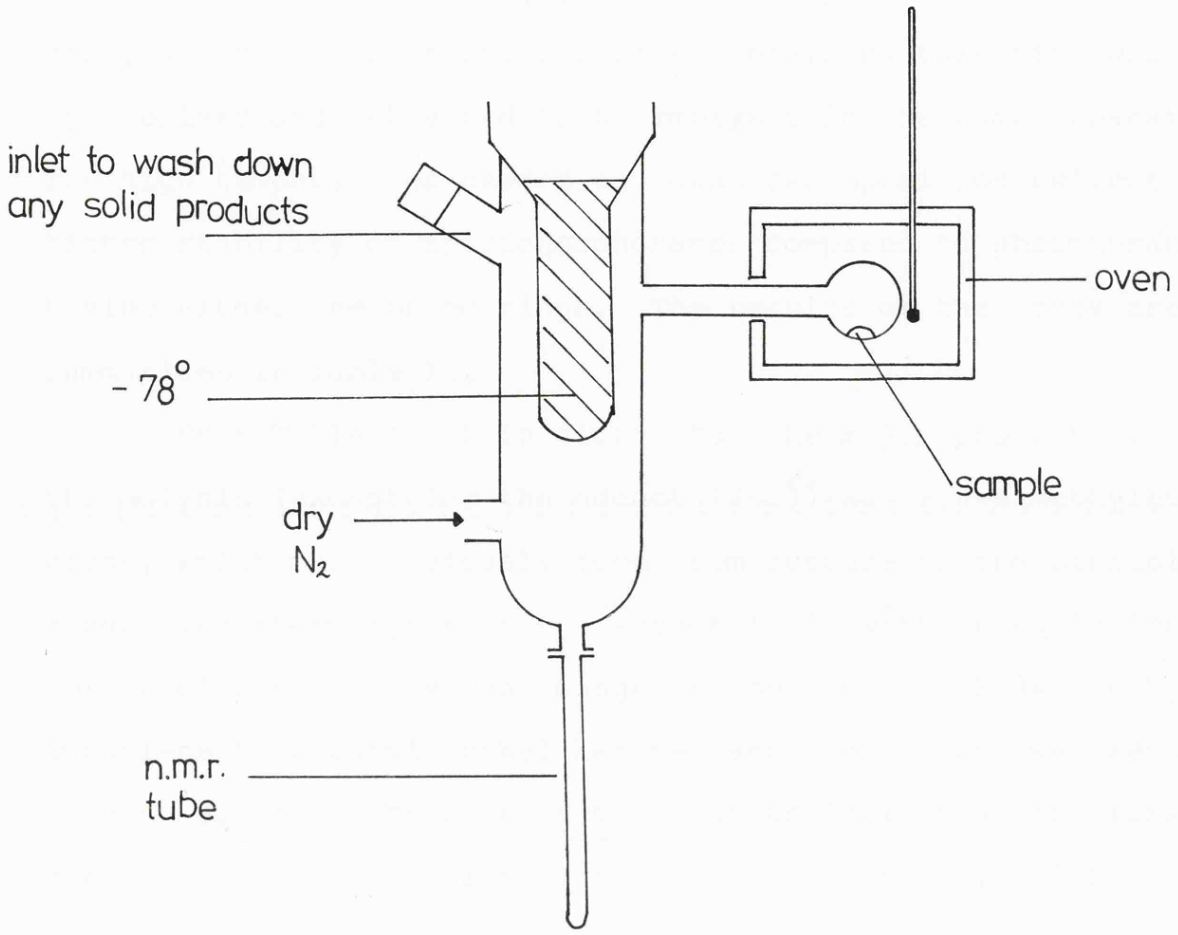


With the preparation of the spirophosphorane (297) from 2-phenyl- 4,4,5,5,-tetramethyl-1,3,2,-dioxaphospholan (266) and acrylic acid, the oxaphospholan ring formed seemed to have

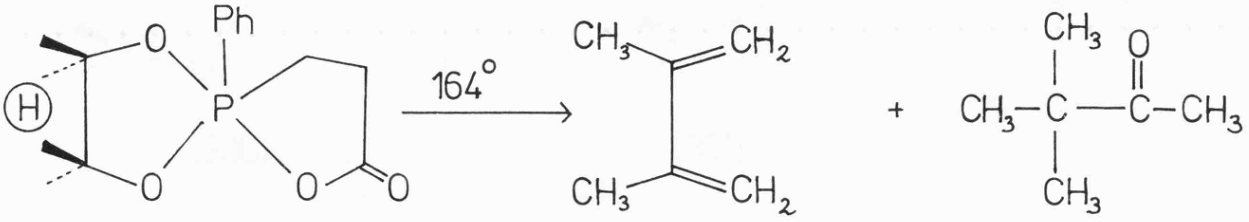


potential for thermolysis reactions. The apparatus used (Diagram 1) was that of Smith and Finlay[167]; the sample is heated in the oven until the point where decomposition takes place. Any volatile products formed collect on the cold-finger and are collected in the n.m.r. tube for spectral analysis and gas-liquid chromatography.

DIAGRAM 1



On heating the spirophosphorane (297) to 164°, a colourless liquid was collected in the n.m.r. tube. From the ^1H n.m.r. spectrum and G.L.C. the mixture was shown to consist of 2,3-dimethylbutadiene (298) as the major constituent and a small amount of t-butyl methyl ketone (299).

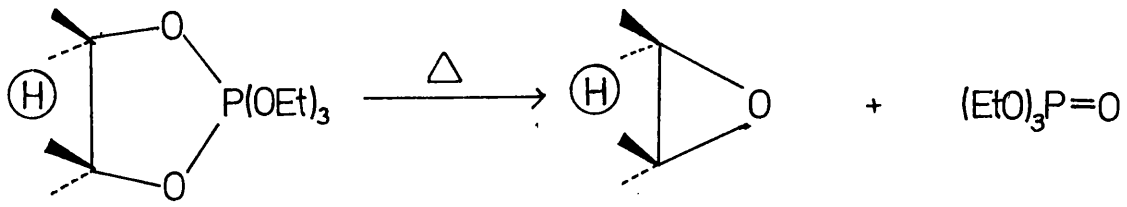


(297) (298) (299)

There was no trace of any tetramethylethylene oxide (301) which Denney[165] obtained from the phosphorane (300). To see if

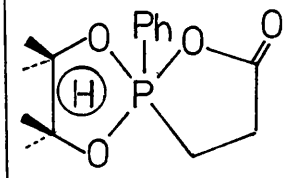
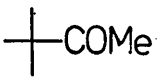
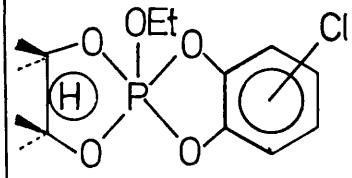
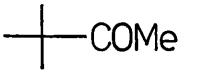
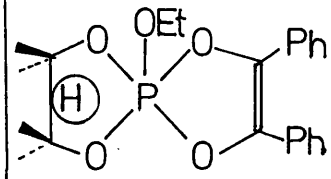
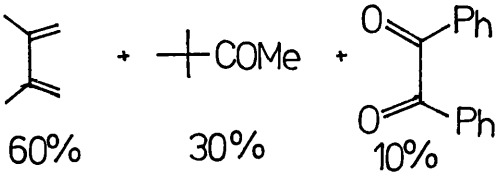
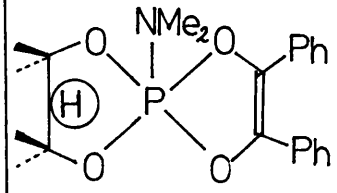
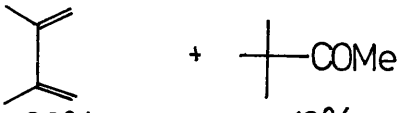
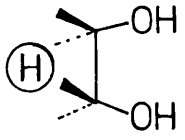
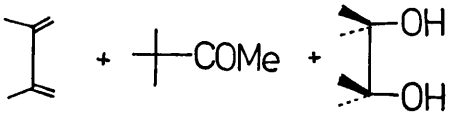
the result for the spirophosphorane (297) was typical of phosphoranes having the 4,4,5,5-tetramethyl-1,3,2-dioxaphospholan ring, a range of spirophosphoranes containing this ring was synthesised and subjected to thermolysis in the same apparatus. The high temperatures needed to cause decomposition reflect the higher stability of spirophosphoranes compared to phosphoranes having either one or no rings. The results of the study are summarised in Table 11.

From Table 11 it is clear that the major product of thermolysis (except for the adduct (302)) was 2,3-dimethylbutadiene, which must obviously come from rupture of the pinacol ring. The thermolysis of the adduct (297) with an equivalent amount of pinacol gave no change in the ratio of 2,3-dimethylbutadiene to t-butyl methyl ketone, and the pinacol was recovered unchanged. This observation makes it unlikely that the first step is loss of pinacol from the spirophosphorane, which then undergoes reaction to give the products isolated. The loss of 2,3-dimethylbutadiene and t-butyl methyl ketone is also mirrored in the mass spectral breakdown patterns of numerous spirophosphoranes containing a pinacol ring.



(300) (301)

TABLE 11

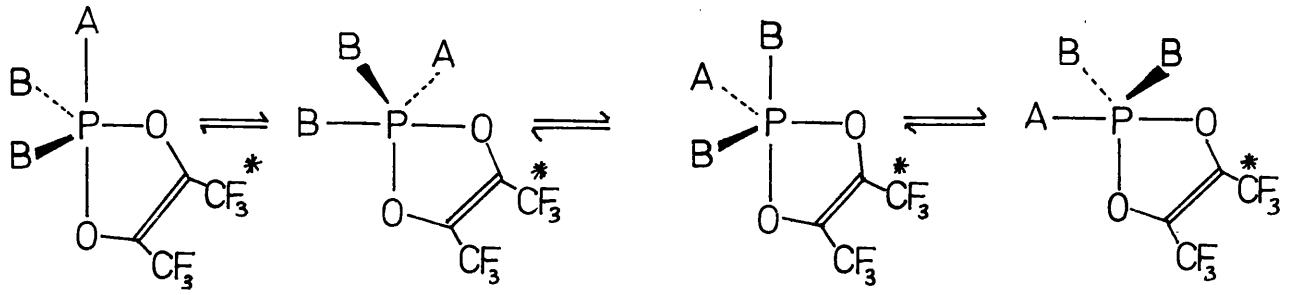
Compound	Decomposition Temperature (°C)	Volatile [a] Products
 (297)	164	 80% +  20%
 (302)	230	 100%
 (303)	250	 60% 30% 10%
 (304)	235	 90% 10%
 + (297)	164	 80% 20%

a) Products identified by ^{1}H n.m.r. and G.L.C. on a 3% O.V. 17 column. The ratios of products were determined from ^{1}H n.m.r. spectra and are only approximate.

7 THE RELATIVE APICOPHILICITIES OF THE CYANIDE AND CHLORINE LIGANDS

7.1 IN HEXAFLUOROBIACETYL ADDUCTS

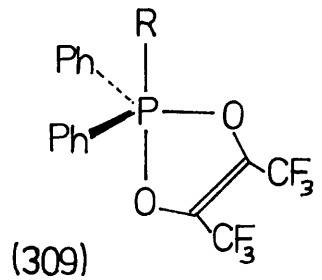
Dickstein and Trippett[154] have shown that the 1,3,2-dioxaphospholens (305) obtained from hexafluorobiacetyl and trivalent phosphorus compounds can be used to gain information on the relative apicophilicities of groups in pentacovalent phosphoranes.



(305) (306) (307) (308)

If A is more apicophilic than B then equivalence of the trifluoromethyl groups can occur via the higher-energy topomers. (306) and (307). The free energy of activation for this process will be a function of the relative apicophilicities of A and B. The more apicophilic A is relative to B, the higher the temperature required to make the process (305)$\rightleftharpoons$(308) become fast on the n.m.r. time-scale.

The actual energies involved in this system, for B = Ph, are quite small (8 - 14 kcal.mol^{-1})[154] which therefore makes this a very useful system for the study of highly apicophilic groups. The actual system employed here was (309) and the results obtained are summarised in Table 12.



(309)

TABLE 12

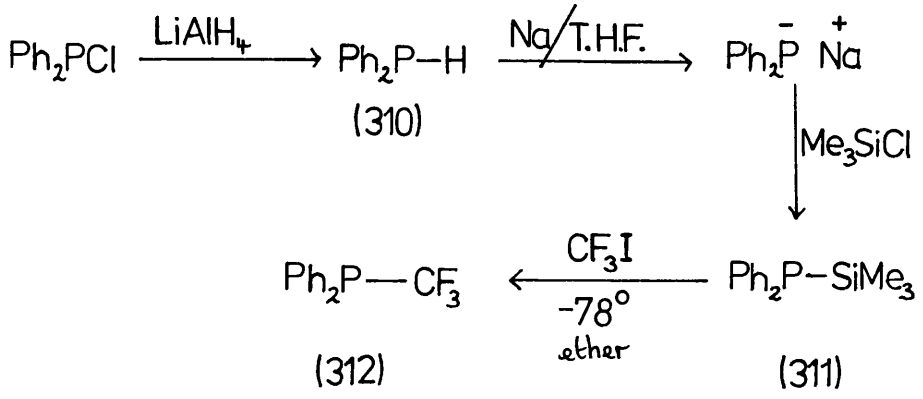
R	$\Delta\nu(H_z)$	$T^c(^oC)^b$	$\Delta G^{\#}$ (kcal.mol^{-1})
-Cl	255	-3 ± 2^o	12.3 ± 0.1
-OPh[a]	151	-4 ± 2	12.6 ± 0.1
-CN	259	30 ± 1	13.9 ± 0.1

a) determined by Dickstein[154]. b) CH_2Cl_2

It is clear that in this system the relative apicophilicities of the phenoxy and chlorine groups are very similar. The interesting thing to note however is the very high apicophilicity of the cyanide group, which must be due to a combination of its π^* acceptor properties and its high electronegativity[96]. This is the first time that the relative apicophilicity of the cyanide group has been determined.

Attempts were made to apply this system to the determination of the relative apicophilicity of the trifluoromethyl group. Unfortunately the trifluoromethyldiphenylphosphine adduct (309, R = CF_3) was not obtained from reaction of trifluoromethyldiphenyl phosphine (312) with hexafluorobiacetyl. From the ^{19}F n.m.r. spectrum of the reaction mixture it was clear that a large number of side-reactions had occurred. Similar results were obtained with the phosphines (310) and (311). Although no apicophilicity value was found for the trifluoromethyl group, a new improved synthesis of trifluoromethyldiphenylphosphine was developed and is outlined in Scheme I. The overall yield by this

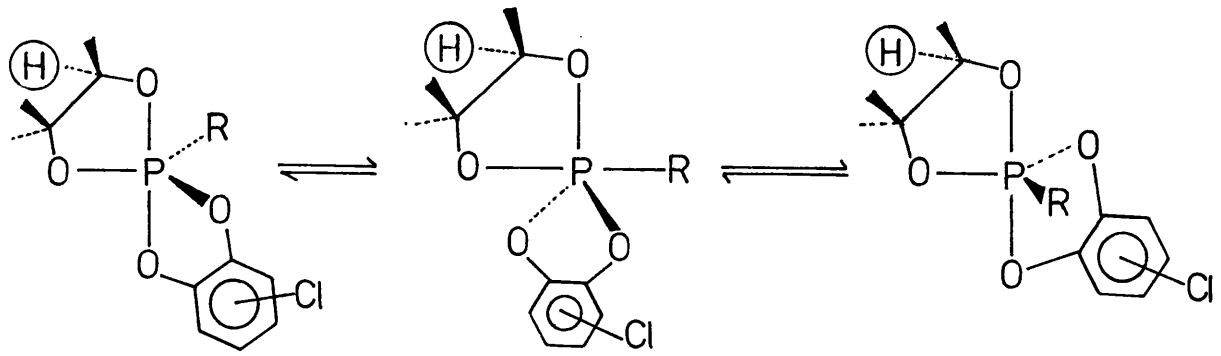
SCHEME I



method is 48% based on chlorodiphenylphosphine which compares well with the methods of Beg and Clark[168] who report yields of 10 - 48% for their high-pressure syntheses.

7.2 IN TETRACHLORO-O-BENZOQUINONE ADDUCTS

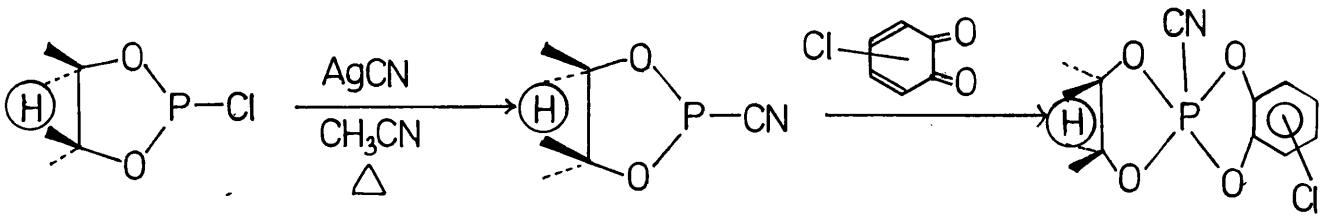
Bone[140] had found in a series of tetrachloro-o-benzoquinone adducts that the chlorine group was more apicophilic than the phenoxy group by approximately 2.5 kcal.mol^{-1} for the system (313) $\rightleftharpoons$ (315).



(313) (314) (315)

Full equivalence of the ring methyls can only occur via the high energy intermediate (314) in which the R group is in an apical position and the tetrachlorocatechol ring diequatorial. The energy required to place this ring diequatorial is high and as such the system can really only be used if R is very apicophilic.

2-Cyano-4,4,5,5-tetramethyl-1,3,2-dioxaphospholan (316) was prepared from 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholan by refluxing with silver cyanide in acetonitrile. The compound (316) readily reacted with tetrachloro-o-benzoquinone



(316) (317)

to give the spirophosphorane (317), its pentacovalent nature being determined from its positive ^{31}P n.m.r. chemical shift. The ^{1}H n.m.r. spectrum in CCl_4 showed two equal intensity signals

for the pinacol methyls at room temperature. At 46 ± 2°C these signals underwent a reversible coalescence, which corresponds to a $\Delta G^{\#}$ of 16.9 ± 0.1 kcal.mol^{-1}, as the process (313)⇌(315), R = CN, becomes fast on the n.m.r. time-scale. When compared to the result of Bone[44] for the spirophosphorane (313, R = Cl), it is clear that the cyanide group is more apicophilic than chlorine by about 1 kcal.mol^{-1} in this system.

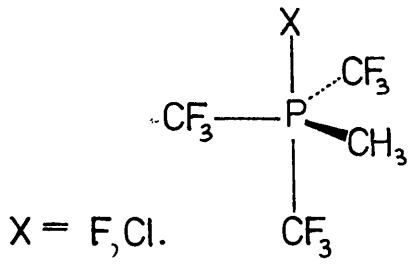
This difference of 1 kcal.mol^{-1} in the relative apicophilicity of cyanide and chlorine compares favourable with the result obtained from the hexafluorobiacetyl adducts (309, R = CN, Cl), in which cyanide was found to be more apicophilic than chlorine by about 1.5 kcal.mol^{-1}.

Of course the coalescences observed in the tetrachloro-o-benzoquinone (313, R = Cl, CN) and hexafluorobiacetyl adducts (309, R = Cl, CN) may be due to irregular processes involving nucleophilic impurities (phosphoranes which contain good leaving groups are very susceptible to hydrolysis). If this were so in the tetrachloro-o-benzoquinone systems, the 'genuine' coalescences would be at higher temperature than observed. This would have the effect of increasing $\Delta G^{\#}$ for the process (313)⇌(315), i.e. the apicophilicity values obtained would be exaggerated and would therefore be closer to the value obtained for the phenoxy group.

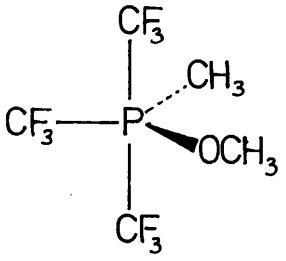
In the case of the hexafluorobiacetyl system the 'genuine' coalescences in the absence of nucleophilic impurities would occur at higher temperatures, thus increasing the $\Delta G^{\#}$ for the process (305)⇌(308) and making the true apicophilicity values greater than the ones recorded.

Cavell[169] has shown from a low temperature analysis of the ^{1}H, ^{31}P and ^{19}F spectra of a series of methyltris(trifluoromethyl) phosphoranes (318), that when X = F or Cl the 'frozen' molecule has X apical, but when X was methoxy, the methoxy group

was in an equatorial position in the frozen phosphorane (319). So on a qualitative scale he showed that the chlorine group is



(318)

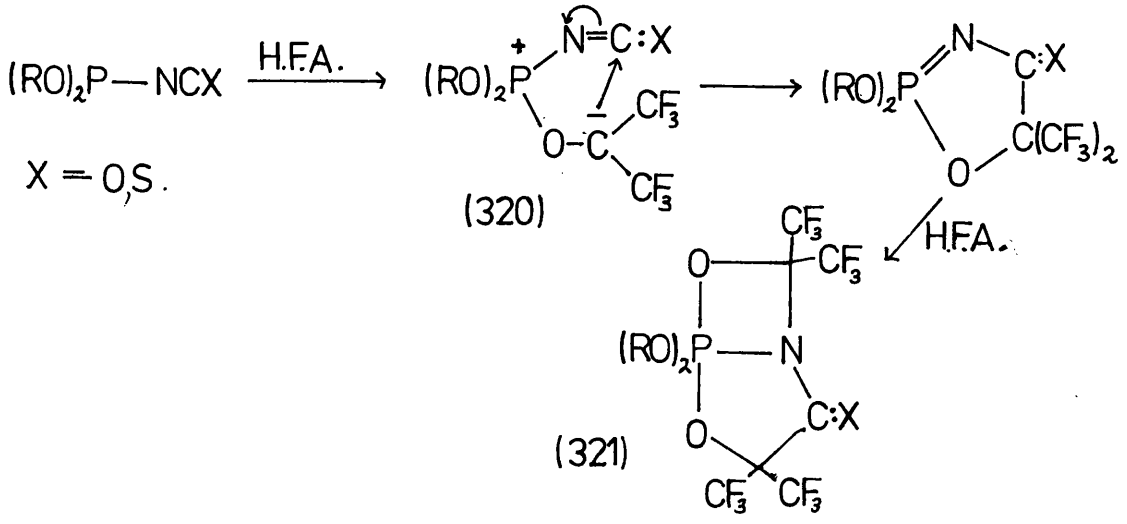


(319)

more apicophilic than the methoxy group, and as the relative apicophilicity of phenoxy and methoxy are close, the results of this experiment go some way to verifying that the cyanide and chlorine groups are indeed more apicophilic than phenoxy in the spirophosphoranes (313, R = CN, Cl, OPh) and the phosphoranes (309, R = CN, Cl, OPh).

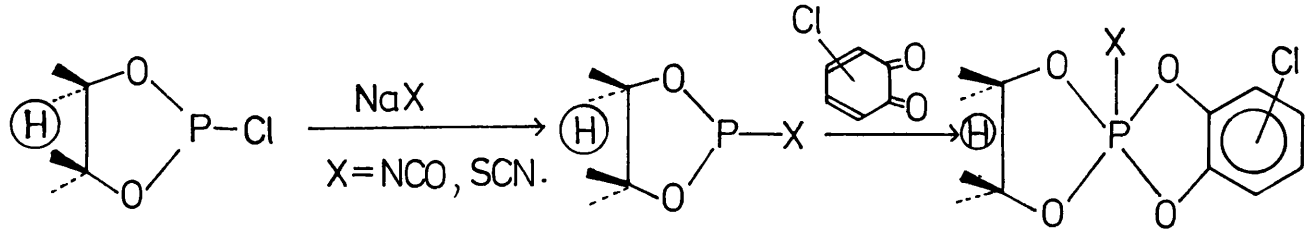
7.3 THE RELATIVE APICOPHILICITY OF THE ISOCYANATE AND ISOTHIOCYANATE GROUPS

The success of the tetrachloro-o-benzoquinone adducts in giving apicophilicity data on groups susceptible to nucleophilic attack (see 7.2) prompted an investigation of the relative apicophilicity of the isocyanate and isothiocyanate groups. Trippett et al[170] have shown how susceptible these groups are to nucleophilic attack from their reactions with hexafluoroacetone to give ultimately the bicyclic phosphoranes. It would appear

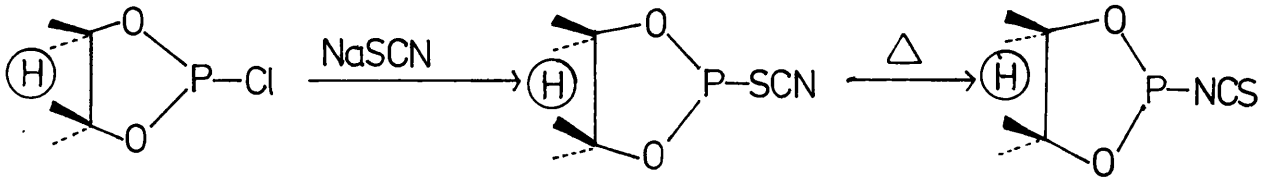


that any attempted synthesis of a phosphorane, bearing these groups, which involved a betaine type intermediate (320) would be unsuccessful.

The 2-substituted 1,3,2-dioxaphospholans (322, R = NCO, NCS) were prepared from 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholan and the appropriate sodium salt on refluxing in benzene-acetonitrile for four hours. The spirophosphoranes (323, R = NCO, NCS) were then prepared in the usual way. In the case of the 1,3,2-dioxaphospholan (322, R = NCS) the initially formed compound is probably a thiocyanate (324) which then rearranges on heating to the isothiocyanate[171].



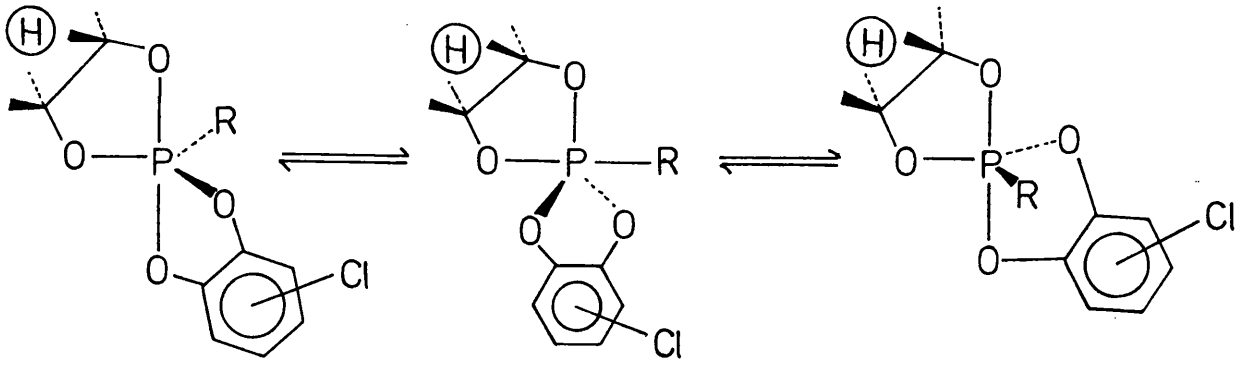
(322) X=NCO, NCS. (323)



(324)

The ^1H n.m.r. spectrum of the spirophosphorane (323, R = NCO) showed two equal intensity signal at room temperature in CCl_4. These underwent a reversible coalescence at 53°C, which corresponds to a $\Delta G^{\#}$ of $\underline{17.5 \pm 0.2\ kcal.mol^{-1}}$ for the process (325)$\rightleftharpoons$(327), R = NCO.

The ^1H n.m.r. spectrum of the spirophorane (323, R = NCS) was a broad singlet in CCl_4. However in sym - tetrachloroethane two signals were observed which coalesced at 57°C, with an



(325) (326) (327)

associated $\Delta G^{\#}$ of 17.8 ± 0.1 kcal.mol^{-1} for the process (325)⇌(327), R = NCS.

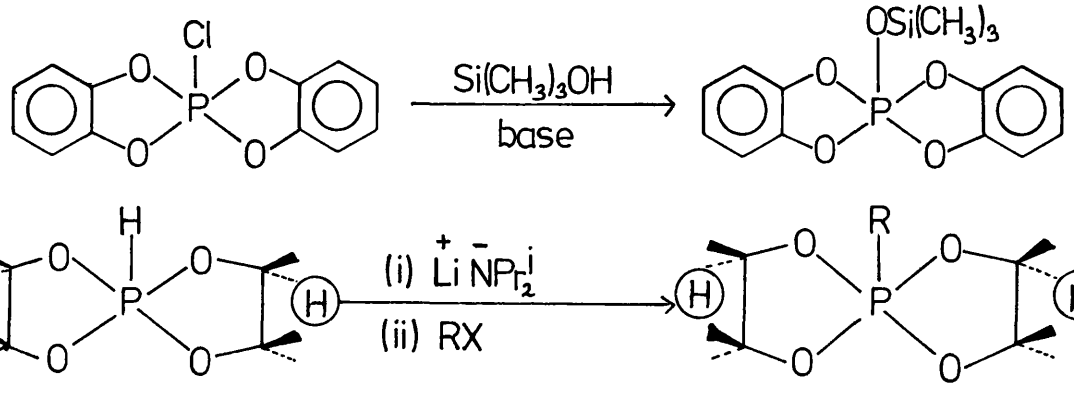
These results show that the relative apicophilicities of isocyanate and isothiocyanate are very similar and that they are very close to the value obtained by Bone[44] for the chlorine group. This would give an order of relative apicophilicities of

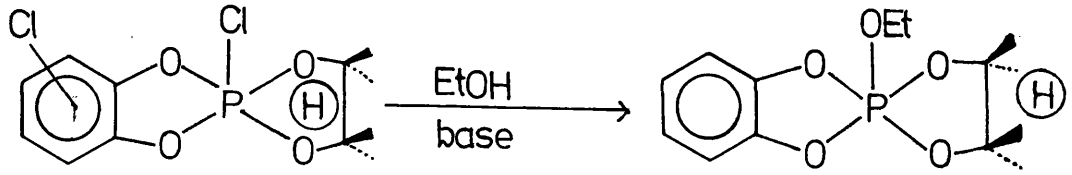
$$-CN > -NCO \approx -NCS \approx Cl > -OPh$$

There have been no other reported values for the relative apicophilicities of the cyanide, isocyanate and isothiocyanate groups in the literature.

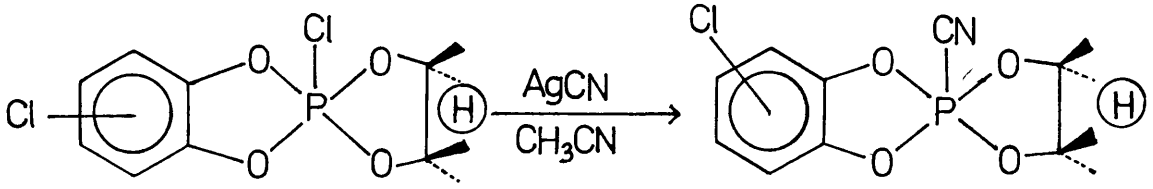
7.4 THE RELATIVE APICOPHILICITY OF THE AZIDE GROUP AND THE ATTEMPTED APICOPHILICITY OF THE BENZOYLOXY GROUP

There have been several reported examples of successful substitution reactions at pentacovalent phosphorus resulting in the formation of new phosphoranes.[82,149,193]





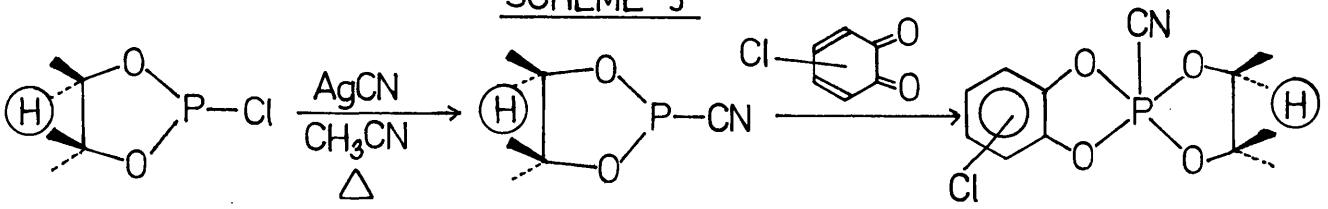
An attempt to prepare the spirophosphorane (329) from anhydrous silver cyanide and the corresponding chloro-compound (328) resulted in the formation of a pale yellow solid.



(328) (329)

The pinacol methyls appeared as two equal intensity signals in CCl_4 at R.T., the ^{31}P n.m.r. was positive as expected and the m^+/e showed the expected mass peak. However on examining the infrared spectrum only a very small obsorption was observed at 2210 cm^{-1}. It was not until an authentic sample of (329) was prepared by an unambiguous route (Scheme J) and its infrared spectrum obtained,

SCHEME J



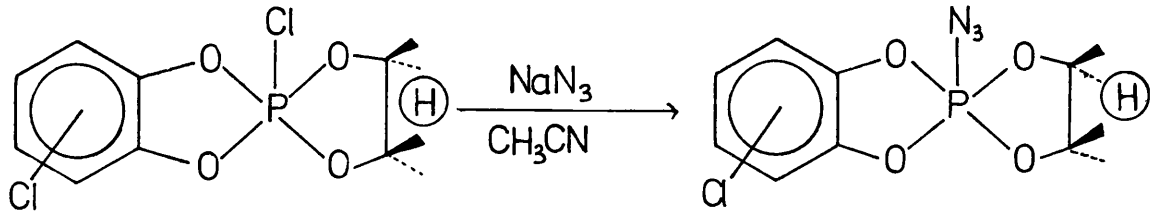
(329)

that the preparation of (329) directly from (328) was substantiated. The very poor absorption of the cyanide group in phosphorus compounds is not unusual ; indeed P-cyano- P,P-diphenylphosphine (Ph_2PCN) has been shown to have no cyanide absorption in the infrared region.[172]

Once the success of the method (328) ⟶ (329) had been established, the possibility of preparing the first pentacovalent phosphorus compound bearing a phosphorus-azide bond was considered. Phosphine oxides containing the azide group are well-known and

reasonably stable.[173] However trivalent phosphorus compounds containing the azide group are very unstable[174] and, as it is the trivalent state which is usually required for phosphorane formation, the usual methods of synthesis are unlikely to be successful.

Sodium azide and P-chloro-4^1,4^1,5^1,5^1-tetramethyl-tetrachloro-1,3,2-benzodioxaphosphole-2-spiro-2^1-1^1,3^1,2^1-dioxaphospholan were stirred at room temperature for two days in acetonitrile. Filtration and careful removal of the solvent under reduced pressure then gave the phosphorane (330).



(329) (330)

Although the ^{31}P n.m.r. chemical shift of -7.8 p.p.m. was a little low for a spirophosphorane of this nature, ^1H n.m.r., infrared and m^+/e evidence was in favour of the structure (330). The ^1H n.m.r. spectrum in sym - tetrachloroethane showed two equal intensity signals which underwent a reversible coalescence at 76 ± 2°C, corresponding to a $\Delta G^{\ddagger}$ of 19.3 ± 0.1 kcal.mol^{-1}. This value shows the azide group to be more apicophilic than the phenoxy group in this system by about 1 kcal.mol^{-1}.

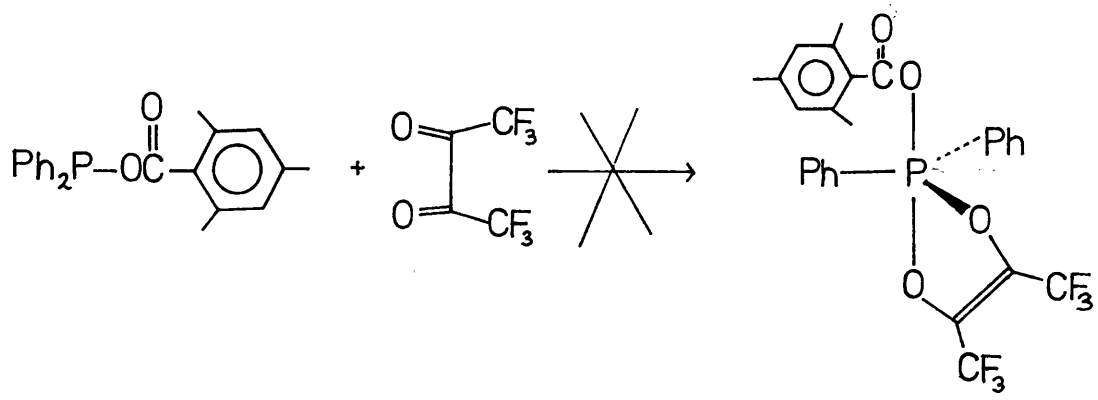
In looking at the very apicophilic groups studied in this chapter the following relative apicophilicity scale can be drawn-up.

$$CN > NCO \approx NCS \approx Cl > N_3 > OPh$$

$\longleftarrow$ increasing apicophilicity.

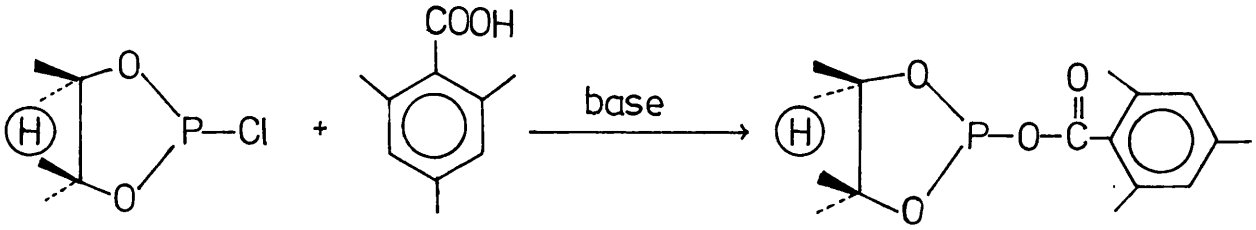
In order to determine the relative apicophilicity of the benzoyloxy group (-OCOAr) the preparation of the following hexafluorobiacetyl adduct (331) was attempted. However no

phosphorane formation was observed in the ^{31}P n.m.r. spectrum.



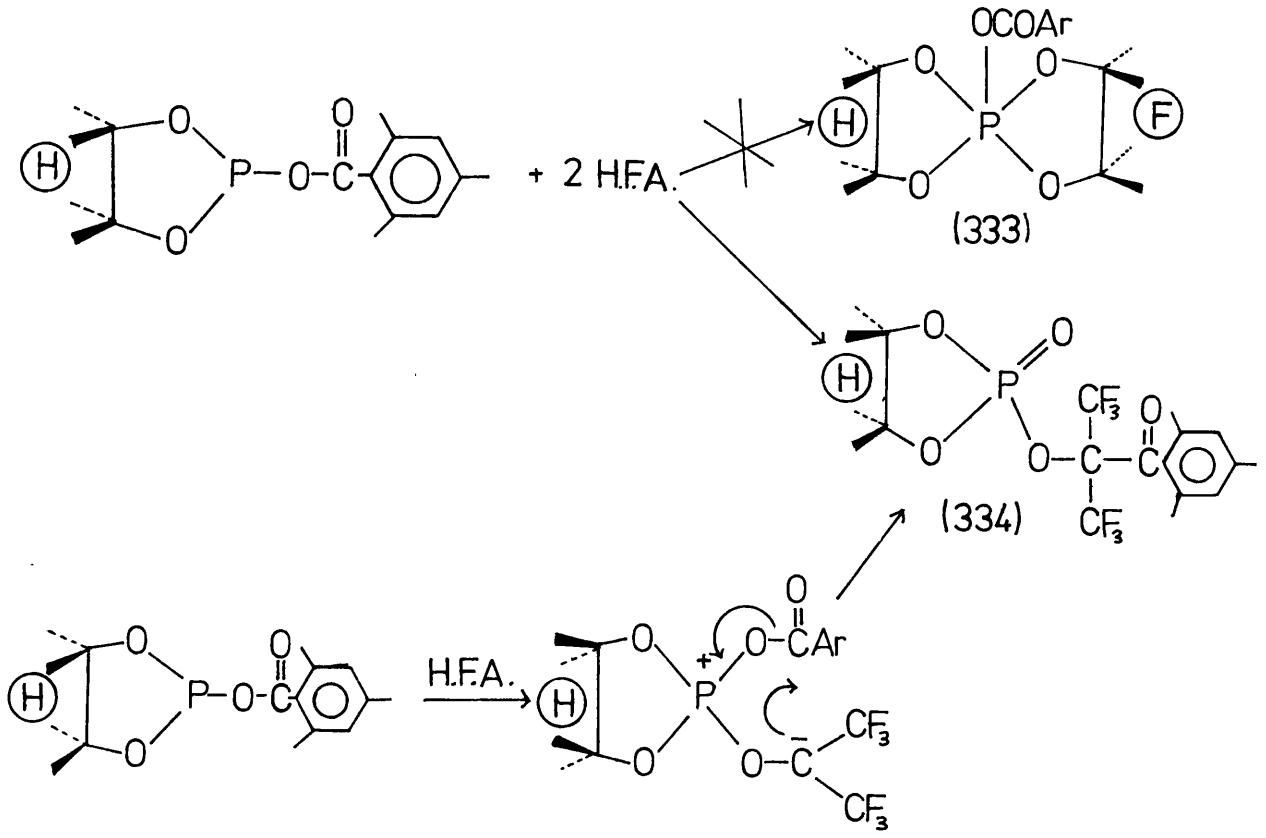
(331)

The phosphite (332) was prepared in good yield in order to prepare spirophosphoranes suitable for a d.n.m.r. study. In

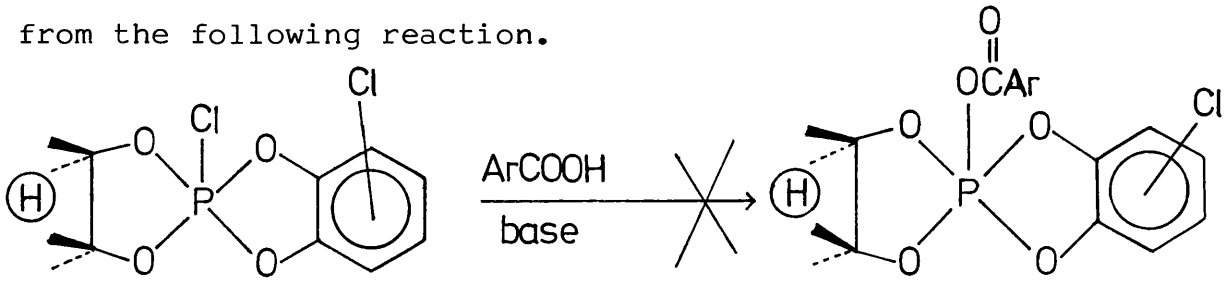


(332)

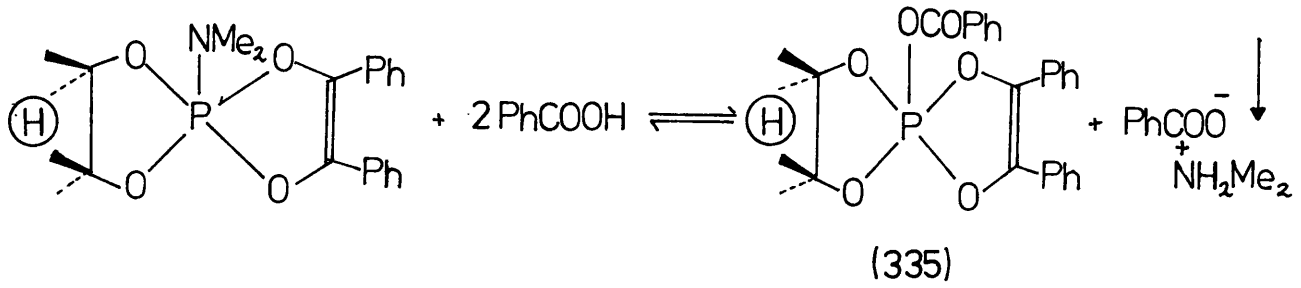
reacting the phosphite (332) with tetrachloro-o-benzoquinone a 1:1 adduct was formed but the low ^{31}P n.m.r. chemical shift was consistent with an oxide. Efforts to characterise fully the reaction product proved impossible due to its extreme instability to water and heat. However an insight into its possible structure resulted from a study of the reaction of (332) with hexafluoro-acetone. Instead of the usual 2:1 adduct (333), the cyclic phosphate (334) was isolated in quantative yield. The formation of (334) was deduced from the low ^{31}P n.m.r. chemical shift of -3.0 p.p.m., the sharp singlet in the ^{19}F n.m.r. spectrum at both high and low temperature, as well as m^+/e and micro-analytical results. The formation of (334) is thought to arise by the following mechanism.



The preparation of a phosphorane containing the benzoyloxy group did not prove possible and no phosphorane was isolated from the following reaction.



In the literature[175] there does exist a method for the preparation of a spirophosphorane (335) containing the benzoyloxy group. However when tried using various solvents and conditions,



no new spirophosphoranes were isolated. It would appear that until further detailed experimental data are released by Bernard and Burgada the possibility of preparing a spirophosphorane containing the benzoyloxy group and hence determining its relative apicophilicity seem remote.

EXPERIMENTAL

Melting points are uncorrected and were determined using a kofler heating stage. Infrared spectra were obtained on a Perkin-Elmer 237 grating spectrometer from nujol mulls unless otherwise stated. Mass spectra were determined with either a V.G. Micromass 16 B machine or an A.E.I. MS9 machine, in each case the molecular ion is given followed by peaks of structural importance. Routine proton n.m.r. spectra were recorded on a Varian T60 instrument using deuterochloroform as solvent unless otherwise stated. Variable temperature proton and fluorine spectra were recorded on a Jeol PS100 instrument using 1-bromonaphthalene as solvent unless stated otherwise. Proton chemical shifts are relative to tetramethylsilane, fluorine n.m.r. spectra are relative to α,α,α- trifluorotoluene as internal standard. Phosphorus chemical shifts were obtained where possible by heteronuclear INDOR spectroscopy using an HD-60 heteronuclear decoupler (N.M.R. Specialities), or by a Jeol PS100 machine. Positive phosphorus chemical shifts are to high field of external 85% H_3PO_4 solution. Proton decoupled Fourier Transform ^{13}C n.m.r. and ^{31}P n.m.r. spectra were obtained on a Jeol JNM FX 60 machine. Carbon -13 chemical shifts are relative to tetramethylsilane.

All operations involving air or moisture sensitive compounds were carried out under dry, oxygen-free, nitrogen. All solvents were dried and distilled before use. Diethyl ether, petroleum spirit, benzene and toluene were dried over sodium wire. Methanol and ethanol were refluxed and distilled from their magnesium alkoxides. Pyridine, di-isopropylamine and triethylamine were refluxed over and distilled from potassium

hydroxide. Tetrahydrofuran was refluxed and distilled from lithium aluminium hydride. Koch-Light Celite was used as a filtering aid and was dried before use by heating to 120° in an oven. Small scale distillations were carried out using a Kugelrohr oven and the boiling points quoted refer to the oven temperatures over which distillation occurred.

Preparation of Phenylphosphorodichloridite

Phosphorus trichloride (0.5 mol) was added dropwise to phenol (0.5 mol) the evolution of hydrogen chloride being moderated by cooling the flask in cold water. After the initial reaction had subsided the mixture was refluxed until no more hydrogen chloride was given off. The reaction mixture was distilled under reduced pressure to give phenylphosphorodichloridite (45%); $b_{0.5}$ 59-64°, Lit. $b_{1.0}$ 90° [176].

Preparation of Phenylphosphorodichloridothioite

A solution of benzene thiol (0.25 mol) in ether (50 ml) was slowly added to a stirred solution of phosphorus trichloride (0.25 mol), and pyridine (0.25 mol) in ether (200 ml). After addition the reaction mixture was refluxed for 1h. Filtration followed by removal of the ether and reduced pressure distillation of the residue gave phenylphosphorodichloridothioite (59%); $b_{0.3}$ 77-79°, Lit. b_{10} 125° [177].

Preparation of 3-Methyl-2-phenoxy-1,3,2-oxaphospholan (193)

This was prepared by addition of 2-methylaminoethanol to phenylphosphorodichloridite in the presence of triethylamine, according to the method of Whittle.[108] (26%); $b_{1.0}$ 108-114°, (Lit. $b_{0.2}$ 85-87°)[108]; δ 2.87 (3H,d,J_{P-H} 12Hz), 2.70 - 3.37 (2H,m), 4.07 - 4.67(2H,m), 6.87 - 7.60(5H,m).

Preparation of 3-Methyl-2-phenylthio-1,3,2-oxazaphospholan

This was prepared by the method of Whittle[108] (30%); $b_{0.4}$ 115-120°, (Lit. $b_{0.4}$ 115-116°);[108] δ 2.73 (3H,d,J_{P-H}14Hz), 2.92 - 3.30 (2H,m), 3.95 - 4.72 (2H,m), 7.08 - 7.67 (5H,m).

Preparation of 2-Phenoxy-1,3,2-oxathiaphospholan

This compound was prepared by the method of Bone[44] (20%); $b_{0.5}$ 116-118°, (Lit. $b_{0.2}$95-98)[44]; δ 4.05 - 4.70(2H,m), 6.80 (2H,t,J_{H-H}6Hz), 6.75 - 7.40 (5H,m).

Preparation of 2-Dimethylamino-3-methyl-1,3,2-oxazophospholan

Prepared by the method of Sanchez et al[67] (36%); b_{15} 68-76°, (Lit. b_{16} 66-68°)[67].

Preparation of 2-Chloro-1,3,2-dioxaphospholan

High yields of this cyclic chlorophosphite were obtained using the method of Lucas[178] (70%); b_{15} 47-50°, Lit. b_{13} 45-47° [178].

General Method for the Preparation of 2-Substituted-1,3,2-dioxaphospholans

The alchohol or thiol (0.05) in ether (20ml) was added dropwise to a stirred mixture of 2-chloro-1,3,2-dioxaphospholan (0.05 mol), and pyridine (0.05 mol) in ether (100 ml) at 0°. When addition was complete the reaction mixture was refluxed for 2h. Filtration and removal of the ether, followed by reduced pressure distillation gave the 2-substituted-1,3,2-dioxaphospholan. By this method, the following compounds were prepared.

2-Ethoxy-1,3,2-dioxaphospholan (134, R = OEt) (75%); b_{15} 54-57°, (Lit. b_{15} 50.5 - 51.0°)[179]; δ 1.20 (3H,t, J_{H-H} 7Hz), 3.50 - 4.39 (6H,m).

2-Ethylthio-1,3,2-dioxaphospholan (134, R = SEt) (61%); $b_{1.0}$ 41-48°, (Lit. $b_{1.5}$ 53-56°)[180]; δ 1.31 (3H,t,J_{H-H} 8Hz), 2.48 - 3.08 (2H,m), 3.81 - 4.57 (4H,m).

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

This compound was obtained in high yields by the method of Bone[44] (86%); $b_{1.0}$ 50-51°, (Lit. b_{11} 80-89°)[181]; δ 1.36 (6H,s), 1.55(6H,s).

Preparation of 2-Substituted-4,4,5,5-tetramethyl-1,3,2-dioxaphospholans

These were prepared by the same method as described for the preparation of 2-substituted-1,3,2-dioxaphospholans. By this method the following were prepared.

2-Ethoxy-4,4,5,5-tetramethyl-1,3,2-dioxaphospholan (143) (83%); b_{18} 94-96°, (Lit. b_{14} 75-76°)[181]; δ 1.16 (6H,s), 1.29 (6H,s), 1.08 - 1.50 (3H,m), 3.46 - 4.08 (2H,m).

2-Ethylthio-4,4,5,5-tetramethyl - 1,3,2-dioxaphospholan (153, R = SEt)

(32%); $b_{1.0}$ 120-124°, (Lit. b_2 135 - 140°)[180]; δ 1.26 (6H,s), 1.32 (6H,s), 1.30 - 1.60 (3H,m), 2.57 - 3.10 (2H,m).

Preparation of 2-Substituted - 1,3,2-benzodioxaphospholes

These were prepared in the usual way by addition of the alcohol or thiol to 2-chloro-1,3,2-benzodioxaphole in ether, in the presence of pyridine. In this way the following compounds were prepared.

2-Ethoxy-1,3,2-benzodioxaphosphole

(75%; b_{20} 108-110°, (Lit. b_{19} 99-100°)[182]; δ 1.11 (3H,t,J_{H-H} 8Hz), 3.55 (2H,q,J_t 8Hz), 6.82 (4H,s).

2 - Ethylthio - 1,3,2-benzodioxaphosphole

(30%); $b_{1.2}$ 109-114°; δ 1.30 (3H,dt,J 1.5 and 7Hz), 2.77 (2H, dq,J 1.5 and 7Hz), 6.81 - 7.16 (4H,m).

Preparation of N-chlorodi-isopropylamine

This was made by the method of Bock and Kompa[183]. (80%), b_{20} 40°, (Lit. b_{10} 43°)[183].

Preparation of Phosphoranes using N-Chlorodi-isopropylamine

A solution of the diol or catechol (5 mmol) in ether (10 ml) was added slowly to a solution of the tervalent phosphorus compound (5 mmol) in ether (25ml) maintained at -78°. N-chlorodi-isopropylamine (5 mmol) in ether (10 ml) was then added slowly and the mixture kept at -78° for 0.5 h. After leaving overnight at room temperature, filtration followed by evaporation gave the crude phosphorane. This was crystallised from or extracted with light petroleum. In this way the following phosphoranes were prepared.

From Perfluoropinacol

5-Ethoxy-2,2,3,3-tetrakistrifluoromethyl-1,4,6,8-tetraoxa-5-phosphaspiro (4.4) nonane (135, R = OEt)

This was recrystallised from 40-60° light petroleum at -20°. (68%); m.p. 45-47°; δ 1.26 (3H,dt,J 7 and $2H_z$), 4.0(4H,d,J_{P-H} $15H_z$) and 3.78 - 4.32 (2H,m); ^{31}P ($CDCl_3$) + 28.8 p.p.m.; ^{19}F (1-bromonaphthalene) + 3.51 (6F,m) and + 3.72(6F,m) p.p.m.; $^m/e$ 468, 439, 438, 423, 421, 411, 410, 399, 380, 371, 311 and 265; ν_{max} (neat film) 2990, 2920, 1480, 1400, 1250, 1220, 1070, 1005, 970, 950, 890, 865, 785, 750 and 705; T^c 116 ± 2°; $\Delta\nu$ $21H_z$; $\Delta G^{\#}$ 20.1 ± 0.2 kcal.mol^{-1}; (Found C,25.7; H,2.1; P,6.55. $C_{16}H_9F_{12}O_5P$ requires C,25.65; H,1.9; P,6.65%).

5-Ethylthio-2,2,3,3-tetrakistrifluoromethyl-1,4,6,8-tetraoxa-5-phosphaspiro (4.4) nonane. (135, R = SEt)

(78%), δ 1.12 - 1.44 (3H,m), 2.46 - 3.22(2H,m) and 4.00 (4H,d, J_{P-H} $15H_z$); ^{31}P ($CDCl_3$) + 2.5 p.p.m.; ^{19}F (1-bromonaphthalene) + 2.60(6F,m) and + 3.60(6F,m) p.p.m.; $^m/e$ 484, 465, 423, 415, 393, 197, 159 and 129; ν_{max} (neat film) 2990, 2900, 1480, 1385, 1245, 1220, 1120, 1060, 1000, 965, 945, 885, 850, 775, 760 and 720; T^c 121 ± 2°; $\Delta\nu$ $104H_z$; $\Delta G^{\#}$ 19.1 ± 0.2 kcal.mol^{-1}.

P-ethoxy-$4^1,4^1,5^1,5^1$-tetrakistrifluoromethyl-1,3,2-benzodioxaphosphole-2-spiro-2^1-(1,3,2)dioxaphospholan. (150, R = OEt)

(85%); δ 1.04 - 1.58 (3H,m), 3.84 - 4.56(2H,m) and 6.90 - 7.04 (4H,m); ^{31}P ($CHCl_3$) + 30.7 p.p.m.; ^{19}F (1-bromonaphthalene) + 4.73 (6F,m) and + 5.60(6F,m) p.p.m.; $^m/e$ 516, 497, 488, 471, 469, 419, 246, 200, 161 and 155; ν_{max} (neat film) 3000, 1495, 1250, 1220, 1100, 1055, 1010, 1000, 970, 900 890, 880, 785, 745 and 715; T^c 180 ± 2°; $\Delta\nu$ $98H_z$; $\Delta G^{\#}$ 22.1 ± 0.2 kcal.mol^{-1}.

P-ethylthio-$4^1,4^1,5^1,5^1$-tetrakistrifluoromethyl-1,3,2-benzodioxaphosphole-2-spiro-2^1-(1,3,2)dioxaphospholan (150, R = SEt).

(82%); δ 1.08 - 1.54 (3H,m), 2.42 - 3.32(2H,m) and 6.82(4H,s); ^{31}P ($CHCl_3$) + 1.0 p.p.m.; ^{19}F (1-bromonaphthalene) + 3.94(6F,m)

and + 4.86(6F,m) p.p.m.; $^{m}/e$ 532, 503, 464, 426, 414, 376, 265, 224, 197 and 147; ν_{max} (neat film) 2970, 2940, 2880, 1490, 1385, 1245, 1220, 1110, 1010, 1000, 965, 895, 870, 775, 745, 720, and 690; T^{c} 163 ± 2°; $\Delta\nu$ 76Hz; $\Delta G^{\#}$ 21.4 ± 0.2 kcal.mol^{-1}.

P-ethoxy-2,2,3,3-tetramethyl-7,7,8,8-tetrakistrifluoromethyl-1,4,6,9-tetraoxa-5-phosphaspiro (4.4) nonane. (147, R = OEt) (81%); δ 1.24(12H,s), 1.32 - 1.48(3H,m) and 4.06 (2H,q,J_{H-H}7Hz); ^{31}P (neat) + 37.1 p.p.m.; ^{19}F (1-bromonaphthalene) + 4.50 (12F,s) p.p.m.; $^{m}/e$ 522, 507, 503, 479, 466, 455, 424, 408, 397, 345, 265 and 245; ν_{max} (neat film) 3000, 2950, 1500, 1420, 1400, 1390, 1250, 1130, 1075, 1020, 1000, 950, 900, 890, 850, 830, 805, 780, 755 and 710; T^{c} could not be obtained as the ^{19}F signal was a singlet in all solvents tried.

P-ethylthio-2,2,3,3-tetramethyl-7,7,8,8-tetrakistrifluoromethyl-1,4,6,9-tetraoxa-5-phosphaspiro (4.4) nonane. (147, R = SEt) (80%), δ 1.28(6H,s), 1.30(6H,s), 1.32 - 1.50 (3H,t,J_{H-H}2Hz) and 2.36 - 3.12(2H,m); ^{31}P ($CDCl_3$) + 7.2 p.p.m.; ^{19}F (1-bromonaphthalene) + 3.06(6F,m) and + 4.52(6F,m) p.p.m.; $^{m}/e$ 538, 523, 501, 464, 439, 426, 414, 376, 281, 265, 224 and 197; ν_{max} (neat film) 3000, 2950, 1450, 1390, 1380, 1370, 1240, 1140, 1120, 1020, 1010, 980, 940, 900, 805, 765, 755 and 735; T^{c} 180°; $\Delta\nu$ 137 Hz; $\Delta G^{\#}$ 21.8 kcal.mol^{-1}.

$2^{1},2^{1}$-trans-$3^{1},4^{1},4^{1}$-pentamethyl-r-1-phenyl-4,4,5,5-tetrakistrifluoromethyl-1,3,2-dioxaphospholan-2-spiro-1^{1}-phosphetan. (234). (78%); Crystallised from methanol, m.p. 94-96°, (Lit. m.p. 95-97), δ 0.72 (3H,dd,J 1.5 and 7Hz), 1.35 (6H,d,J_{P-H}19Hz), 1.40 (6H,d,J_{P-H}17Hz) and 7.17 - 8.17 (5H,m); ^{31}P ($CDCl_3$) - 3.4 p.p.m.

From Pinacol

P-ethoxy-2,2,3,3,7,7,8,8-octamethyl-1,4,6,9-tetraoxa-5-phosphaspiro (4.4) nonane. (149, R = OEt)

(82%); δ 1.22 (24H,s), 1.30 - 1.54 (3H,m) and 4.05 (2H,m); ^{31}P (40-60° petroleum) + 42.4 p.p.m.; $^{m}/e$ 308, 248, 222, 208, 193, 166, 150, 138, 127 and 99; ν_{max} (neat film) 2990, 2940, 1470, 1385, 1295, 1155, 1080, 1015, 975, 930, 845, 820, 780 and 655; T^{c} the ring methyl groups gave two equal intensity signals; $\Delta\nu$ 5Hz, however the compound decomposed before coalescence.

P-ethylthio-2,2,3,3,7,7,8,8-octamethyl-1,4,6,9-tetraoxa-5-phosphaspiro(4.4)nonane. (149, R = SEt)

(85%); δ 1.22 (12H,s), 1.32 - 1.55 (3H,m) and 2.35 - 3.12 (2H,m); ^{31}P (neat) + 23.0 p.p.m.; $^{m}/e$ 263 (loss of SEt), 240, 224, 208, 181, 166, 143, 127, 105 and 99; ν_{max} (neat film) 3000, 2940, 1470, 1385, 1220, 1150, 1015, 970, 930, 890, 840, 800, 780, 715 and 655; T^{c} (Cl_3CBr) decomposition before coalescence; $\Delta\nu$ 4.5Hz.

From Ethylene Glycol

P-ethoxy-2,2,3,3-tetramethyl-1,4,6,8-tetraoxa-5-phosphaspiro(4.4)nonane. (144)

(76%); δ 1.22(12H,s), 1.25 - 2.42 (3H,m), 3.78-4.14(2H,m) and 3.65 (4H,d,J_{P-H}14Hz); ^{31}P (neat) + 34.9 p.p.m.; $^{m}/e$ 253, 208, 193, 166, 151, 137, 127, 125, 108, 99 and 82; ν_{max} (neat film) 2990, 2910, 1460, 1395, 1385, 1375, 1295, 1220, 1165, 1060, 1010, 985, 930, 880, 840, 775 and 735; T^{c} 92 $\pm$ 2°; $\Delta\nu$ 8Hz; $\Delta G^{\ddagger}$ 19.4 $\pm$ 0.2 kcal.mol^{-1}.

P-ethylthio-2,2,3,3-tetramethyl-1,4,6,8-tetraoxa-5-phosphaspiro(4.4)nonane. (139, R = SEt)

78%); δ 1.22 (12H,s), 1.28 - 2.56 (3H,m), 2.32 - 2.94 (2H,m) and 3.80 (4H,d,J_{P-H}14Hz); ^{31}P ($CDCl_3$) + 10.5 p.p.m.; $^{m}/e$ 268, 240, 224, 208, 181, 152, 125, 99 and 88; ν_{max} (neat film) 2990, 2940, 1460, 1395, 1385, 1370, 1270, 1215, 1160, 1065, 1010, 970, 920, 870, 830, 765, 680 and 650; T^{c} only one signal for the ring methyl protons in all solvents tried.

P-ethylthio-1,4,6,8-tetraoxa-5-phosphaspiro(4.4)nonane. (146, R = SEt) (57%); δ 1.0 - 1.52 (3H,m), 2.64 (2H,dq,J7 and 1.5Hz) and 3.90 (8H,d,J_{P-H}15Hz); ^{31}P ($CDCl_3$) + 7.3 p.p.m.; m/e 212, 201, 184, 156, 152, 138, 125, 109, 94 and 91; ν_{max} (neat film) 2985, 2900, 1475, 1270, 1240, 1055, 1030, 945, 925, 850, 745 and 705; T^c the methylene ring protons show only the phosphorus splitting in all solvents investigated, c.f. the P-ethoxy analogue[63].

From 3-Methylcatechol

The following phosphoranes were obtained as approximately 1 : 1 mixtures of the 4- and 7- methyl isomers and as such could not be prepared crystalline.

3^1,4(7)-Dimethyl-P-phenoxy-1,3,2-benzodioxaphosphole-2-spiro-2^1-(1,3,2)-oxazaphospholidine. (195)

(68%); δ 1.90 (3H,s), 2.30 (3H,s), 2.94 (6H,d,J_{P-H}10Hz), 2.68 - 4.16 (8H,m) and 6.48 - 7.28 (16H,m); ^{31}P ($CDCl_3$) + 41.2 p.p.m.; m/e 319, 276, 262, 246, 226, 218, 213, 163, 153, 140, 120, 104 and 94; ν_{max} (neat film) 3060, 3040, 2950, 2870, 1635, 1600, 1495, 1355, 1260, 1220, 1190, 1080, 1045, 960, 920, 870, 815, 760, 730 and 695; T^c 127 ± 2 for the 4- and 7- methyl groups; $\Delta\nu$ 35Hz; $\Delta G^{\#}$ 20.2 ± 0.2 kcal.mol^{-1}.

3^1,4(7)-Dimethyl-P-phenylthio-1,3,2-benzodioxaphosphole-2-spiro-2^1-(1,3,2)-oxazaphospholidine. (200)

(60%); δ 1.64 (3H,s), 2.40 (3H,s), 2.82 (6H,d,J_{P-H}10Hz), 2.46 - 3.38 (4H,m), 3.40 - 4.46 (4H,m), 6.05 - 6.74 (6H,m) and 6.84 - 7.45 (10H,m); ^{31}P ($CDCl_3$) + 23.4 p.p.m.; m/e 335, 261, 226, 212, 163, 120, 110, 104 and 84; ν_{max} (neat film) 3070, 2950, 2800, 1585, 1485, 1470, 1440, 1350, 1265, 1255, 1220, 1180, 1060, 1035, 955, 860, 815, 745 and 690; T^c 137 ± 2° for the 3^1-methyl group; $\Delta\nu$10Hz; $\Delta G^{\#}$ 21.7 ± 0.2 kcal.mol^{-1}.

3^1,4(7)-Dimethyl-P-dimethylamino-1,3,2-benzodioxaphosphole -2-spiro-2^1-(1,3,2)-oxazaphospholidine. (201)

(85%); δ 2.22 (3H,s), 2.26 (3H,s), 2.70 (12H,d,J_{P-H}11Hz), 2.90 (6H,d,J_{P-H}10Hz), 2.26 - 3.34 (6H,m), 3.48 - 4.22 (4H,m) and 6.80 (6H,m); ^{31}P ($CDCl_3$) + 37.9 p.p.m.; m/e 270, 226, 197, 185, 170, 153, 135 and 104; ν_{max} (neat film) 2960, 1600, 1490, 1480, 1360, 1270, 1185, 1080, 1000, 965, 870, 800, 765 and 745; T^c 180° for the 3^1-methyl group; $\Delta\nu$ 8Hz; $\Delta G^{\#}$ 724.3 kcal.mol^{-1}.

4(7)-Methyl-P-phenoxy-1,3,2-benzodioxaphosphole -2- spiro -2^1-(1,3,2)-oxathiophospholan. (203)

(66%); δ 1.66 (3H,s), 2.24 (3H,s), 2.85 (6H,d,J_{P-H}10Hz), 2.45 - 3.35 (4H,m), 3.40 - 4.32 (4H,m), 6.0 - 6.72 (6H,m) and 6.82 - 7.45 (10H,m); ^{31}P (1-bromonaphthalene) + 1.3 p.p.m.; m/e 324, 268, 262, 232, 181, 169, 135 and 94; ν_{max} (neat film) 2940, 2870, 1605, 1505, 1445, 1350, 1290, 1175, 1150, 1080, 980, 750 and 705; T^c 112 ± 2° for the 4,7-methyl signals; $\Delta\nu$ 45.7Hz; $\Delta G^{\#}$ 19.2 ± 0.1 kcal.mol^{-1}.

P,4(7)-dimethyl-P-phenoxy-P-phenyl-1,3,2-benzodioxaphosphole. (206)

(89%); δ 2.27 (6H,s), 2.35 (6H,d,J_{P-H}16Hz) and 6.60 - 8.10 (26H,m), at -95° in CH_2Cl_2 the 4-methylgroup split out into two signals; ^{31}P ($CDCl_3$) + 12.8 p.p.m.; m/e 338, 262, 245, 231, 215, 201, 182, 165, 153, 139 and 121; ν_{max} (neat film) 3045, 2950, 1600, 1490, 1440, 1350, 1270, 1225, 1200, 1125, 1080, 940, 895, 855, 760 and 690; T^c (CH_2Cl_2) - 65 ± 2°; $\Delta\nu$ 4.0 Hz; $\Delta G^{\#}$ 11.1 ± 0.1 kcal.mol^{-1}.

From 4-methycatechol

3^1,5(6)-Dimethyl-P-phenoxy-1,3,2-benzodioxaphosphole -2-spiro-2^1-(1,3,2)-oxazophospholidine.

(55%); δ 2.20 (3H,s), 2.26 (3H,s), 2.85 (3H,d,J_{P-H}9Hz),

2.95 (3H,d,J_{P-H}10Hz), 2.54 - 3.26 (4H,m), 3.35 - 4.20 (4H,m), 6.50 (6H,m) and 6.62 - 7.25 (10H,m); ^{31}P ($CDCl_3$) + 43.9 p.p.m.; m/e 319, 276, 262, 226, 218, 213, 163, 140, 120, 104 and 94; ν_{max}(neat film) 3040, 2950, 2870, 1610, 1595, 1505, 1490, 1345, 1260, 1220, 1080, 1040, 1025, 965, 945, 920, 870, 780, 755 and 690; No coalescence possible as only one signal for the 6-methyl group in all solvents tried.

3^1,5(6)-Dimethyl-P-phenylthio-1,3,2-benzodioxaphosphole-2-spiro-2^1-(1,3,2)-oxazophospholidine (200)

(70%); δ 2.18 (3H,s), 2.20 (3H,s), 2.80 (6H,d,J_{P-H}10Hz), 2.42 - 3.30 (4H,m), 3.35 - 4.35 (4H,m), 6.15 - 6.80 (6H,m) and 6.95 - 7.40 (10H,m); ^{31}P ($CDCl_3$) + 22.5 p.p.m.; m/e 335, 261, 226, 212, 163, 120, 110, 104 and 84; ν_{max}(neat film) 3050, 2920, 2870, 1590, 1510, 1485, 1445, 1345, 1285, 1260, 1220, 1190, 1125, 1070, 1030, 965, 950, 865, 805, 750, 705 and 695; T^c only one signal for the 5-methyl group in all solvents tried.

3^1,5(6)-Dimethyl-P-dimethylamino-1,3,2-benzodioxaphosphole-2-spiro-2^1-(1,3,2)-oxazaphospholidine (202)

(70%); δ 2.26 (6H,s), 2.70 (12H,d,J_{P-H}10Hz), 2.88 (6H,d,J_{P-H}9Hz), 2.60 - 3.40 (4H,m), 3.50 - 4.20 (4H,m) and 6.28 - 6.86 (6H,m); ^{31}P ($CDCl_3$) + 33.8 p.p.m.; m/e 270, 226, 197, 185, 170, 153, 135 and 104; ν_{max}(neat film) 2940, 2830, 1650, 1610, 1495, 1450, 1345, 1250, 1075, 990, 850, 755 and 725, T^c decomposition occurred at 111°.

5(6)-Methyl-P-phenoxy-1,3,2-benzodioxaphosphole-2-spiro-2^1-(1,3,2) - oxathiophospholan

(75%); δ 2.12 (3H,s), 2.20 (3H,s), 2.52 - 3.18 (4H,m), 3.38 - 4.42 (4H,m), 6.10 - 6.54 (6H,m) and 6.64 - 7.22 (10H,m); ^{31}P (1-bromonaphthalene) - 1.4 p.p.m; m/e 324, 268, 262, 232, 181, 169, 135, 94 and 77; ν_{max}(neat film) 2940, 2870, 1605, 1505, 1445, 1350, 1290, 1175, 1150, 1080, 980, 750 and 705; T^c 82 ± 2° for the 5(6)-methyl signals; $\Delta\nu$ 7.6 Hz; $\Delta G^{\#}$ 18.9 ± 0.1 kcal.mol^{-1}.

From 4-Fluorocatechol

5(6)-Fluoro-3^1-methyl-P-phenoxy-1,3,2-benzodioxaphosphole -2-spiro-2^1-(1,3,2)-oxazaphospholidine

(60%); δ 2.86 (6H,d,J_{P-H}10Hz), 2.35 - 4.32 (8H,m), 6.08 - 6.50 (6H,m) and 6.55 - 7.25 (10H,m); ^{31}P ($CDCl_3$) + 41.3 p.p.m.; ^{19}F ($CDCl_3$) + 55.96 (1F,m) and + 58.97 (1F,m) p.p.m.; m/e 323, 285, 230, 208, 206, 189, 164, 127, 120, 104 and 94; ν_{max}(neat film) 3050, 2920, 2850, 1610, 1595, 1565, 1505, 1380, 1255, 1205, 1140, 1080, 1025, 960, 860, 790, 765, 690 and 650; T^c 168 ± 2° for the 5(6)-fluoro signals; $\Delta\nu$ 300Hz; $\Delta G^{\#}$ 20.3 ± 0.1 kcal.mol^{-1}.

Reaction of 2-Substituted-4,4,5,5-tetramethyl-1,3,2-dioxaphospholans with 3-Benzylidene-2,4-pentanedione

A solution of 3-benzylidene-2,4-pentanedione (0.05 mol) and the 2-substituted-4,4,5,5-tetramethyl-1,3,2-dioxaphospholan (0.05 mol) in a mixture of benzene and hexane (10 ml of a 1 : 4 mixture v/v) was allowed to react at 40° overnight. Evaporation of the solvent gave near quantitative yields of the 1 : 1 adduct. Recrystallisation from light petroleum gave predominently the trans isomer. The following 1 : 1 adducts were prepared by this method.

8-Acetyl-2,2,3,3,7-pentamethyl-r-9-phenyl-trans-5-ethoxy-1,4,6-trioxa-5-phosphaspiro (4.4) non-7-ene. (155, R = OEt) Recrystallised from light petroleum, m.p. 108-109°; δ 0.21 (3H,s), 0.98 (3H,s), 1.26 (3H,s), 1.35 (3H,s), 1.34 - 1.60 (3H,m), 1.96 (3H,s), 2.60 (3H,d,J_{P-H}1Hz), 3.75 - 4.4 (3H,m) and 7.30 (5H,s); ^{31}P (CH_2Cl_2) + 10.9 p.p.m.; m/e 380, 338, 323, 298, 280, 265, 255, 209, 188, 171, 154 and 127; ν_{max}1660, 1565, 1495, 1320, 1150, 1060, 975, 930, 770, 750, 700, 670 and 640; $^{1st}T^c$ (chlorobenzene) 80 ± 3°; $\Delta\nu$14Hz; $\Delta G^{\#}$ 18.3 ± 0.2 kcal.mol^{-1}; $^{2nd}T^c$ 100 ± 3°; $\Delta\nu$108 Hz; $\Delta G^{\#}$ 18.0 ± 0.2

kcal.mol^{-1}; (Found C, 63.2; H, 7.75; P, 7.85. $C_{20}H_{29}O_5P$ requires C,63.15; H,7.7; P,8.15%).

8-Acetyl-2,2,3,3,7-pentamethyl-r-9-phenyl-cis-5-ethylthio-1,4,6-trioxa-5-phosphaspiro (4.4) non-7-ene (156, R = -SEt) Recrystallised from light petroleum, m.p. 136 - 137°; δ(chlorobenzene) 0.7 (3H,dt,J 3 and 8 H_3), 1.08 (3H,s), 1.18 (3H,s), 1.22 (3H,s), 1.26 (3H,s), 1.84 (3H,s), 2.36 (3H,d,J_{P-H}1H_3), 1.94 - 2.5 (2H,m) and 4.36 (1H,d,J_{P-H}24H_3); ^{31}P (chlorobenzene) - 2.9 p.p.m.; ^{m}/e 396, 353, 335, 297, 253, 224, 208, 189, 171, 147 and 129; ν_{max} 1660, 1395, 1375, 1320, 1155, 1135, 965, 925, 820, 740, 700 and 660; ^{1st} T^c (o - dichlorobenzene) 85 ± 3°; $\Delta\nu$35H_3; $\Delta G^{\#}$ 18.0 ± 0.2 kcal.mol^{-1}; ^{2nd} T^c 100 ± 3°; $\Delta\nu$112 H_3; $\Delta G^{\#}$ 17.9 ± 0.2 kcal.mol^{-1}; (Found: C,60.5; H, 7.4; $C_{20}H_{29}O_4PS$ requires C, 60.6; H, 7.3%). The trans ethylthio analogue (155, R = SEt) had δ 0.23 (3H,s), 0.82 (3H,s), 1.25 (3H,s), 1.33 (3H,s), 1.88 (3H,s), 2.38 (3H,d,J_{P-H}1 H_3), 4.08 (1H, d,J_{P-H} 17.5 H_3) and 7.08 (5H,s).

8-Acetyl-2,2,3,3,7-pentamethyl-r-9-phenyl- trans-5-trimethylsiloxy -1,4,6-trioxa-5-phosphaspiro (4.4) non-7-ene (182) Recrystallised from ethylacetate/light petroleum, m.p. 145 - 146°, change of crystal form between 130 - 133°; δ 0.14 (3H,s), 0.23 (9H,s), 0.92 (3H,s), 1.17 (3H,s), 1.28 (3H,s), 1.89 (3H,s), 2.48 (3H,d,J_{P-H}1 H_3), 4.03 (1H,d,J_{P-H}21H_3) and 7.18(5H,s); ^{31}P ($CDCl_3$) + 18.2 p.p.m.; ^{m}/e 424, 409, 381, 366, 341, 324, 309, 299, 281, 253, 248, 236, 185, 171, 155, 147 and 121; ν_{max} 1665, 1500, 1380, 1260, 1155, 1040, 985, 940, 850, 760, 700 and 695; T^c 70 ± 5°;$\Delta\nu$12H_3; $\Delta G^{\#}$ 17.9 ± 0.2 kcal.mol^{-1}; (Found: C, 59.45; H, 7.80; P, 7.65. $C_{27}H_{33}O_5PS$: requires C, 59.0; H, 7.80; P, 7.30%). The cis - trimethylsiloxy analogue (188) had δ 0.19 (9H,s), 1.10 (3H,s), 1.32 (3H,s), 1.43 (3H,s), 1.48 (3H,5), 1.86 (3H,s), 2.39 (3H,d,J_{P-H} 1 H_3), 4.01 (1H,d, J_{P-H}20H_3) and 7.18 (5H,s).

Preparation of P-trimethylsiloxy-2,2,3,3-tetramethyl-7,7,8,8-tetrakistrifluoromethyl-1,4,6,9-tetroxa-5-phosphaspiro(4.4) nonane (175)

Hexafluoroacetone (0.3 mol) was passed into a stirred solution of 2-trimethylsiloxy-4,4,5,5-tetramethyl-1,3,2-dioxaphospholan (0.1 mol) in ether (30 ml) at -78°C. The solution was kept at -78°C for 1h, and then the solvent removed under reduced pressure. The spirophosphorane was then extracted with light petroleum.

δ 0.27 (9H,s), 1.42 (6H,s) and 1.56 (6H,s); ^{31}P (CH_2Cl_2) + 42.7 p.p.m.; ^{19}F (1-bromonophthalene) + 4.4 (6F,m) and 4.8 (6F,m) p.p.m.; $^{m}/e$ 568, 553, 449, 511, 464, 454, 417, 397, 386, 304, 236, 197, 155, 121, 105 and 97; ν_{max}(neat film) 3000, 1460, 1150 - 1325, 1020, 990, 950, 915, 860, 815, 765, 715 and 660; T^c 168 ± 2°; $\Delta\nu_{40H_z}$; $\Delta G^{\#}$ 22.2 ± 0.1 kcal.mol^{-1}.

Preparation of 4,4,5,5-tetramethyl-1,3,2-dioxaphospholan-2-oxide (181)

This was prepared from 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholan by the method of Zwierzak[194]. (97%), m.p. 104-106°, (Lit. m.p. 104-106°)[194].

Preparation of 2-trimethylsiloxy-4,4,5,5-tetramethyl-1,3,2-dioxaphospholan (168)

This was prepared according to the procedure of Issleid and Walther[147]. To a stirred solution of 4,4,5,5-tetramethyl-1,3,2-dioxaphospholan-2-oxide (0.15 mol), triethylamine (0.25 mol) in benzene (150 ml) was added freshly distilled chlorotrimethylsilane (0.25 mol). After addition the mixture was heated under reflux for 1h, and then left to stand overnight. Filtration, removal of the benzene, excess triethylamine and chlorotrimethylsilane followed by reduced pressure distillation of the residue gave the title compound. (70%); $b_{0.05}$ 50-55°; δ 0.20 (9H,s), 1.22 (6H,s) and 1.36 (6H,s); ^{31}P (CH_2Cl_2) - 126.9 p.p.m.;

^{m}/e 236, 210, 155, 149, 122 and 106; ν_{max} (neat film) 2985, 1400, 1380, 1260, 1150, 985, 950, 900, 855, 805, and 760.

Preparation of 2-trimethysiloxy-4,4,5,5-tetramethyl-1,3,2-dioxaphospholan-2-sulphide (169)

A mixture of 2-trimethylsiloxy-4,4,5,5-tetramethyl-1,3,2-dioxaphospholan (0.02 mol), sulphur (0.02 mol) in benzene, (20 ml) was refluxed until the sulphur had disappeared. The benzene was removed and the residue recrystallised from 40-60° light petroleum. (96%); m.p. 50-53°; δ 0.30 (9H,s), 1.32 (6H,s) and 1.40 (6H,s); ^{31}P (CH_2Cl_2) - 54.6 p.p.m.; ^{m}/e 268, 253, 210, 187, 171, 153, 137, 131, 121 and 106; ν_{Max} 1400, 1380, 1260, 1145, 1035, 945, 855, 800, 765 and 740; (Found: C, 40.65; H,7.55; P,11.85. $C_9H_{21}O_3PSiS$ requires C,40.30; H,7.85; P,11.55%).

Preparation of 2,2-trans-3,4,4-pentamethyl-r-1-phenylphosphetan-1-oxide (227)

Was prepared by the method of Hawes and Trippett[184]. m.p. 125°-126°; δ 1.05 (3H,dd,J 1.5 and 7Hz), 1.12 (6H,d,J_{P-H}19Hz), 1.43 (6H,d,J_{P-H}16Hz), 1.90 - 2.30 (1H,m), 7.45 - 7.70 3H,m) and 7.83 - 8.20 (2H,m); ^{31}P ($CDCl_3$) -53.0 p.p.m.

Preparation of 2,2-cis-3,4,4-pentamethyl-r-1-phenylphosphetan-1-oxide (230)

Was prepared by the method of Corfield[155]. m.p. 116-117°; δ 1,03 (3H,dd,J 1.5 and 7Hz), 1.23 (6H,d,J_{P-H}19Hz), 1.42 (6H,d, J_{P-H} 17Hz), 1.9 - 2.8 (1H,m) and 7.40 - 8.0 (5H,m); ^{31}P ($CDCl_3$) - 55.5 p.p.m.

Preparation of r-1-chloro-2,2-trans-3,4,4-pentamethylphosphetan-1-oxide

Was prepared by the method of McBride, Jungermann, Killheffer and Clutter[185]. (60%); m.p. 72-75°.

Preparation of r-1-benzyl-2,2-trans-3,4,4-pentamethylphosphetan-1-oxide.

Was prepared by the method of Corfield[155]. m.p. 180-182°.

Preparation of r-1-chloro-2,2-cis-3,4,4-pentamethylphosphetan-1-oxide

Was prepared by the method of Cremer and Trivedi.[186]

Preparation of r-1-benzyl-2,2-cis-3,4,4-pentamethylphosphetan-1-oxide (239)

This was prepared as a cis rich mixture of the cis and trans benzylpentamethylphosphetan-1-oxides by the method of Gray and Cremer[158]. (The ratio of cis : trans was 60 : 40 as determined by ^{1}H n.m.r. in pyridine solution.)

Trichlorosilane reduction of phenyl and benzylpentamethylphosphetan-1-oxides

The cis and trans phenyl and benzylpentamethylphosphetan-1-oxides were reduced stereospecifically to the corresponding phosphetans, using trichlorosilane, by the method of Corfield.[155] The phosphetans were used after removal of the solvent without any further purification.

Preparation of r-1-dimethylamino-2,2-trans-3,4,4-pentamethyl-phosphetan (244)

This was prepared by the method of Oram,[156] b_6 71-73°.

Reaction of r-1-benzyl-2,2-trans-3,4,4-pentamethylphosphetan with perfluoropinacol in the presence of N-chlorodi-isopropylamine

The reaction was carried out in the usual way, however no spirophosphorane was formed. The reaction mixture after leaving overnight was chromatographed on basic alumina (40:1) using ether as the elvent, and gave the following compounds. r-1-Benzyl-2,2-trans-3,4,4-pentamethylphosphetan-1-oxide (219)

Recrystallised from light petroleum, m.p. 180-182°, (Lit. m.p 180-182°)[155]; δ 1.10 (3H,dd,J 1.5 and 7Hz), 1.35 (6H,d,J_{P-H}17Hz), 1.45 (6H,d,J_{P-H}16Hz), 3.44 (2H,d,J_{P-H}10Hz) and 7.12 - 7.66 (5H,m).

r-1- -chlorobenzyl-2,2-trans-3,4,4-pentamethylphosphetan-1-oxide (220) Recrystallised from light petroleum, m.p. 173-174°;

δ 0.9 (3H,m), 1.20 (6H,m), 1.52 (6H,m), 2.16 (1H,m), 5.2 (1H,d,J_{P-H}4Hz) and 7.1 - 7.75 (5H,m); ^{31}P ($CDCl_3$) - 60.7 p.p.m.; m/e 286, 284, 269, 250, 232, 216, 180, 178, 159, 141, 132, 125, 117 and 97; ν_{max} 1495, 1240, 1190, 1160, 1075, 930, 790, 725, 700 and 655; (Found: C, 63.2; H,7.75; Cl, 12.6. $C_{15}H_{22}ClOP$ requires C,63.3; H,7.75; 12.5%.) r-1-α,α-Dichlorobenzyl-2,2-trans-3,4,4-pentamethylphosphetan-1-oxide (221)

Recrystallised from light petroleum, m.p. 116-116.5°; δ 0.88 (3H,dd,J 1.5 and 7Hz), 1.28 (6H,d,J_{P-H}16Hz), 1.44 (6H,d,J_{P-H} 17Hz), 2.15 (1H,m) and 7.05 - 7.98 (5H,m); ^{31}P ($CDCl_3$) - 64.8 p.p.m; m/e 324, 322, 320, 318, 284, 250, 235, 178, 159, 141, 103 and 97; ν_{max} 1495, 1450, 1245, 1205, 1170, 845, 775, 740, 695 and 640; (Found: C,56.5; H,6.5; Cl,22.6. $C_{15}H_{21}Cl_2OP$ requires C,56.4; H,6.6; Cl,22.3%).

The following compounds were prepared from the corresponding phosphetans and catechol using N-chlorodi-isopropylamine.

P-r-phenyl-$2^1,2^1$- trans -$3^1,4^1,4^1$-pentamethyl-1,3,2,-benzodioxaphosphole-2-spiro-1^1-phosphetan (229)

Recrystallised from light petroleum, (83%); m.p. 124-125°; δ 0.85 (3H,dd,J 2 and 7Hz), 1.26 (6H,d,J_{P-H}19Hz), 1.44 (6H,d,J_{P-H} 16Hz), 1.9(1H,m), 6.62 (4H,s) and 7.14 - 7.86 (5H,m); ^{31}P ($CDCl_3$) + 5.7 p.p.m.; m/e 328, 256, 236, 221, 216, 168, 166, 139, 125, 119, 110, 108, 97 and 77; ν_{max} 1495, 1255, 1115, 1020, 880, 830, 740, 720 and 655; (Found: C,73.2; H,7.6; P, 9.5. $C_{20}H_{25}O_2P$ requires C,73.2; H,7.6; P,9.5%).

P-r-phenyl-$2^1,2^1$- cis -$3^1,4^1,4^1$-pentamethyl-1,3,2-benzodioxaphosphole-2-spiro-1^1-phosphetan (231)

Recrystallised from 40-60° petroleum at -20°C, (80%); m.p. 65-67°; δ 0.84 (3H,dd,J 2 and 4Hz), 1.20 (6H,d,J_{P-H}18Hz), 1.40 (6H,d,J_{P-H}15Hz), 2.02 (1H,m), 6.5 (4H,s) and 7.0 - 7.7 (5H,m); ^{31}P ($CDCl_3$) + 1.9 p.p.m.; m/e 328, 258, 243, 216, 168, 166, 150, 139, 119, 108, 97, 92 and 79; ν_{max} 1495, 1285, 1255,

1140, 1115, 1100, 1020, 880, 830, 740, 720, 700 and 650; (Found: C,72.9; H,7.7. $C_{20}H_{25}O_2P$ requires C,73.2; H,7.6%).

P-r-benzyl-2^1,2^1-trans-3^1,4^1,4^1-pentamethyl-1,3,2-benzodioxaphosphole-2-spiro-1^1-phosphetan (234)

Recrystallised from light petroleum, (64%); m.p. 140-141°; δ 0.82 (3H,dd, J 2 and 7Hz), 1.35 (6H,d,J_{P-H}18Hz) 1.30 (6H,d,J_{P-H} 16Hz), 3.28 (2H,d,J_{P-H}7Hz), 6.34 (4H,s) and 6.82 (5H,s); ^{31}P ($CDCl_3$) + 4.2 p.p.m.; m/e 342, 272, 257, 250, 230, 182, 180, 163, 139, 110, 97 and 92; ν_{max} 1600, 1460, 1250, 1100, 1010, 905, 880, 830, 775, 730, 695 and 650; (Found: C,73.55; H,7.9; P,8.95. $C_{21}H_{27}O_2P$ requires C,73.7; H,7.9; P,9.1%).

P-r-benzyl-2^1,2^1-cis-3^1,4^1,4^1-pentamethyl-1,3,2-benzodioxaphosphole-2-spiro-1^1-phosphetan (232)

This was prepared from the cis rich sample of the phosphetan (60 : 40) and on subsequent work-up and extraction with 40 - 60° petroleum at -20°C gave the title compound. The isomer ratio was determined by ^1H n.m.r. using a Jeol PS100 machine and 1-bromonaphthalene as solvent. The isomer ratio of tne adduct was also found to be 60 : 40. δ (1-bromonaphthalene) 0.80 (3H,dd,J 2 and 7Hz), 1.38 (6H,d,J_{P-H}19Hz), 1.32 (6H,d,J_{P-H}18Hz); 3.28 (2H,d,J_{P-H}7Hz); m/e 342, 272, 257, 250, 230, 182, 180, 163, 139, 110, 97 and 92.

P-r-1-(dimethylamino)-2^1,2^1-trans-3^1,4^1,4^1-pentamethyl-1,3,2-benzodioxaphosphole-2-spiro-1^1-phosphetan (246)

Recrystallised from light petroleum, (90%); m.p. 120°; δ 0.80 (3H,dd,J 1.5 and 7Hz), 1.25 (6H,d,J_{P-H}18Hz), 1.30 (6H,d, J_{P-H}17Hz), 1.80 (1H,m), 2.56 (6H,d,J_{P-H}12Hz) and 6.65 (6H,s); ^{31}P($CDCl_3$) - 8.0 p.p.m.; m/e 295, 280, 251, 225, 198, 182, 156, 139, 97 and 92; ν_{max}(neat film) 2900, 2805, 1620, 1495, 1360, 1285, 1260, 1210, 1100, 1012, 975, 880, 830, 760, 740, 720 and 640; (Found C,65.3; H,8.90; P,9.60; N,4.75. $C_{16}H_{26}NO_2P$ requires C,65.1; H,8.80; P,10.50; N,4.75%).

Preparation of 2-dimethylamino-4,4,5,5-tetramethyl-1,3,2-dioxaphospholan (264)

This was prepared by the method of Bone[44] (90%), $b_{1.0}$ 54-57°, (Lit. $b_{2.0}$ 63°)[63]; δ 1.23 (6H,s), 1.30 (6H,s) and 2.64 (6H,d,J_{P-H}8Hz).

Preparation of 4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaphospholan (266)

To a well stirred solution of pyridine (0.4 mol) in ether (1000 ml) at 0°C, was added dropwise and simultaneously a solution of dichlorophenylphosphine (0.2 mol) in ether (50 ml) and a solution of pinacol (0.2 mol) in ether (50 ml). After addition the mixture was left overnight, filtered, the solvent removed and the residue distilled under reduced pressure. (51%); $b_{0.3}$ 90-94°, Lit. $b_{0.5}$99-115°[141], (Lit. m.p. 103-104°)[187]; δ 1.25 (6H,s), 1.40 (6H,s) and 6.60 - 7.17 (5H,m).

Preparation of 2-t-butyl-4,4,5,5-tetramethyl-1,3,2-dioxaphospholan (272)

Sodium hydride (0.2 mol) was suspended in ether (50 ml) and to this was added a solution of pinacol (0.1 mol) in ether (20 ml). The mixture was refluxed for 1.5h, cooled, and then a solution of t-butyldichlorophosphine (0.1 mol) in ether (20 ml) added, the mixture was then refluxed for a further 3h. After filtration, removal of solvent, reduced pressure distillation gave the title compound as an extremely air-sensitive colourless liquid. (52%); $b_{0.7}$ 48-54°; δ 0.97 (9H,d,J_{P-H}12Hz) and 1.36 (12H,s); ^{31}P ($CDCl_3$) - 204.1 p.p.m.; m/e 204, 164, 149, 139, 123, 106, 101 and 94; ν_{max} (neat film) 2995, 1490, 1475, 1405, 1270, 1150, 975, 900, 805, 760 and 680.

Reactions of Acrylic Acid with Trivalent Phosphorus Compounds

To a stirred solution of the phosphorus compound (5 mmol) in ether (20 ml) was added a solution of acrylic acid (5 mmol) in ether (5 ml) and the mixture left stirring overnight. The

ether was removed and the residue taken-up in light petroleum. In this way the following 1 : 1 adducts were prepared.

P-phenyl-2,2,3,3-tetramethyl-1,4,6-trioxa-5-phospha (5-P^V) - spiro (4.4) non-7-one (267)

Recrystallised from ethyl acetate-light petroleum. (100%); m.p. 131-131.5°; δ 0.80 (3H,s), 1.16 (3H,s), 1.22 (3H,s), 1.31 (3H,s), 1.74 - 2.96 (4H,m), 7.01 - 7.46 (3H,m) and 7.52 - 8.08 (2H,m); ^{31}P ($CDCl_3$) + 10.7 p.p.m.; ^{13}C-22.87, -23.52, -24.30, -24.49, -24.88, -26.31, -27.61, -33.92, -77.0 (J_{P-C}80 Hz), -127.48, -128.19, -128.52, -128.97, -131.05, -131.25, -131.90, -132.61 and -172.8 (J_{P-C}24 Hz) p.p.m.; $^m/e$ 296, 281, 252, 238, 224, 197, 180, 171, 152, 142 and 124; ν_{max} 1725, 1440, 1425, 1305, 1155, 980, 920, 845, 760, 720 and 700; 1st T^c (CCl_3Br) 63 ± 3°; $\Delta\nu$9Hz; $\Delta G^{\#}$ 17.7 ± 0.1 kcal.mol^{-1}; 2nd T^c (CCl_3Br) 77 ± 1°; $\Delta\nu$35Hz; $\Delta G^{\#}$ 17.5 ± 0.1 kcal.mol^{-1}; (Found: C,60.35; H,7.24, P,10.40. $C_{15}H_{21}O_4P$ requires C,60.80; H,7.15; P,10.45%).

P-dimethylamino-2,2,3,3-tetramethyl-1,4,6-trioxa-5-phospha-(5-P^V) - spiro (4.4) non-7-one. (265)

(85%); δ 1.23 (6H,s), 1.40 (3H,s), 1.50 (3H,s), 2.71 (6H,d, J_{P-H}10Hz) and 2.00 - 3.14 (4H,m); ^{31}P ($CDCl_3$) + 18.7 p.p.m.; $^m/e$ 264, 263, 237, 219, 182, 164, 147, 137, 119 and 100; ν_{max}(neat film) 2995, 1730, 1610, 1380, 1275, 1150, 965, 940 and 885; T^c decomposition before coalescence.

P-t-butyl-2,2,3,3-tetramethyl-1,4,6-trioxa-5-phospha(5-P^V) -spiro (4.4) non-7-one (273)

Recrystallised from ethyl acetate - light petroleum. (100%); m.p. 113.5 - 115°; δ 1.28 (9H,d,J_{P-H}18Hz), 1.30 (12,H,s) and 2.00 - 2.89 (4H,m); ^{31}P ($CDCl_3$) - 10.5 p.p.m.; $^m/e$ 276, 261, 232, 218, 204, 176, 161, 148, 134, 120 and 100; ν_{max} 1715, 1380, 1210, 1160, 1010, 985, 920, 835, 780, 755 and 705; T^c singlet for the pinacol methyl's in all solvents tried; (Found: C,56.35; H,9.00; P,11.10. $C_{13}H_{25}O_4P$ requires C,56.50; H,9.10;

P,11.20%).

Reaction between Acrylic acid and 2-Trimethylsiloxy-4,4,5,5-tetramethyl-1,3,2-dioxaphospholan.

This reaction was carried out in the usual way but no adduct was formed, instead 4,4,5,5-tetramethyl-1,3,2-dioxaphospholan-2-oxide was recovered in a quantitative yield. M.p. and mixed m.p. 104-106°; δ 1.40 (6H,s), 1.52 (6H,s) and 5.44 (1H,d,J_{P-H}689 Hz)

Preparation of Ethyl-3-(diethoxyphosphonyl) propionate.

(291)

To a solution of triethyl phosphite (0.1 mol) in ether (50 ml) at 0°C was added acrylic acid (0.1 mol) and the mixture was allowed to reach room temperature slowly, and left overnight. Removal of the ether, followed by reduced pressure distillation gave the title compound. (45%); $b_{0.05}$100-110°) (Lit.$b_{0.5}$111-112)[164]; δ 1.33 (6H,dt,J 4 and 7Hz), 1.40 (3H,m), 1.80 - 3.04 (4H,m) and 3.66 - 4.60 (6H,m); ^{31}P ($CDCl_3$) - 30.6 p.p.m., there was no phosphorane species detactable by ^{31}P F.T. n.m.r.

Preparation of Isopropyl-3-(di-isopropoxyphosphonyl) propionate

To a solution of tri-isopropyl phosphite (0.1 mol) in ether (50 ml) at 0°C was added acrylic acid (0.1 mol). The mixture was then allowed to reach room temperature slowly and then left overnight. Removal of solvent, followed by reduced pressure distillation gave the title compound. (70%); $b_{0.05}$105-110°; δ 1.34 (9H,d,J_{H-H}5Hz), 1.70 - 2.84 (4H,m) and 4.37 - 5.10 (3H,m); ^{31}P ($CDCl_3$) - 28.4 p.p.m.; m/e 280, 239, 197, 179, 163, 155, 137, 120, 109 and 99; ν_{max} (neat film) 2900, 1735 1470, 1375, 1245, 1180, 1110, 980, 890 and 770.
There was no phosphorane species detectable by ^{31}P F.T. n.m.r.
After distillation the residue was recrystallised from ethyl acetate - light petroleum at -20°C to give 3 - Di-isopropoxy-phosphonyl propionic acid.

(20%); δ 1.30 (6H,d,J_{H-H}6Hz); 1.72 - 2.92 (4H,m), 4.30 - 5.09 (2H,m) and 11.44 (1H,s); ^{31}P ($CDCl_3$) -27.2 p.p.m., m/e 238, 217, 197, 179, 163, 155, 137, 121, 109 and 99; ν_{max} 2720, 2640, 2565, 2500, 1730, 1265, 1215, 1180, 1105, 1010, 995, 815, 775, 760 and 710.

Preparation of Diphenylphosphine (310)

This was prepared by the method of Kuchen and Buckwald[188]. (97%); $b_{0.5}$122-118°, (Lit. b_{16}156-157° [188]).

Preparation of P-trimethylsilyl-P,P-diphenylphosphine (311)

To a solution of diphenylphosphine (0.08 mol) in dry T.H.F. was added an excess of sodium wire (5g). After the initial effervescence had finished the mixture was refluxed for 2h and the excess sodium removed. The solution was colled to 0°C and freshly distilled trimethylchlorosilane (0.08 mol) added dropwise, with stirring, after addition the mixture was refluxed for 1h and then allowed to cool. The precipitate was filtered off in the dry-box, the solvent removed and the residue distilled under reduced pressure. (58%); $b_{0.6}$ 126-128°, (Lit $b_{0.6}$122-126° [189]); δ 0.20 (9H,d,J_{P-H}5Hz) and 7.10 - 7.65 (10H,m); ^{31}P ($CDCl_3$) + 54.5 p.p.m., (Lit. ^{31}P (CH_3CN) + 53.7 p.p.m.[189]).

Preparation of P-trifluoromethyl-P,P-diphenylphosphine (312)

To a stirred solution of P-trimethylsilyl-P,P-diphenylphosphine (0.02 mol) in ether (20 ml) at -78°C was added a previously trapped amount of trifluoro-iodomethane (0.02 mol). The reaction mixture was then allowed to reach room temperature, the ether removed and the residue distilled under reduced pressure. (78%); b_{15}150-160°, (Lit. b 255-257[168]); ^{19}F (CH_2Cl_2) - 7.83 (3F,d,J_{P-F}72Hz) p.p.m.; ν_{max}(neat film) 3060, 3000, 1585, 1485, 1440, 1275, 1150, 1105, 1070, 1027, 1000, 745 and 695.

Preparation of P-cyano-P,P-diphenylphosphine

To a solution of chlorodiphenylphosphine (0.05 mol) in xylene

(25 ml) was added anhydrous silver cyanide (0.05 mol). The mixture was then heated under reflux overnight. Filtration, removal of solvent, followed by reduced pressure distillation gave the title compound. (56%); $b_{1.5}$ 180-182°, (Lit. $b_{13.5}$ 187-188°)[190]; ν_{max} (neat film) very small band at 2190 cm^{-1}.

Preparation of P-cyano-P,P-diphenylphosphine sulphide

This was prepared by refluxing P-cyano-P,P-diphenylphosphine (0.01 mol) with phosphorusthiochloride according to the method of Johns and DiPietro[191]. The sulphide was recrystallised from ethyl acetate-light petroleum in 98% yield, m.p. 49-50°, (Lit. m.p. 50-50.2° [191]); ν_{max} 2180 (C≡N).

Preparation of Hexafluorobiacetyl

This was prepared by the method of Ramirez and Kugler,[192] (12%)

Preparation of 1,3,2-Dioxaphospholens from Hexafluorobiacetyl and Trivalent Phosphorus Compounds

Hexafluorobiacetyl (5 mmol) was allowed to distil into a stirred solution of the phosphine (5 mmol) in dichloromethane (5 ml) at -78°C, the apparatus being fitted with a dry-ice condenser. After addition the reaction mixture was allowed to come to room temperature over a period of 0.5h. The solvent was removed under reduced pressure and the residue taken up in light petroleum. In this way the following 1 : 1 adducts were prepared in almost quantitative yields.

P-cyano-P,P-diphenyl-4,5-bistrifluoromethyl-1,3,2-dioxaphospholene. (309, R=CN)

δ 7.1 - 7.9 (10H,m); ^{31}P (CH_2Cl_2) + 43.6 p.p.m.; ^{19}F (CH_2Cl_2) + 10.31 (3F,m) and + 13.06 (3F,m) p.p.m.; $^m/_e$ 405, 384, 379, 342, 327, 298, 260, 201, 183, 154, 143 and 110; ν_{max} (neat film) 3350, 2200, 1710, 1600 1495, 1450, 1360, 1230-1190, 1000, 750 and 700; T^c (CH_2Cl_2) 30-31°; $\Delta\nu$ 259 Hz; $\Delta G^{\#}$ 13.9 ± 0.1 $kcal.mol^{-1}$.

P-chloro-P,P-diphenyl-4,5-bistrifluoromethyl-1,3,2-dioxaphospholene (309, R=Cl)

δ 7.0 - 7.9 (10H,m); ^{31}P (CH_2Cl_2) + 4.9 p.p.m.; ^{19}F (CH_2Cl_2) + 0.42 (3F,m) and+3.08 (3F,m) p.p.m. at -40°C; $^m/e$ 416, 414, 395, 380, 326, 298, 235, 220, 201, 183, 154, 143 and 107; ν_{max} (neat film) 3350, 1790, 1600, 1490, 1450, 1250-1200, 1005, 950, 730 and 695; T^c (CH_2Cl_2) - 3 ± 2°; $\Delta\nu$ 255 Hz; $\Delta G^{\ddagger}$ 12.3 ± 0.1 kcal.mol^{-1}.

The reaction of hexafluorobiacetyl with diphenylphosphine, P-trimethylsilyl-P,P-diphenylphosphine, P-trifluoromethyl-P,P-diphenylphosphine and P-2,4,6-trimethylbenzoyloxy-P,P-diphenylphosphinite gave no pentacovalent phosphorus adducts.

Preparation of P-2,4,6-trimethylbenzoyloxy -P,P-diphenyl phosphinite

To an ice-cold,stirred solution of chlorodiphenylphosphine (0.05 mol) and triethylamine (0.05 mol) in ether (150 ml) was slowly added a solution of 2,4,6-trimethylbenzoic acid (0.05 mol) in ether (50 ml). After addition the mixture was stirred at room temperature for 1h, then refluxed for a further 1h. Filtration, removal of the solvent and recrystallisation of the residue from ethyl acetate - light petroleum gave the title compound. (87%); m.p. 112-114°; δ 2.25 (6H,s), 2.35 (3H,s), 6.90 (2H,s) and 7.30 - 8.20 (10H,m); ^{31}P (CH_2Cl_2) - 103.2 p.p.m.; $^m/e$ 348, 325, 319, 293, 262, 219, 201, 183, 164 and 146; ν_{max} 1745, 1710, 1610, 1440, 1250, 1230, 1160, 1130, 1015, 995, 950, 835, 760, 720 and 695; (Found: C,75.45; H,6.00; P,8.89. $C_{22}H_{21}O_2P$ requires C,75.85; H,6.08, P,8.89%).

Preparation of P-2,4,6-trimethylbenzoyloxy-P,P-diphenylphosphinothionate

A mixture of P-2,4,6-trimethylbenzoyloxy-P,P-diphenylphosphinite (5 mmol) and sulphur (5 mmol) in benzene (10 ml) was refluxed until the sulphur had disappeared, (c.a. 2h). The benzene was

removed and the residue recrystallised from ethyl acetate - light petroleum. (95%); m.p. 115-116°; δ 2.30 (3H,s), 2.40 (6H,s), 6.95 (2H,s) and 7.30 - 8.35 (10H,m); ^{31}P (CH_2Cl_2) - 77.1 p.p.m.; $^m/e$ 380, 341, 325, 277, 260, 234, 217, 199, 164, 146 and 119; ν_{max} 1745, 1610, 1250, 1230, 1160, 1010, 950, 910, 820, 795, 735 and 690; (Found: C,69.60; H,6.0; P,8.70. $C_{22}H_{21}O_2PS$ requires C,69.46; H,5.56; P,8.43%).

Preparation of 2-2,4,6-trimethylbenzoyloxy-4,4,5,5-tetramethyl-1,3,2-dioxaphospholan (332)

To a stirred, ice-cold solution of 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholan (0.1 mol), triethylamine (0.1 mol) in ether (150 ml) was added a solution of 2,4,6-trimethylbenzoic acid (0.1 mol) in ether (100 ml). After addition the mixture was refluxed for 1h, filtered and the ether removed. Reduced pressure distillation of the residue gave the title compound. (80%); $b_{0.45}$ 180-185°; δ 1.31 (6H,s), 1.40 (6H,s), 2.29 (3H,s), 2.36 (6H,s) and 6.80 (2H,s); ^{31}P (CH_2Cl_2) - 135.6 p.p.m.; $^m/e$ 310, 295, 281, 252, 227, 205, 170, 164, 147 and 119; ν_{max} (neat film) 2980, 1710, 1615, 1450, 1260, 1165, 1140, 1065, 960, 915, 850, 765 and 670.

Reaction of Hexafluoroacetone with 2-2,4,6-trimethylbenzoyloxy-4,4,5,5-tetramethyl-1,3,2-dioxaphospholan

The reaction was carried out in the usual way, however no 2 : 1 adduct was formed. After the solvent was removed, recrystallisation from ethyl acetate - light petroleum gave 2-1,1,1,3,3,3-hexafluoro-2(2,4,6-trimethylbenzoyloxy)-2-propoxy-4,4,5,5-tetramethyl-1,3,2-dioxapholan-2-oxide, (334), (100%), m.p. 120.5 - 121°; δ 1.11 (6H,s), 1.43 (6H,s), 2.24 (6H,s), 2.30 (3H,s) and 6.94 (2H,s); ^{31}P (CH_2Cl_2) - 3.0 p.p.m.; ^{19}F ($CDCl_3$) + 3.23 (6F,s) p.p.m.; $^m/e$ 476, 395, 377, 321, 296, 280, 227, 211, 169, 147 and 119; ν_{max} 1730, 1610, 1405, 1320, 1230, 1135, 965, 945, 840, 810, 750, 725 and 665; (Found:

C,48.0; H,4.85; P,6.50. $C_{19}H_{23}O_5PF_6$ requires C,47.90; H,4.85; P,6.50%).

Preparation of 2-cyano-4,4,5,5-tetramethyl-1,3,2-dioxaphospholan (316)

A stirred mixture of 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholan (0.1 mol), silver cyanide (0.1 mol) and acetonitrile (50 ml) was heated under reflux for 6h. The solids were filtered off, the solvent removed and the residue distilled under reduced pressure. (50%); $b_{0.75}$ 74-78°; δ 1.34 (6H,s), and 1.50 (6H,s); ^{31}P (neat) - 174.6 p.p.m.; $^m/e$ 173, 149, 147, 122, 106 and 83; ν_{max} (neat film) 3000, 2950, 2095, 1470, 1390, 1180, 1145, 1020, 950, 845, 820 and 770.

Preparation of 2-isocyanato-4,4,5,5-tetramethyl-1,3,2-dioxaphospholan (322, X=NCO)

A stirred mixture of 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholan (0.1 mol), sodium isocyanate (0.1 mol) in acetonitrile (30 ml) and benzene (60 ml) was refluxed for 4h and left standing overnight. Filtration, removal of solvent, followed by reduced pressure distillation gave the title compound, (56%); $b_{1.3}$ 95-97°; δ 1.40 (12H,s); ^{31}P ($CDCl_3$) - 175.2 p.p.m.; $^m/e$ 189, 149, 147, 124, 122, 106, 85 and 83; ν_{max} (neat film) 2990, 2240, 1455, 1375, 1300, 1170, 1135, 955, 905, 825 and 760.

Preparation of 2-isothiocyanato-4,4,5,5-tetramethyl-1,3,2-dioxaphospholan (322, X = NCS)

A stirred mixture of 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholan (0.1 mol), sodium thiocyanate (0.1 mol) in acetonitrile (30 ml) and benzene (60 ml) was refluxed for 4h and left overnight. Filtration, removal of solvent, followed by reduced pressure distillation gave the title compound (40%); $b_{1.3}$ 115-118°; δ 1.28 (6H,s) and 1.40 (6H,s); ^{31}P ($CDCl_3$) - 127.6 p.p.m.; $^m/e$ 205, 190, 147, 122, 107, 100, 89 and 83;

ν_{max}(neat film) 2995, 2000, 1470, 1385, 1305, 1175, 1145, 1015, 965, 915, 840 and 770.

Preparation of Spirophosphoranes using Tetrachloro-o-benzoquinone

To a stirred solution of the trivalent phosphorus compound (5 mmol) in ether (5 ml) was added a solution of tetrachloro-o-benzoquinone (5 mmol) in ether (20 ml). The reaction mixture was left until the colour had discharged, the solvent was then removed and the residue taken up in ethyl acetate - light petroleum. In this way the following spirophosphoranes were prepared in almost quantitative yields.

P-chloro-$4^1,4^1,5^1,5^1$-tetramethyl-tetrachloro-1,3,2-benzodioxaphosphole-2-spiro-2^1-$1^1,3^1,2^1$-dioxaphospholan (328)

This was prepared by Bone[44]. δ (CCl_4) 1.00 (6H,s) and 0.95 (6H,s); ^{31}P ($CDCl_3$) + 14.5 p.p.m., (Lit. ^{31}P (CCl_4) + 13.6 p.p.m.)[44]

P-ethoxy-$4^1,4^1,5^1,5^1$-tetramethyl-tetrachloro-1,3,2-benzodioxaphosphole-2-spiro-2^1-$1^1,3^1,2^1$-dioxaphospholan (302)

Recrystallised from ethyl acetate - light petroleum. M.p. 145-146°; δ 1.37 (12,H,s), 1.12 - 1.41 (3H,m) and 3.84 - 4.52 (2H,m); ^{31}P ($CDCl_3$) + 31.5 p.p.m.; $^m/e$ 442, 440, 438, 436, 356, 337, 328, 310, 291, 248, 211, 165 and 141; ν_{max} 1600, 1395, 1305, 1160, 1055, 1025, 980, 930, 855, 825, 795 and 675; T^c singlet for the pinacol methyls in all solvents tried; (Found: C,38.50; H,3.95; Cl,32.20. $C_{14}H_{17}O_5PCl_4$ requires C,38.40; H,3.90; Cl,32.25%).

P-trimethylsiloxy-$4^1,4^1,5^1,5^1$-tetramethyl-tetrachloro-1,3,2-benzodioxaphosphole-2-spiro-2^1-$1^1,3^1,2^1$-dioxaphospholan.

(170, R = $-OSiMe_3$)

Recrystallised from ethyl acetate - light petroleum. M.p. 171 - 172° (decomposition); δ 0.34 (9H,s) and 1.49 (12H,s); ^{31}P ($CDCl_3$) + 35.9 p.p.m.; $^m/e$ 486, 484, 482, 480, 424, 399, 382, 366,

304, 269, 237, 171, 155, 147 and 121; ν_{max} 1660, 1440, 1310, 1260, 1140, 1020, 990, 960, 950, 865, 850 and 800; T^c singlet for the pinacol methyls in all solvents tried; (Found: C,37.75; H,4.20; P,7.15. $C_{15}H_{21}O_5PSiCl_4$ requires C,37.35; H,4.40; P,6.40%).

P-Cyano-$4^1,4^1,5^1,5^1$-tetramethyl-tetrachloro-1,3,2-benzodioxaphosphole-2-spiro-2^1-$1^1,3^1,2^1$-dioxaphospholan (329)

δ 1.43 (12H,broad singlet); ^{31}P (CH_2Cl_2) + 38.9 p.p.m.; $^m/e$ 423, 421, 419, 417, 393, 328, 310, 294, 248, 218, 183, 165, 155, 147, 118 and 99; ν_{max} 2210, 1590, 1400, 1280, 1140, 1015, 975, 950, 875, 820, 755 and 670; T^c (CCl_4) 46 $\pm$ 2°; $\Delta\nu 8H_z$; $\Delta G^{\#}$ 16.9 $\pm$ 0.1 kcal.mol^{-1}.

P-Isocyanato-$4^1,4^1,5^1,5^1$-tetramethyl-tetrachloro-1,3,2-benzodioxaphosphole-2-spiro-2^1-$1^1,3^1,2^1$-dioxaphospholan. (323, X = NCO)

δ 1.42 (12H, broad singlet); ^{31}P ($CDCl_3$) + 14.5 p.p.m.; $^m/e$ 439, 437, 435, 433, 393, 371, 345, 328, 312, 294, 277, 248, 232, 211, 183, 165, 155, 118 and 100; ν_{max} (neat film) 3000, 2270, 1660, 1410, 1395, 1270, 1150, 1010, 970, 945, 855, 825, 785, 760 and 660; T^c (CCl_4) 53 $\pm$ 2°; $\Delta\nu 6H_z$; $\Delta G^{\#}$ 17.5 $\pm$ 0.2 kcal.mol^{-1}.

P-Isothiocyanato-$4^1,4^1,5^1,5^1$-tetramethyl-tetrachloro-1,3,2-benzodioxaphosphole-2-spiro-2^1-$1^1,3^1,2^1$-dioxaphospholan (323, X = NCS)

δ (CCl_4) 1.40 (6H,s) and 1.46 (6H,s); ^{31}P ($CDCl_3$) + 42.7 p.p.m.; $^m/e$ 455, 453, 541, 449, 408, 393, 368, 352, 328, 310, 294, 218, 183, 155, 147 and 118; ν_{max} (neat film) 2990, 2000, 1465, 1400, 1275, 1155, 1010, 975, 950, 865, 830 and 790; T^c ($Cl_2CHCHCl_2$) 57 $\pm$ 2°; $\Delta\nu 5H_z$; $\Delta G^{\#}$ 17.8 $\pm$ 0.1 kcal.mol^{-1}.

Preparation of P-Azido-$4^1,4^1,5^1,5^1$-tetramethyl-tetrachloro-1,3,2-benzodioxaphosphole-2-spiro-2^1-$1^1,3^1 2^1$-dioxaphospholan. (330) A mixture of P-chloro-$4^1,4^1,5^1,5^1$-tetramethyl-tetrachloro-1,3,2-benzodioxaphosphole-2-spiro-2^1-$1^1,3^1,2^1$-dioxaphospholan (10 mmol) and sodium azide (10 mmol) in acetonitrile (30 ml) was stirred at room temperature for two days. The solids were filtered off, the solvent carefully removed under reduced pressure and the resulting solid was extracted with cold ethyl acetate - light petroleum to give the title compound. (60%); δ 1.49 (12H, broad singlet); ^{31}P (CH_3CN) - 7.8 p.p.m.; $^m/e$ 439, 437, 435, 433, 407, 356, 328, 310, 296, 248, 218, 209, 183, 155 and 118; ν_{max} 2180, 1475, 1435, 1405, 1315, 1275, 1145, 975, 835, 750 and 715; T^c ($Cl_2CHCHCl_2$) 76 $\pm$ 2°; $\Delta\nu_{3H_3}$; $\Delta G^{\#}$ 19.3 $\pm$ 0.1 kcal.mol^{-1}. By a similar procedure using silver syanide, P-cyano-$4^1,4^1,5^1,5^1$-tetramethyl-tetrachloro-1,3,2-benzodioxaphosphole-2-spiro-2^1-$1^1,3^1,2^1$-dioxaphospholan was prepared.

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SUMMARY

A review of phosphorane chemistry is presented. From a range of spirophosphoranes the relative apicophilicity of sulphur and oxygen containing ligands was determined. The conclusion reached was that the relative apicophilicities of ethylthio, ethoxy and trimethylsiloxy were similar.

The N-chlorodi-isopropylamine method for the preparation of spirophosphoranes was developed, enabling the preparation of various unsymmetrical phosphoranes, from which the relative apicophilicities of phenoxy and phenylthio groups were determined. The preparation of spirophosphoranes from phosphetans was shown to go with retention of configuration at phosphorus. The interconversion of the cis and trans spirophosphoranes prepared from phenyl and benzylphosphetans was followed kinetically, and from this study the phenyl group was shown to be more apicophilic than the benzyl group.

Cyclic and acyclic phosphites were reacted with acrylic acid. In the case of cyclic phosphites spirophosphoranes were prepared from which the relative apicophilicity of the phenyl group was determined. A series of spirophosphoranes was prepared containing a 4,4,5,5-tetramethyl-1,3,2-dioxaphospholan ring. On thermolysis these were found to give 2,3-dimethylbutadine as the major component and some t-butyl methyl ketone.

From a series of hexafluorobiacetyl and tetrachloro-o-benzoquinone adducts the relative apicophilicities of chlorine, cyanide, isocyanate and isothiocyanate were determined. It was shown that the cyanide was more apicophilic than chlorine, whilst the isocyanate and isothiocyanate were found to have a similar apicophilicity to chlorine.

The first pentaco-ordinate phosphorane containing an azide ligand was prepared by direct substitution of a chloro-spirophosphorane. From this spirophosphorane the relative apicophilicity of the azide group was determined; it was found to be slightly more apicophilic than the phenoxy group. By a similar procedure a spirophosphorane containing a cyanide ligand was prepared.