Some Aspects of the Chemistry of Spirophosphoranes.

by

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A Thesis

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in the Faculty of Science

of the

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STATEMENT

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

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

signed

S.A. Bone.

September, 1975.

ACKNOWLEDGEMENTS

First and foremost I would like to thank my supervisor, Professor S. Trippett for his guidance and constant encouragement during all stages of the work for this degree.

I would like to thank Dr. P.J. Whittle and Dr. M.W. White for many valuable discussions and my fellow research students who made my stay at Leicester seem so short and happy.

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

The Apicophilicity of Thio-substituents in Trigonal Bipyramidal Phosphoranes.
By S.A. Bone, S. Trippett* and P.J. Whittle,
J.C.S. Perkin I, 1974, 2125.

Strain Factors in Five-membered Pentacovalent Phosphoranes.
S.A. Bone, S. Trippett*, M.W. White, and P.J. Whittle,
Tetrahedron Letters, 1974, 1795.

A Convenient Synthesis of Spirophosphoranes.
S.A. Bone and S. Trippett*,
Tetrahedron Letters, 1975, 1583.

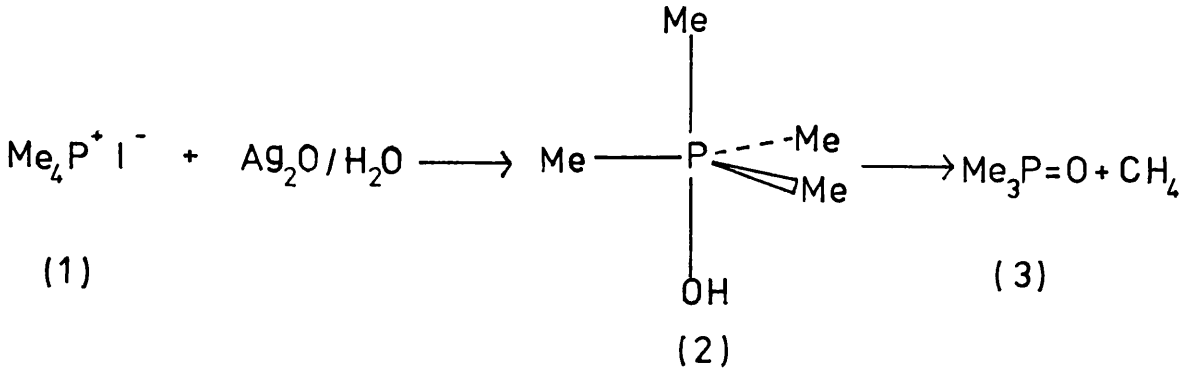
Application of Diethyl Azodicarboxylate in the Synthesis of Spirophosphoranes.
S.A. Bone and S. Trippett*,
J.C.S. Perkin I (accepted for publication).

1. PHOSPHORANES.

1.1 Introduction.

The term 'phosphorane' is used to describe a phosphorus atom with five covalently bonded ligands around it.

The first phosphorane reported in the Literature was the intermediate (2) proposed by C.K. Ingold in 1929[1] in the reaction of tetramethylphosphonium iodide (1) with moist silver oxide. When these two compounds are heated together methane gas is liberated with the formation of trimethylphosphine oxide (3).

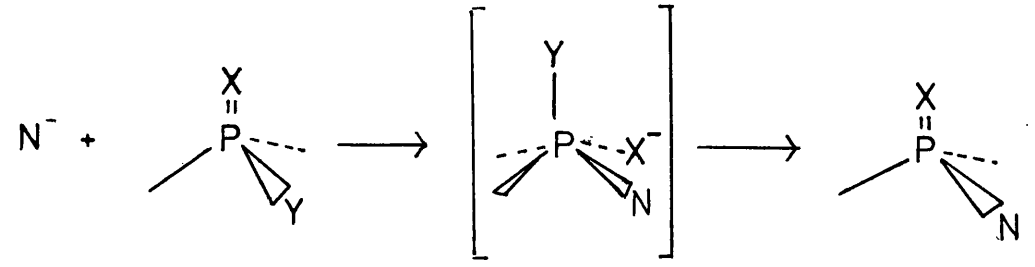


(1) (2) (3)

Ingold proposed that unlike the analogous ammonium series where discrete Me_4N^+ and OH^- ions exist, the intermediate (2) existed as a pentacovalent phosphorane, i.e. with a covalent phosphorus-oxygen bond.

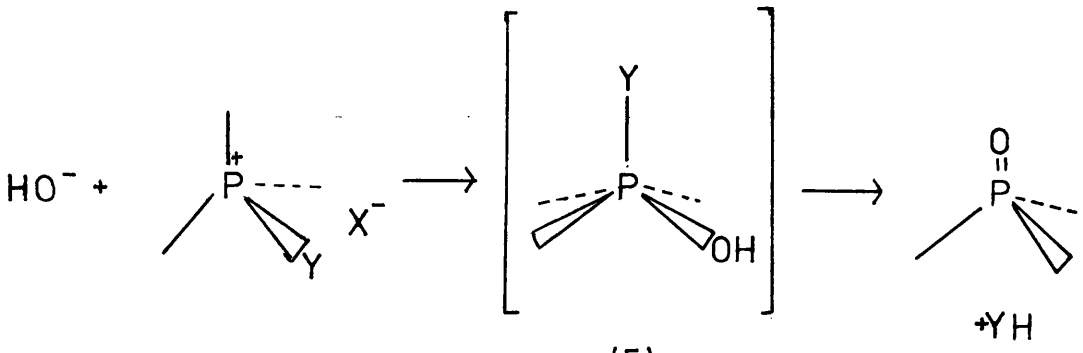
Since this work was published, many papers have appeared concerning the intermediacy of pentacovalent phosphoranes in the reaction of a nucleophile with a tetracoordinated phosphorus compound.[2-12]

Intermediates (4) and (5) in these substitution reactions have very short life times and have never been isolated. The evidence for these intermediates is therefore indirect. These typesof intermediates



(4)

X = O, S



(5)

form one of the two main classes of phosphoranes. The other class is the type of phosphorane which is reasonably stable and may be isolated and fully characterised.

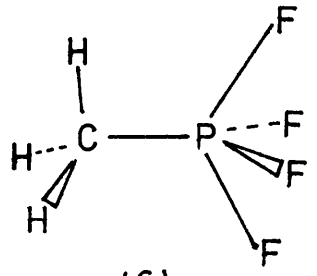
As it is impossible to study the intermediate type of phosphorane directly, it is generally assumed that properties and structure of stable phosphoranes are also applicable to the unstable phosphorane intermediates.

1.2 Structure of Phosphoranes.

The data obtained from the X-ray diffraction study of pentaphenylphosphorane,[13] electron diffraction[14] and infra red and Raman studies[15] of pentafluorophosphorane and the electron diffraction study of pentachlorophosphorane[16] indicate that for acyclic phosphoranes

with five identical ligands a trigonal bipyramidal geometry is adopted.

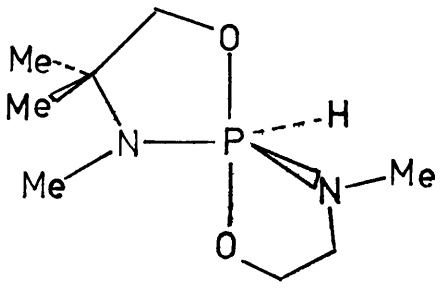
Electron diffraction studies of CH_3PF_4 [17] showed that the molecule was definitely trigonal bipyramidal but there was a small amount of distortion, the four fluorine atoms being bent away from the methyl group (6).



(6)

For cyclic phosphoranes containing small (4 or 5 membered) rings, distortion away from trigonal bipyramidal geometry sometimes occurs.

Phosphoranes (7)[18] and (8)[19] have been studied by X-ray diffraction and shown to be almost perfect trigonal bipyramids.



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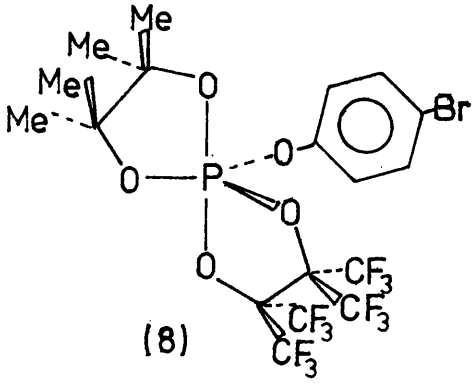

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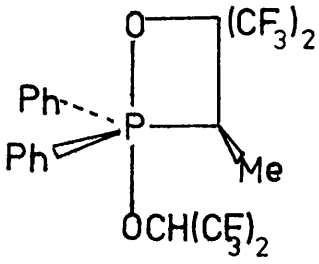
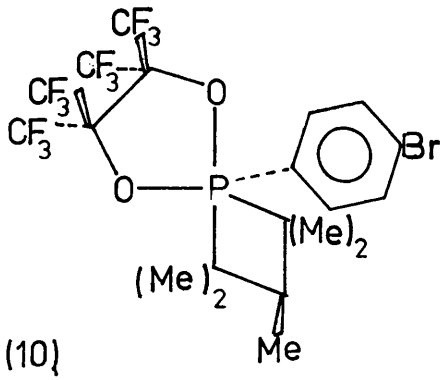
X-ray diffraction studies of (9)[20] showed that the oxaphosphetan ring



(9)

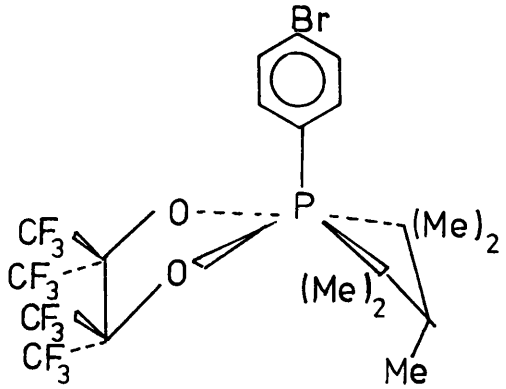
induced small distortions in the molecule, in particular, the Ph–P–Ph angle had decreased from 120° to 112·7°.

X-ray diffraction of (10)[21] showed that the presence of the four-



(10)

and the five-membered ring caused severe distortions. In fact, this phosphorane possesses almost a perfect square pyramidal structure, the p-bromophenyl group taking the apical position and the four ring atoms the basal positions (11).



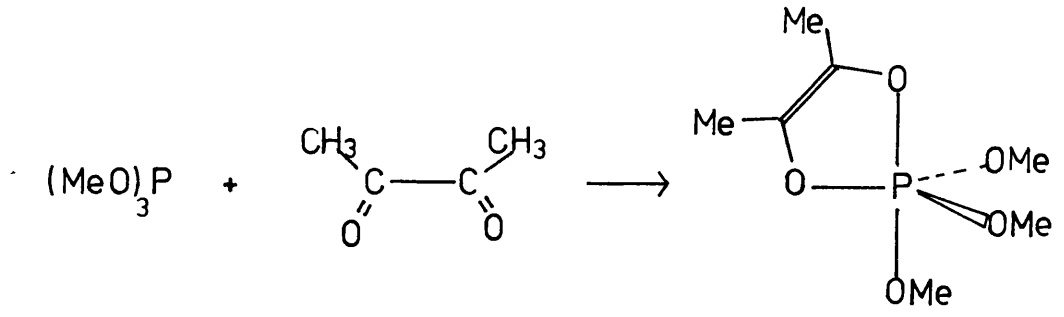
(11)

The X-ray studies described here indicate that the more asymmetrically substituted the phosphorus the more distorted the phosphorane.

Generally, distortions are fairly small and so for the purpose of discussion phosphoranes will be regarded as trigonal bipyramids. The significance of this assumption will become clear in the following chapters.

1.3 Synthesis of Oxyphosphoranes.

The early work on the preparation of cyclic phosphoranes was largely carried out by Ramirez and co-workers[22,23]. They found that phosphites, phosphonites and phosphinites react readily with ∝-diketones and o-quinones to form unsaturated 1,3,2-dioxaphospholens, e.g.



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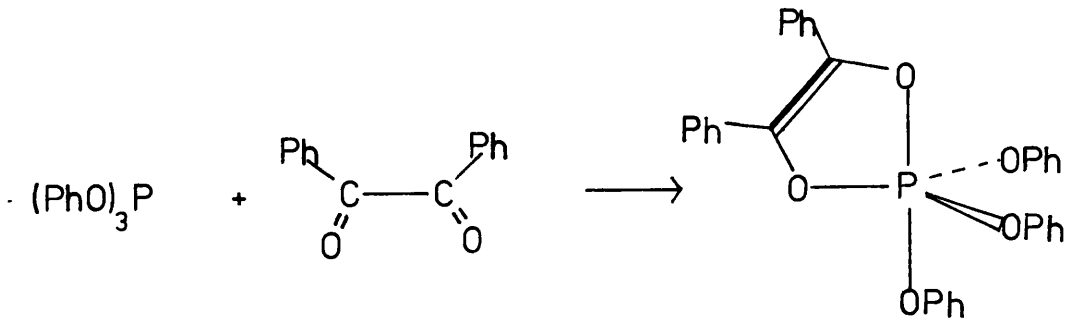
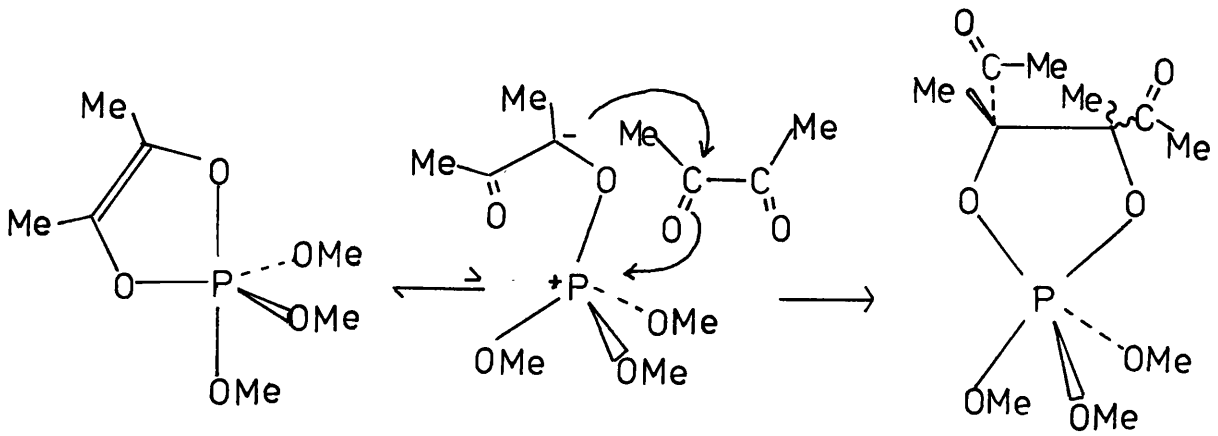


(13)

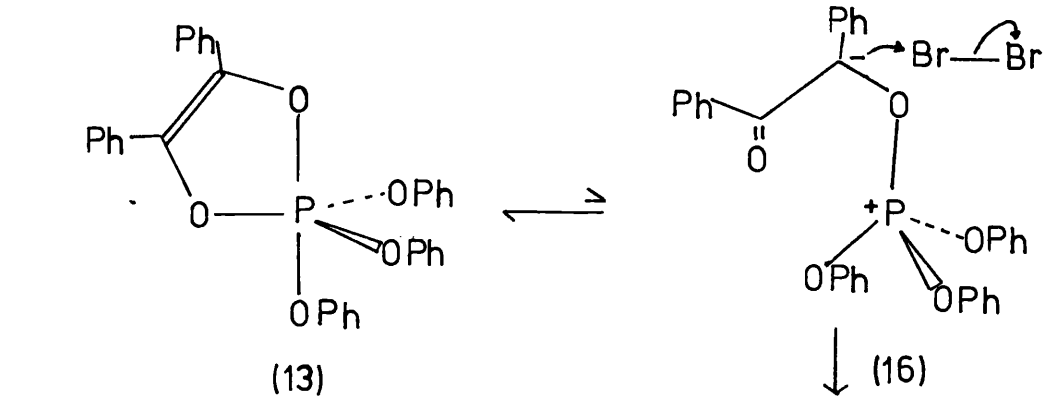
The phosphoranes (12) and (13) are fairly reactive species. They react readily with a further molecule of ∝-diketone to form a 2:1 adduct e.g. (15)



(12) (14) (15)

The reaction is believed to go through intermediate (14) where ring opening has occurred. The stabilised negative charge attacks the carbonyl of a second molecule of α -diketone followed by ring closure to form the 2:1 adduct (15).

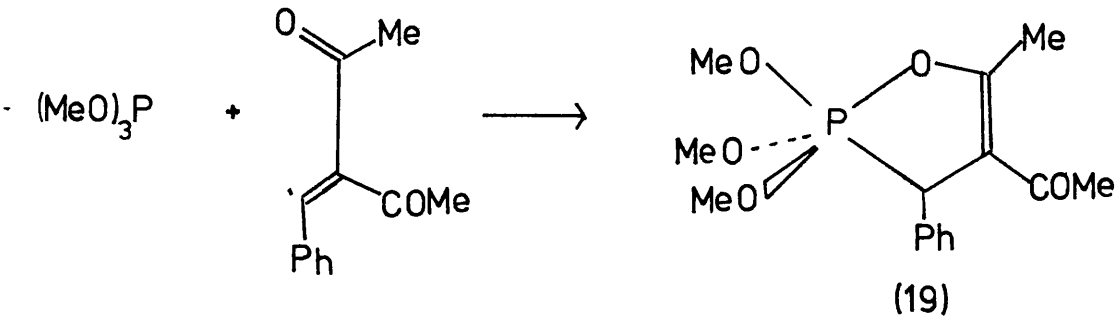
It is through the analogous intermediate (16) that the benzil adduct (13) reacts with bromine at low temperatures ultimately forming the dibromoketone (18) and triphenylphosphate.



The stabilised anion of (16) reacts with a molecule of bromine liberating a bromide ion to give intermediate (17). The bromide ion attacks the carbon atom to displace triphenylphosphate which is a thermodynamically favourable process, yielding the dibromide (18).

Trivalent phosphorus compounds react with a wide variety of 1,3-unsaturated compounds to give stable phosphoranes, e.g. (19),[24]

(20),[25], (21)[26] and (22)[27].



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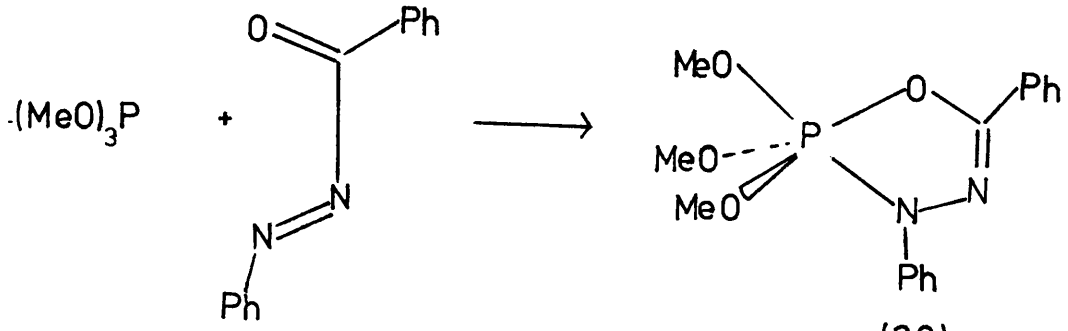

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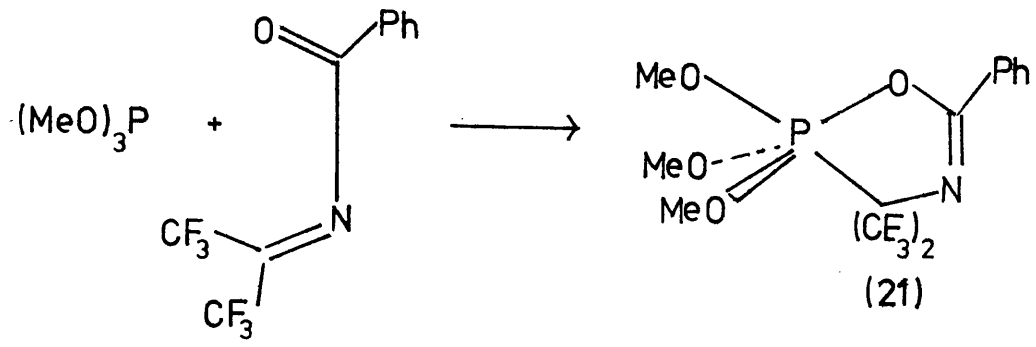

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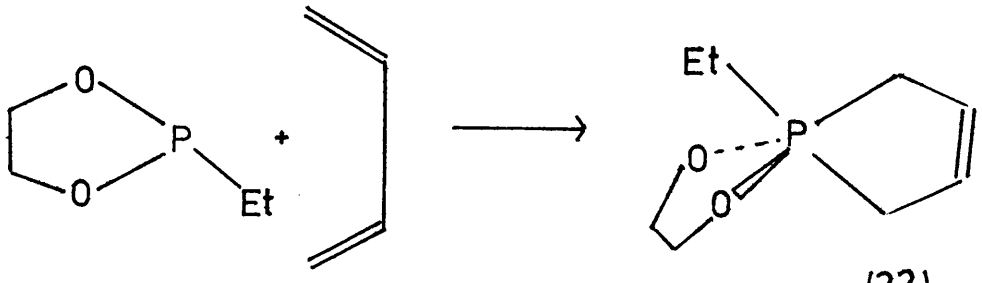
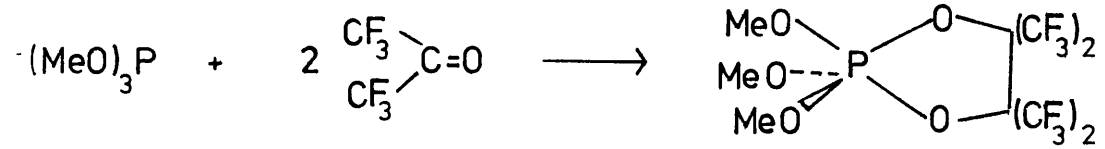


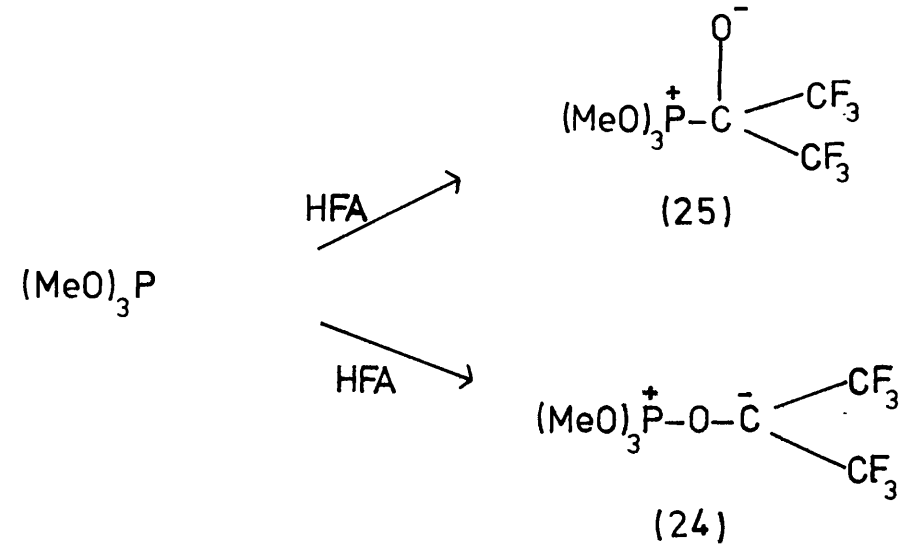
(22)

Certain activated carbonyl compounds react with trialkyl phosphites to give 2:1 adducts. For example hexafluoroacetone,[28] o- and p-nitrobenzaldehydes,[29] fluorenone,[30] phthalaldehydes,[31] and methyl pyruvate[32] all react to give 1,3,2-dioxaphospholans.

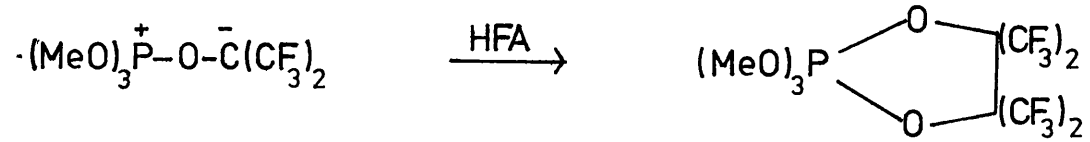


(23)

The mechanism of this reaction is believed to go via a dipolar intermediate (24) although it is not known for certain whether this intermediate is formed directly or through isomerisation of intermediate (25).

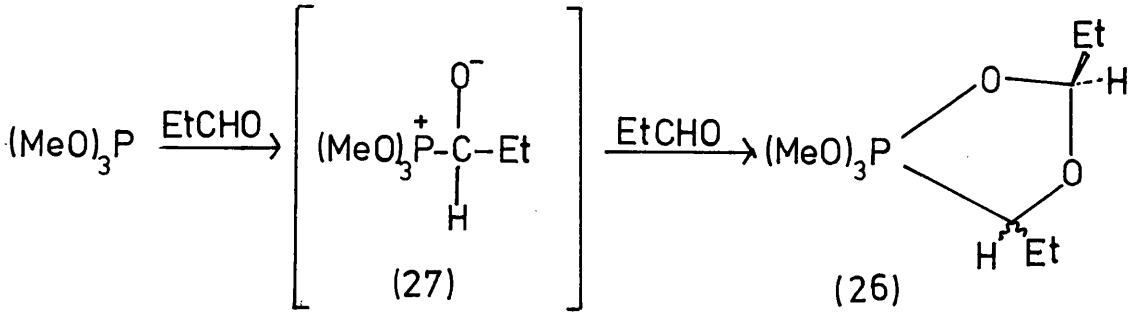


In this case the second molecule of hexafluoroacetone (HFA) reacts with intermediate (24) to yield (23) the 1,3,2-dioxaphospholan.



(23)

For non-activated carbonyl compounds, e.g. simple aliphatic aldehydes,[33] the reaction takes a different course resulting in a 1,4,2-dioxaphospholan (26).

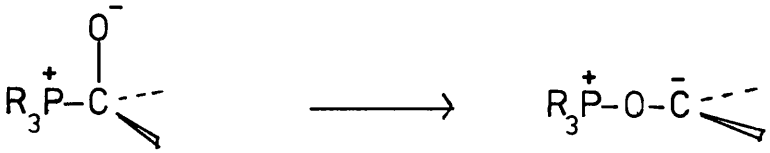


In this case the trimethylphosphite must attack the carbon atom of the carbonyl to form intermediate (27). This intermediate cannot rearrange because the carbon atom of the carbonyl of propionaldehyde cannot stabilise a negative charge. Therefore the second molecule of propionaldehyde reacts with (27) to form the 1,4,2-dioxaphospholan (26).

Ramirez[34] studied the reaction between trialkyl phosphites and pentafluorobenzaldehyde and found that the 2:1 adduct initially formed was a 1,4,2-dioxaphospholan which on standing isomerised to the 1,3,2-dioxaphospholan.

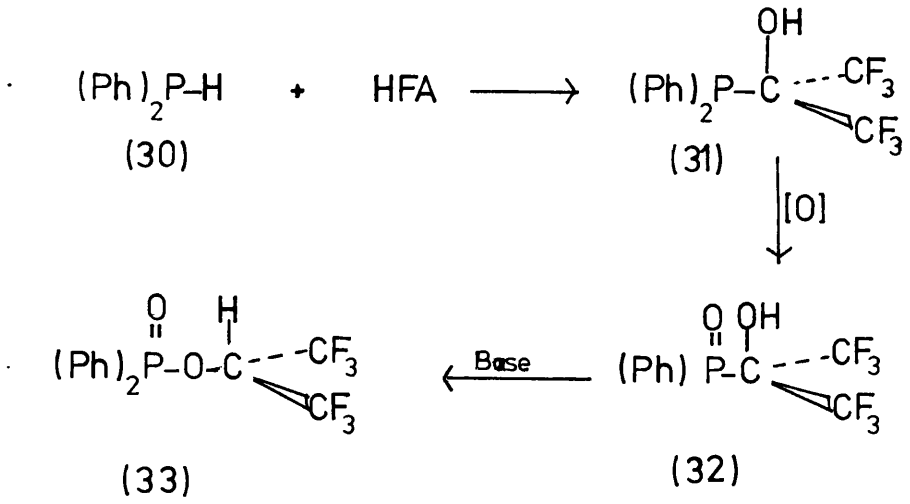
1,4,2-Dioxaphospholans have been isolated from the reaction of hexafluoroacetone and certain trivalent phosphorus compounds (see Chapter 6). These adducts are thermally stable and show no tendency to isomerise to the 1,3,2-dioxaphospholans. This indicates that 1,4,2-dioxaphospholans are not intermediates in the formation of 1,3,2-dioxaphospholans.

For the formation of a 1,4,2-dioxaphospholan to occur, the phosphorus must attack the carbon of the carbonyl first to give an intermediate (28).



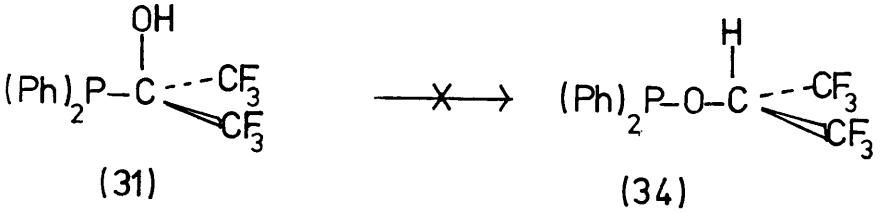
(28) (29)

As even hexafluoroacetone can form 1,4,2-dioxaphospholans it is possible that initial attack always occurs at the carbon of the carbonyl and not the oxygen. This view is supported by the work of Janzen and Vaidya[35] who studied the reaction of hexafluoroacetone with diphenylphosphine (30) and concluded that the initial product was the phosphorus (III) alcohol (31).



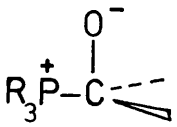
(30) (31) (33) (32)

The structure of (31) was assigned from n.m.r. data. (31) was found to be very susceptible to oxidation yielding (32); again the structure is assigned from n.m.r. data. Finally, in the presence of base (32) rearranged to (33). They found the intermediate (31) was stable and showed no isomerisation to (34).



(31) (34)

This could be taken as evidence that the isomerisation (28) to (29) will not occur.



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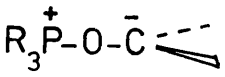
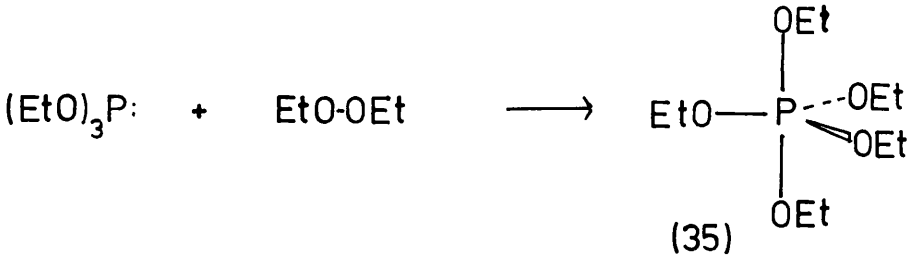


(29)

However, this assumption is not strictly valid as isomerisation of the charged betaine (28) is likely to be easier than for the uncharged phosphorus (III) alcohol (31).

Hence, although it appears that initial attack occurs at the carbon of the carbonyl followed by rearrangement of the type (28) to (29), the possibility of direct attack on oxygen in certain cases cannot be ruled out.

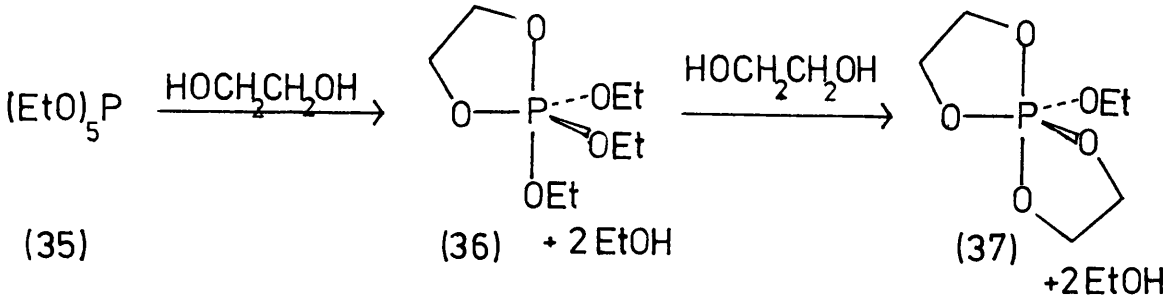
In 1964 Denney and Relles[36] found that diethyl peroxide and triethyl phosphite reacted to give a substance which was characterised as pentaethoxyphosphorane (35).



(35)

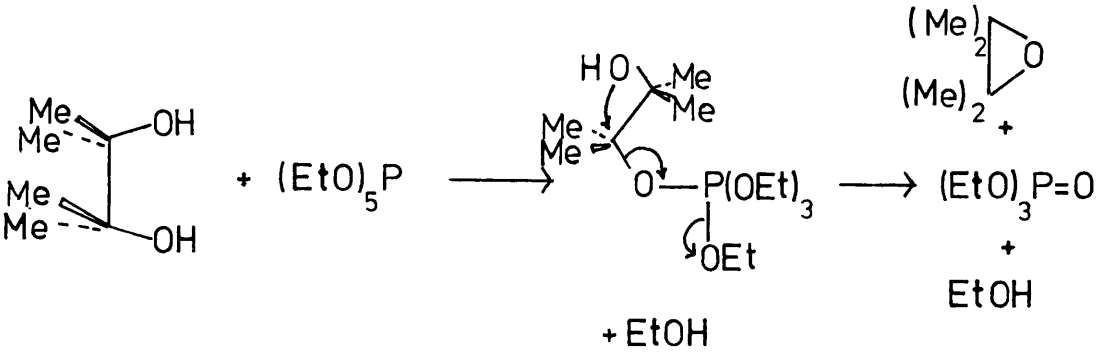
By this method, many oxyphosphoranes were synthesised.

Denney later discovered[37] that acyclic oxyphosphoranes reacted with certain diols forming cyclic and spiro-phosphoranes.



When pentaethoxyphosphorane is treated with one mole of ethylene glycol, two moles of ethanol are displaced with the formation of the cyclic phosphorane (36). This cyclic phosphorane reacts with a second mole of ethylene glycol to form the spirophosphorane (37) with the displacement of a further two moles of ethanol.

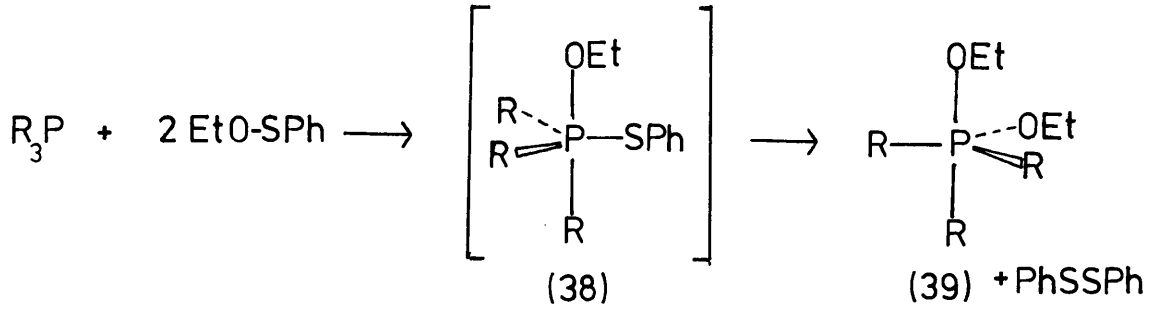
Denney found that similar displacements occur with neopentyl glycol , propylene glycol, d l - 2.3-butanediol and styrene glycol. With pinacol, 1,4-butanediol and 1,5-pentanediol mono exchanges occurred followed by a displacement reaction which yielded the heterocycle and the tetrasubstituted phosphorus compound, e.g.



When pinacol is reacted with pentaethoxyphosphorane the products are tetramethylethylene oxide, triethyl phosphate and two moles of ethanol.

Denney[38] also discovered that two moles of ethyl benzenesulphenate react with one mole of a trivalent phosphorus compound yielding the

diethoxyphosphorane (39) and diphenyl disulphide.



Denney observed by ^{31}P n.m.r. the initial formation of (38) which as the reaction proceeded disappeared with the formation of (39) by an unknown mechanism. The diethoxyphosphorane formed by this reaction can now be treated with a suitable diol to yield cyclic or spiro-phosphoranes depending on the nature of the groups labelled R.

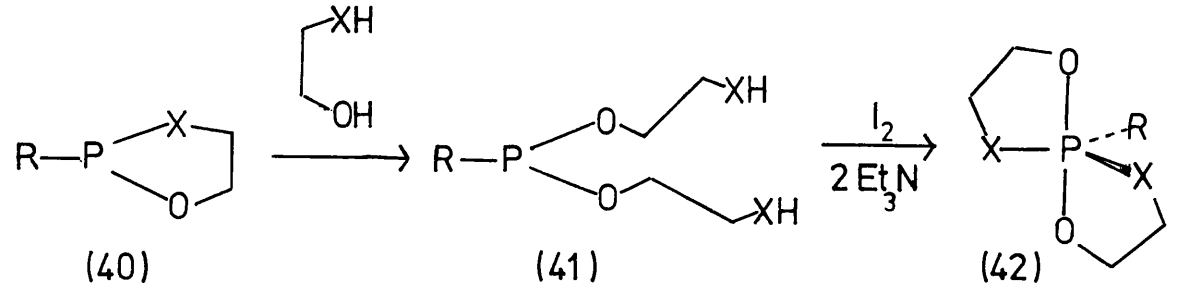
The major disadvantage of this route to phosphoranes is that the peroxide reaction is often very slow, as much as four days at room temperature in some cases. It is found that the starting trivalent phosphorus compound is oxidised by diethyl peroxide to the $R_3P = O$. This may occur to an extent of 25% in some cases.

The use of ethyl benzenesulphenate reduces the reaction time but introduces diphenyldisulphide into the reaction mixture which is difficult to remove.

The displacement of two moles of ethanol by a diol is often slow as well. When the exchange has taken place the phosphorane is contaminated with $R_3P=O$ by oxidation or diphenyl disulphide from the ethyl benzene-sulphenate. Consequently, Denney was rarely able to isolate and fully characterise the phosphoranes made by this exchange route.

In a recent publication[39] a new route to spirophosphoranes is described. A cyclic phosphonite 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.



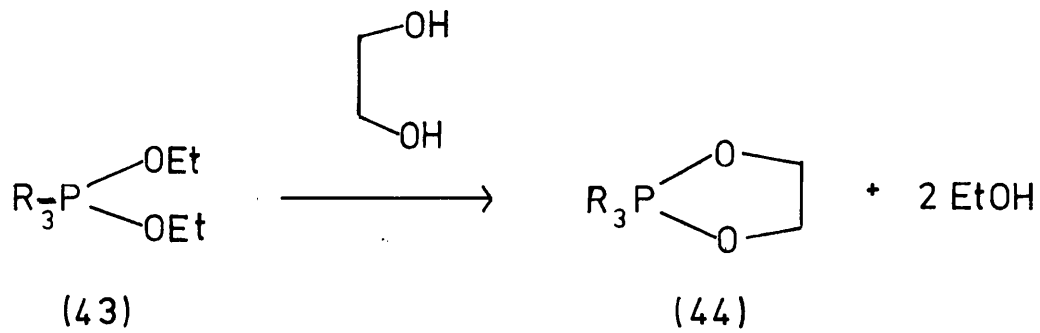
R = Ph or Me

X = O or NH

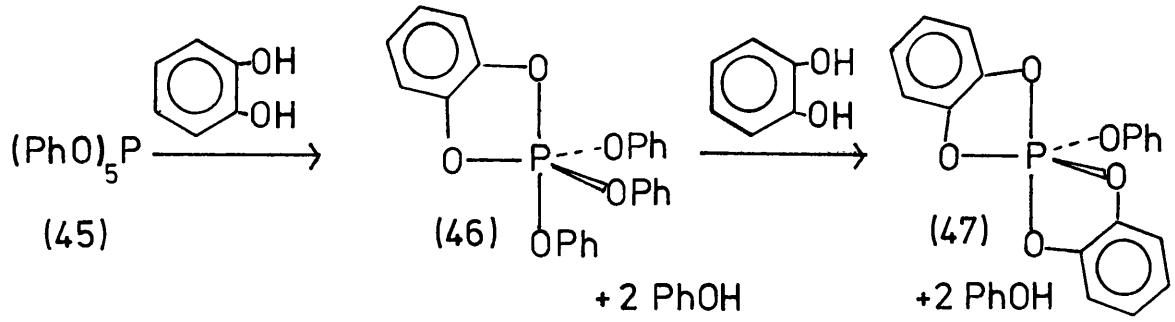
This reaction gives rise to spirophosphoranes (42) in high yields. All spirophosphoranes prepared in this way had both rings the same. The authors did not state whether mixed ring spirophosphoranes could be made in this way.

1.4 Stability of Phosphoranes.

X-ray diffraction studies[20,51] have shown that considerable crowding exists in the oxaphosphorane trigonal bipyramidal. Ramirez has suggested[34] that when phosphorus forms part of a small-membered ring in a phosphorane, steric interaction is reduced and the phosphorane structure is stabilised. There is much evidence in the literature to support this theory. Denney's exchange route to oxyphosphoranes[37] is an example.



Similarly catechol[54] reacts readily with pentaphenoxyphosphorane (45) to form cyclic and spirophosphoranes (46,47) with the displacement



of two moles of phenol for each catechol ring. This type of exchange strongly indicates that cyclic and spirophosphoranes are thermodynamically more stable than acyclic oxyphosphoranes.

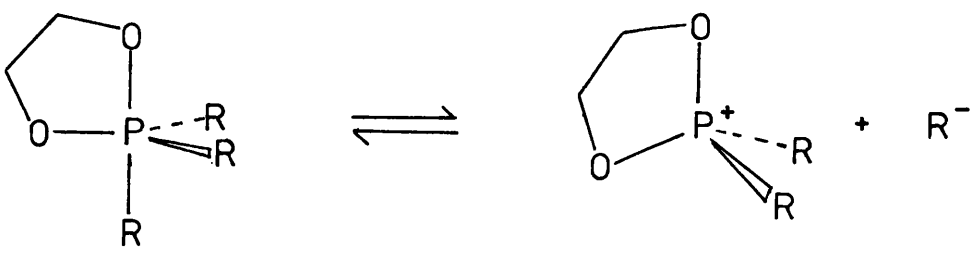
The ease with which a phosphorane dissociates into ions according to the equation

$$R_5P \rightleftharpoons R_4P^+ R^-$$

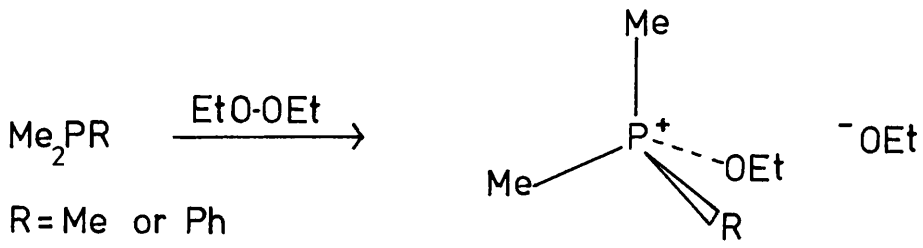
is termed kinetic stability. There appear to be two main factors that influence this equilibrium:

(i) Incorporation of phosphorus into a small ring.

As there is a great deal of crowding in a phosphorane[20,51] there will be a tendency to dissociate into ions thereby reducing the amount of crowding. The small ring (4 or 5 membered) has a two-fold effect; it reduces the steric crowding and causes ring strain to build up in going from a trigonal bipyramidal to a tetrahedron, i.e. (48) $\rightleftharpoons$ (49).

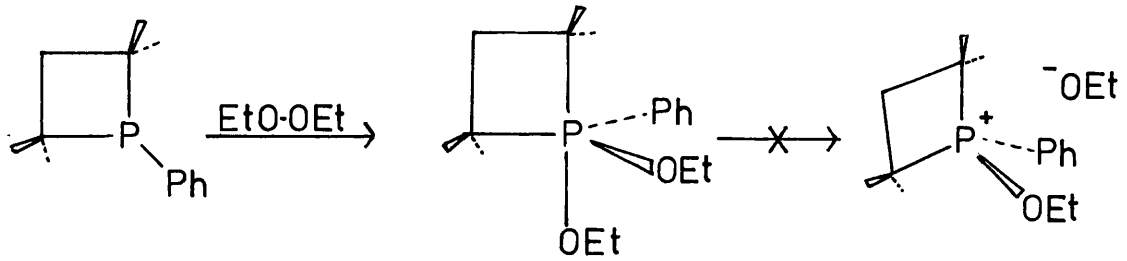


This point is well illustrated by the work of Denney[52] on the reaction of diethyl peroxide with various phosphines. With trimethylphosphine and dimethylphenylphosphine, the oxyphosphoranes formed with diethyl peroxide were best described as phosphonium ethoxides (51).



(50) (51)

The methylene group of the O-Et groups was a simple quartet and showed no coupling to phosphorus indicating rapid exchange via (51). The phosphetan (52), reacted with diethyl peroxide to form a stable phosphorane (53).



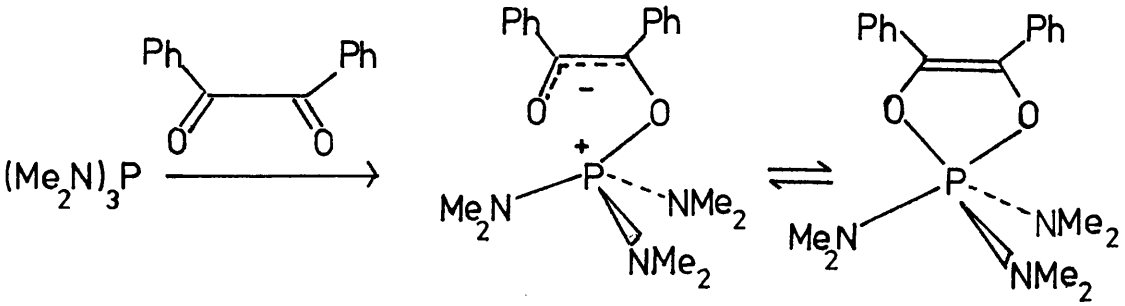
(52) (53) (54)

Ionisation of (53) $\rightleftharpoons$ (54) does not occur because this would cause a large increase in ring strain as the angle in the phosphetan ring is increased from 90^{o} to 109^{o}.

(ii) Electronegativity of the Ligands Bonded to Phosphorus.

There appears to be a general trend in oxyphosphorane chemistry that as alkoxy groups are replaced by alkyl or amino groups the stability of the phosphorane decreases. The adduct formed between

benzil and trimethyl phosphite is very stable[22,23] whereas the adduct between benzil and trisdimethylaminophosphine exists as two forms (55) and (56) in solution.[53]



(55) (56)

The presence of the dipolar form (55) was deduced from the fact that the ^{31}P n.m.r. was solvent dependent, shifting to lower field as the polarity increased. As the open dipolar form (55) has a negative ^{31}P shift and the oxyphosphorane (56) has a positive ^{31}P shift then the observed shift is a weighted average of the two. Separate signals are not observed because equilibration (55) $\rightleftharpoons$ (56) is fast on the n.m.r. time-scale.

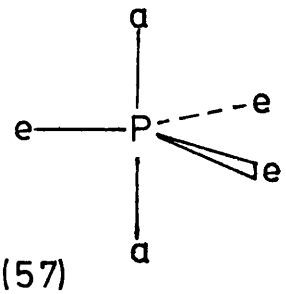
Ramirez suggested[34] that the instability of the trisdimethylamino adduct was due partly to the lower electronegativity of nitrogen and partly to the fact that dimethylamino groups are more bulky than alkoxy groups.

2. LIGAND PERMUTATIONAL ISOMERISM IN PHOSPHORANES.

2.1 Evidence for Ligand Permutational Isomerism.

The ^{19}F n.m.r. spectrum of pentafluorophosphorane[40] showed only one type of fluorine atom in the temperature range $+60^{o}$ to -197^{o}.

It can be seen clearly that in a trigonal bipyramid (57) there are two distinct positions, apical (a) and equatorial (e).



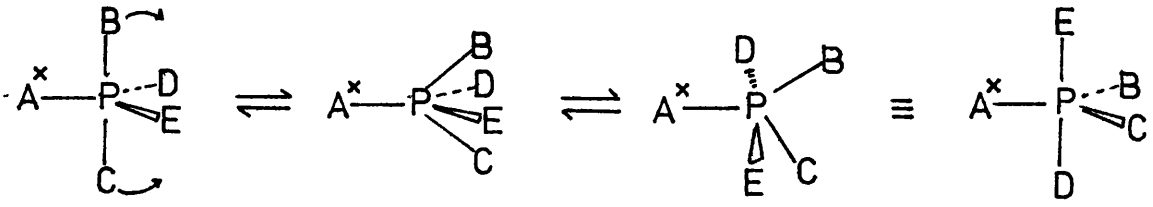
(57)

If the trigonal bipyramid in pentafluorophosphorane were static, a complex ^{19}F n.m.r. spectrum would be expected. There must be a mechanism of low energy that allows the fluorine atoms in this molecule to become equivalent.

2.2 Berry Pseudorotation.

In 1960 Berry[41] attempted to explain the behaviour of pentafluorophosphorane by postulating that the fluorine atoms were rapidly becoming equivalent by a ligand reorganisation process which he termed pseudorotation.

SCHEME 1



(58) (59) (60) (60)

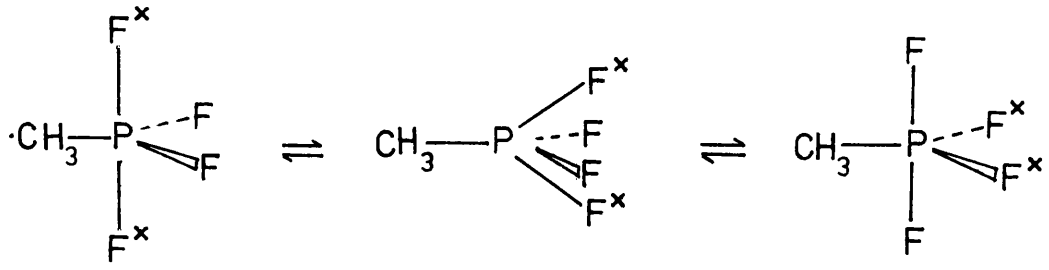
The process as illustrated in Scheme 1 may be explained as follows.

One of the equatorial positions, in this case A^* acts as a pivot. The apical atoms B and C move in the direction shown towards the two remaining equatorial positions D and E. At the same time, D and E move apart to form the square base pyramid (59) which can be regarded as a transition state or an intermediate. Continuation of this motion increases the angle between D and E until it reaches 180^o; by this time the angle between B and C has decreased from 180^o to 120^o. At this stage, A^* the pivot, B and C have become the new equatorial positions and D and E have become the new apical positions.

This pseudorotation has made B and C equivalent with D and E. If B or C is now used as a pivot and a second pseudorotation is then carried out, all the positions A to E become equivalent.

Quite simply apical and equatorial atoms are exchanged in a pairwise manner by a Berry pseudorotation.

Extending this idea further, the predicted ^{19}F n.m.r. for CH_3PF_4 would be expected to have only one type of fluorine atom, as in this case the CH_3 group can act as the pivot and the fluorine atoms will become equivalent by one Berry pseudorotation.



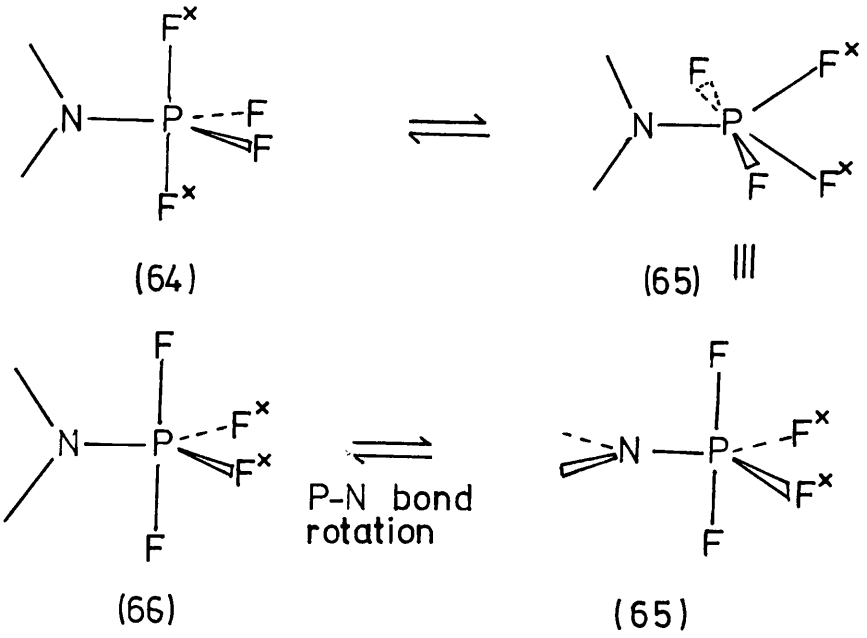
(61) (62) (63)

The two apical fluorine atoms (starred) become two equatorial fluorine atoms, therefore $F^* \equiv F$. The ^{19}F n.m.r. of this species is a doublet[42] due to P-F spin-spin coupling in the temperature range 100^o to -120^o.

2.3 Alternative Mechanisms to Berry Pseudorotation.

Muetterties has considered several alternative mechanisms[43] by which the fluorine atoms of pentafluorophosphorane may become equivalent but eliminated them on the basis of the experiment of Whitesides and Mitchell.[44] This experiment involved the analysis of the temperature-dependent ^{31}P n.m.r. of $Me_2N\text{-}PF_4$. At first sight, this appears to be a similar case to CH_3PF_4 where the four fluorine atoms are equivalent even at the lowest temperature observable in the ^{19}F n.m.r. Closer inspection shows that, irrespective of the nitrogen co-ordination geometry - planar or pyramidal, rotation about the P-N bond must be rapid to achieve ultimate fluorine atom equivalence via the Berry pseudorotation shown in Scheme 2.

SCHEME 2



If, with the methyl groups in the plane of the apical fluorines (F^*) (64) a Berry pseudorotation occurs without P-N bond rotation, the new trigonal bipyramid (65) has the methyl groups parallel to the plane of the equatorial fluorines; only after rotation of 90^o about the P-N bond do the four fluorines become equivalent (66). Equivalence may also occur by rotation about the P-N first followed by a Berry pseudorotation i.e. the reverse of Scheme 2.

From Hoffmann's theories[45] (see Section 3.1) the phosphorane (65) is of higher energy than (64) - the amount found experimentally[46] to be approximately nine kcals mol^{-1}. Thus to get (65) by either pseudorotation or by P-N bond rotation an energy barrier of nine kcals mol^{-1} must be overcome.

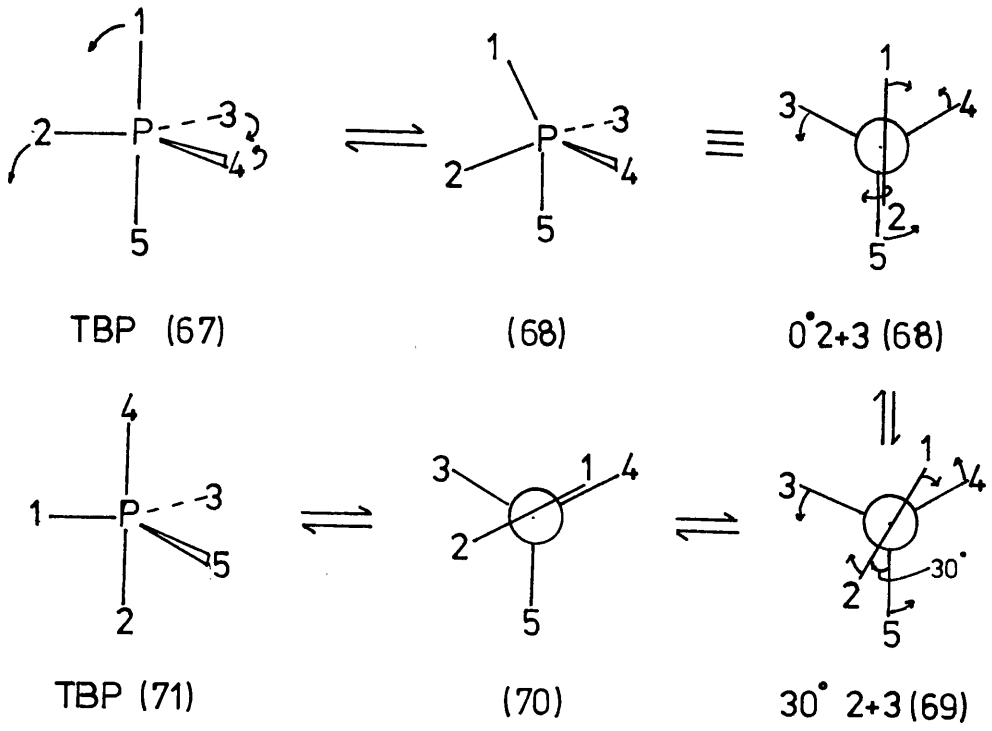
On cooling this molecule down to -100^o the ^{31}P n.m.r. spectrum showed a triplet of triplets expected for a static trigonal bipyramid with the dimethyl amino group equatorial, i.e. two sets of two fluorine atoms. At -50^o however the ^{31}P n.m.r. spectrum showed a regular quintet i.e. four equivalent fluorines. From a full line shape analysis in the region -50 to -100^o Whitesides and Mitchell concluded that fluorine equivalence was achieved by simultaneous interchange of two apical with two equatorial fluorine atoms.

Of the mechanisms considered by Muetterties, only Berry pseudorotation was consistent with the experiment by Whitesides and Mitchell.

2.4 Turnstile Rotation.

An alternative to Berry pseudorotation not considered by Muetterties was suggested by Ugi, Ramirez, and their co-workers[47] and termed Turnstile Rotation.

SCHEME 3



The turnstile rotation process is illustrated in Scheme 3. First of all, ligands 1 and 2 move down by about 9° in the plane of the paper. These ligands are referred to as 'the pair'. Ligands 3 and 4 now move together until the 3-P-4 angle is about 90°. Ligands 3,4 and 5 are referred to as 'the trio'. This bending would give the intermediate (68) referred to by Ugi and Ramirez as a 0° (2+3), but in fact this intermediate is never actually formed because synchronous to the bending of 1 and 2 and 3 and 4 is a 30° internal rotation of the pair against the trio. In other words, the pair rotates 18° one way and the trio rotates 12° in the opposite direction; thus the pair and the trio have rotated 30° relative to each other. The effect of this 30° rotation is clearly seen from the Newman projection of the hypothetical intermediate (68) and the intermediate (69). The intermediate (69) is referred to as a 30° (2+3). The name is derived from

the smallest dihedral angle between ligands in the Newman projection. If the rotations are continued in the same directions through a further 30^{o} intermediate (70) would be produced. The smallest angle is between 1 and 4 which is 0^{o} therefore this intermediate would be called a 0^{o} (2+3). Synchronous to this rotation is the bending back to a trigonal bipyramid (71), i.e. the reverse of the first motion.

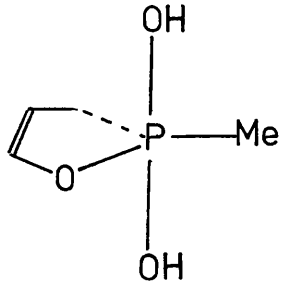
This process is known as a $(TR)^{1}$ and gives the same result as a Berry pseudorotation with 3 as the pivot.

The overall process exchanges ligands in a pairwise manner in accord with the experiment of Whitesides and Mitchell.

Calculations[45] have shown that for symmetrical acyclic phosphoranes (pentafluorophosphorane etc.) the Berry pseudorotation process is energetically preferred, but in the cases where the square base pyramid is destabilised, and in less symmetrically substituted phosphoranes, other mechanisms may operate.

The major difference between Berry and Turnstile rotation is the possibility of multiple Turnstile rotations called $(TR)^{2}$ and $(TR)^{3}$.

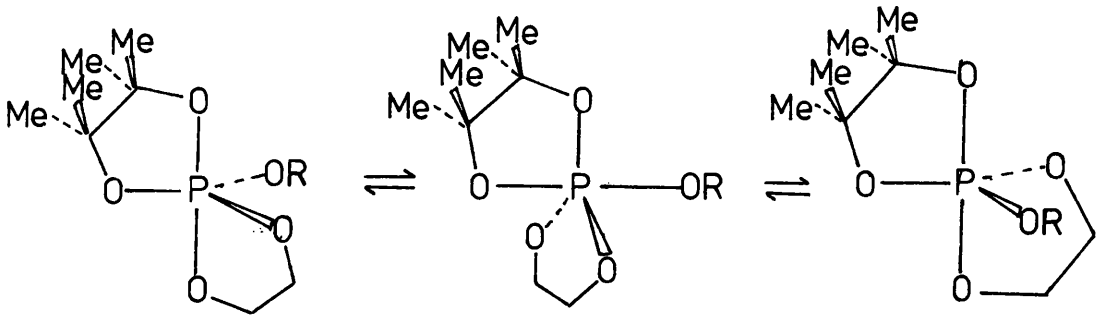
Ugi and Ramirez[47d,e] calculated the energy required for an oxaphospholen ring to span the diequatorial position as in (72) to be 40 kcals mol^{-1} (c.f. Chapter 6).



(72)

Similarly, they calculated the energy to exchange an apical oxygen for an equatorial carbon to be 37 kcals mol^{-1}. Ugi and Ramirez[47] have claimed that high energy trigonal bipyramids of this type may be avoided by a multiple TR process.

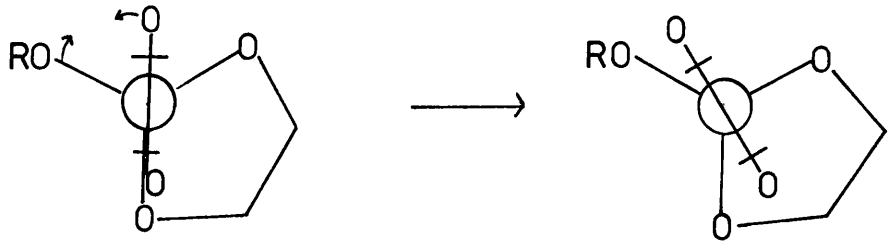
This process is best described with an example:-



(73) (74) (75)

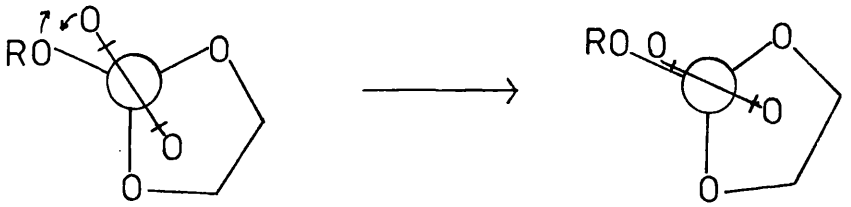
In terms of Berry pseudorotation, (73) may pseudorotate to (74) with the ethylene glycol ring diequatorial. This is a very high energy intermediate. A second pseudorotation brings (74) to (75) with equilibration of the pinacol methyl groups.

In terms of Turnstile rotation, the pinacol ring of (73) becomes the pair and the other three groups become the trio. Distortion of the angles as described for (67) would lead to the 0° (2+3) (76). However, a synchronous 30° internal rotation gives the 30° (2+3) (77).



0° (2+3) (76) 30° (2+3) (77)

Continuation of this internal rotation by a further 30° leads to a second 0°(2+3) (78).



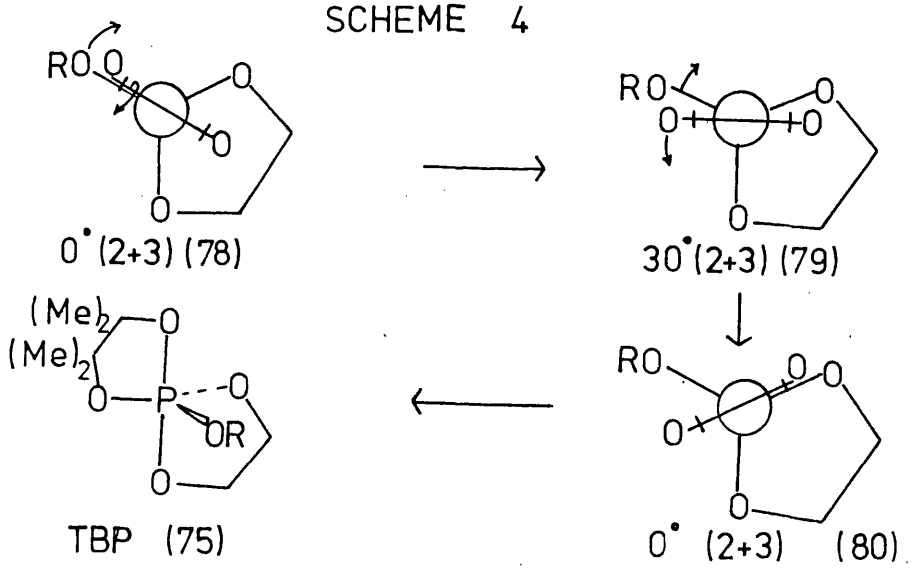
30°(2+3) (77) 0°(2+3) (78)

Ramirez and Ugi claim that the 0°(2+3) (78) can do one of two things,

(i) distort to a trigonal bipyramid which in this case is the high energy (74) with the ring diequatorial,

(ii) continue the internal rotation by a further 30° to the next 30°(2+3) (79), then again to the next 0°(2+3) (80) followed by distortion to the low energy trigonal bipyramid (75) Scheme 4.

SCHEME 4



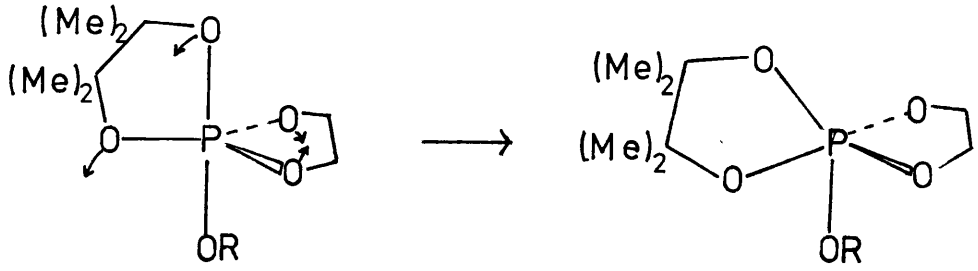
0°(2+3) (78) 30°(2+3) (79)

TBP (75) 0° (2+3) (80)

By using this second alternative Ugi and Ramirez claim that the high energy trigonal bipyramid (74) may be avoided. This process is called a $(TR)^2$, two rotations of 60° missing out the intermediate trigonal bipyramid. When three successive rotations occur missing out the two intermediate trigonal bipyramids the process is known as a $(TR)^3$.

The phosphorane (74) with the ethylene glycol ring diequatorial has been drawn as a trigonal bipyramid in the interests of clarity.

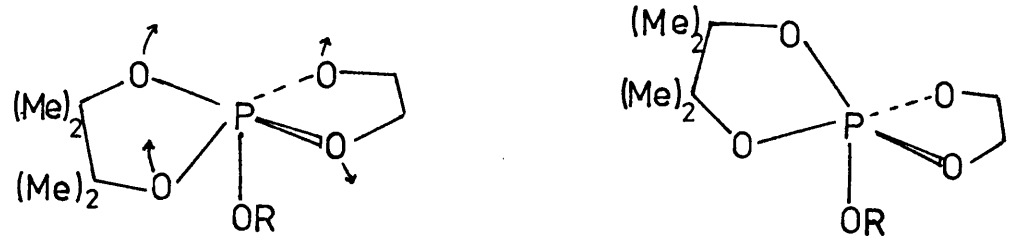
Clearly such a phosphorane can not be expected to remain as a perfect trigonal bipyramid.



(74) (81)

The oxygen atoms of the diequatorial ring will move together reducing the O-P-O angle in order to reduce the ring strain. This motion forces the pinacol ring down in the direction of the phenoxy group. If the pinacol ring moves too far down the repulsion term between the phenoxy group and the oxygen in the pinacol ring becomes large. Therefore a balance is achieved between the strain in the ethylene glycol ring and the repulsion between the phenoxy and pinacol oxygen. This intermediate structure (74) is more accurately represented by (81).

Considering the intermediate (78) in the Turnstile process - a $0^{o}(2+3)$



(78) (81)

In a perfect $0^{o}(2+3)$ the O-P-O angle in the ethylene glycol ring is 90^{o}, therefore ring strain is very small. The phenoxy group and the pinacol oxygen are eclipsed and in very close proximity. There will clearly be a distortion where the pinacol ring moves upwards to reduce

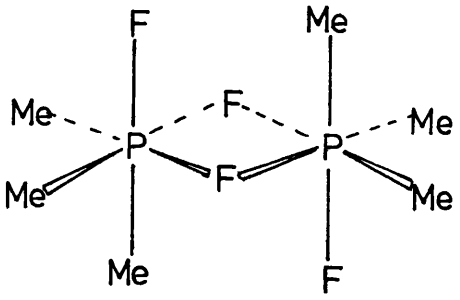
this repulsion term but such a movement increases the O-P-O angle in the ethylene glycol ring causing ring strain to increase. A balance between these two factors leads to the same intermediate (81) as from distortion of the trigonal bipyramid (74). The important point that can be drawn from this analysis is that Berry pseudorotation and Turnstile rotation describe different routes through the same intermediates.

For the purpose of explaining variable temperature n.m.r. data presented in this thesis Berry pseudorotation or Turnstile rotation may be used equally well, but for the sake of simplicity, permutational isomerisation processes will be described formally in terms of Berry pseudorotation.

2.5 Irregular Processes.

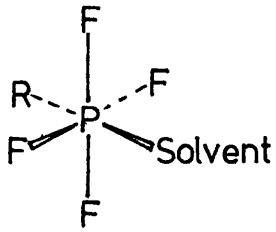
The ligand permutational isomerisation processes discussed so far have all been regular processes, i.e. unimolecular and involving no bond rupture or formation. Irregular processes, however, may be unimolecular or bimolecular and always involve bond making and breaking. Fluorophosphoranes with more than one fluorine atom are particularly susceptible to irregular processes. In a recent paper by Moreland and Doak[48] they discovered that in Teflon n.m.r. tubes the ligand permutational isomerism of Ph_2PF_3 was an intramolecular process with first order kinetics. In pyrex n.m.r. tubes the process was intermolecular but still first order. This was thought to be caused by impurities present in the pyrex tubes.

Second order kinetics and large negative entropies of activation observed by Cowley[49] for Me_2PF_3 and Me_3PF_2 led him to postulate the presence of a fluorine-bridged dimeric intermediate (82).



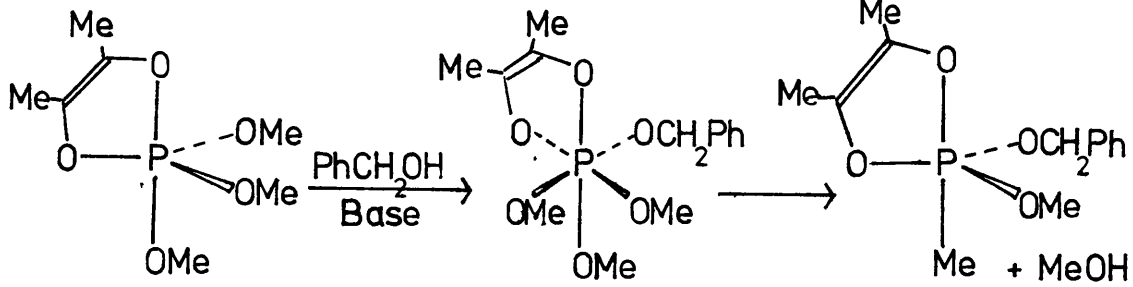
(82)

Musher[50] suggested for RPF_4 phosphoranes that apart from fluorine bridging, fluorine equivalence could be caused by co-ordination to a solvent molecule as in (83).



(83)

Hexa-co-ordinate species (85) have been postulated by Ugi and Ramirez[12] in the base-catalysed exchange of alkoxy groups in the oxyphosphorane (84).

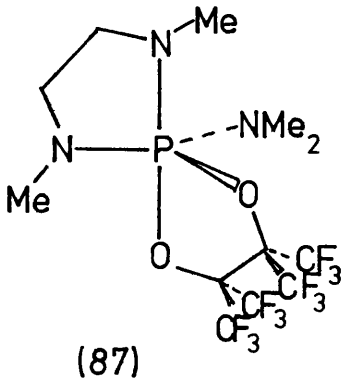


(84) (85) (86)

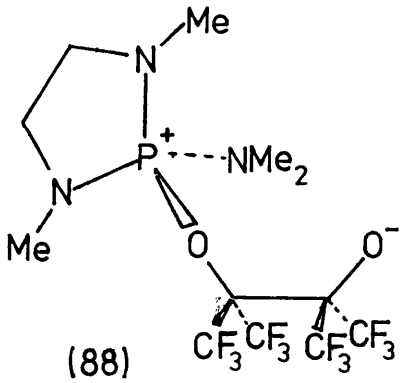
The presence of nucleophilic impurities in the phosphorane or solvent could cause equilibration by an analogous mechanism.

One of the most common irregular processes in oxyphosphoranes is that of ionisation, usually ring opening. The adduct (87) prepared

by Whittle[19] showed only a singlet in the ^{19}F above 0^{o}. This could be explained in terms of an irregular process where reversible dissociation was taking place (87) $\rightleftharpoons$ (88).



(87)



(88)

When interpreting ligand permutational isomerism from n.m.r. data the possibility of irregular processes must be considered and where possible eliminated by experiment (see Section 3.5).

3. ARRANGEMENT OF LIGANDS IN PHOSPHORANES.

3.1 Bonding in Phosphoranes.

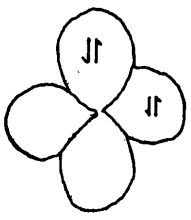
The fact that in a trigonal bipyramid apical bonds are longer than equatorial and that the more electronegative elements prefer the apical position has led to a large number of approaches to bonding in phosphoranes.[17,47b-f,45,55-57]

From a Molecular Orbital study Hoffmann, Howell, and Muetterties[45] concluded that apical bonds will be longer than equatorial and more electronegative atoms will prefer the apical position, but unlike other workers[47b-f] they concluded that d-orbitals participated only to a small extent and had only a small effect in determining the ligand arrangement around phosphorus.

Hoffmann considered the effect of substituents bearing filled or unfilled π orbitals on phosphorus in a pentaco-ordinate phosphorane.

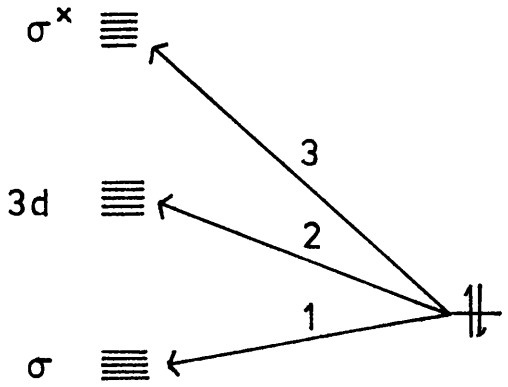
(i) π donation.

A π donor was defined as a substituent bearing one or two high-lying occupied molecular orbitals.



(89)

Three interactions were considered for this donor orbital with the phosphorus atom

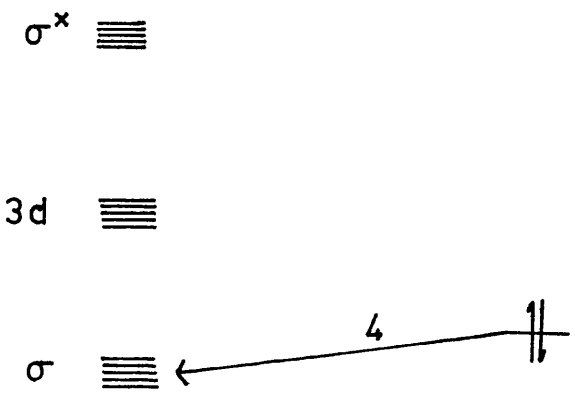


Interaction 1, inherently destabilising[58-60], is between a filled π donor and filled P^V skeletal orbitals. Interaction 2, inherently stabilising, is between the potentially active phosphorus 3d orbitals and the donor. Interaction 3, inherently stabilising, is between donor and unfilled skeletal orbitals. The energy of σ^* is so high that little trace of interaction with normal donors has been found.

Interaction 2 is considered to be small and thus the major interaction is 1 which is considered to be destabilising.

(ii) π Acceptance.

The situation is simpler for π acceptors as there is only one chemically significant interaction.



A π acceptor is defined as a substituent with one or two low-lying unoccupied molecular orbitals. Interaction 4, inherently stabilising, is between the acceptor orbital and the filled P^V skeletal orbitals. It was concluded that π acceptors have a stabilising effect.

Hoffmann considered the interaction of π orbitals of a substituent in both the apical and equatorial positions. From the amounts of overlap between molecular orbitals it was concluded that the greatest interaction occurred in the apical position for both acceptors and donors. It then follows that π donors having a destabilising effect will prefer the equatorial position where interaction is less and π acceptors having a stabilising effect will prefer the apical position where interaction is greater.

3.2 Apicophilicity of Ligands.

From Hoffmann's molecular orbital calculations three factors have emerged relating to a ligand's preference for the apical position, electronegativity, π donation, and π acceptance. This preference for the apical position is referred to as 'apicophilicity'.[47d]

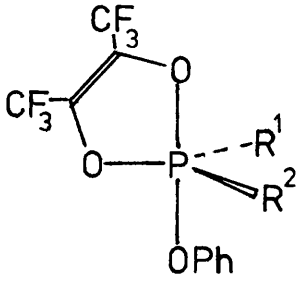
Early attempts at predicting relative apicophilicities came from n.m.r. studies of fluorophosphoranes[42,61] and cyclic oxyphosphoranes[24,62,63] and kinetic studies of cyclic and acyclic phosphate, phosphonate and phosphinite esters[5,64]; these were referred to as the 'Preference Rules'. They stated simply that when phosphorus was part of a small (four- or five-) membered ring, the ring prefers to span the apical-equatorial position of a trigonal bipyramid, and also that electronegative groups prefer the apical position. X-ray studies have confirmed that small rings prefer the apical-equatorial arrangement[18-20] but it has since

been discovered that there are other factors apart from electronegativity that affect the apicophilicity of a ligand.

Hoffmann's Molecular Orbital calculations on PH_5 [45] indicated an accumulation of negative charge at the apical positions; this has also been found for other phosphoranes.[47d,55,65] This means that electronegative groups will prefer the apical position.

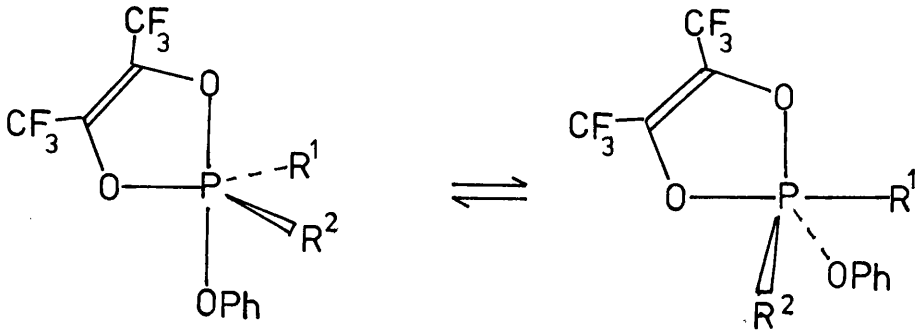
Using electronegativity, π donation, and π acceptance the relative apicophilicity of ligands may be rationalised except in cases where there are large steric interactions.

The apical position, having three neighbours at 90^{o} may be considered to be more hindered than the equatorial position having only two. However, the apical bond is longer therefore steric interactions will be smaller. Whittle[19] studied a series of perfluorobiacetyl adducts (90) in order to determine which site was the more hindered.



(90)

The pseudorotation (90) $\rightleftharpoons$ (91) can be slowed on the n.m.r. time-scale. From this information can be calculated the 'Free Energy of Activation' (see Section 3.4).



(90) (91)

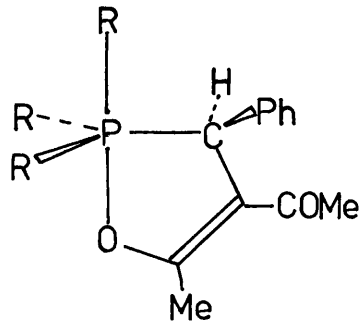
Where R^1 is less apicophilic than R^2.

The results may be summarised:

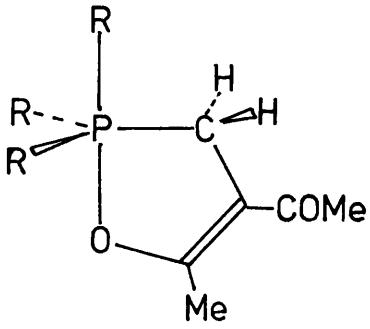
R^1 = Me	R^2 = Me	ΔG^*	10·0 kcals mol^{-1}
R^1 = Me	R^2 = Bu^t	ΔG^*	11·1 kcals mol^{-1}
R^1 = Bu^t	R^2 = Bu^t	ΔG^*	14·6 kcals mol^{-1}

As there are no π orbitals on methyl or t-butyl and the electronegativities are very close the increase in energy required to put t-butyl apical as the group remaining equatorial changes from methyl to t-butyl must be due to increased steric hindrance in the apical position, i.e. the apical site is morehindered than the equatorial. It was also concluded from this experiment that steric effects in a trigonal bipyramid are relatively small unless there are at least two bulky groups attached directly to phosphorus.

Another type of steric hindrance to pseudorotation can be seen when there are bulky substituents on the α-carbon atom. Gorenstein[63b] noted that the barriers to pseudorotation in the benzylideneacetylacetone adducts (92) were considerably greater than in the corresponding methyleneacetylacetone adducts (93).

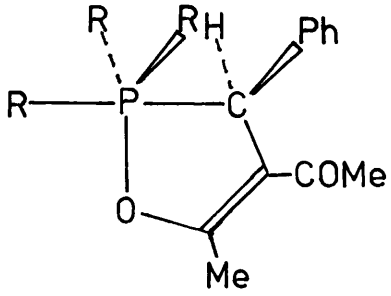


(92)



(93)

The reason for this is clearly steric as in the case of (92) there is complete eclipsing of the phenyl group and an equatorial R group when the ring carbon atom is apical (94).



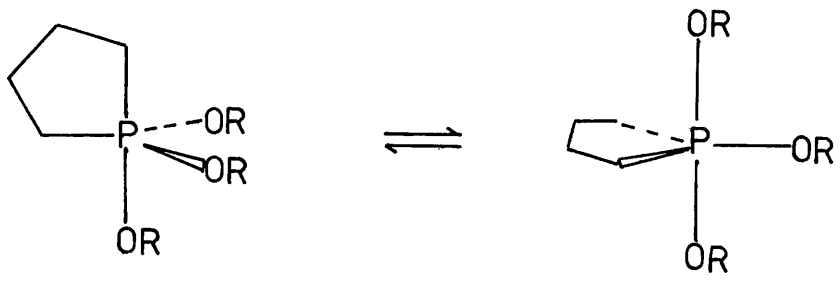
(94)

Conclusion.

The apicophilicity of a group is determined primarily by the electronegativity but corrections have to be made when π acceptor or donor orbitals are present on the group and when steric effects are important.

3.3 Use of Apicophilicity Values.

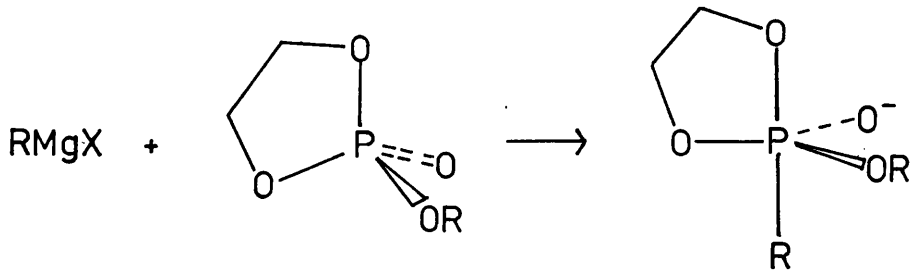
If apicophilicity values were available for various groups then it would be theoretically possible to predict the energetically most favoured arrangement of ligands in an acyclic phosphorane. In a cyclic phosphorane however the value of the ring strain may be important e.g. (95).



(95) (96)

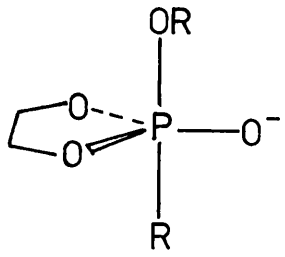
On apicophilicity predictions alone, (96) is favoured as oxygen is more apicophilic than carbon. A knowledge of ring strain is important here to decide whether the gain in energy on going from (95) to (96), replacing the apical carbon by an equatorial oxygen, is greater than the increase in ring strain caused by expanding the ring angle at phosphorus from 90^{o} to 120^{o}. The importance of apicophilicity and ring strain values is in the reaction of nucleophiles with tetraco-ordinated phosphorus compounds. Although the phosphorane intermediates are very short lived there is much evidence[2-12] to indicate that they are sufficiently long lived to undergo pseudorotation processes. An assumption made by most workers[5] is that the nucleophile attacks one of the faces of the tetrahedral phosphorus thus occupying an apical position in the trigonal bipyramidal intermediate, i.e. apical attack by the nucleophile. Also the leaving group is assumed to leave from an apical position. Using these assumptions a nucleophile can attack any of the four faces of the tetrahedral phosphorus forming four possible trigonal bipyramids; if these are sufficiently long lived pseudorotation can occur producing up to twenty trigonal bipyramids any of which may decompose to products. Hence there is a possibility of forming a large variety of products. If two further assumptions are made then apicophilicity values and ring strains may be used to predict the course

of these reactions. The first assumption is that the nucleophile attacks in such a way that the thermodynamically most stable phosphorane (with the nucleophile apical) is initially produced. The second is that decomposition to products will occur from the most stable phosphorane which has the leaving group apical. These assumptions can best be illustrated by an example, e.g. attack by Grignard reagent on a five-membered cyclic phosphate (97).



(97) (98)

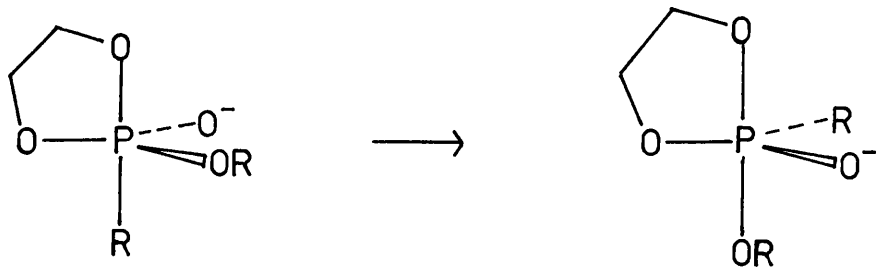
The R^- nucleophile could not attack opposite the phosphoryl oxygen as O^- is very poorly apicophilic. If the nucleophile had attacked opposite the OR group the phosphorane produced would have the ring in the diequatorial position (99) which would be highly unfavourable.



(99)

Thus attack must occur opposite a ring oxygen in order that the assumption that with the nucleophile apical, the most thermodynamically stable phosphorane is produced, i.e. (98). The assumption that decomposition occurs from the most stable phosphorane which has the leaving group apical requires that (98) must pseudorotate to the most

stable phosphorane. The phosphorane (98) is a high energy species because it has an alkyl group apical, i.e. the nucleophile, which is poorly apicophilic and an alkoxy group equatorial which is highly apicophilic. Using this apicophilicity data it could be predicted that before loss of the ring oxygen of (98) can occur a pseudorotation will take place putting the alkoxy apical and the alkyl equatorial, i.e. (98) ⟶ (100).



(98) (100)

This pseudorotation produces the more stable trigonal bipyramid (100). A second pseudorotation will put either the alkyl group or the O^- group apical which will be of high energy, therefore decomposition of the phosphorane occurs from (100). Here, the ring oxygen may be lost to give (101) or the alkoxy group to give (102).

(101) (102)

The group that is lost is determined by the anion stability, i.e. the better leaving group is displaced. If both groups have a similar leaving group ability then a mixture of products (101) and (102) will be observed.

Clearly, with a full knowledge of apicophilicity and ring strain values coupled with a knowledge of leaving group ability, the stereochemical pathway of nucleophilic displacement at tetraco-ordinated phosphorus may be predicted, except where bulky groups are directly bonded to phosphorus when steric effects become important.[66]

3.4 Determination of Apicophilicity Values.

There are three methods described in the literature for the determination of apicophilicity.

(a) DeBruin[67] reasoned that if by knowledge of apicophilicities and leaving group abilities the stereochemical course of nucleophilic substitution at tetraco-ordinate phosphorus could be predicted then the reverse must also be true. Thus from a prior knowledge of the reaction pathway and stereochemistry of various substitutions he was able to build up a semi-quantitative apicophilicity scale.

(b) A qualitative assessment of apicophilicity in certain asymmetrically substituted phosphoranes can be made by studying the ground state arrangement of ligands.[42, 61,68-70] This is accomplished by cooling the sample until all pseudorotations are slow on the n.m.r. time-scale. Analysis of the n.m.r. spectra of the frozen molecule can determine the ligand arrangement. This has led to the formation of a limited apicophilicity scale[69] but this is not particularly useful for obtaining quantitative data.

(c) The rate of pseudorotation is dependent on the energy difference between interconverting phosphoranes. Suitable phosphoranes have been prepared which allow the rate of pseudorotation to be monitored by d.n.m.r. spectroscopy,[71-75] or, in the case of higher energy pseudorotations

by 'conventional' kinetic determinations. Free energies of activation ΔG^{*} were then calculated from the coalescence temperature and the maximum frequency separation of the signals below coalescence, $\Delta\nu$ using the Eyring equation;[77a]

$$k_1 = (kT/h) \exp(-\Delta G^{*}/RT)$$

k = Boltzmann's constant

T = Temperature of coalescence

h = Planck's constant

R = Gas constant.

where the rate of pseudorotation k_1 at the coalescence temperature is given by the Gutowsky-Holm[77b] approximation

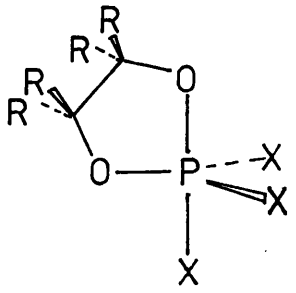
$$k_1 = \frac{\pi \Delta\nu}{\sqrt{2}}$$

The values of ΔG^{*} calculated in this way at different temperatures can be compared only if the entropies of activation ΔS^{*} are zero. Gorenstein[63b] and Wolf[76] have concluded that the values of ΔS^{*} are very small and to the first approximation may be regarded as zero.

3.5 Application of D.N.M.R. to Determine 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 two systems.

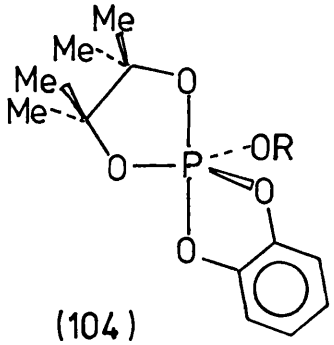
1(a) The first system utilises a five-membered 1,3,2-dioxaphospholan ring with four identical groups on the carbon atoms 4 and 5 which can readily be monitored by n.m.r. (103)



where R = CF_3, CH_3 or H.

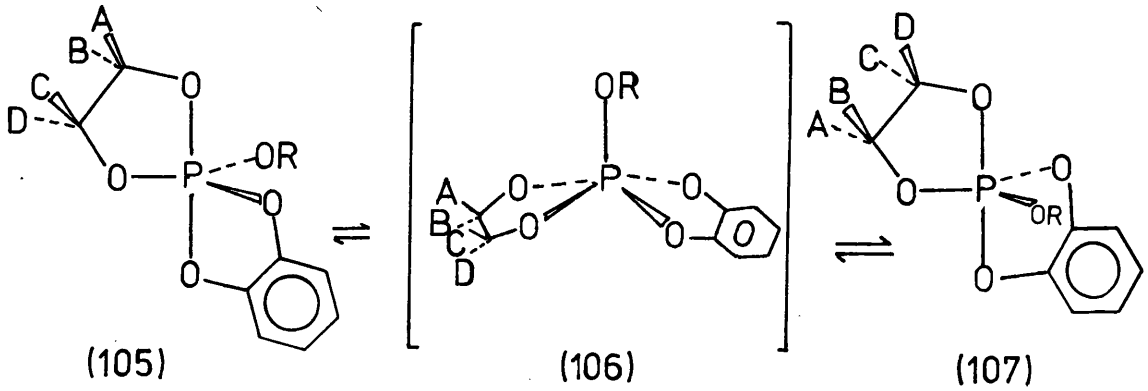
(103)

The four groups are usually methyl, trifluoromethyl, or hydrogen. For a particular example (104), consider the methyl groups to be labelled



(104)

A - D (105). Pseudorotation of (105) to (107) passes through the square base pyramidal intermediate (106). This intermediate contains a plane of symmetry which makes A equivalent with C and B equivalent with D.

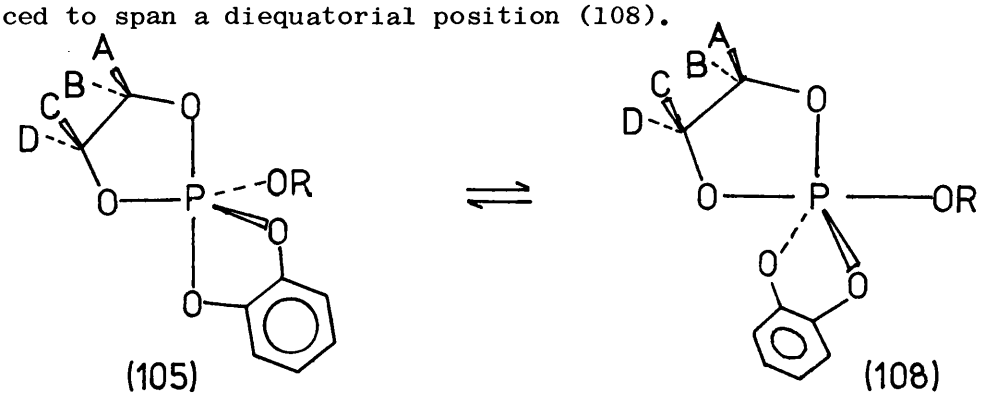


(105) (106) (107)

A ≡ C and B ≡ D

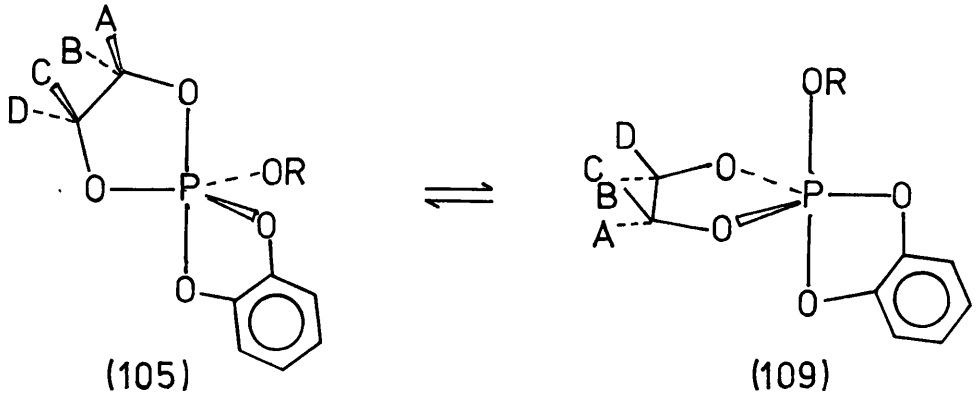
Phosphoranes (105) and (107) are of equal energy and known as topomeric species. This pseudorotation has a very low energy of activation and cannot be slowed on the n.m.r. time-scale. Due to this topomeric pseudorotation the methyl signals of adduct (104) appear as two sharp singlets in the ^{1}H n.m.r. at room temperature.

A second pseudorotation may occur in which the catechol ring is forced to span a diequatorial position (108).



In (108) there is a plane of symmetry in the plane of the paper which makes A equivalent with B and C equivalent with D. This pseudorotation will be of high energy because the catechol ring is in an unfavourable diequatorial position and the OR group has been moved to the apical position. This process will have a free energy of activation of about 20 kcals. mol^{-1} (see Chapter 4). This pseudorotation will be slow on the n.m.r. time-scale at room temperature but as the temperature is raised, the methyl signals will eventually broaden, coalesce to a single broad peak which will sharpen as the temperature is raised further. When this pseudorotation is fast on the n.m.r. time-scale, all the methyl groups are equivalent in the n.m.r.

A third pseudorotation may occur in this molecule where the pinacol ring moves out diequatorial and the OR group moves to an apical position (109).

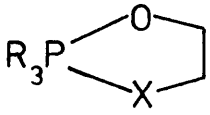


(105) (109)

The plane of symmetry in the plane of the paper makes methyls A equivalent with C and B equivalent with D which has the same effect as the low energy topomeric pseudorotation (105) ⇌ (107).

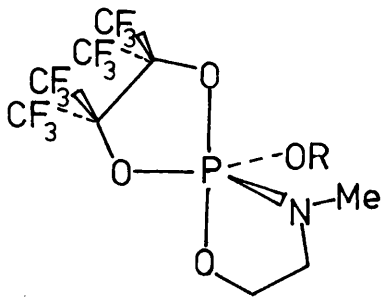
Complete equivalence of the methyl signals can occur only if the catechol ring spans the diequatorial position and the OR group moves to an apical position.

1(b) The same ring (103) may be used to obtain information on apicophilicity and ring strain when the second ring is not symmetrical, i.e.



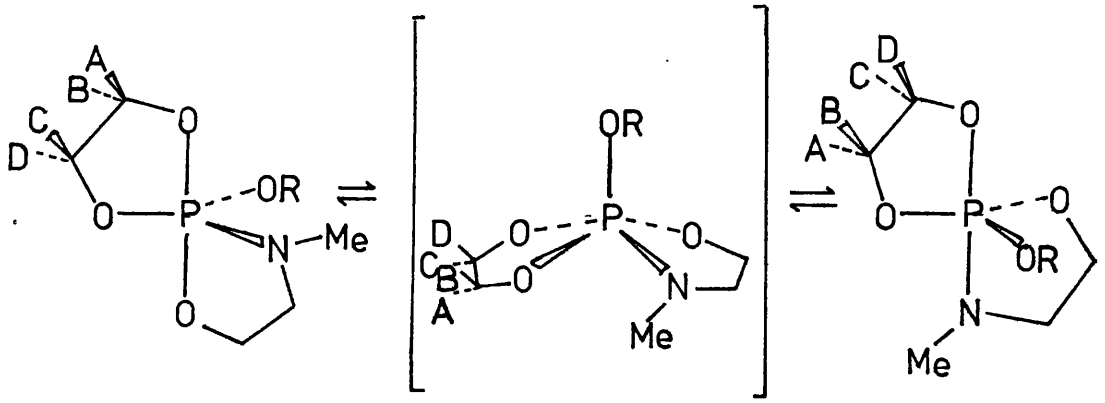
where X = NMe, S.

e.g. (110)



(110)

Consider the trifluoromethyl groups to be labelled A-D (111). The lowest energy pseudorotation (111) - (113) does not make any of the trifluoromethyl groups equivalent.

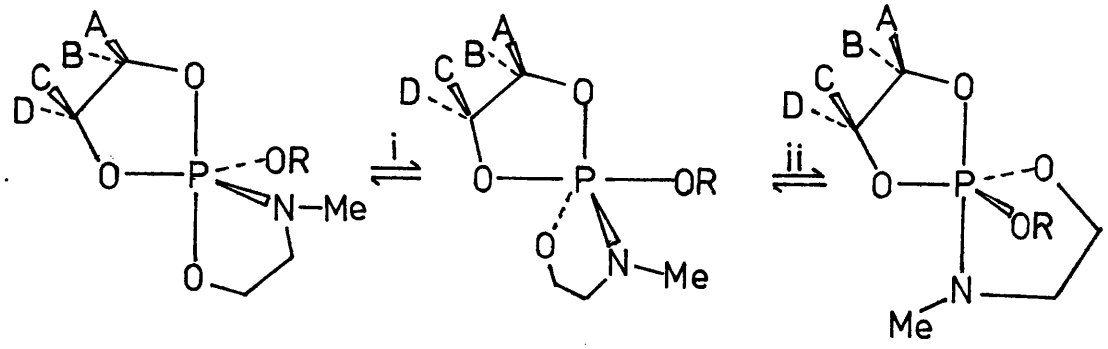


(111) (112) (113)

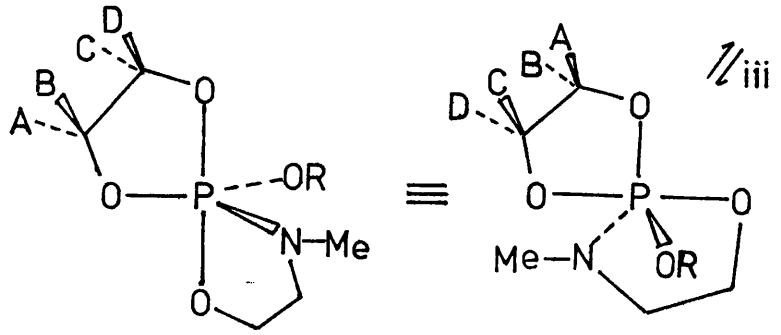
As this is the only pseudorotation which is rapid on the n.m.r. time-scale at room temperature the ^{19}F n.m.r. consists of four equal signals.

Partial equivalence of the trifluoromethyl groups can occur by a multistep pseudorotation pathway which includes the high energy species with the oxazaphospholan ring diequatorial and the OR group apical. The pathway is set out in Scheme 5.

SCHEME 5



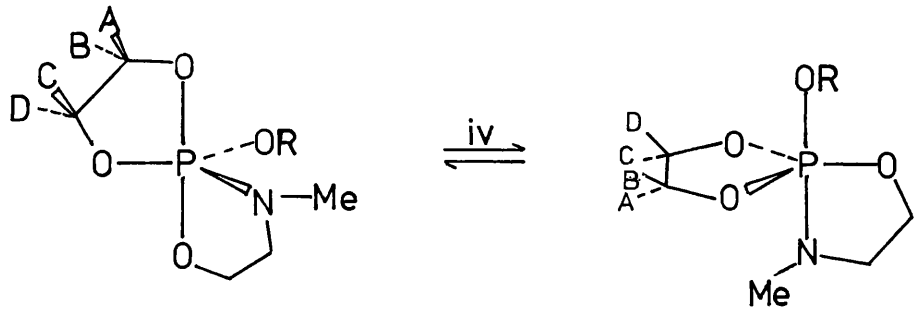
(111) (114) (115)



(116) (116)

Pseudorotation (i) puts the oxazaphospholan ring diequatorial and OR apical; this is the highest energy species (114). Pseudorotation (ii) may now occur to give intermediate (115). This has an apical nitrogen group which is unfavourable so pseudorotation (iii) occurs to give (116). Comparing (111) with (116), A of (111) has been replaced by D in (116), i.e. A and D have become equivalent. Similarly B of (111) has been replaced by C in (116), i.e. B and C have become equivalent. When Scheme 5 becomes fast on the n.m.r. time-scale then the four trifluoromethyl signals coalesce to two.

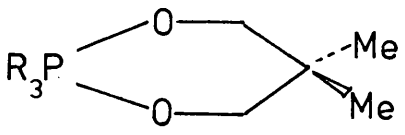
The pseudorotation (iv) that puts the perfluoropinacol ring diequatorial must also be considered.



(111) (117)

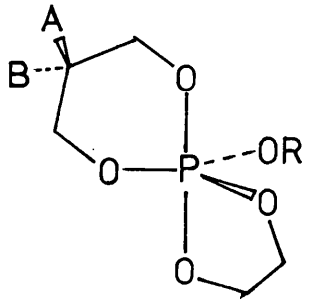
Pseudorotation (iv) would give the high energy intermediate (117) which contains a plane of symmetry in the plane of the paper which makes A equivalent with C and B equivalent with D. As pseudorotations (i)- (iii) make A equivalent with D and B equivalent with C if all four pseudorotations are fast on the n.m.r. time-scale complete equivalence of the trifluoromethyl groups will be observed. In a molecule of this type it is theoretically possible to observe two coalescences as the temperature is raised, four signals coalescing to two as one ring goes out diequatorial then two signals coalescing to one as both rings go out diequatorial.

2(a) The second system employs the 5,5-dimethyl-1,3,2-dioxaphosphorinan system (118).



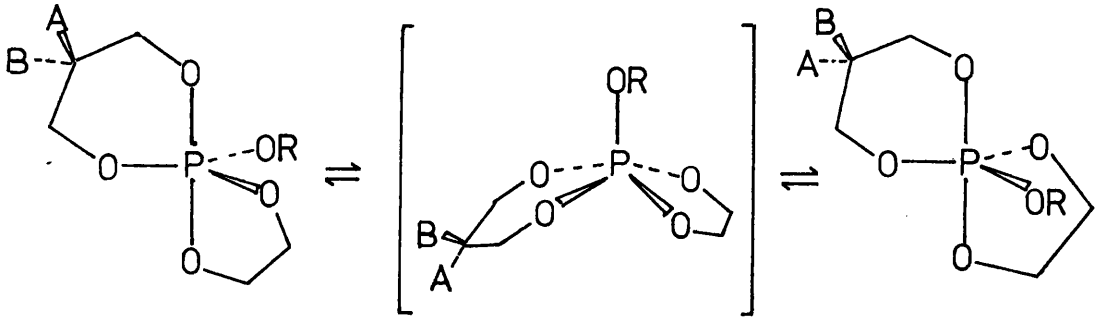
(118)

Using (119) as an example with the methyls labelled A and B



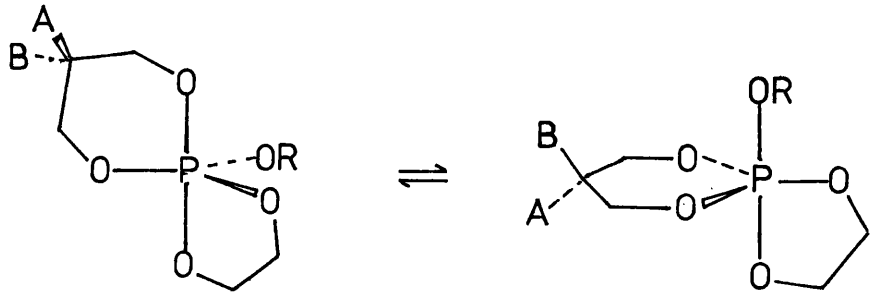
(119)

The low energy topomeric pseudorotation (119) $\rightleftharpoons$ (121) does not make the methyl groups A and B equivalent.



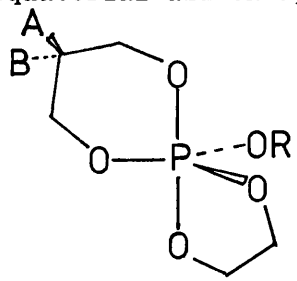
(119) (120) (121)

Similarly the relatively low energy pseudorotation (119) $\rightleftharpoons$ (122) that puts the dioxaphosphorinan ring diequatorial does not make A and B equivalent.

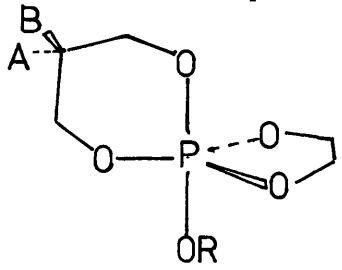


(119) (122)

Only the high energy pseudorotation putting the five-membered ring diequatorial and OR apical allows A and B to become equivalent.



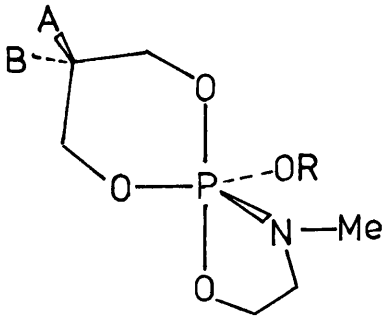
(119)



(123)

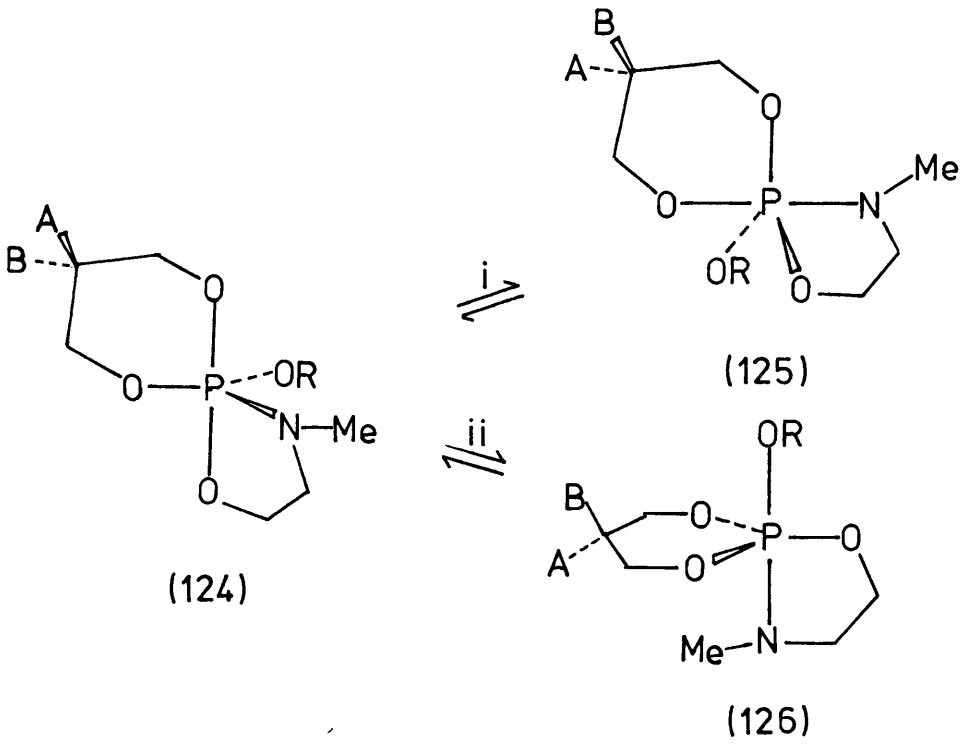
The plane of symmetry through (123) in the plane of the paper makes A and B equivalent.

2(b) In the case where the second ring is unsymmetrical the 5,5-dimethyldioxaphosphorinan system (118) is potentially very useful, e.g. (124).

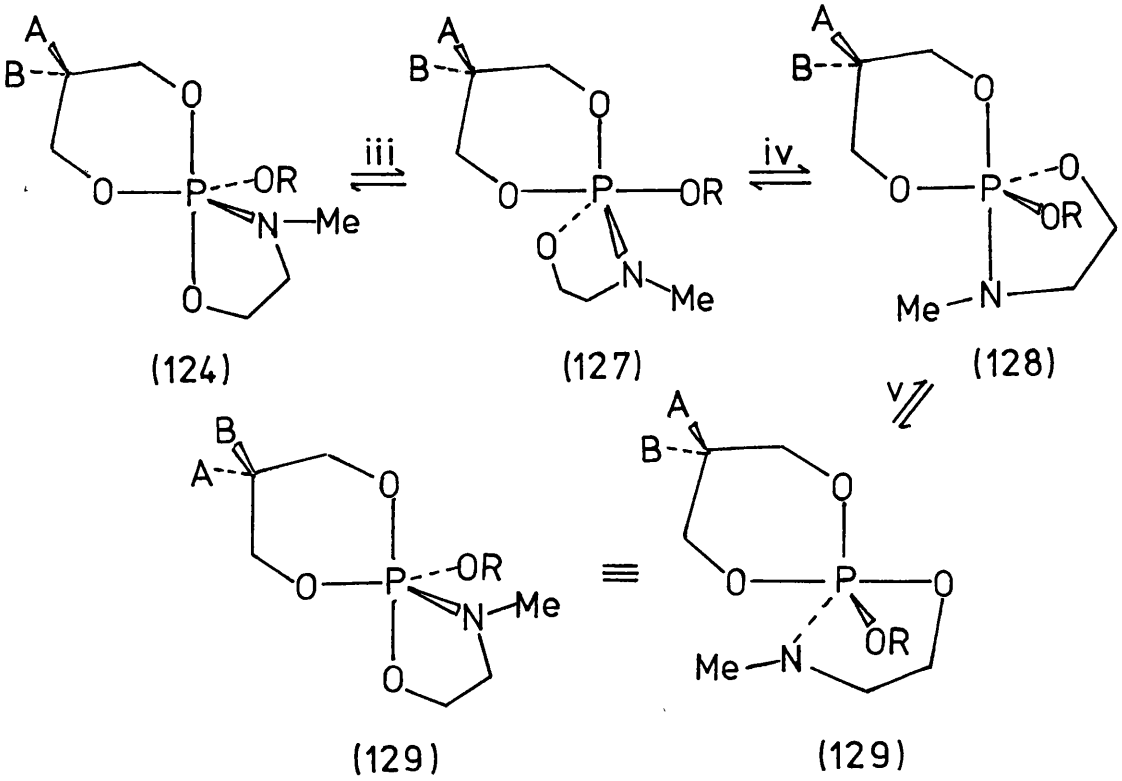


(124)

As in the case where the second ring was symmetrical (119) the relatively low energy pseudorotations (i) and (ii) do not make A and B equivalent.



A and B may only become equivalent by a multistep pseudorotation pathway including the high energy intermediate with the oxazaphospholan ring diequatorial. This pathway is set out in Scheme 6.



SCHEME 6

Pseudorotation (iii) gives the highest energy phosphorane (127) with the oxazaphospholan ring diequatorial. Pseudorotation (iv) may now take place giving intermediate (128) which has a nitrogen group apical; pseudorotation (v) then gives (129). Comparing (124) with (129), A in (124) is on the opposite side to the OR group, whereas A in (129) is on the same side as the OR group the position held by (B) in (124), i.e. A and B have become equivalent.

The importance of the dimethyldioxaphosphorinan system is that equivalence of the methyls only occurs when the other ring goes out diequatorial, even if the second ring is unsymmetrical.

3.6 Accuracy and Limitation of the D.N.M.R. Method.

Accuracy.

For systems where coalescence of signals of equal intensity is observed, the Gutowsky-Holm equation has been shown to be almost as accurate as a complete line shape analysis.[78] The main sources of error in the calculation of the free energy of activation ΔG^* lie in:

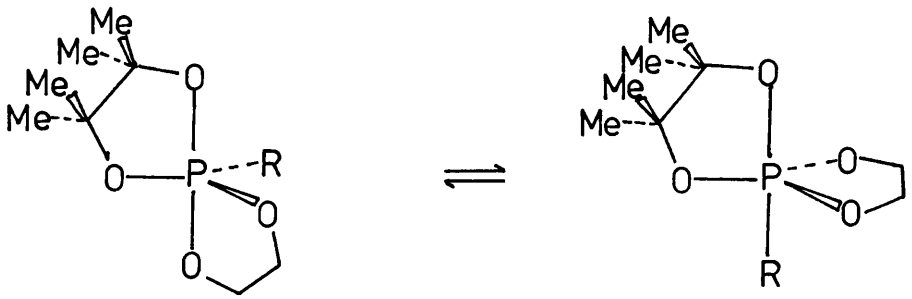
(a) Temperature Measurements.

The total error in measurement of a coalescence temperature is $\pm 5^{o}$ which corresponds to an error in the ΔG^* value of $\pm 0{\cdot}3$ kcals. mol^{-1}.

(b) Measurement of the Maximum Frequency Separation Between the Signals that Coalesce.

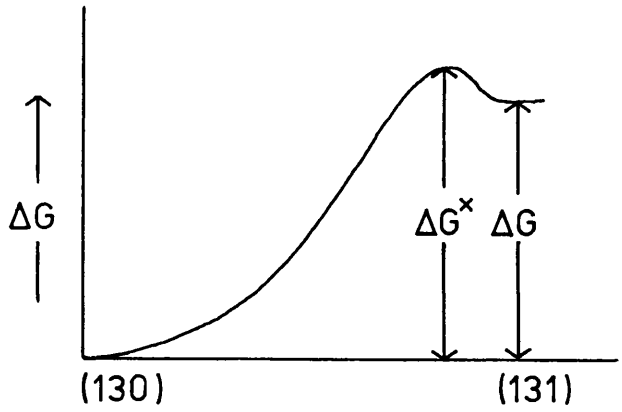
This figure can normally be obtained quite accurately but in cases where coalescence is close to the lower limit of the n.m.r. spectrometer temperature range the frequency separation cannot be measured accurately. This however is only a very minor source of error.

Consider the pseudorotation (130) ⇌ (131)



(130) (131)

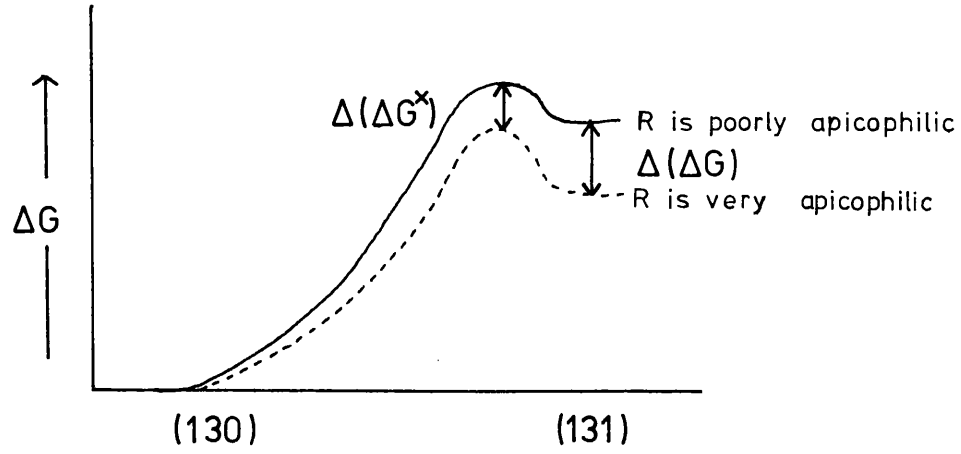
The reaction co-ordinate may be drawn as follows:-



To compare the difference in energy between (130) and (131) the value required is ΔG but the Gutowsky-Holm equation measures ΔG^* the free energy of activation. Clearly, ΔG^* is an overestimate of ΔG. The phosphorane (131) with the ring diequatorial is a very high energy species and according to Hammond's Postulate the product will closely resemble the transition state. In fact (131) itself may be the transition state, in which case $\Delta G^* = \Delta G$. Thus it seems reasonable to assume that the difference between ΔG^* and ΔG will be small.

Small errors can arise when determining the relative apicophilicity between two groups. This can be seen by comparing the reaction

co-ordinates for the two phosphoranes (130) where in one the R group is very apicophilic and in the other the R group is poorly apicophilic.



From Hammond's Postulate the phosphorane (131) with R poorly apicophilic will more closely resemble the transition state than with R very apicophilic. This means that the measured $\Delta(\Delta G^{*})$ value is smaller than the actual difference in energy between the two phosphoranes (131) $\Delta(\Delta G)$. The error will be very small unless comparing a very poorly apicophilic group like phenyl with a very apicophilic group like fluorine. Hence for comparison of groups with reasonably similar apicophilicities $\Delta(\Delta G^{*})$ is regarded as being equal to $\Delta(\Delta G)$ in this way a quantitative apicophilicity scale may be built up.

Limitations.

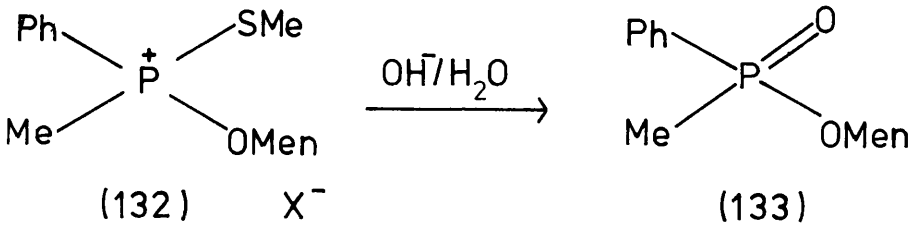
The major limitation of the d.n.m.r. method of determining apicophilicities is that the changes observed in the n.m.r. may be due to some process other than the speeding up or slowing down of a pseudo-rotation. Coalescence may be caused by the groups under observation becoming accidentally magnetically equivalent. This usually only occurs when the signals under observation are very close together to begin with.

It is possible to distinguish between accidental equivalence and genuine coalescence by studying the line widths of the signals as they approach coalescence. If a genuine rate process is becoming fast or slow on the n.m.r. time-scale the signal decreases in height and the line widths are significantly increased. For accidental equivalence there should be no variation in the line width.

The most likely alternative mechanism is an irregular process previously discussed in Section 2.5. The method used by Ramirez[12,79,8] for deciding if ionic species are present in solution is to obtain the ^{31}P n.m.r. in solvents of different polarity. If a marked variation in ^{31}P n.m.r. is observed in highly polar solvents it is a good indication that ion species are present in solution.

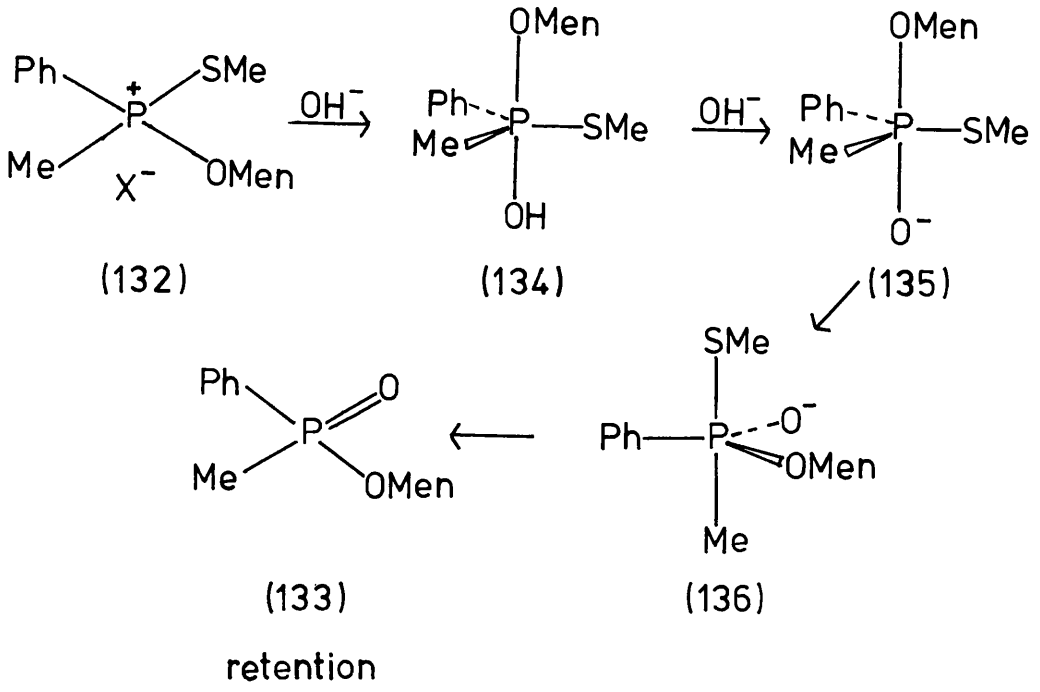
4. THE RELATIVE APICOPHILICITY OF SULPHUR LIGANDS.

Some semi-quantitative evidence was available on the relative apicophilicity of sulphur ligands from hydrolysis of tetraco-ordinated phosphorus compounds.[81,82] Alkaline hydrolysis of the optically active phosphonium salt (132) gives the phosphinate (133) with retention.



Using the assumptions set out in 3.3, i.e. apical attack to form the most stable trigonal bipyramid followed by apical loss from the most stable trigonal bipyramid, two possible intermediates may be formed by attack of a hydroxyl ion.

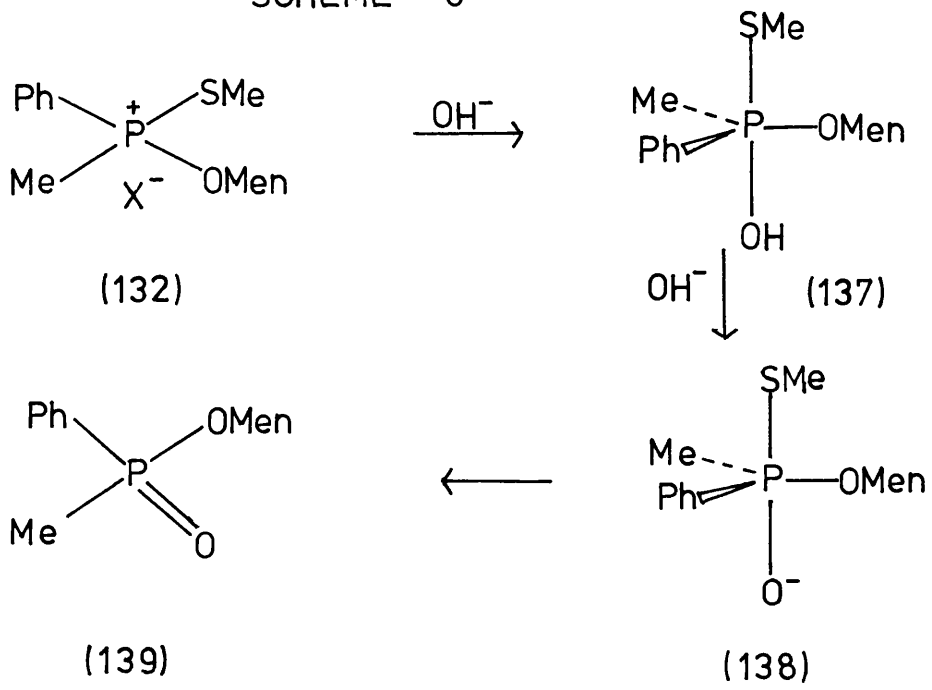
(i) Opposite O-Menthyl.



SCHEME 7

(ii) Opposite SMe.

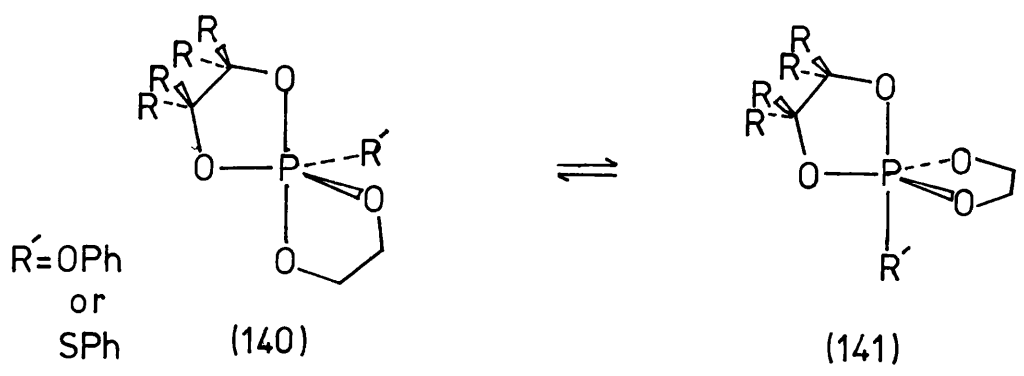
SCHEME 8



If attack opposite -O-menthyl occurs (Scheme 7) then the result is retention of configuration. If attack opposite -SMe occurs then inversion would be the result (Scheme 8). The result found experimentally is retention; this means that the trigonal bipyramid with o-menthyl apical is more stable than with SMe apical, i.e. -O-menthyl is more apicophilic than -SMe.

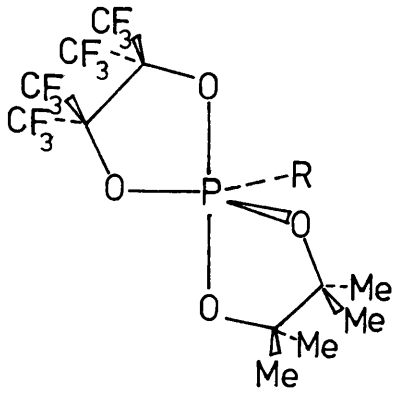
It was decided to try and obtain quantitative data on this difference between sulphur and oxygen substituents.

Using spirophosphoranes of the type (140)



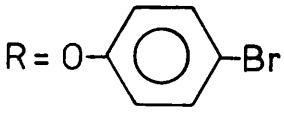
Where R' is OPh and SPh and observing the energies for the speeding up of pseudorotation 140 ⇌ 141 the relative apicophilicity of -OPh and -SPh can be measured (see Section 3.6).

Duff[93] made an attempt to do this by preparing adducts (142) and (143).



R = OPh (142)

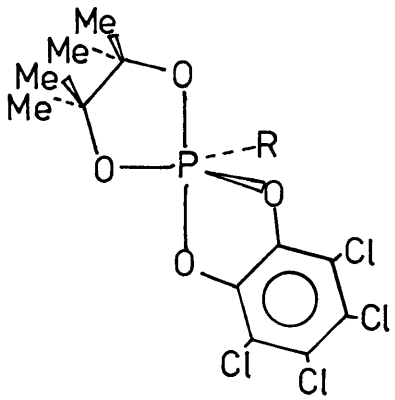
R = SPh (143)



(144)

The thiophenyl adduct (143) showed a reversible coalescence in the ^{19}F n.m.r. at 180° corresponding to a ΔG^{*} value of 22·4 kcals.mol^{-1}., but the phenoxy adduct showed only a singlet in the ^{19}F down to -90° at which temperature coalescence was observed in dichloromethane but not in ether. An X-ray structure determination of the p-bromophenoxy adduct (144) showed it to have an almost perfect trigonal bipyramidal structure. The singlet in the ^{19}F for this adduct is thought to arise from accidental equivalence of the trifluoromethyl groups. As no direct comparison was available from this system, others were investigated.

Adducts (145)-(147) were readily synthesised by treatment of the respective trivalent phosphorus compound with tetrachloro-o-benzoquinone.



R = OPh (145)

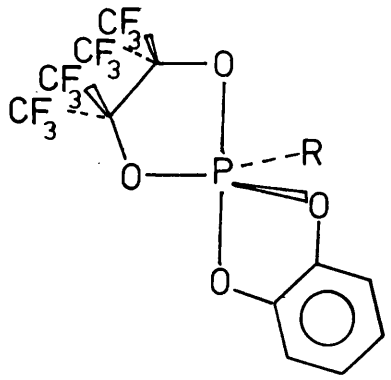
R = SPh (146)

R = NMe_2 (147)

The phenoxy adduct (145) showed a reversible coalescence in the ^1H n.m.r. at 106° corresponding to a ΔG^* value of 20·5 kcals. mol^{-1}. The dimethylamino adduct (147) showed no coalescence even at 180° (the upper limit of the n.m.r. spectrometer). This was expected in view of the large difference in apicophilicity between phenoxy and dimethylamino.[72,84] Unfortunately the thiophenyl adduct (146) decomposed at 130° before coalescence. The figure obtained for the phenoxy adduct (145) seemed much more reasonable than that obtained by Duff (142). All that can be concluded from this experiment is that thiophenyl is less apicophilic than phenoxy.

In order to make a quantitative assessment other systems were considered.

e.g.

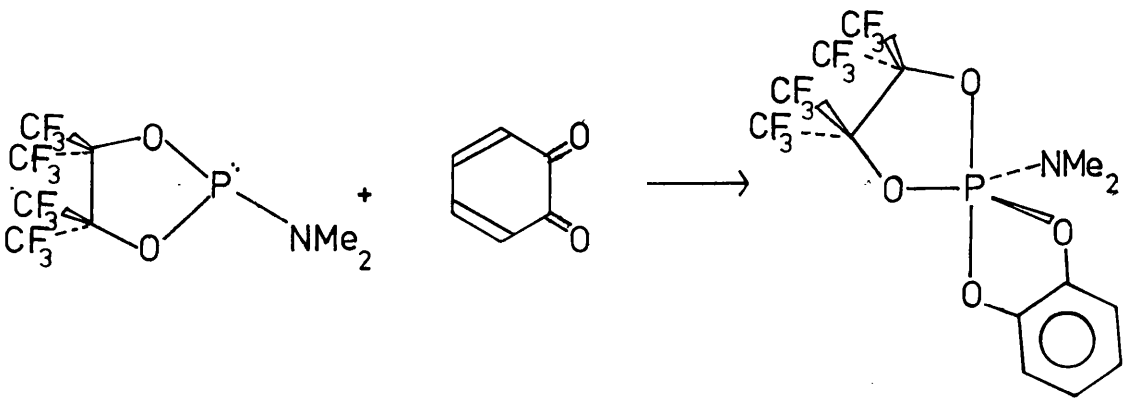


R=OPh (148)

R=SPh (149)

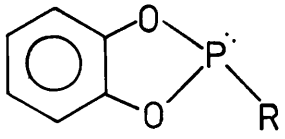
R=NMe_2 (150)

A problem of synthesis was encountered with this system. Adduct (150) was prepared by the reaction of cyclic amino phosphite (151) with o-benzoquinone



(151) (150)

This reaction gave only a poor yield of adduct because reaction was very slow, consequently much of the o-benzoquinone polymerised before reacting with the phosphite. No product could be obtained in the reaction of o-benzoquinone with the phenoxy or thiophenyl analogues of (151). Whittle[19] had reacted the three trivalent compounds (152)-(154) with two moles of hexafluoroacetone.



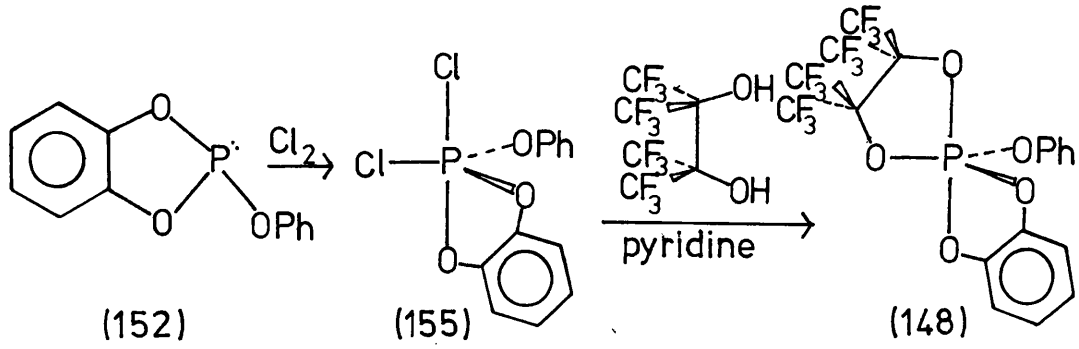
R=OPh (152)

R=SPh (153)

R=NMe_2 (154)

After one month at -40° (154) had reacted to give adduct (150) but even after two months at room temperature the phosphites (152) and (153) had not reacted with the HFA.

Adduct (148) was prepared by the addition of one mole of molecular chlorine to the cyclic phosphite (152) to give the dichlorophosphorane (155) followed by the addition of one mole of perfluoropinacol in the presence of two moles of pyridine.

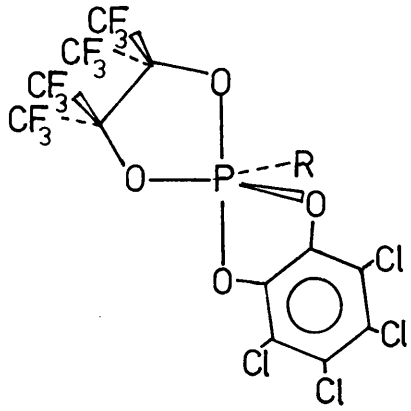


(152) (155) (148)

By this method, adduct (148) was prepared in 70% yield. A reversible coalescence was observed in the ^{19}F n.m.r. at 152° corresponding to a ΔG^{*} value of 20·5 kcals. mol^{-1}. When the same

procedure was carried out for the thiophenyl analogue (153) none of the corresponding adduct (149) was obtained.

The system (156)-(158) was considered next because a route was available to the thiophenyl adduct which avoided the addition of molecular chlorine.



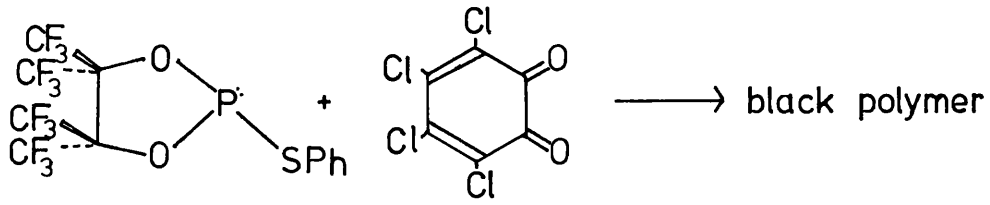
R = OPh (156)

R = SPh (157)

R = NMe_2 (158)

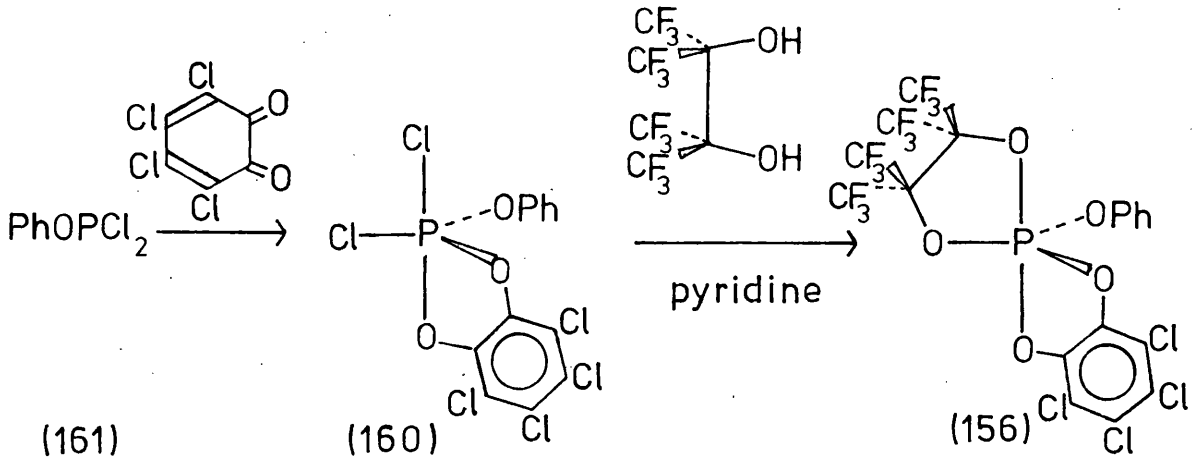
The dimethylamino adduct (158) was simply prepared by the reaction of the cyclic amino phosphite (151) with tetrachloro-o-benzoquinone. As expected, no coalescence was observed for this compound.

Reaction of the cyclic phosphite (159) with tetrachloro-o-benzoquinone led to polymerisation of the quinone.



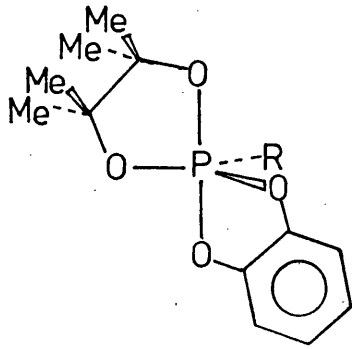
(159)

The phenoxy adduct was prepared by the following sequence.



Reaction of tetrachloro-o-benzoquinone with $PhOPCl_2$ (161) produces the dichlorophosphorane (160) without the use of molecular chlorine. Addition of perfluoropinacol in the presence of two moles of pyridine yields the adduct (156) in 57%. Reversible coalescence at 152° corresponded to a ΔG^* value of 21·8 kcals. mol^{-1}. When the same procedure was carried out with $PhSPCl_2$ no thiophenyl adduct (157) could be isolated.

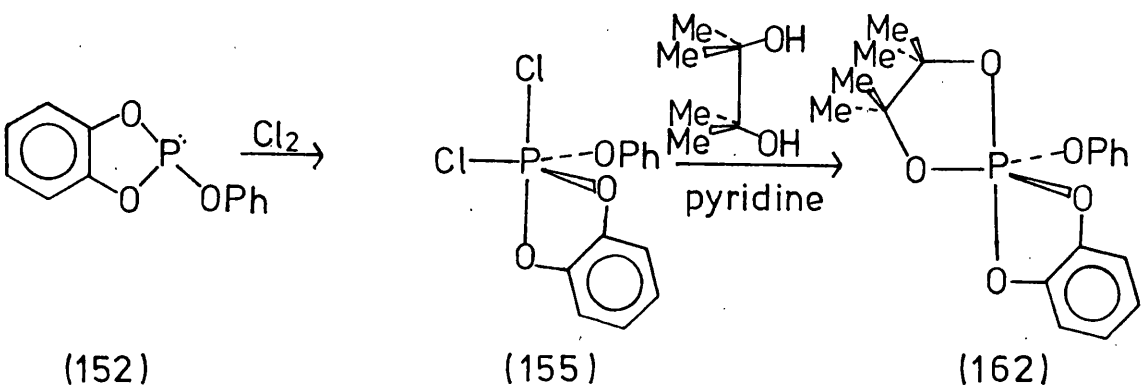
The next system to be studied was (162) - (163).



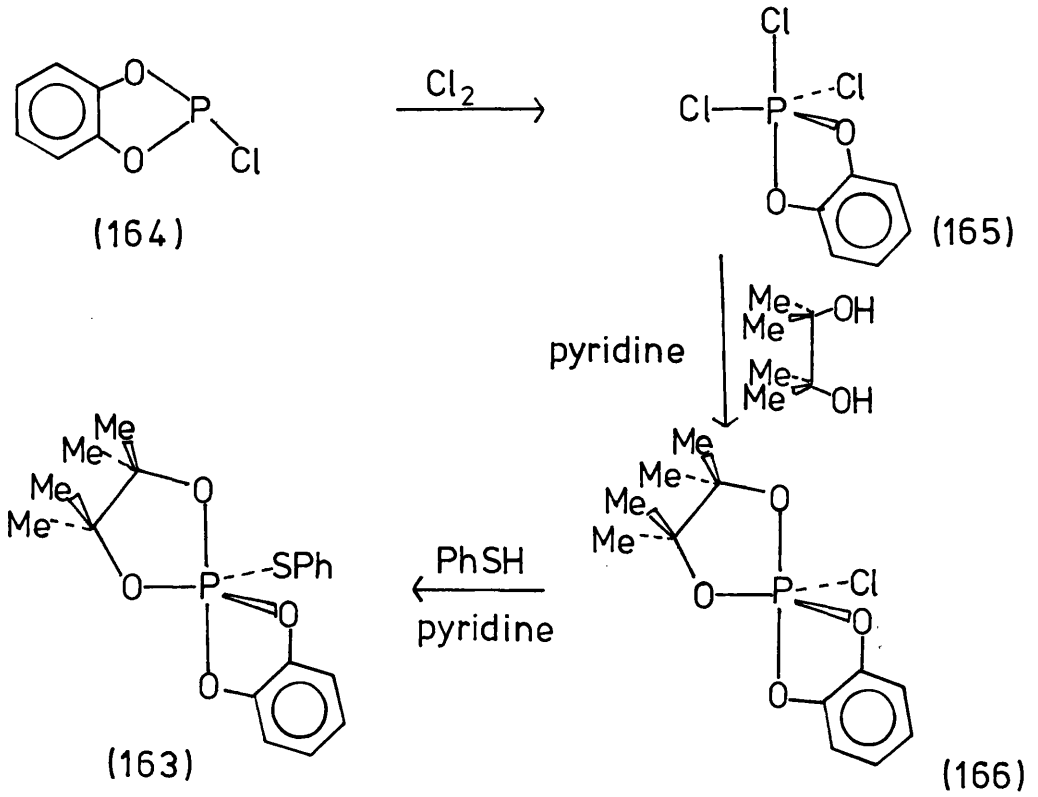
R=OPh (162)

R=SPh (163)

The phenoxy adduct was simply prepared by addition of chlorine to the cyclic phosphite (152) followed by addition of pinacol in the presence of two moles of pyridine.



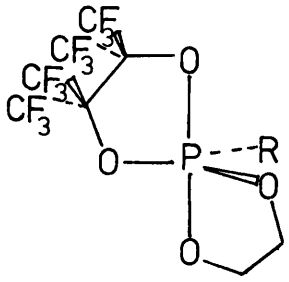
By this method the phenoxy adduct (162) was obtained in 51% yield. Reversible coalescence at 101° corresponded to a ΔG^* value of 20·5 kcals. mol^{-1}. The thiophenyl adduct was prepared by the following reaction pathway. Molecular chlorine was added to the cyclic chlorophosphite (164) to give the trichlorophosphorane (165), this intermediate was treated with one mole of pinacol in the presence of two moles of pyridine to give the chlorospirophosphorane (166) to which was added one mole of benzene thiol in the presence of one mole of pyridine.



(164) (165) (163) (166)

By this method, the thiophenyl adduct (163) was isolated in 30% yield. A reversible coalescence at 104° in the ^1H n.m.r. corresponded to a ΔG^* value of 20·7 kcals. mol^{-1}. Thus from the first direct comparison of phenoxy and thiophenyl, it appears that the apicophilicities are very similar, phenoxy being the more apicophilic by 0·2 kcals. mol^{-1}.

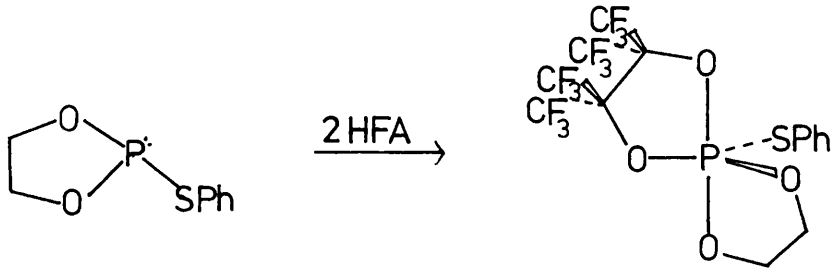
To confirm this similarity, a further system was considered (167), (168).



R=OPh (167)

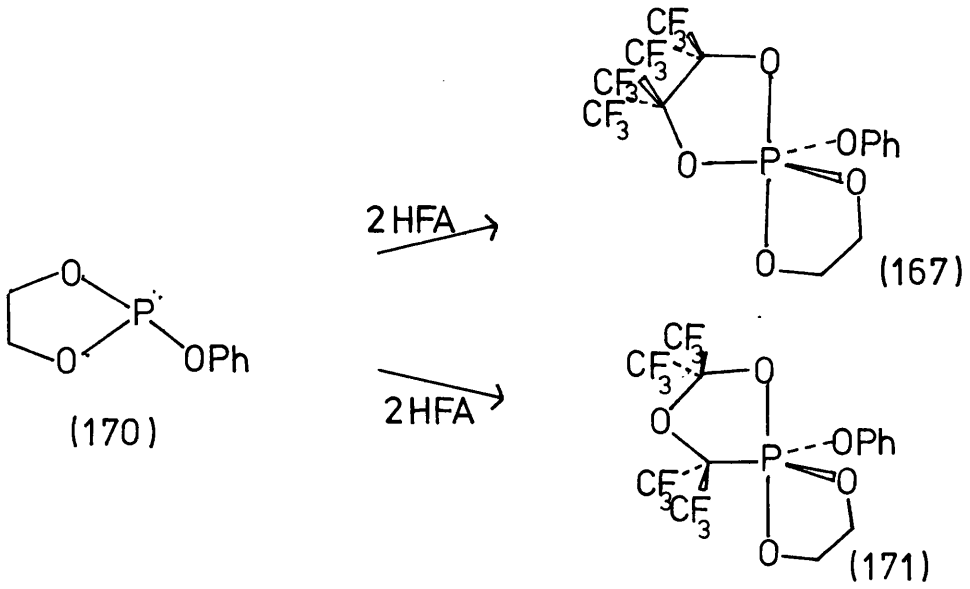
R=SPh (168)

Treatment of the cyclic thiophosphite (169) with two moles of hexafluoroacetone (HFA) yields the adduct (168) in almost quantitative yield.



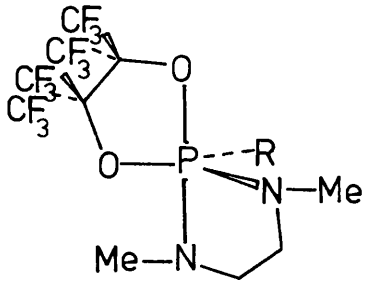
(169) (168)

This adduct coalesced reversibly at 69° (ΔG^{*} = 17·3 kcals. mol^{-1}.). When the phenylethylenephosphite (170) was treated with two moles of HFA two products were obtained, the 1,3,2-dioxaphospholan adduct (167) in 20% yield and the 1,4,2-dioxaphospholan adduct (171) in almost 80% yield.



The 1,4,2-dioxaphospholan adduct (171) was the least soluble in petrol and was thus obtained pure. Its structure was assigned from the four signals in the ^{19}F n.m.r. and the ^{31}P chemical shift. By fractional crystallisation, the ratio of the 1,3,2- : 1,4,2-dioxaphospholan adducts was improved from 1:4 to 2·5:1. This was sufficient to observe the two signals in the ^{19}F n.m.r. corresponding to the 1,3,2-dioxaphospholan coalesce reversibly at 74° (ΔG^{*} = 17·5 kcals. mol^{-1}.). In this system, the thiophenyl group is very slightly more apicophilic than phenoxy by 0·1 kcals. mol^{-1}.

Whittle[19] prepared the HFA adducts (172) - (175)



R=OPh (172)

R=SPh (173)

$R=NMe_2$ (174)

$R=OCH(CF_3)_2$ (175)

In this case, the phenoxy adduct (172) coalesced at 155° (ΔG^{*} = 20·4 kcals. mol^{-1}.) and the thiophenyl adduct (173) coalesced at 116° (ΔG^{*} = 19·4 kcals. mol^{-1}.).

In this system, thiophenyl is rather more apicophilic than phenoxy. However, this system may not be entirely reliable; the dimethylamino adduct (174) showed only one signal in the ^{19}F n.m.r. above 0°. Below this temperature two signals were observed for this adduct. Clearly as the dimethylamino group is so poorly apicophilic, equivalence of the CF_3 groups must be due to an irregular process. A possible mechanism has already been discussed in Section 2.5 for this system. On dissolving the dimethylamino adduct in the acidic hexafluoroisopropanol to see if the ^{31}P changes with solvent polarity it was converted rapidly and quantitatively into the hexafluoroisopropoxy adduct (175). In the case of the thiophenyl adduct (173) the possibility of an irregular process causing the observed changes in the n.m.r. cannot be ruled out.

On the basis of these experiments the relative apicophilicity of the thiophenyl group is very similar to that of phenoxy, the balance being influenced by the other substituents around the phosphorus atom. This result is surprising in view not only of the low electronegativity but also of the strong π donor properties of sulphur ligands.

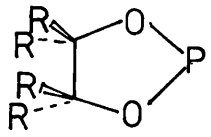
There is evidence from the high energy barrier to rotation around P-S bonds[46,85] that π donation from sulphur to phosphorus is almost as strong as from nitrogen to phosphorus. Both these factors make sulphur ligands poorly apicophilic according to the predictions of Hoffmann.[45] However, sulphur has empty 3d orbitals which may act as an acceptor of π electron density from the phosphorus atom. This

factor makes sulphur prefer the apical position. These opposing factors must be balancing each other out leaving sulphur ligands as apicophilic as the corresponding oxygen ligands.

CHAPTER 5

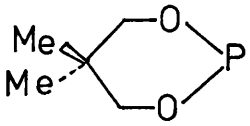
New Methods for the Synthesis of Phosphoranes.

Existing methods for preparing phosphoranes containing two saturated rings are rather limited, (see Section 1.3). For analysis by d.n.m.r. methods it is necessary to have a ring bearing groups that can be readily monitored by n.m.r., e.g. (176) or (177).



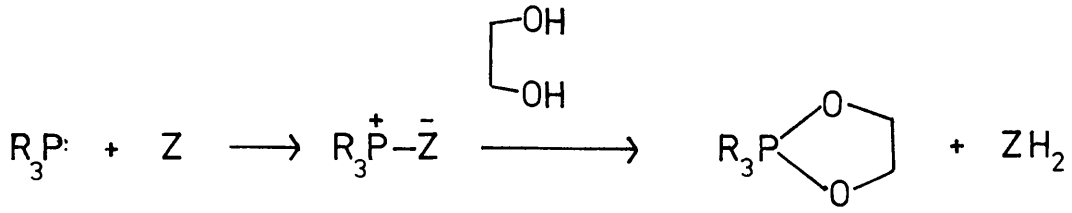
R = CF_3, CH_3 or H.

(176)

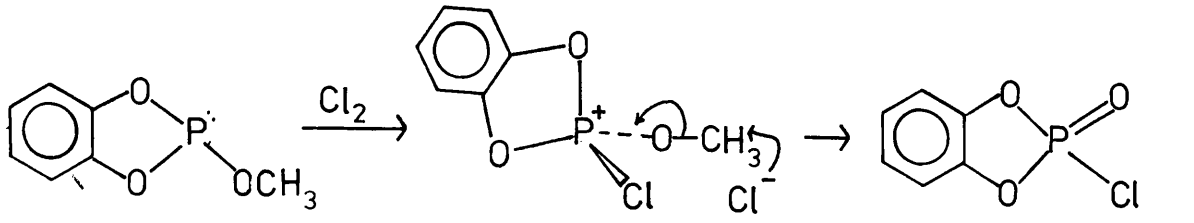


(177)

A method was required to oxidatively add these rings to cyclic phosphites using the parent diol, i.e. a reagent (Z) was required that would oxidise trivalent phosphorus compounds and then readily be displaced by a diol to yield spirophosphoranes.



The only known reagent that would behave in this manner was molecular chlorine. This had only limited application because very few cyclic phosphites could be chlorinated without further reactions taking place, e.g. dealkylation reactions, (178) ⟶ (180).



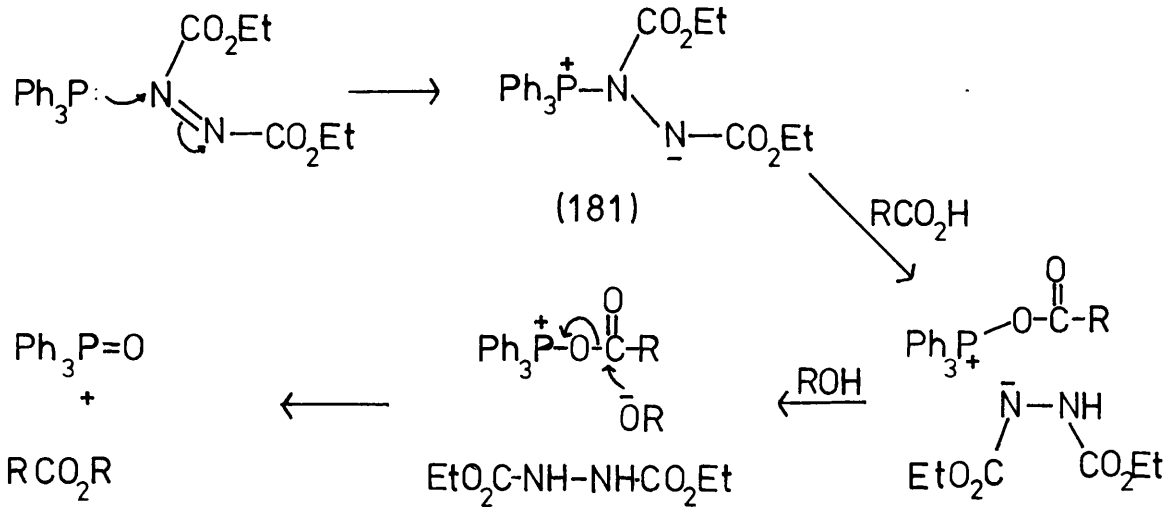
(178) (179) (180)

This dealkylation process is known as the Arbusov reaction.[86] Even in cases where Arbusov reactions cannot occur the yield of phosphorane is usually quite low, (see Chapter 4).

In the literature,[87] the reaction of equimolar amounts of triphenylphosphine, diethylazodicarboxylate (DAD), a carboxyclic acid and an alcohol was well known.

$$Ph_3P: + EtO_2C\text{-}N{=}N\text{-}CO_2Et \xrightarrow{RCO_2H+ROH} Ph_3P{=}O + RCO_2\text{-}R + EtO_2C\text{-}NH\text{-}NH\text{-}CO_2Et.$$

The mechanism of this reaction is set out in Scheme 9.

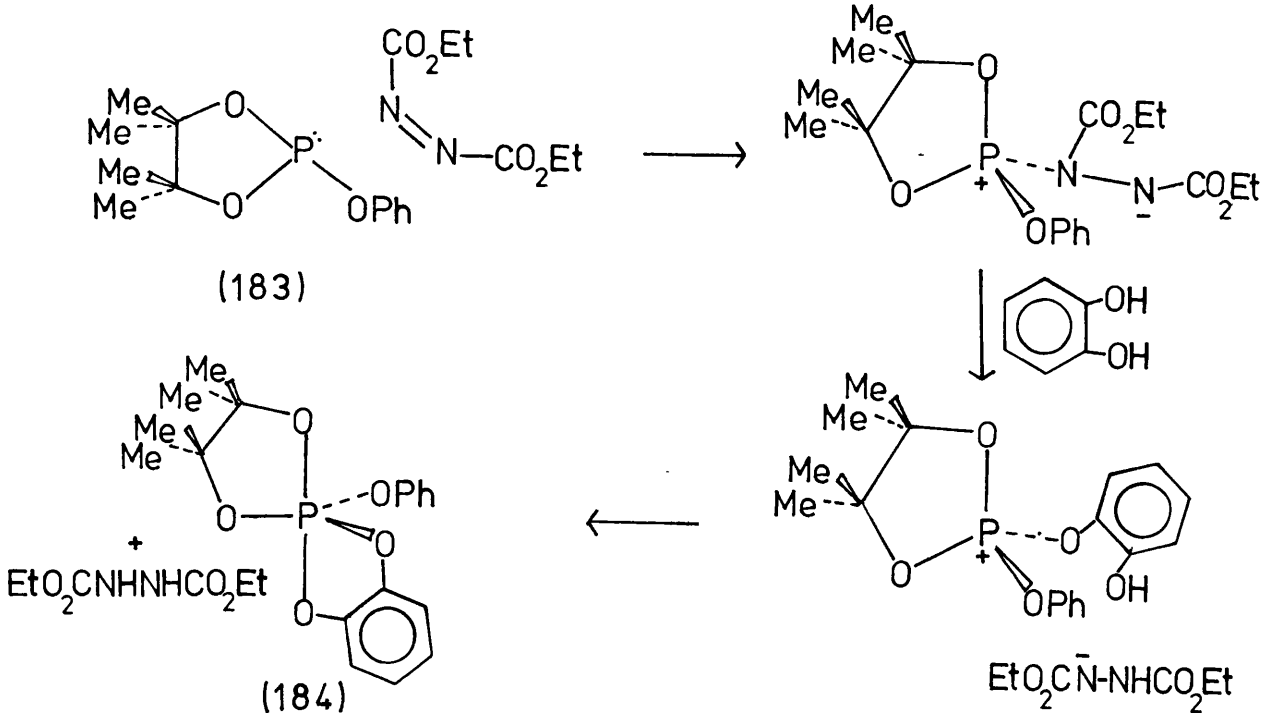


SCHEME 9

The triphenylphosphine is thought to attack the DAD forming the betaine structure (181); this intermediate may be protonated by the acid and the anion produced displace the DAD as the anion which may be protonated by the alcohol to give the reduced form of DAD, diethyl hydrazodicarboxylate. The RO^- may attack the phosphorus to form a phosphorane or attack the carbonyl of the RCO_2^- group already attached to phosphorus to give the ester RCO_2R and triphenyl-

phosphine oxide.

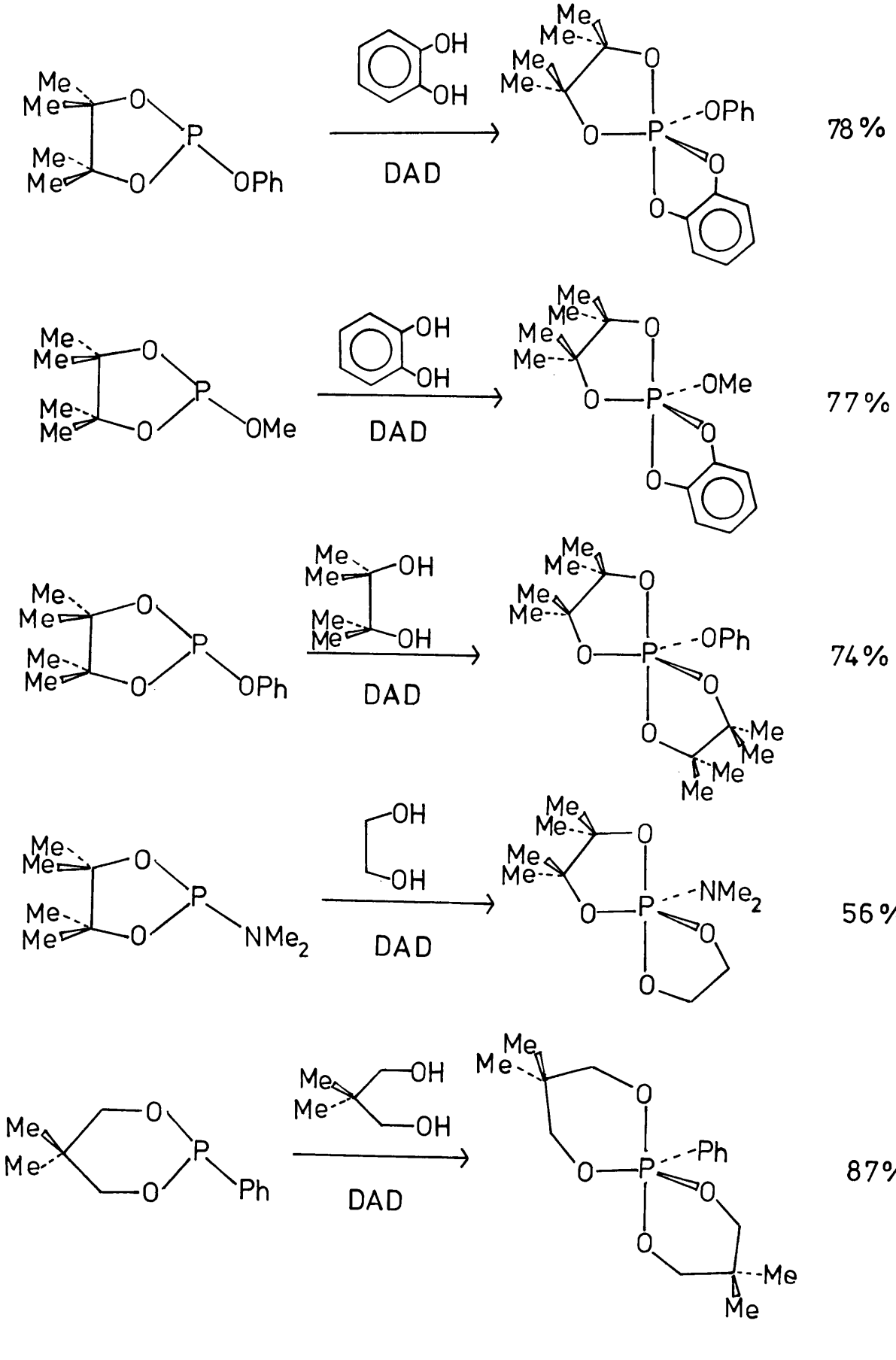
It was decided to try and apply this reaction to phosphorane synthesis. The cyclic phosphite (183) was treated with one mole equivalent of DAD and after five minutes one mole equivalent of catechol was added. The reaction was carried out in ether and almost immediately a white precipitate of diethyl hydrazodicarboxylate was formed. Filtration followed by removal of ether and recrystallisation of the residue from 60-80° petrol yielded the adduct (184) in 78%. This reaction is thought to go by a similar mechanism to the triphenylphosphine reaction.



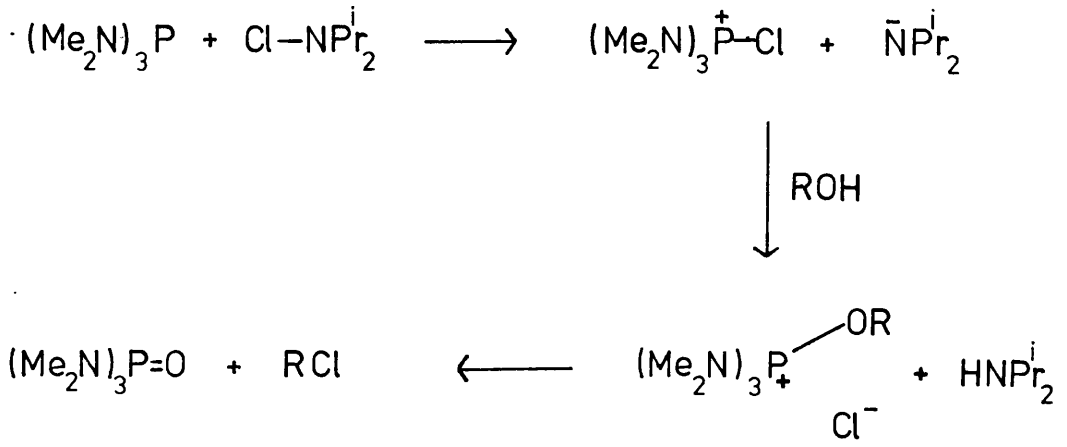
This reaction proved very successful for the addition of various 1,2- and 1,3-diols including catechol, pinacol, ethylene glycol, and neopentyl glycol. It was not possible to add perfluoropinacol by this method.

Using this method many phosphoranes were prepared including some that could not be prepared by any of the known methods (see Table one).

TABLE 1



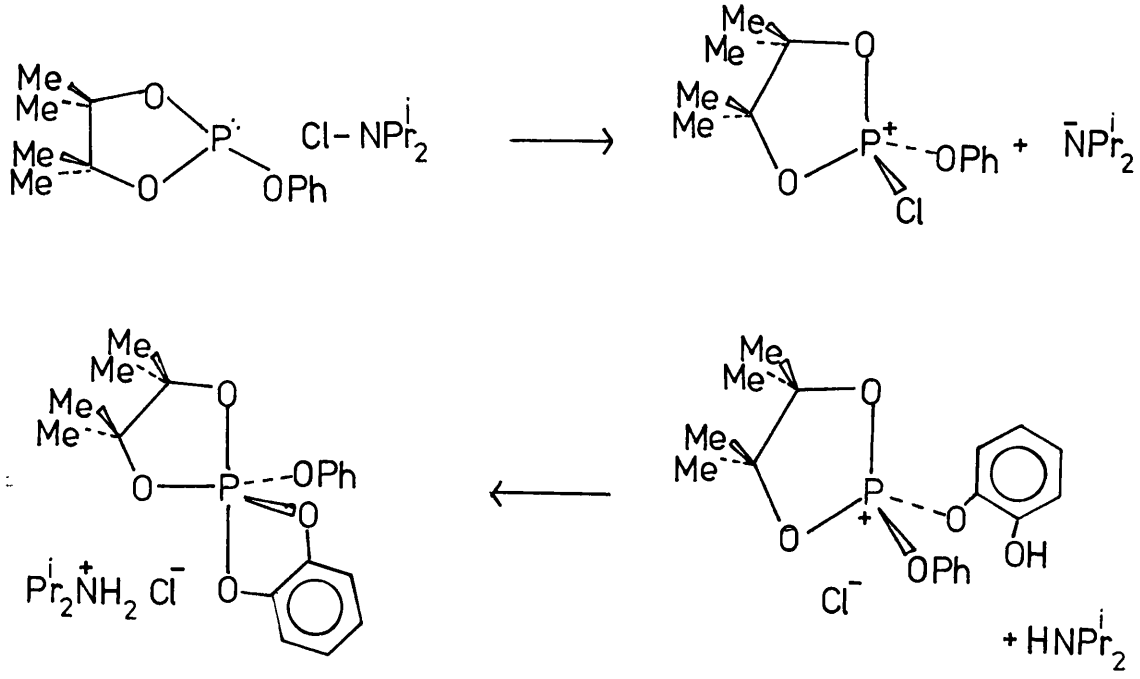
In a recent paper by Castro, Chapleur and Gross[88a] trisdimethylaminophosphine was reacted with N-chlorodi-isopropylamine at -40° in dichloromethane in the presence of an alcohol. From this reaction they reported yields of up to 98% of the alkyl chloride derived from the alcohol. The mechanism is believed to be as follows:



nucleophilic attack by the phosphorus on the chlorine formally displaces the non-nucleophilic di-isopropylamide anion which is protonated by the alcohol. The OR^- anion attacks the phosphorus and the chloride ion does an Arbusov reaction to give the alkyl chloride and hexamethylphosphoric triamide.

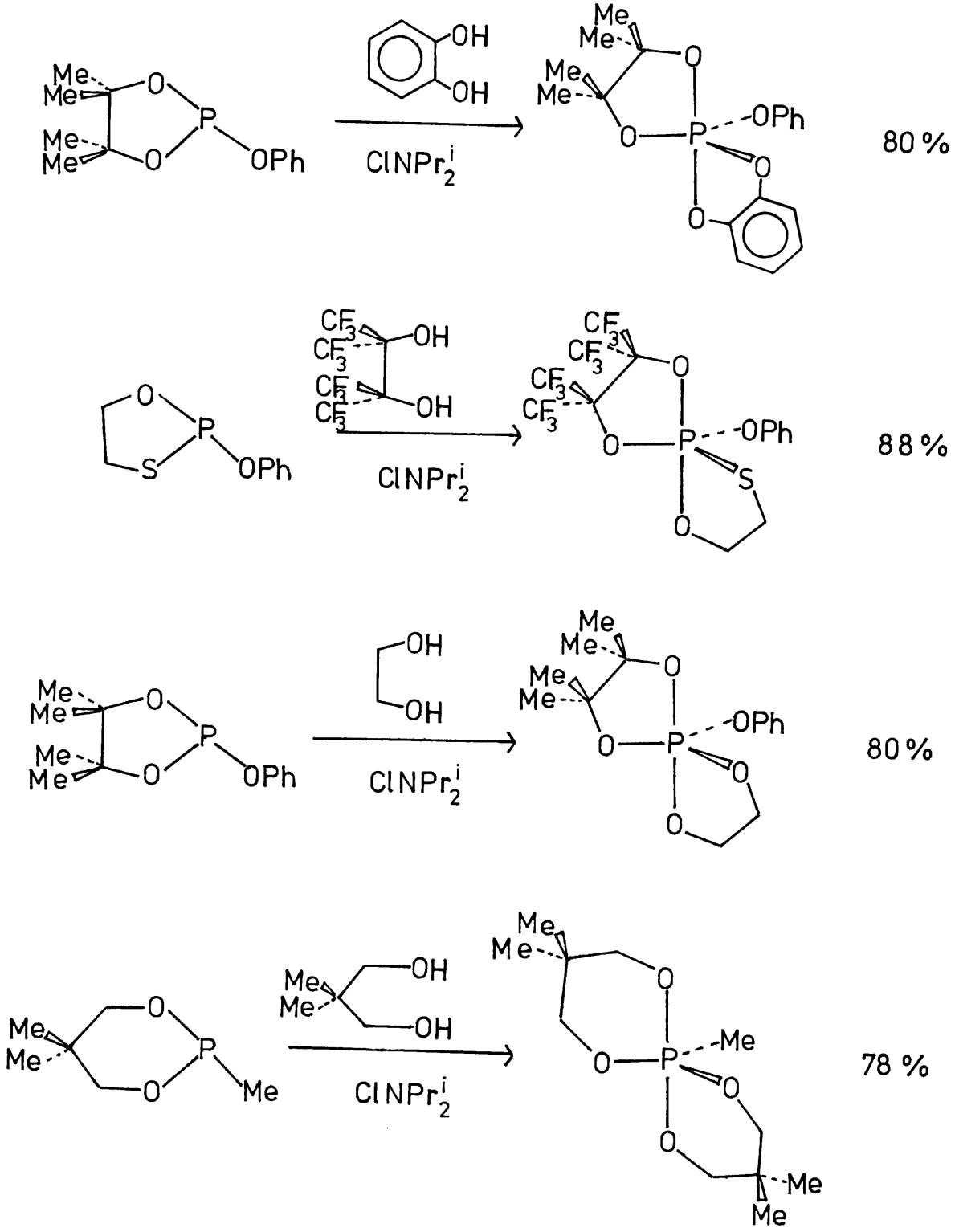
It was decided to try and apply this reaction to the synthesis of phosphoranes. Using ether as the solvent, equimolar quantities of the cyclic phosphite (183) and catechol were mixed at -78° and an equimolar quantity of N-chlorodi-isopropylamine was added dropwise. A white precipitate of di-isopropylamine hydrochloride was quickly formed. The solution was allowed to warm to room temperature and stirred for a further three hours. Filtration followed by removal of ether and crystallisation from petrol yielded adduct (184) in 80%. In this case,

nucleophilic attack by phosphorus on the chlorine occurs formally displacing the di-isopropylamide anion which is protonated by the catechol. This anion of catechol attacks the phosphorus and the other hydroxyl group of catechol attacks the phosphorus displacing hydrogen chloride which reacts immediately with the di-isopropylamine and precipitates out of the reaction mixture, leaving the phosphorane in solution.



This reaction works very well with 1,2- and 1,3-glycols including perfluoropinacol, and is the easiest route to many phosphoranes (see Table two). The use and importance of this method will become clear in later chapters.

TABLE 2



CHAPTER 6

6.1 Ring Strain in Five-membered Cyclic Phosphoranes.

Hoffmann et al[45] in their molecular orbital approach to bonding in phosphoranes were able to predict the preferred orientation of π acceptors and 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 thus there would be little preferential orientation. A substituent in an equatorial site however was found to interact more strongly when the π orbital was parallel to the apical bonds than when it was in the equatorial plane: i.e.

(i) (ii)

interaction (i) is stronger than interaction (ii). Hoffmann concluded that these π donor interactions are destabilising; therefore the π donor orbital will prefer to lie in the equatorial plane (ii) where interaction is less.

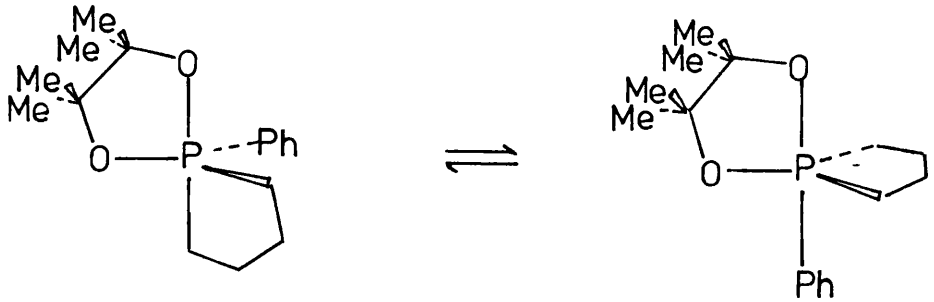
π Acceptors stabilise the molecule therefore the π acceptor orbital will prefer to lie parallel with the apical bonds (i) where interaction is stronger. This implies that for a substituent with a single π donor orbital in an equatorial position there will be a barrier to rotation around the sigma bond to phosphorus as the orbital rotates from being parallel to the equatorial plane through 90^{o} to an unfavourable apical plane.

X-ray work[18-21] has shown that heteroatoms bonded to phosphorus

are sp^2 hybridised which means that they act as single π systems. There is much evidence for the slowing down of P-N[44,46,88-90] and P-S[85] bond rotation as the temperature is lowered. Slow rotation around a P-O bond has never been observed experimentally; the only experimental evidence relating to P-O bond rotation[91] indicates that the barrier is less than 8 kcal. $mol.^{-1}$.

6.2 Ring Strain of the Phospholan Ring.

For the adduct (185),[92] complete equivalence of the pinacol methyls may be achieved when the five-membered phospholan ring spans a diequatorial position and the phenyl group moves apical (186).



(185) (186)

The free energy of activation, ΔG^*, for this process as calculated from the Gutowsky-Holm equation is 9 kcal. $mol.^{-1}$. This energy term is made up of two factors:

(i) the increase in ring strain in opening up the phospholan ring angle at phosphorus from 90^o to 120^o, which can be represented by the term S_{90-120} (phospholan).

(ii) the difference in apicophilicity between the ring carbon and the phenyl group which can be represented by A(ring C-Ph).

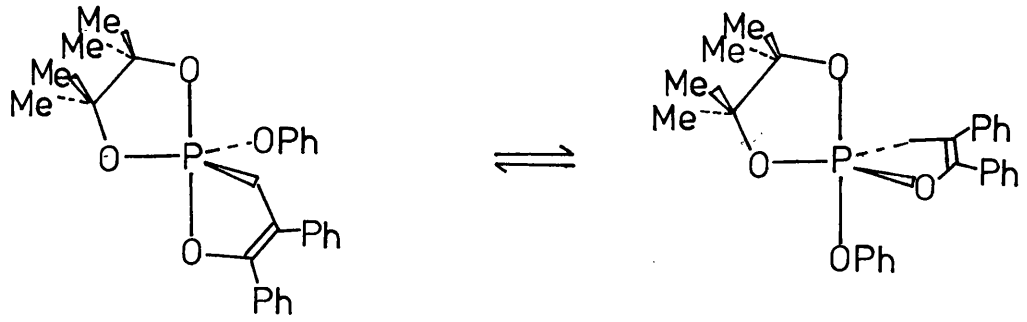
The problem may now be expressed as an equation:

$$\Delta G^* = S_{90-120}(\text{phospholan}) + A(\text{ring C - Ph}) \qquad (1)$$

From data obtained in acyclic systems[72,84] alkyl groups are more apicophilic than phenyl groups by about one kcal. mol.$^{-1}$ Substitution of this value into equation (1) allows the S_{90-120}(phospholan) to be determined, i.e. 8 kcal. mol.$^{-1}$

6.3 Estimation of the Energy of Rotation about a P-O Sigma Bond.

The ΔG^* value for the methylenedeoxybenzoin adduct (187)[92] associated with putting the oxaphospholen ring diequatorial and phenoxy apical is 14.1 kcal. mol.$^{-1}$



(187) (188)

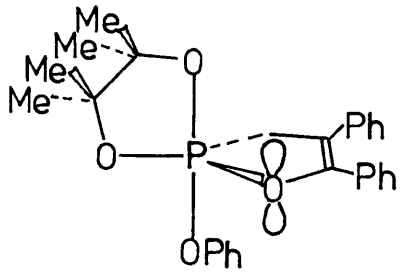
The strain on the five-membered oxaphospholen ring will be greater than the 8 kcal. mol.$^{-1}$ of the phospholan because of the double bond. The value of 10 kcal. mol.$^{-1}$ may be used for the oxaphospholen ring strain.

The equation for this system may be written:

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

The difference between the apicophilicity of the ring oxygen and phenoxy is about -1 kcal. mol.$^{-1}$, i.e. phenoxy is the more apicophilic, Substituting these values in equation (2) it appears that there must be another energy factor of about 5 kcal. mol.$^{-1}$ to be added on.

Considering the oxaphospholen ring in the diequatorial position (188), it can be seen that as the oxygen atom is sp^2 hybridised the donor orbital is parallel to the apical bonds which Hoffmann[45] concluded is the less favourable position.



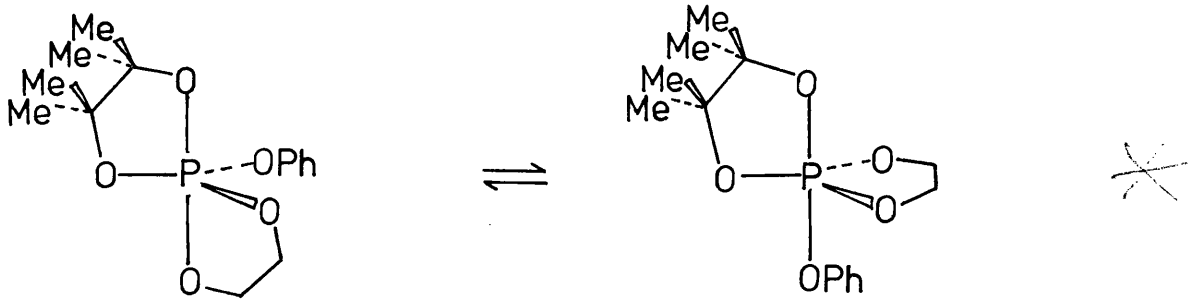
(188)

The 5 kcal. mol.$^{-1}$ must be equivalent to the energy barrier to rotation around to P-O bond, termed Rot O. Equation (2) may be rewritten as

$$\Delta G^* = S_{90-120}(\text{oxaphospholen}) + A(\text{ring O - OPh}) + \text{Rot O} \quad (3)$$

6.4 Ring Strain of the 1,3,2-Dioxaphospholan Ring.

In the case of the ethylene glycol adduct (189) (preparation described in Chapter 4) the energy required for complete equilibration of the CH_3 groups via (190) is 17.4 kcal. mol.$^{-1}$.



(189) (190)

The strain in the dioxaphospholan ring is likely to be very close to that of the phospholan, but when the dioxaphospholan ring is diequatorial both oxygen atoms have their π donor orbital in the wrong orientation. The equation for this system may be expressed:

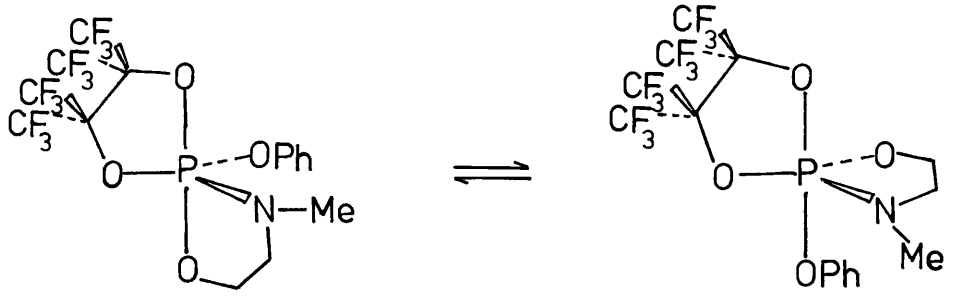
$$\Delta G^* = S_{90-120}(\text{dioxaphospholan}) + A(\text{ring O-OPh}) + 2\ \text{Rot O} \qquad (4)$$

$$= \quad 8 \quad + \quad (-1) \quad + \quad 10$$

The predicted value of ΔG^*, 17kcal. $mol.^{-1}$ is very close to the value determined experimentally of 17.4kcal. $mol.^{-1}$

6.5 Estimation of the Energy of Rotation about a P-N Sigma Bond.

Using the values for ring strain and rotation around P-O bonds derived from these simple phosphoranes it is possible to estimate the energy barrier to rotation around a P-N bond from the ΔG^* value of the adduct (191).



(191) (192)

With the oxazaphospholan ring diequatorial, the oxygen atom and the nitrogen atom have their lone pairs in an unfavourable orientation. The energy equation may be written,

$$\Delta G^* = S_{90-120}(\text{oxazaphospholan}) + A(\text{ring O-OPh}) + \text{Rot O} + \text{Rot N} \qquad (5)$$

ΔG^* for this process was found to be 20.7 kcal. $mol.^{-1}$. Using the values

S_{90-120}(oxazaphospholan) = 8 kcal. $mol.^{-1}$

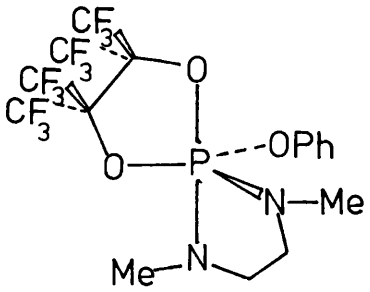
A (ring O-OPh) = -1 " "

Rot O = 5 " "

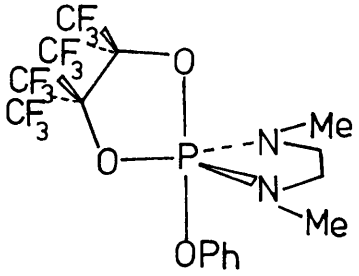
Rot N - the energy barrier to rotation around the P-N bond is approximately 9 kcal. $mol.^{-1}$ This value corresponds very well to the value of 9.5 kcal. $mol.^{-1}$ obtained from Me_2NPF_4 in the Whitesides and Mitchell experiment.[46]

6.6 Estimation of the Difference in Apicophilicity Between Oxygen and Nitrogen.

Knowing the value of the energy barrier to rotation around P-N bonds allows an estimate of the difference in apicophilicity between nitrogen and oxygen to be made from the ΔG^* value of the adduct (193).[19]



(193)



(194)

The energy equation for this process may be written,

$$\Delta G^* = \text{Strain}_{90-120}(\text{diazaphospholan}) + A(\text{ring N-OPh}) + 2\ \text{Rot N} \quad (6)$$

ΔG^* found experimentally is 20.5 kcal. $mol.^{-1}$

Strain_{90-120}(diazaphospholan) is 8 " "

2 Rot N is 18 " "

From this data the value of A (ring N-OPh) is approximately -5.5 kcal. $mol.^{-1}$, i.e. phenoxy is more apicophilic than the ring nitrogen by 5.5 kcal. $mol.^{-1}$ This value is very close to the result obtained from the acyclic system (195) described in Chapter 7.4.

From the study of this series of phosphoranes, general rules have emerged for predicting the ΔG^* value for the process where a phosphorane with a five-membered ring apical-equatorial moves to a phosphorane with a five-membered ring diequatorial.

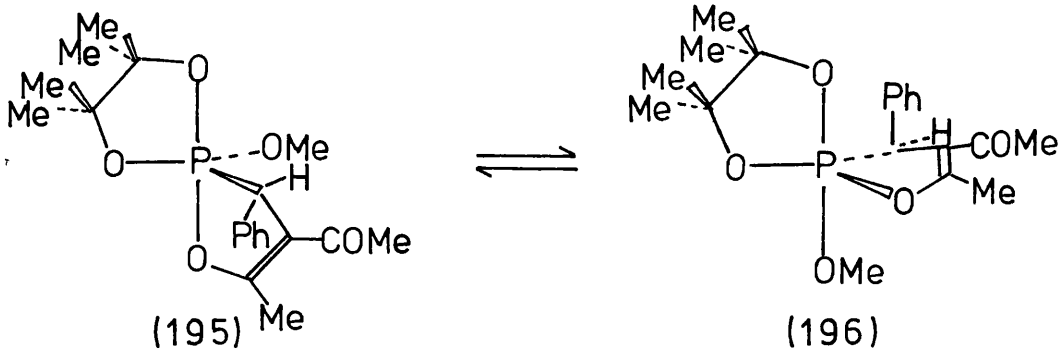
From these experiments, the following assignments have been suggested:

TABLE THREE

FACTOR	ENERGY kcal. $mol.^{-1}$
Ring strain of phospholan	8
Ring strain of phospholen	10
Rotation around oxygen	5
Rotation around nitrogen	9
Apicophilicity difference (ring oxygen-phenoxy)	-1
Apicophilicity difference (ring nitrogen-phenoxy)	-5.5

Using these data the ΔG^* values of a large number of adducts may be predicted quite accurately. It is only when steric effects become important that large differences between observed and predicted ΔG^* values are found. Steric effects are mostly found where bulky groups are attached to the atom next to phosphorus, i.e. the α position.

In the benzylideneacetylacetone adduct (195)[63b] the ΔG^* value found experimentally is 17.6 kcal. mol.$^{-1}$



(195) (196)

The energy equation for this process may be written:

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

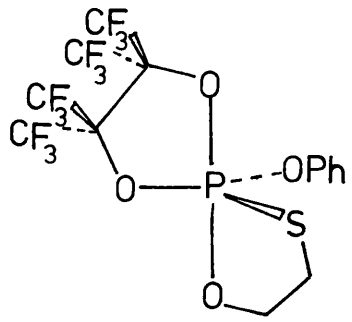
$$10 \qquad\qquad 0 \qquad\qquad 5 \quad \text{kcal. mol.}^{-1}$$

The predicted ΔG^* value is 15 kcal. mol.$^{-1}$ The extra 2.6 kcal. mol.$^{-1}$ could arise from the interaction between the phenyl group and the pinacol oxygen as these groups are almost eclipsed when the oxaphospholan ring is diequatorial.

6.7 Determination of Ring Strain in Sulphur-Containing Rings.

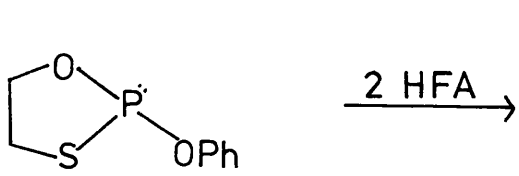
Although a considerable amount of work had been done on phosphoranes with five-membered rings containing oxygen and nitrogen heteroatoms, there were no data available for the same systems containing sulphur as the heteroatom. It was decided that various phosphoranes should be synthesised containing five-membered rings with sulphur atoms adjacent to phosphorus in order to obtain ring strain data for these systems.

The first system considered was the hexafluoroacetone (HFA) adduct (197).

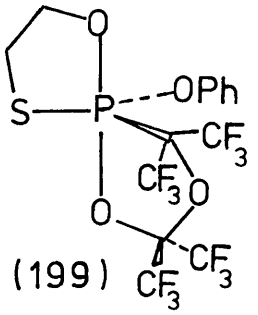


(197)

However, treatment of the cyclic thiophosphite (198) with HFA led to the formation of the 1,4,2-dioxaphospholan (199) as the only product.

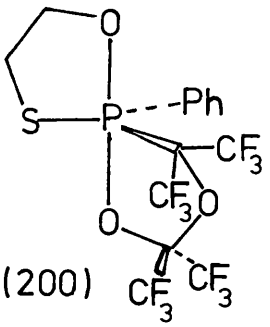


(198)



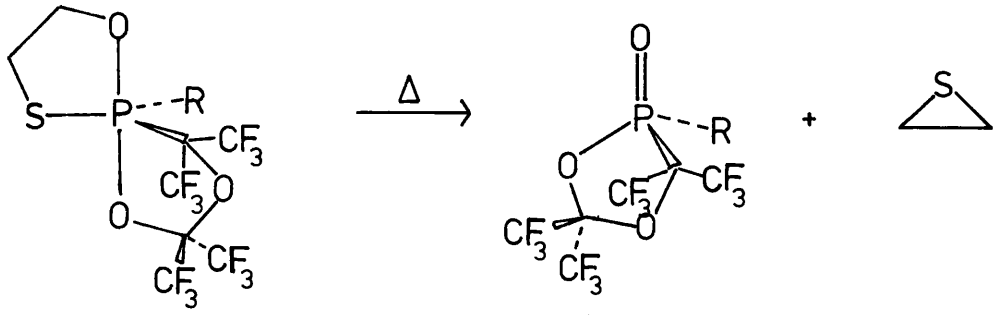
(199)

The adduct (199) was shown to be the 1,4,2-dioxaphospholan from ^{31}P and ^{19}F n.m.r. data and comparison with the adduct (200)[83] for which an X-ray structure was obtained.[109]



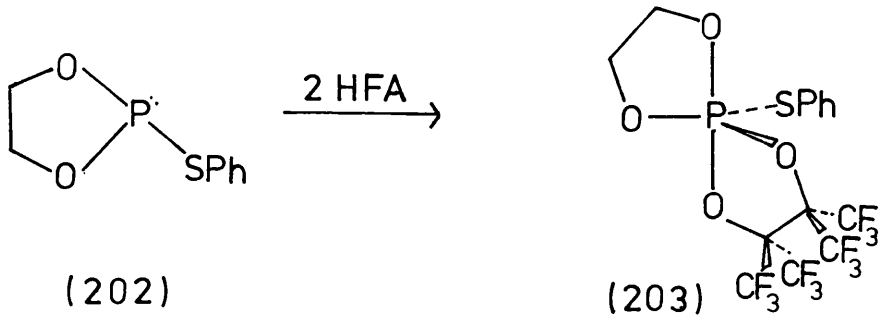
(200)

Both (199) and (200) are thermally stable up to 160° above which decomposition occurs with loss of episulphide to give (201).



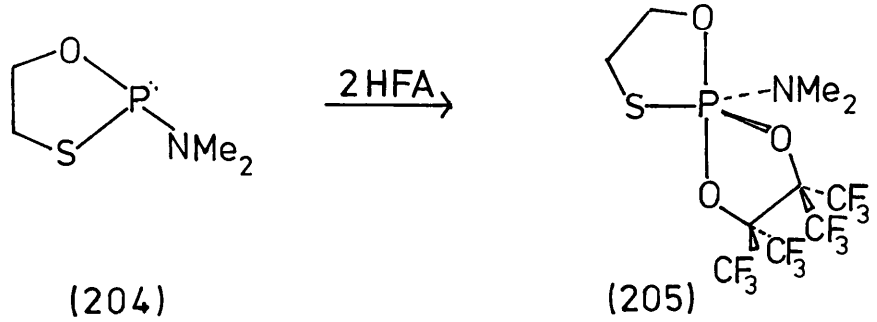
R = Ph or OPh (201)

No rearrangement to the 1,3,2-dioxaphospholan adduct was observed. It appears that the balance between the formation of the 1,3,2- or the 1,4,2-dioxaphospholan is critical as the cyclic thiophosphite (202) gives entirely the 1,3,2-dioxaphospholan (203) with HFA.



(202) (203)

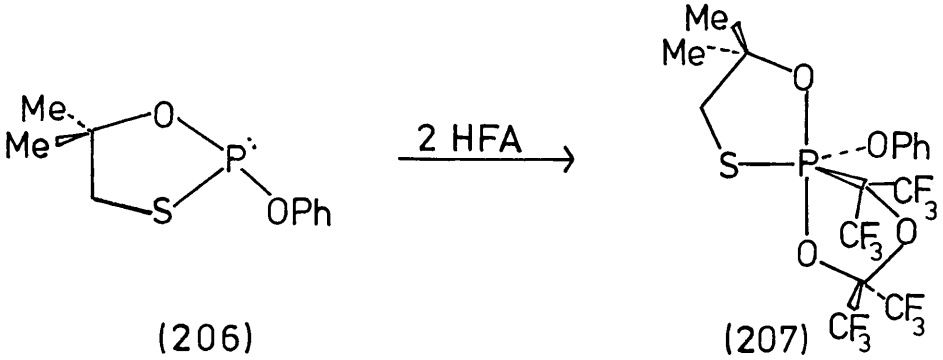
Similarly, when the cyclic aminothiophosphite (204) is treated with HFA only the 1,3,2-dioxaphospholan (205) is produced.



(204) (205)

The adduct (205) was dissolved and refluxed in the acidic solvent hexafluoroisopropanol in the hope that the dimethylamino group would be displaced by hexafluoroisopropoxy. However, no displacement occurred at room temperature and, on refluxing, the adduct decomposed.

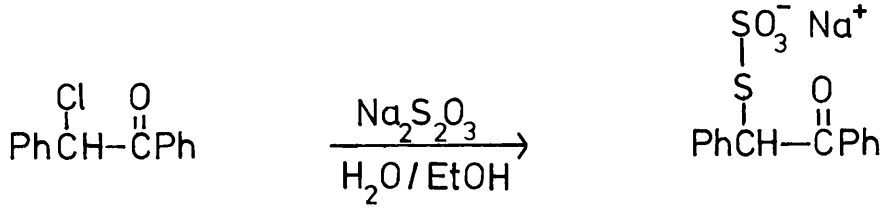
As the balance between the formation of the 1,3,2- and 1,4,2-dioxaphospholans is so critical it was decided to prepare (206) and treat it with HFA in the hope that the two methyl groups would tip the balance in favour of the 1,3,2-dioxaphospholan.



(206) (207)

Unfortunately only the 1,4,2-dioxaphospholan (207) was obtained from this reaction. At the time, no other route to these phosphoranes was available so other systems were considered.

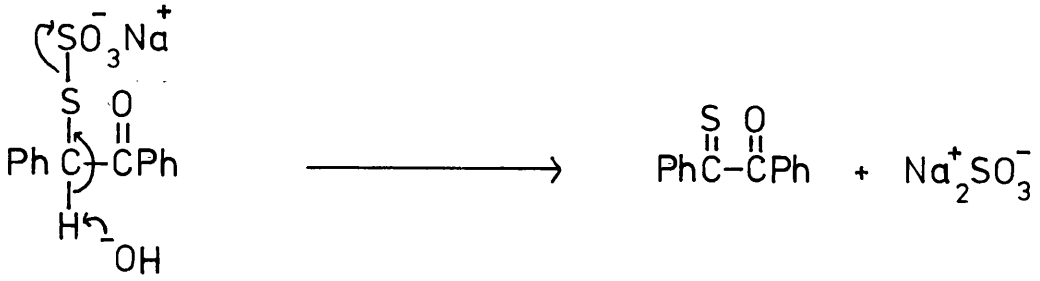
A relatively simple procedure for the preparation of monothiobenzil (208), PhC(O)C(S)Ph, appeared in the literature described by Saville and Steer.[93] Treatment of desyl chloride (209) with sodium thiosulphate in aqueous ethanol gave sodium S-desylthiosulphate (210).



(209) (210)

When an aqueous solution of (210) is added to sodium hydroxide solution in the presence of dichloromethane as a co-solvent, monothiobenzil (208) is formed and immediately taken up into the dichloromethane as shown by the deep blue colouration. The dichloromethane layer was washed and dried and used without isolation of the monothiobenzil. The mechanism of this reaction is thought to be removal of the benzyl hydrogen

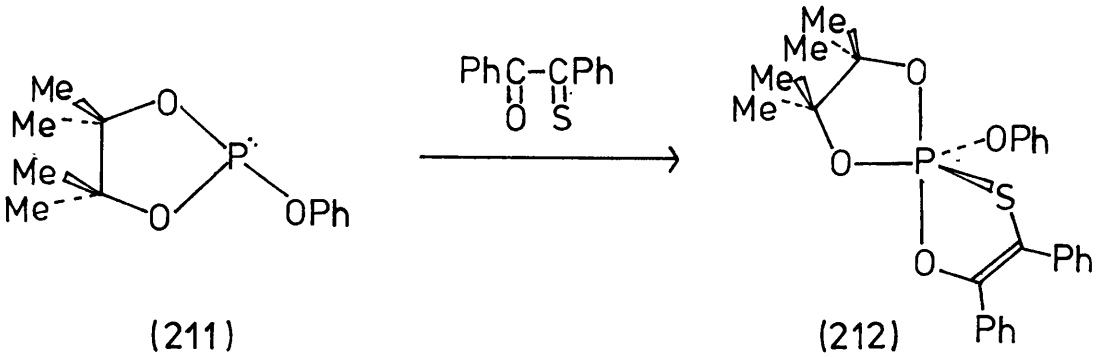
by the base followed by displacement of the sulphite anion.



(210) (208)

An investigation was made into the possibility of obtaining phosphoranes from the reaction of monothiobenzil with trivalent phosphorus compounds.

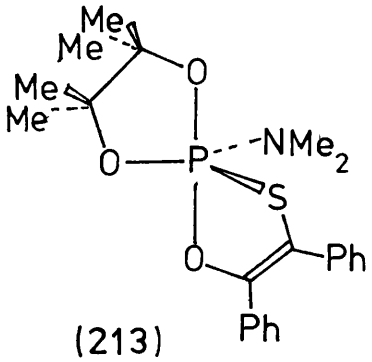
The cyclic phosphite (211) was treated with a solution of monothiobenzil; even at -78°, the blue colour was immediately discharged.



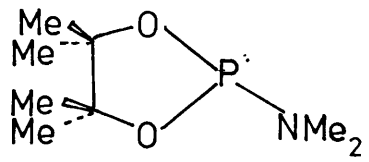
(211) (212)

After warming to room temperature, removal of the solvent followed by crystallisation gave the adduct (212) in fairly low yield. The room temperature ^{1}H n.m.r. showed four signals for the pinacol methyl groups as expected. On raising the temperature, the four signals were expected to coalesce to two as one ring went out diequatorial and on raising the temperature further the two signals would coalesce to one as both rings went out diequatorial. When the sample was warmed up however, the four signals coalesced to one. This meant that the two signals that should have been obtained were either accidentally equivalent in the n.m.r. or both rings were going out diequatorial at the same rate in which case only one signal would be expected.

A third possibility was that of an irregular process where ring opening of the oxathiaphospholen ring was occurring. To test for this, the dimethylamino adduct (213) was prepared. The idea of this is that the pseudorotation which puts the dimethylamino group apical and a ring diequatorial will be too high in energy to be observed in the n.m.r. Dimethylamino groups stabilise a positive charge on phosphorus better than oxygen so if ring opening is occurring in the phenoxy adduct (212) then it should occur at an even lower temperature in the dimethylamino adduct (213).



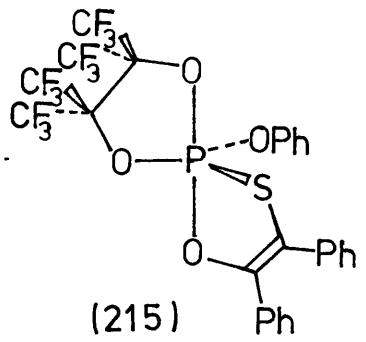
(213)



(214)

The adduct (213) was readily prepared from monothiobenzil and the respective cyclic aminophosphite (214). The room temperature ^{1}H n.m.r. of this adduct showed four signals for the pinacol methyl as expected and on warming the spectrum remained unchanged up to 157° above which rapid decomposition took place. From this experiment it was concluded that genuine pseudorotation processes must account for the equilibration observed in the phenoxy adduct (212).

An attempt was made to prepare adduct (215).



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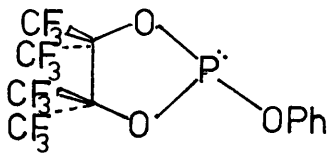
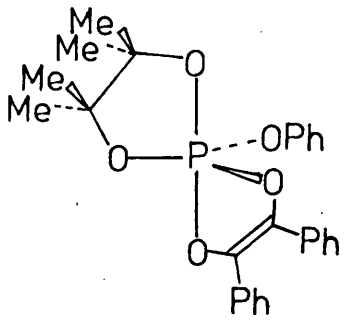


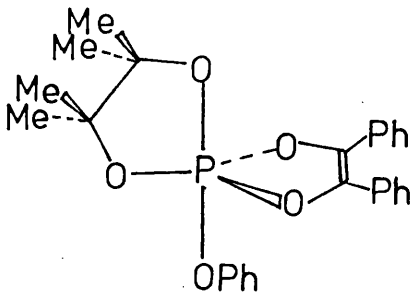
(216)

This would have given an unambiguous answer to this problem because the perfluoropinacol ring has never been observed to span a diequatorial position on then.m.r. time-scale. Unfortunately monothiobenzil would not react with the cyclic phosphite (216) even after stirring overnight at room temperature.

The benzil adduct (217) was prepared to determine the ring strain in this type of system.



(217)



(218)

The ΔG^* value for the process (217) $\rightleftharpoons$ (218) was found experimentally to be 21.4 kcal. $mol.^{-1}$ Substituting this value into an energy equation, the strain factor may be estimated:

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

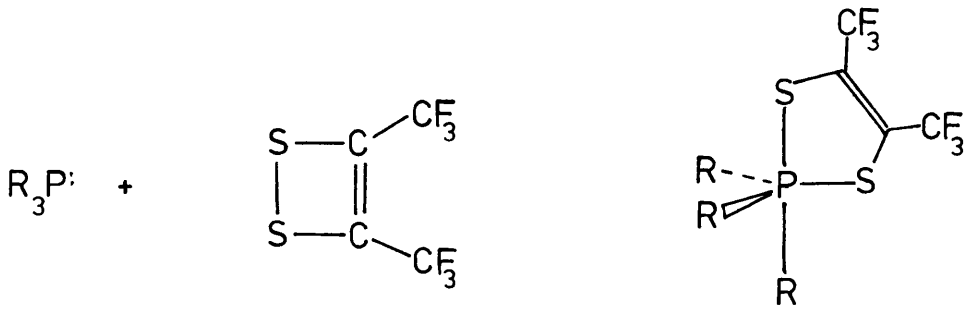
$$21.4 \qquad \text{'strain'} \qquad + \quad (-1) \qquad + \quad 10$$

therefore 'strain' = 12.4 kcal. $mol.^{-1}$

The ΔG^* value obtained from the coalescence temperature of the monothiobenzil adduct (212) was 21 kcal. $mol.^{-1}$ This would be a reasonable value for the pinacol ring spanning a diequatorial position but the predicted ΔG^* value for the oxathiaphospholen ring will be higher than the dioxaphospholen adduct (217) by the difference in rotation energy between P-S and P-O. The P-S value[85] is thought to be

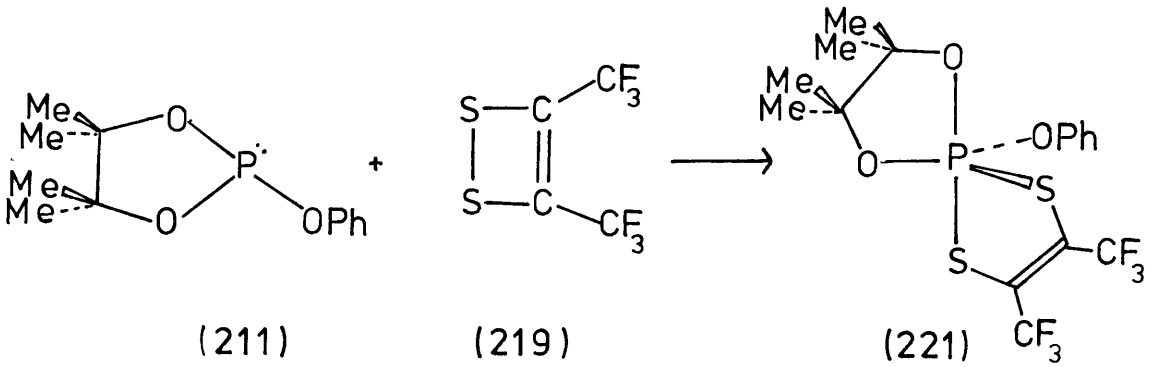
about 9 kcal. mol.$^{-1}$ therefore the predicted ΔG^* value for putting the oxathiaphospholen ring diequatorial will be approximately 25 kcal. mol.$^{-1}$ At the time, the n.m.r. data were interpreted as involving the pinacol ring going out diequatorial and the resulting two signals being accidentally equivalent in the n.m.r.

In 1972, Denney[94] described the reaction of the dithieten (219) with various trivalent phosphorus compounds.



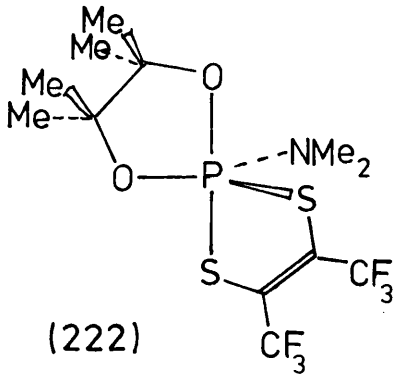
(219) (220)

The products of these reactions (220) were stable phosphoranes containing a dithiaphospholen ring. The adduct (221) was therefore prepared by reaction of the dithietene with the cyclic phosphite (211).



(211) (219) (221)

The ^{1}H n.m.r. of the adduct showed two signals for the pinacol methyls which showed a reversible coalescence at 136^o corresponding to a ΔG^* value of 22.3 kcal. mol.$^{-1}$ To check that coalescence was not being caused by an irregular process with ring opening, the dimethylamino analogue (222) was prepared. In this case, no change in the n.m.r. was observed up to 151^o, above which rapid decomposition took place.



(222)

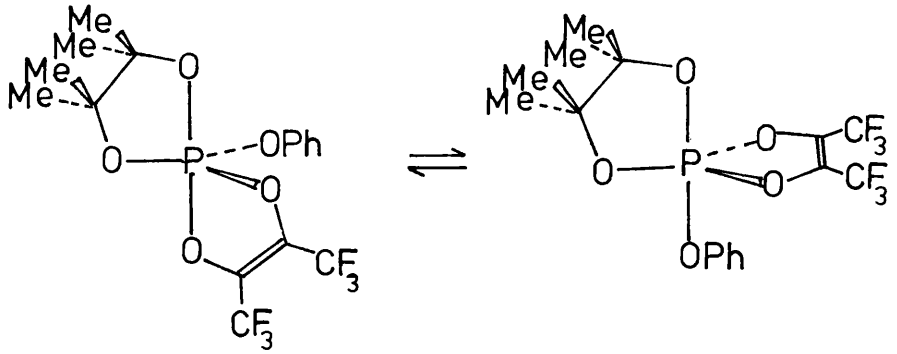
This evidence suggests that the methyl groups in the phenoxy adduct (221) become equivalent by a regular pseudorotation. This was surprising because the predicted ΔG^* value is much higher than the value found experimentally.

$$\Delta G^* = \text{strain}_{90\text{-}120}(\text{dithiaphospholen}) + A\ (\text{ring S-OPh}) + 2\ \text{Rot S}$$

$$= \qquad 10 \qquad\qquad -1 \qquad\qquad 18$$

i.e. $\Delta G^* = 27$ kcal. mol.$^{-1}$

There are two factors in this equation that are not known accurately, the strain in the dithiaphospholen ring and the rotation around P-S bonds. The strongly electron-withdrawing CF_3 groups may possibly be reducing the π donation of sulphur to phosphorus thus making the P-S rotation energy smaller. If this were the case then a similar, though smaller effect would be observed for the hexafluoro-biacetyl adduct (223).



(223) (224)

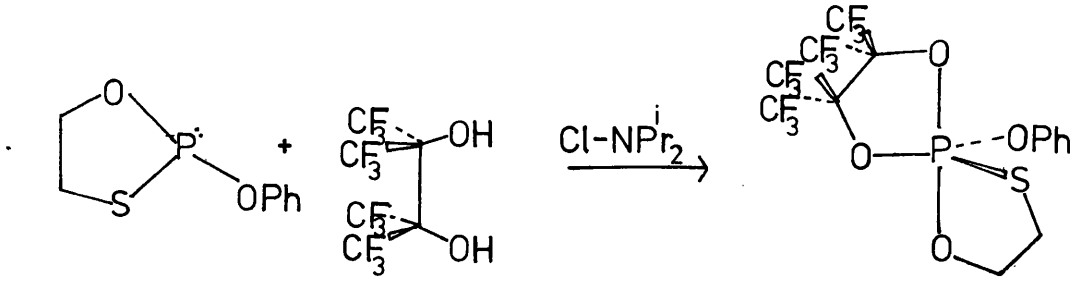
This adduct was readily prepared by the reaction of hexafluorobiacetyl with the cyclic phosphite (211). The ΔG^* value for the process (223) $\rightleftharpoons$ (224) was found to be 22.9 kcal. mol.$^{-1}$ From the energy equation,

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

$$22.9 = \qquad S \qquad (-1) \quad + \quad (10)$$

the strain factor is 13 kcal. mol.$^{-1}$, if the rotation around each oxygen is 5 kcal. mol.$^{-1}$ If the CF_3 groups caused the rotational term to be less than 5 kcal. mol.$^{-1}$ then the strain factor would have to be greater to compensate and as 13 kcal. mol.$^{-1}$ is a high value already it seems unlikely that the CF_3 groups have an effect on the π donation of oxygen to phosphorus.

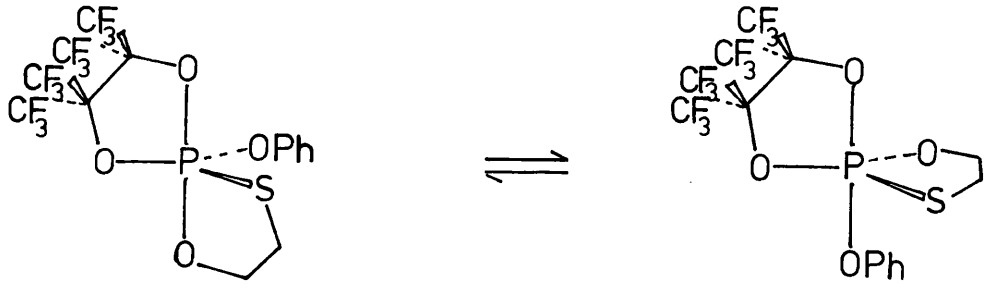
Before valid assumptions could be made from these experiments more examples were required to verify the facts. However, at that time, no synthetic methods were available. With the development of the N-chlorodi-isopropylamine route to phosphoranes it was possible to prepare the adduct that had been considered first, i.e. (197).



(198) (197)

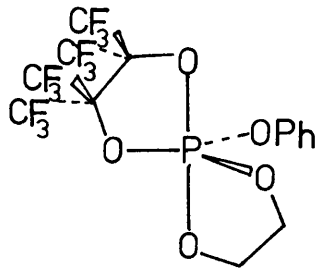
Reaction of the cyclic thiophosphite (198) in the presence of perfluoropinacol with N-chlorodi-isopropylamine gave adduct (197) in 88% yield.

The ΔG^* value for the process (197) $\rightleftharpoons$ (225)



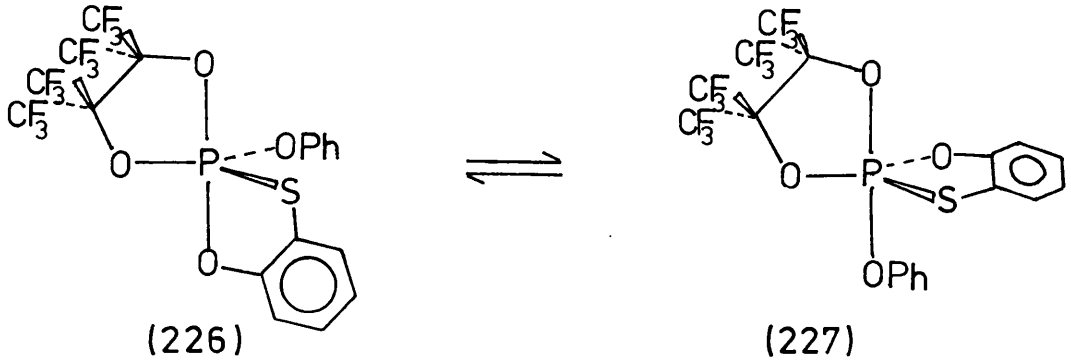
(197) (225)

was found to be 17.7 kcal. $mol.^{-1}$ which is very close to the value of 17.4 kcal. $mol.^{-1}$ for the ethylene glycol adduct (189).



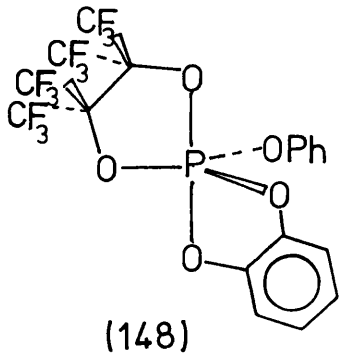
(189)

Using the N-chlorodi-isopropylamine method, adduct (226) was synthesised.



(226) (227)

The ΔG^* value for the process (226) $\rightleftharpoons$ (227) was found to be 20.7 kcal. $mol.^{-1}$, again very close to the oxygen analogue (148) which has a ΔG^* value of 20.5 kcal. $mol.^{-1}$.

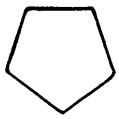
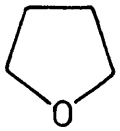
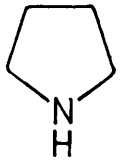
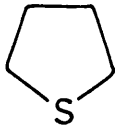


(148)

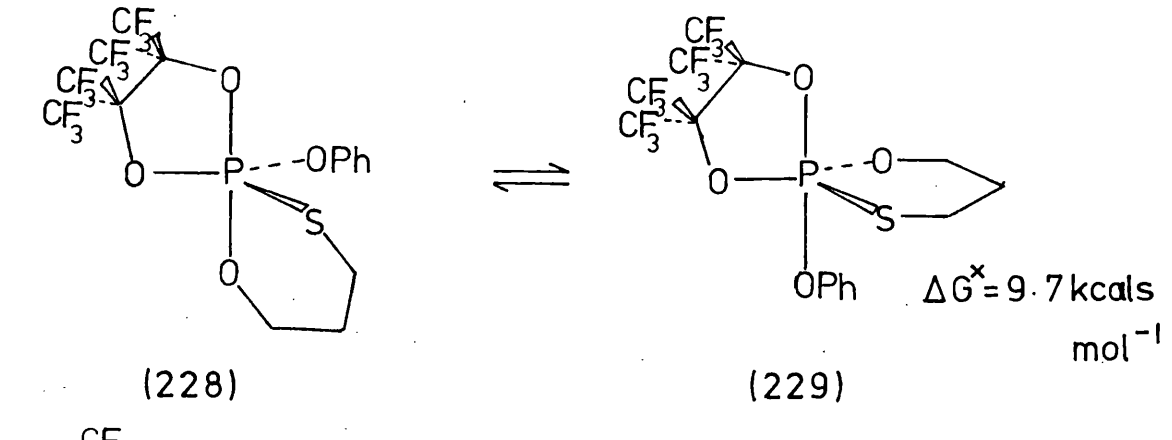
From the results of these experiments, it has become clear that exchanging sulphur for oxygen in a five-membered ring does not alter significantly the energy required to put that ring out into a diequatorial position. The energy of rotation around a P-S bond has been shown experimentally[85] to be greater than around a P-O bond, therefore some other factor must be smaller to compensate for this. The only factor which could be smaller with sulphur in the ring is 'ring strain'.

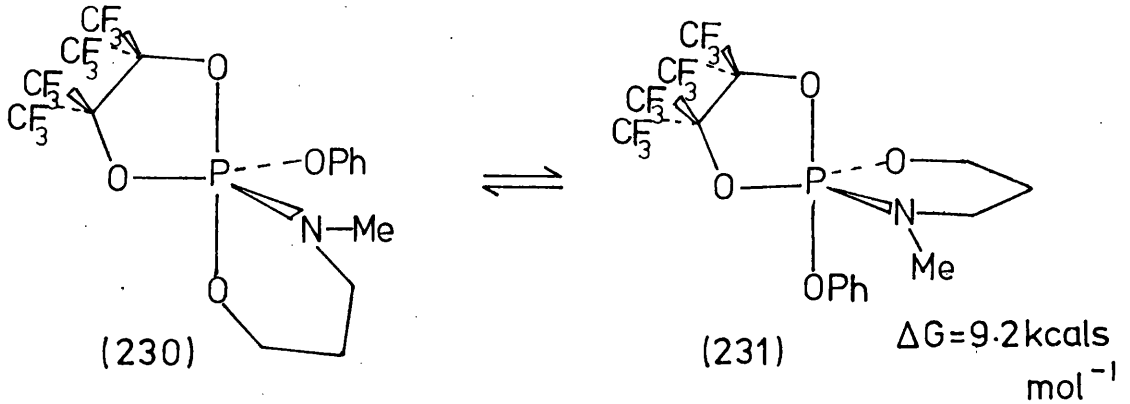
Pell and Pilcher[95] compared the ring strains of cyclopentane, tetrahydrofuran, pyrolidine, and tetrahydrothiophene obtained from heats of combustion. The results are summarised in Table four.

TABLE FOUR

	ring strain kcals mol^{-1}
	6.05
	5.63
	5.80
	1.97

The strain in tetrahydrothiophene is about 3.5 kcal. mol.$^{-1}$ less than in tetrahydrofuran. However in these simple heterocycles, the heteroatoms are sp^3 hybridised whereas in the phosphorus analogues they are sp^2 hybridised so a direct comparison cannot be strictly made, nevertheless it seems reasonable to assume that the strain in sulphur containing five-membered rings will be significantly lower than the oxygen analogues. Before ring strains can be predicted with confidence, more information is required on the rotation energy for the P-S bond. This information may be obtained by comparing the ΔG^* value for the oxathiaphosphorinan (228) with the oxazaphosphorinan prepared by Whittle[19] (230).





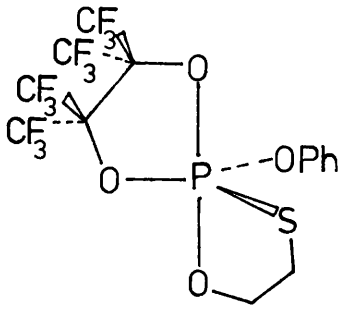
A six-membered ring containing phosphorus is less rigid than a five-membered ring, consequently when the six-membered ring is diequatorial it is possible for the molecule to distort so that the

donor orbitals are moved from the unfavourable position where they are parallel to the apical bonds to a more favourable intermediate orientation. This has the effect of reducing the unfavourable interaction between the donor orbital and the phosphorus. Pell and Pilcher[95] also worked out the ring strain for the six-membered ring analogues of Table 4 and found that they were virtually strain free. The difference in ring strain between piperidine and thiocyclohexane was only 0.1 kcal. $mol.^{-1}$ Although it cannot be assumed that the ring strain in the oxathiaphosphorinan (229) and the oxazaphosphorinan (231) is zero it does seem reasonable to assume that the strain factor will be the same in both molecules. The other terms that may be assumed to be identical in both molecules are the A (ring O-OPh) and the rotation around the P-O bond energy. If the energy equations for the two molecules are substracted then the strain factor, A (ring O-OPh) and Rot O factors disappear leaving:

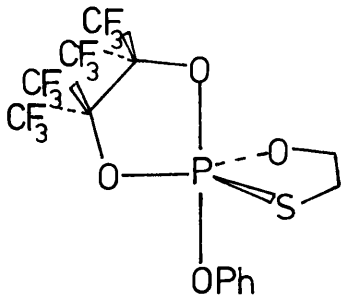
$$\Delta G^{*}_{(229)(O\text{-}S)} - \Delta G^{*}_{(231)(O\text{-}NMe)} = \text{Rot S} - \text{Rot N}$$

As the difference between the ΔG^{*} values for the two molecules is very small, about 0.5 kcal. $mol.^{-1}$, it can be assumed that Rot S = Rot N. This is not a very satisfactory method for obtaining a figure of the energy of rotation around a P-S bond because so many assumptions have to be used but as there are no accurate values reported in the literature from direct measurements there is no alternative but to assume that Rot S = Rot N = 9 kcal. $mol.^{-1}$.

The energy equation for (197) $\rightleftharpoons$ (225)



(197)



(225)

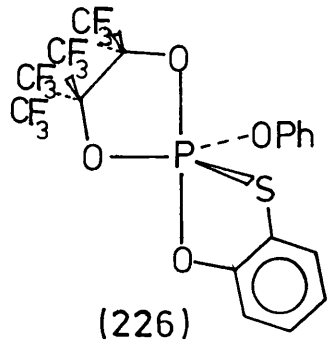
may be written,

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

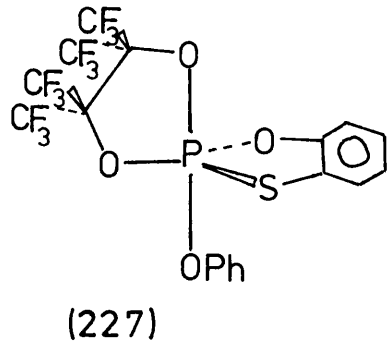
$$= \quad ? \quad + \quad (-1) \quad + \quad 5 \quad + \quad 9$$

ΔG^* found experimentally is 17.7 kcal. mol.$^{-1}$ which means that the strain factor in the oxathiaphospholan ring is only 4.7 kcal. mol.$^{-1}$ compared to the value of 8 kcal. mol.$^{-1}$ for the dioxaphospholan. The difference in ring strain of approximately 3.5 kcal. mol.$^{-1}$ is very close to the difference between tetrahydrofuran and tetrahydrothiophene found by Pell and Pilcher.[95]

Similarly for the equilibrium (226) ⇌ (227)



(226)



(227)

The energy equation may be written,

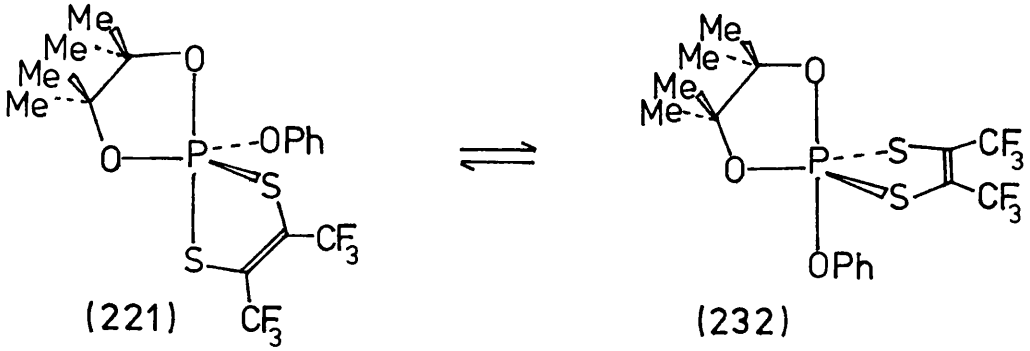
$$\Delta G^* = S_{90-120}(\text{oxathiaphospholen}) + A\ (\text{ring O-OPh}) + \text{Rot O} + \text{Rot S}$$

$$20.7 = \quad ? \quad + \quad 0 \quad + \quad 5 \quad + \quad 9$$

i.e. strain in the oxathiaphospholen ring is only 6.7 kcal. mol.$^{-1}$ again about 3.5 kcal. mol.$^{-1}$ less than the strain in the dioxaphospholan (148).

From these experiments, it appears that replacing an oxygen atom by sulphur causes the ring strain to be lowered by about 3.5 kcal. mol.$^{-1}$ when the ring spans the diequatorial position.

Considering the ring containing two sulphur atoms



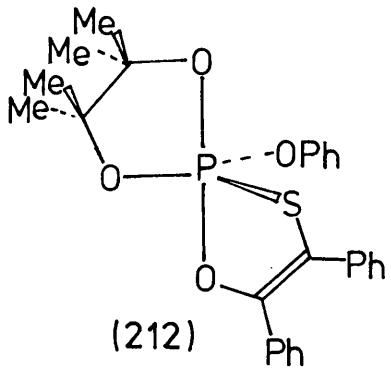
The energy equation may be written,

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

$$22.3 = \quad ? \quad + \quad (-1) \quad + \quad 18$$

The strain in the dithiaphospholen ring is only 5.3 kcal. mol.$^{-1}$ whereas the strain in the dioxaphospholen analogue (223) is 13 kcal. mol.$^{-1}$, a difference of about 7.5 kcal. mol.$^{-1}$ From this experiment it appears that for each oxygen atom replaced by sulphur the ring strain is lowered by approximately 3.5 kcal. mol.$^{-1}$

Looking once again at the monothiobenzil adduct (212) for which the coalescence of four signals to one was observed,



(212)

The energy equation may be written,

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

$$21.0 = \quad ? \quad + \quad (-1) \quad + \quad 5 \quad + \quad 9$$

The strain for the oxathiaphospholen ring spanning a diequatorial position would be 8kcal. $mol.^{-1}$ The strain in the benzil adduct (217) is about 12 kcal. $mol.^{-1}$ so the difference between these two ring strain values could be accounted for by the presence of the sulphur atom. 21 kcal. $mol.^{-1}$ is therefore a reasonable value for ΔG^* of the process where the oxathiaphospholen ring moves diequatorial and phenoxy apical. The observed coalescence of four signals going to one may well be caused by both rings going out diequatorial alternately, the two high energy processes having very similar ΔG^* values.

Conclusion.

It has been found experimentally that the ΔG^* value for a process where a five-membered ring with two oxygens adjacent to phosphorus moves to a diequatorial position does not vary very much as the oxygen atoms are successively replaced by sulphur atoms. This is surprising because the energy associated with P-S bond rotation is about

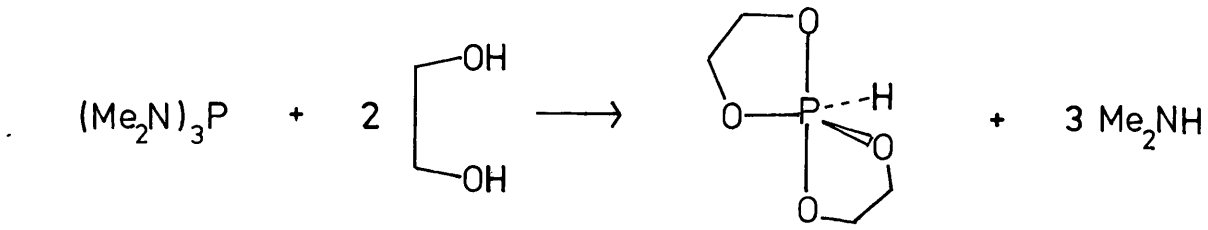
4 kcal. mol.$^{-1}$ greater than P-O bond rotation. It is suggested that the extra energy associated with P-S bond rotation is compensated by a drop in ring strain of about 3.5 kcal. mol.$^{-1}$ for each oxygen atom replaced by sulphur. This suggestion is in accord with the work of Pell and Pilcher[95] who discovered that the difference in ring strain between the five-membered ring heterocycles tetrehydrofuran and tetrahydrothiophene was also about 3.5 kcal. mol.$^{-1}$.

With the information obtained on energies of rotation around the bonds between various heteroatoms and phosphorus, differences in apicophilicities and ring strains it is possible to predict ΔG^* values for a large number of phosphoranes containing five-membered rings.

CHAPTER 7

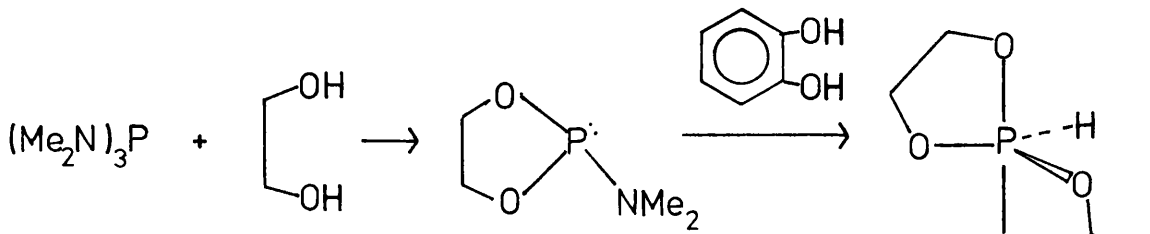
7.1 The Relative Apicophilicity of Hydrogen

Spirophosphoranes containing P-H bonds are very readily prepared by the action of two moles of either a 1,2-diol or a 1,2-aminoalcohol on trisdimethylaminophosphine, e.g.



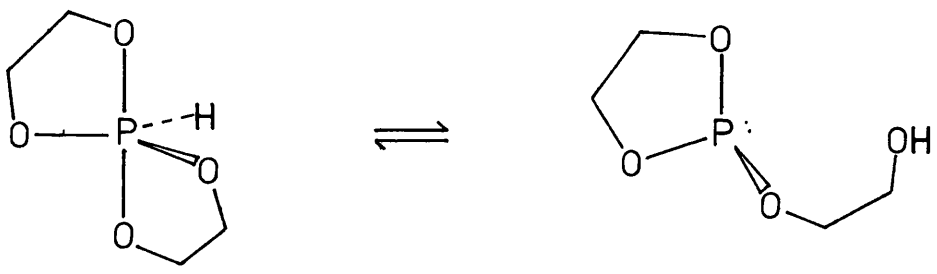
(233)

Unsymmetrical spirophosphoranes can be made by reacting one mole of a diol with trisdimethylaminophosphine to form the cyclic aminophosphite (234) which may then be reacted with a second diol to form the spirophosphorane (235).



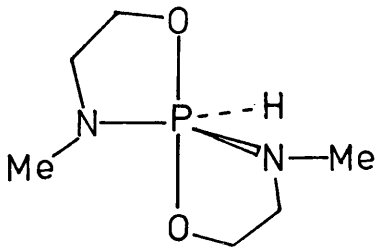
(234) (235)

In this type of phosphorane an equilibrium between the P^{V} and the ring opened P^{III} forms often exists. i.e.



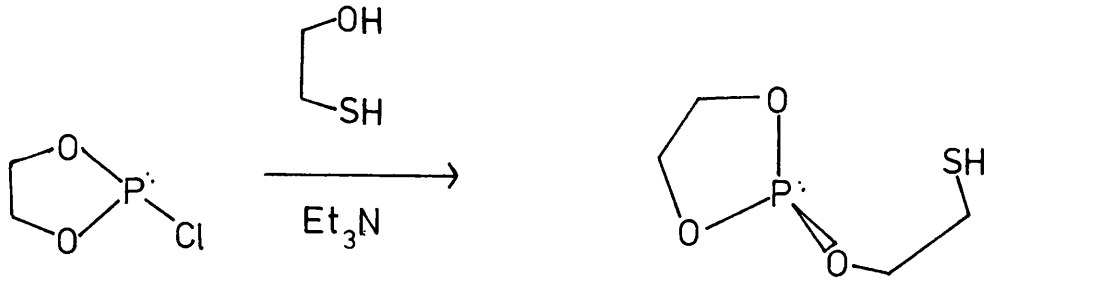
P^{V} P^{iii}

The ratio of P^{V} to P^{III} may be observed by ^{31}P n.m.r. The spirophosphoranes have large positive chemical shifts and the phosphites have large negative shifts relative to 85% H_3PO_4. 1,2-Aminoalcohols also react with trisdimethylaminophosphine forming spirophosphoranes, e.g. (236)



(236)

The reaction of 2-mercapto-ethanol with the cyclic chlorophosphite (237) yields the phosphite (238) which exists entirely as the trivalent species.[96]

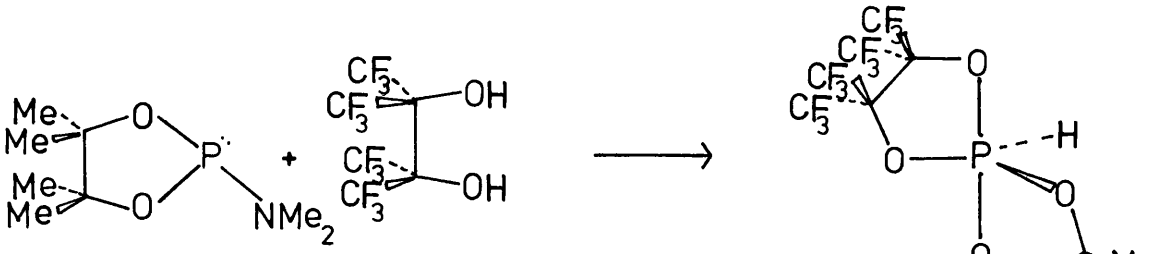


(237) (238) $Et_3\overset{+}{N}H\ Cl^-$

Although a very large number of spirophosphoranes containing P-H bonds have been prepared,[97-99] surprisingly little work has been done of the determination of the relative apicophilicity of hydrogen. A great problem associated with this type of phosphorane is that as the temperature is raised, the $P^{V} \rightleftharpoons P^{III}$ equilibrium may become fast on the n.m.r. time-scale.

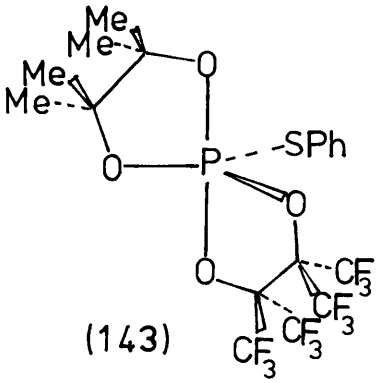
To try and gain a little more information on the relative apicophilicity of hydrogen, the adduct (239) was prepared by treating

the cyclic aminophosphite (240) with perfluoropinacol.



(240) (239)

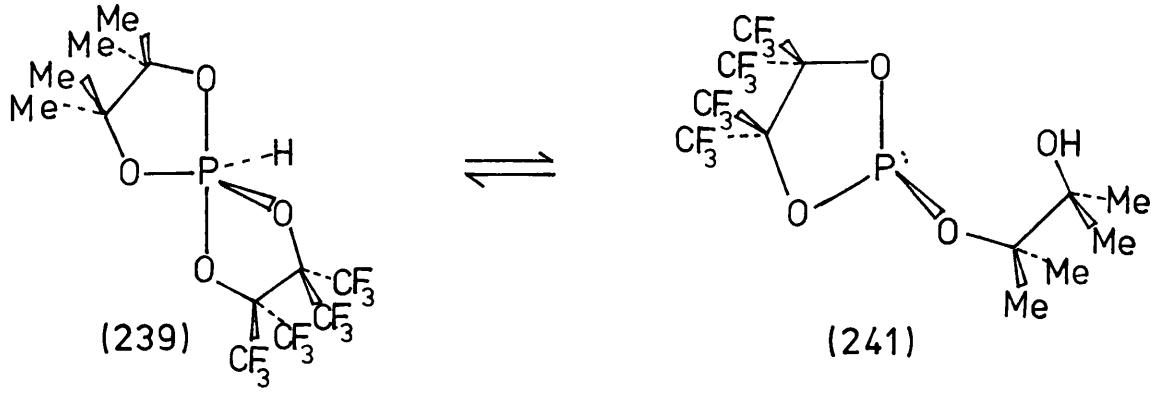
The adduct (239) was found to exist entirely in the P^V form. There was a complete absence of an OH band in the infra red spectrum and no trivalent form was detected in the ^{31}P n.m.r. The variable temperature ^{19}F n.m.r. showed a coalescence of the two signals to one at 92° corresponding to a ΔG^* value of 18.8 kcal. $mol.^{-1}$. This value may be compared directly with the adduct (143).[83]



(143)

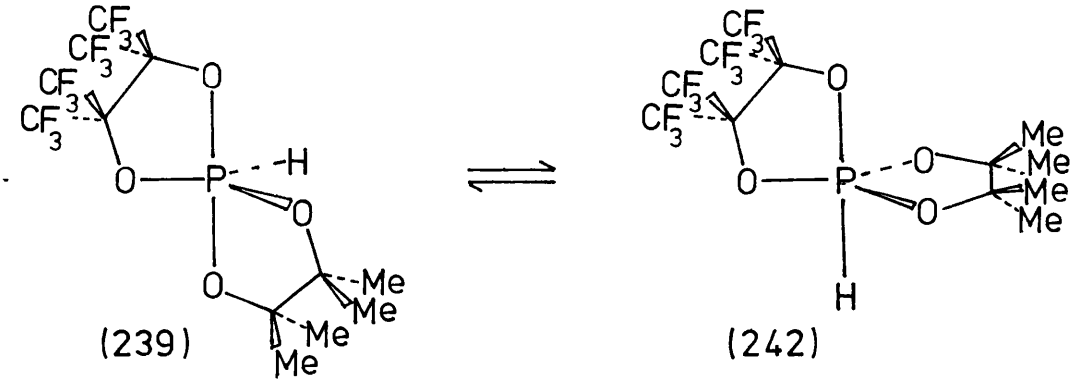
The ΔG^* value for the equivalence of the CF_3 groups in (143) is 22.4 kcal. $mol.^{-1}$ This indicates that hydrogen is highly apicophilic.

Equivalence of the CF_3 groups in the phosphorane (239) could also be achieved by rapid ring opening of either ring, e.g. (239) $\rightleftharpoons$ (241).



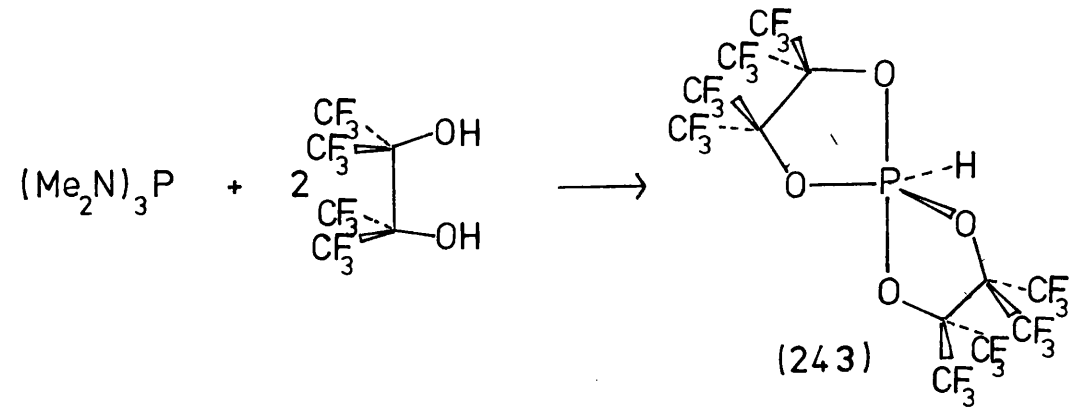
(239) (241)

To investigate this possibility the variable temperature ^1H n.m.r. was monitored. The spectrum of the adduct (239) remained unchanged even at 167°. If the process (239) $\rightleftharpoons$ (241) becomes fast on the n.m.r. time-scale then P-H coupling will be lost, however, no loss of P-H coupling was observed even at 167°. The pinacol methyls appeared as two singlets as expected at room temperature and did not alter as the temperature was raised. These methyl groups can become equivalent by either the perfluoropinacol ring spanning a diequatorial position (something that has never been observed by d.n.m.r. methods) or by rapid ring opening of either ring. This means that the same irregular process makes both the methyls of thepinacol ring and the CF_3 groups of the perfluoropinacol ring equivalent. The fact that the methyl groups on the pinacol ring do not become equivalent even at 167° indicates that the CF_3 groups must become equivalent by a regular process, i.e. a pseudorotation which puts the pinacol ring diequatorial and the hydrogen apical (242).



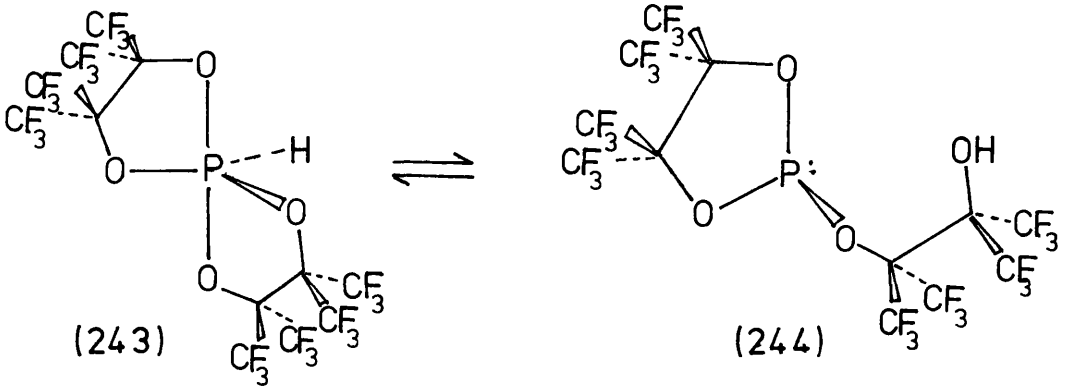
(239) (242)

The adduct (243) was prepared by the action of trisdimethylamino-phosphine with two moles of perfluoropinacol.



(243)

This adduct was found to exist as an equilibrium between the P^{V} form (243) and the P^{III} form (244)



(243) (244)

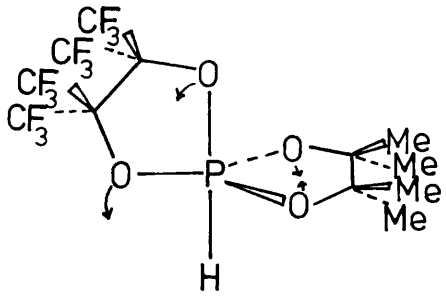
This equilibrium must be fast on the n.m.r. time-scale at room temperature because the ^{1}H n.m.r. showed an OH proton but no P-H coupling, the ^{19}F n.m.r. showed only a sharp doublet (P-F coupling J = 14.5 Hz) and the ^{31}P showed a broad signal at -88 p.p.m. from 85% H_3PO_4, a value which is not negative enough to be a normal phosphite and much too negative to be a phosphorane, it must therefore be a weighted average value of the phosphite and the phosphorane caused by the rapid equilibrium, (243) $\rightleftharpoons$ (244).

Equilibration of all the CF_3 groups in this way can only be caused by the rapid equilibration (243) $\rightleftharpoons$ (244). The ^{19}F n.m.r. was monitored as the temperature was lowered and at low temperatures, the ^{19}F n.m.r. consisted of three signals in the ratio of 2:1:1 which is consistent with the trivalent form (244) but not with the phosphorane (243).

It is strange that the tetraoxyphosphorane (239) with one perfluoropinacol ring should exist in the P^{V} form even at 167° whereas the phosphorane (243) with two perfluoropinacol rings prefers to exist in the P^{III} form. There appears to be no rational explanation for this behaviour.

The apicophilicity of hydrogen is rather anomolous. The electronegativity is as low as for carbon, and hydrogen has no apparent acceptor orbitals and yet it is an extremely apicophilic group as

determined using spirophosphoranes of the type (239). The high apicophilicity of hydrogen may be understood by considering the intermediate (242) with hydrogen apical and the pinacol ring diequatorial.



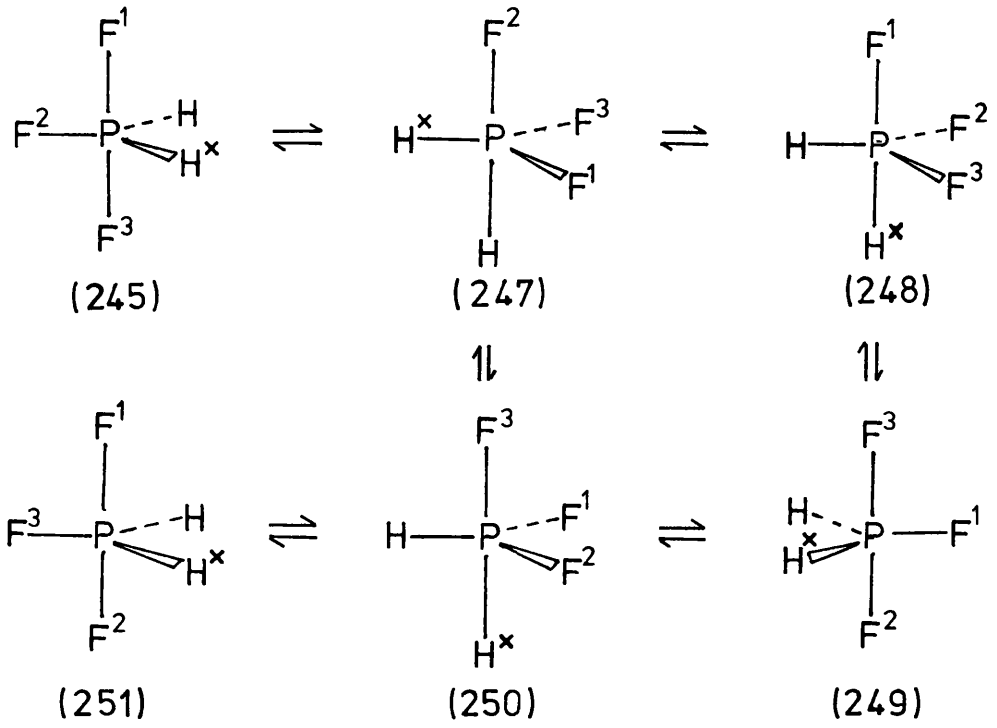
(242)

The intermediate (243) is not expected to be a perfect trigonal bipyramid (see Chapter 2.4). The oxygens of the pinacol ring will move together to reduce the ring strain, this motion forces the perfluoropinacol ring down in the direction shown, towards the apical hydrogen. These motions continue until a balance is set up between strain in the pinacol ring and the repulsion term between the oxygen of the perfluoropinacol ring and the apical hydrogen. As hydrogen is so small, the perfluoropinacol ring will be able to move further down towards it before the repulsion term becomes large, this means that the strain in the pinacol ring is reduced which lowers the energy of intermediate (242) considerably giving rise to a low ΔG^* value and making hydrogen appear highly apicophilic.

If this reasoning is correct then in acyclic phosphoranes, hydrogen will show its true apicophilicity as the steric effects described for spirophosphoranes will not be operating in acyclic systems.

Cowley[75] studied the d.n.m.r. behaviour of H_2PF_3 (245) and $H(CF_3)$-PF_3 (246). Equivalence of the fluorine atoms in (245) can be achieved

by the following pseudorotations set out in Scheme 10.



SCHEME 10

The high energy intermediates for this process have hydrogen apical. Cowley calculated the following activation parameters from the variable temperature ^{19}F n.m.r. $\Delta H^* = 14.2$ kcal. mol.$^{-1}$ and $\Delta G^* = 10.2$ kcal. mol.$^{-1}$

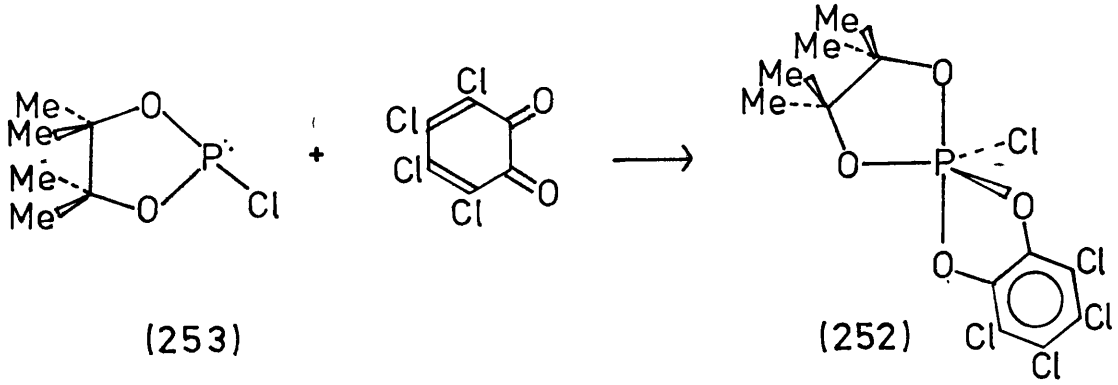
Equivalence of the fluorine atoms in $H(CF_3)PF_3$ (246) requires that the same pseudorotations described in Scheme 10 take place except H* is replaced by CF_3. The high energy intermediate is now (247) (H* = CF_3) as CF_3 has been found to be more apicophilic than hydrogen,[69] i.e. the high energy intermediate has hydrogen apical and should therefore have the same activation parameters as H_2PF_3 (245). However Cowley calculated the following activation parameters for $H(CF_3)PF_3$, $\Delta H^* = 8.8$ kcal. mol.$^{-1}$ and $\Delta G^* = 6.3$ kcal. mol.$^{-1}$ This means that the two results are not consistent with each other. The value

of ΔS^* in these two cases is much greater than the expected value for a genuine pseudorotation which is zero[63b,76] which implies that equivalence of the fluorine atoms in H_2PF_3 and $H(CF_3)PF_3$ is due to an irregular process probably involving fluorine-bridged intermediates, or possibly due to interactions with the walls of the pyrex n.m.r. tubes.

As equivalence of the fluorine atoms in H_2PF_3 and $H(CF_3)PF_3$ is due to irregular processes there is no quantitative apicophilicity data on hydrogen in acyclic systems. Until reliable data is produced for acyclic phosphoranes containing P-H bonds comparison with the relative apicophilicity of hydrogen in spirophosphoranes is impossible.

7.2 The Relative Apicophilicity of Chlorine.

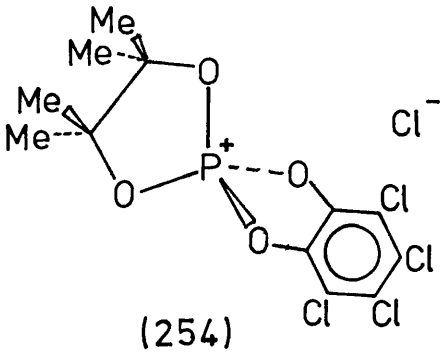
The adduct (252) was prepared by addition of tetrachloro-o-benzoquinone to the chlorophosphite (253)



(253) (252)

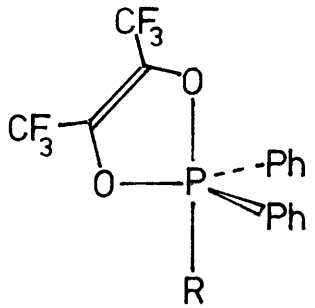
The chlorophosphorane was extremely hydrolytically unstable and could not be isolated in a pure state. The reaction was carried out in anhydrous carbon tetrachloride, and when the reaction was complete the solution was concentrated and the n.m.r. data were obtained from aliquots of this solution. The positive chemical shift in the ^{31}P n.m.r. relative to 85% H_3PO_4 indicated that the adduct existed as a

phosphorane (252) and not a tetraoxyphosphonium chloride (254).



(254)

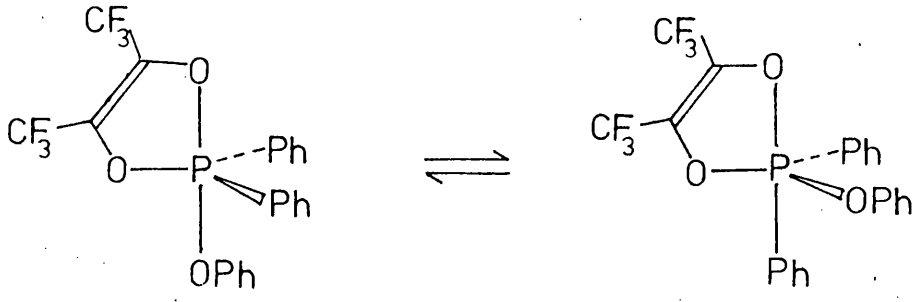
The ^{1}H n.m.r. consisted of two singlets for the pinacol methyls as expected and as the temperature was raised a reversible coalescence at 51° was observed corresponding to a ΔG^* value of 17.8 kcal. mol.$^{-1}$ This value may be compared directly with the ΔG^* value of 20.5 kcal. mol.$^{-1}$ for the phenoxy analogue (145), i.e. chlorine is more apicophilic than phenoxy by about 2.5 kcal. mol.$^{-1}$ In such an adduct as the chlorophosphorane (252) it is almost impossible to preclude the possibility that the equivalence of the pinacol methyls in the ^{1}H n.m.r. is caused by an irregular process involving small amounts of nucleophilic impurities, e.g. chloride ions. It is possibly for this reason that the results of this experiment compare so poorly with the results obtained by J.I. Dickstein,[100] who prepared the adducts (255) and (256).



R = OPh (255)

R = Cl (256)

The CF_3 groups in this molecule can only become equivalent when the pseudorotation which puts a phenyl group apical and the R group equatorial, e.g. (255) $\rightleftharpoons$ (257), is fast on the n.m.r. time-scale.

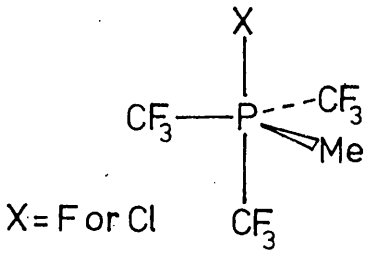


(255) (257)

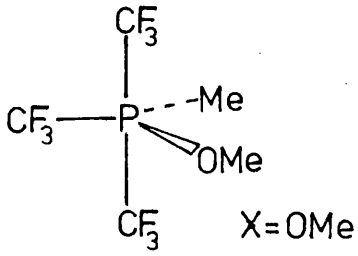
The intermediate (257) with phenyl apical is of high energy and the more apicophilic R is, the higher in energy (257) will be. This means that themore apicophilic R is the higher the coalescence temperature. The results of these experiments show that the phenoxy adduct (255) has a ΔG^* value of 12.6 kcal. $mol.^{-1}$ and the chloro adduct (256) a ΔG^* value of 12.0 kcal. $mol.^{-1}$, i.e. phenoxy is the more apicophilic.

The coalescences in both the cyclic phosphorane (256) and the spirophosphorane (252) may be caused by nucleophilic impurities. In the case of the spirophosphorane (252), the coalescence caused by a genuine pseudorotation may be at a higher temperature than 51^{o} so the ΔG^* value obtained from this experiment may only be a minimum value which would make chlorine appear more apicophilic than it really is. In the case of the cyclic phosphorane (256) the coalescence caused by pseudorotation may be at a higher temperature than that caused by the irregular process, this has the effect of making chlorine appear less apicophilic than it really is. These experiments provide an upper and lower limit to the range of the apicophilicity of chlorine relative to phenoxy.

In a recent paper,[101] the methyltris(trifluoromethyl)phosphoranes $Me(CF_3)_3PX$ with X as fluorine, chlorine and methoxy were prepared. At low temperature, the frozen molecules were analysed by ^{1}H, ^{31}P and ^{19}F n.m.r. and from the size of the coupling constants, etc. it was concluded that when X was fluorine or chlorine, the phosphorane had the structure (258) but when X was methoxy the phosphorane had the structure (259).



(258)



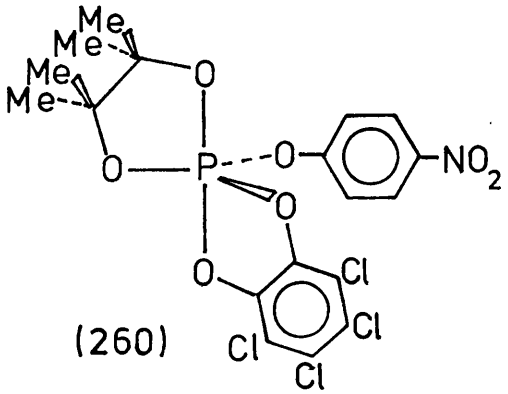
(259)

On a qualitative scale, this experiment shows that chlorine is more apicophilic than methoxy but does not say by how much. Methoxy groups are usually found to be about one kcal. $mol.^{-1}$ less apicophilic than phenoxy groups so the results of this experiment agree with the apicophilicity of chlorine falling in a range 0.5 to +2.5 kcal. $mol.^{-1}$ relative to phenoxy.

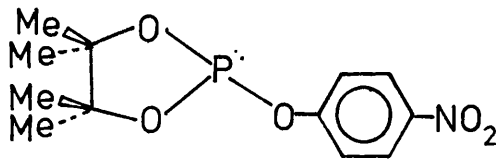
There is a slight doubt as to the reliability of the results obtained from hexafluorobiacetyl adducts[100] as the difference between phenoxy and methoxy in this system was found to be 2.8 kcal. $mol.^{-1}$, a larger value than is usually observed. It is likely that these hexafluorobiacetyl adducts will be more susceptible to irregular processes involving ionic species than spirophosphoranes as the HFBA adducts contain only one ring and have two phenyl groups attached to phosphorus which help to stabilise a positive charge on phosphorus, (see Section 1.4). Although it is not possible to state categorically which result is nearer the correct answer for the relative apicophilicity of chlorine, more reliable results have been obtained from spirophosphoranes.

7.3 Relative Apicophilicity of the p-Nitrophenoxy Group.

The leaving group ability of p-nitrophenoxy is virtually the same as that of the chloride anion. The adduct (260) was therefore prepared in order to determine what effect the p-nitro group would have on the relative apicophilicity of phenoxy.



(260)

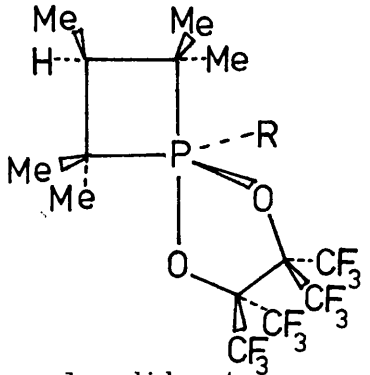


(261)

The preparation of this adduct posed some problems because although the cyclic phosphite (261) was readily prepared, distillation was impossible as deoxygenation reactions of the nitro group would have occurred. For this reason it was necessary to react the crude phosphite with tetrachloro-o-benzoquinone to obtain the adduct (260). ^{1}H and ^{31}P n.m.r. indicated thepresence of only a small amount of impurities in solution with the adduct (260). As this adduct was as hydrolytically unstable as the chloro adduct (252) further purification was impossible. The methyl groups for the adduct (260) appeared as two singlets in the ^{1}H n.m.r. as expected and on warming a reversible coalescence was observed at 110^{o} corresponding to a ΔG^{*} value of 20 kcal. $mol.^{-1}$ This value is very close to that of the phenoxy analogue (145) (ΔG^{*} = 20.5 kcal. $mol.^{-1}$) and may be compared with the value for the chloro adduct (252) (ΔG^{*} = 17.8 kcal. $mol.^{-1}$). The results of this experiment indicate that electron-withdrawing groups in the para position of a phenoxy substituent have very little effect on the apicophilicity of the phenoxy group.

7.4 Relative Apicophilicity of the Dimethylamino Group.

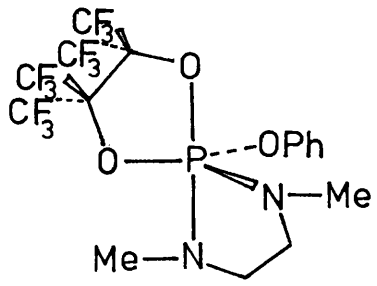
In the series of HFA phosphetan adducts (262 - 263) prepared by Oram[72] a difference of about 7.5 kcal. mol.$^{-1}$ between phenoxy and dimethylamino was found.



R = OPh (262)

R = NMe_2 (263)

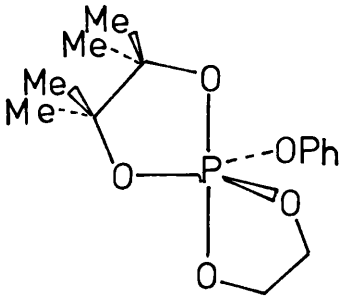
This value did not correspond well to the difference estimated from the ΔG^* value of the adduct (193)[19] (see Chapter 6).



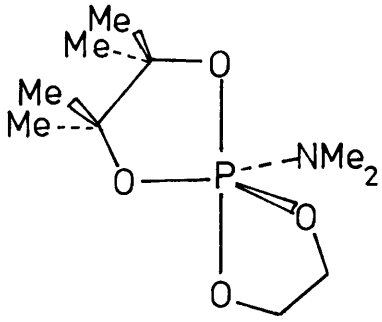
(193)

Using the energy equation for this process, the value of the term A (ring N-OPh) was estimated at -5.5 kcal. mol.$^{-1}$, i.e. a much smaller value. It is difficult to find suitable systems for comparing the relative apicophilicities of phenoxy and dimethylamino due to the large difference between them.

The adduct (264) was prepared by both the 'DAD' and the 'N-chlorodi-isopropylamine' methods and the coalescence temperature associated with the ethylene glycol ring spanning a diequatorial position and phenoxy becoming apical was found to be only 41^{o} corresponding to a ΔG^* value of 17.4 kcal. mol.$^{-1}$.



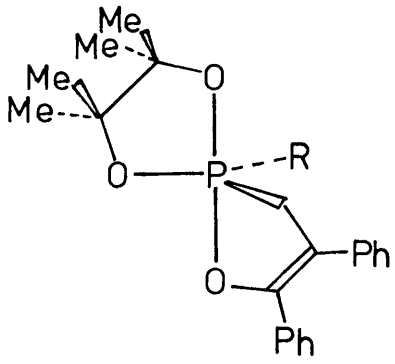
(264)



(265)

Using the 'DAD' method, the dimethylamino analogue (265) was prepared, from the reversible coalescence of the methyl signals at 157°, ΔG^* was found to be 22.7 kcal. mol.$^{-1}$ From this experiment the difference in apicophilicity between dimethylamino and phenoxy is 5.3 kcal. mol.$^{-1}$ which is in excellent agreement with the value estimated from the ΔG^* value of adduct (193).

The reliability of this experiment has been confirmed by M.W. White[92] in his study of methylenedesoxybenzoin adducts (266 - 267).

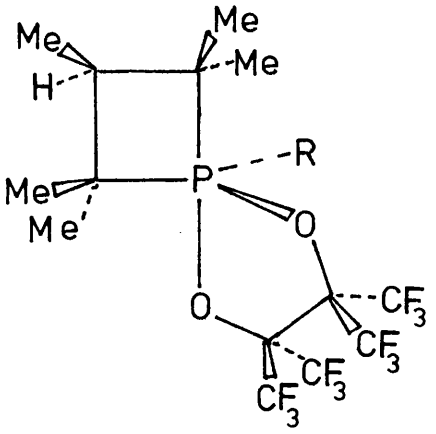


	$\Delta G^{\ddagger}$ kcals mol^{-1}	
R = OPh	14.1	(266)
R = NMe_2	19.0	(267)

In this case, the difference in apicophilicity between dimethylamino and phenoxy was found to be 5 kcal. mol.$^{-1}$.

7.5 The Relative Apicophilicity of Phenyl, Benzyl, and Methyl Groups.

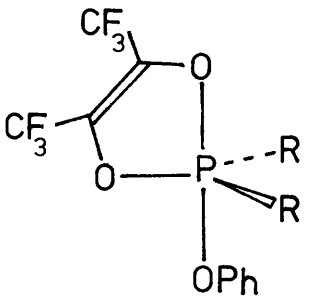
The work by Oram and Trippett[72] showed that the phenyl group was considerably less apicophilic than methyl or isopropyl in the HFA phosphetan adducts (268-271).



R	ΔG^{x} kcals mol^{-1}	
Me	16.9	(268)
Pr^{i}	17.8	(269)
Ph cis	19.6	(270)
Ph trans	> 22	(271)

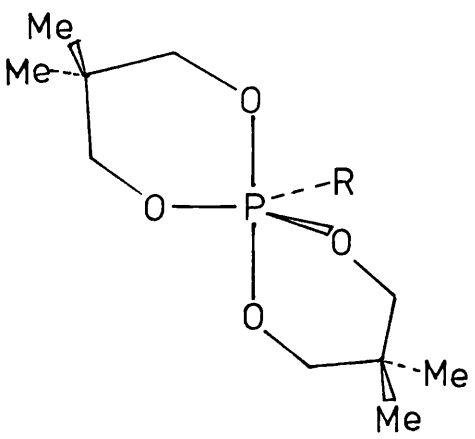
In the case of the trans phenyl adduct (271) the coalescence temperature was much higher than for the cis adduct (270) and was even above the upper limit of the n.m.r. spectrometer.

The work by Whittle[19] showed that phenyl was about as apicophilic as isopropyl in the adducts (272-273).



R	ΔG^{x} kcals mol^{-1}	
Ph	12.6	(272)
Pr^{i}	12.9	(273)

In order to obtain more information on this subject the adducts (274 - 276) were prepared using the 'N-chlorodi-isopropylamine' method.

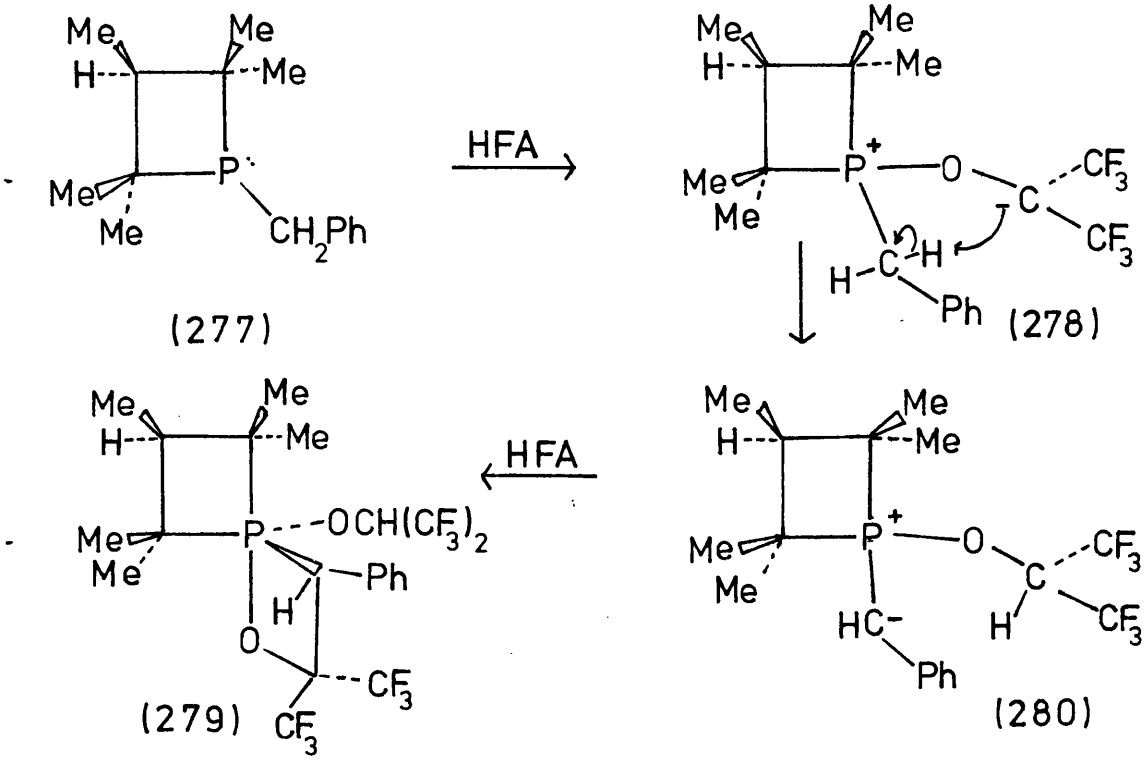


R	$\Delta G^{\times}$ kcals mol^{-1}	
Ph	13·2	(274)
CH_3	12·7	(275)
CH_2Ph	12·2	(276)

The methyl (275) and phenyl (274) adducts had previously been prepared by Denney[37] in an impure state by his exchange route to phosphoranes. Denney calculated the ΔG^* value for the methyl adduct (275) but not for the phenyl adduct (274).

In these adducts, the difference in apicophilicity between methyl and phenyl was only 0.5 kcal. $mol.^{-1}$. This result confirms that phenyl and alkyl groups have similar apicophilicities. It is difficult to explain why the phenyl group in the phosphetan series (268 - 271) is so much less apicophilic.

The benzyl group was found to be about one kcal. $mol.^{-1}$ more apicophilic than phenyl. This is an interesting result as it is the first time that the relative apicophilicity of the benzyl group has been determined. Oram[72] tried to obtain this value from his phosphetan series but found that the reaction of the benzylphosphetan (277) with HFA took an unusual course.

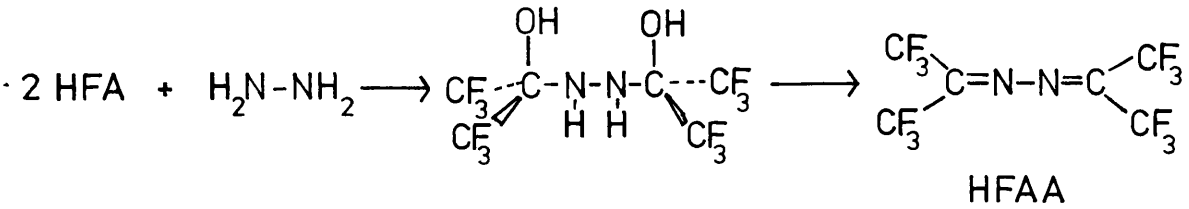


The first molecule of HFA is believed to attack the phosphorus forming the betaine (278). Proton transfer occurs from the benzyl to the hexafluoroisopropoxy group forming the ylide (279). Attack of a second molecule of HFA on the ylide gives the oxaphosphetan (280).

CHAPTER 8

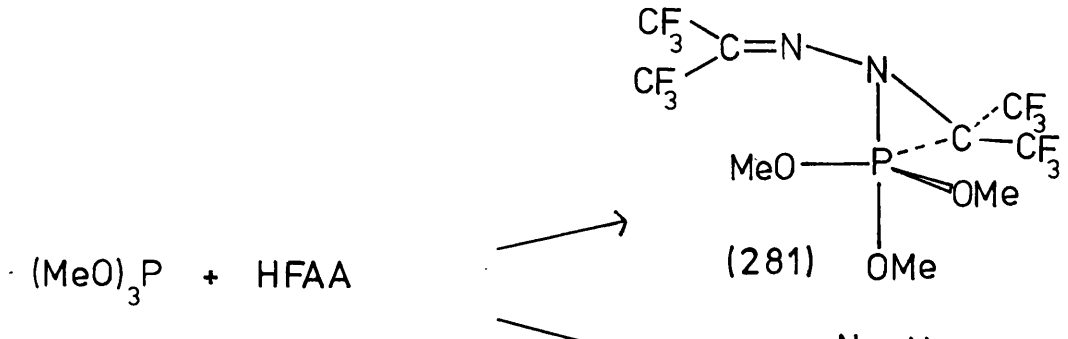
The 1:1 Adduct from Hexafluoroacetone Azine and Trimethyl Phosphite.

Burger[102] reported a simple synthesis of hexafluoroacetone azine (HFAA) by reaction of HFA with hydrazine followed by dehydration with phosphorus oxychloride and a tertiary base.

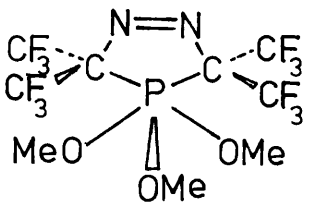


HFAA

He then went on to describe the reaction of HFAA with trialkyl phosphites and trisdimethylaminophosphine. The products of these reactions were 1:1 adduct between the trivalent phosphorus compound and HFAA. The adducts were found to have remarkable thermal stability and could be distilled under reduced pressures. Burger considered two structures (281) and (282) for the adduct from trimethyl phosphite.



(281)



(282)

The ^{1}H n.m.r. of the trimethyl phosphite adduct showed three equivalent methoxy groups. The ^{19}F showed two signals, one broad at

-12.45 p.p.m. and the other quoted as a multiplet at -0.32 p.p.m. relative to external CF_3CO_2H. The ^{19}F n.m.r. is not consistent with structure (282) with the five-membered ring as this structure should have just one signal probably split into a doublet by coupling to phosphorus. Mass spectral data showed a very strong peak associated with loss of $-N=C(CF_3)_2$ and no fragmentation due to loss of N_2. Furthermore, these adducts had absorptions on the infra red at around 1720 cm^{-1}, which was assigned to the imine stretching frequency $-N=C(CF_3)_2$. From this evidence, Burger concluded that the adduct could not have structure (282) with a five-membered ring, so it must have the structure (281) with a three-membered ring.

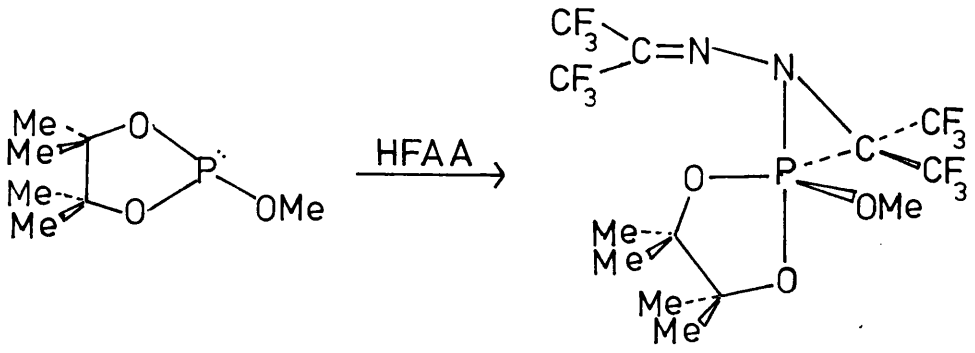
Having made extensive studies on four-, five- and six-membered rings it was decided to study some three-membered ring adducts of which these HFAA adducts were the only reported examples. A three-membered ring should have an even greater preference for an apical equatorial position than a four-membered ring.

The trimethyl phosphite adduct was prepared to check the n.m.r. data given by Burger and to obtain the ^{31}P curiously omitted in the original publication. The chemical shifts in the ^{19}F were found to be approximately the same as the published values. The broad peak at -11.8 p.p.m. (CF_3CO_2H) was found to split into two equal signals on cooling, one a well defined quartet and the other a less well defined quartet (J = 8.5 Hz). The other signal at 0.7 p.p.m. (CF_3CO_2H) was found to be a sharp singlet even at -87^{o}.

The coalescence of the broad signal can be attributed to rotation around the imine bond $N=C(CF_3)_2$ which is very similar to the results of other HFA imines.[103] This confirms the presence of the imine group $N=C(CF_3)_2$. If the broad signal in the ^{19}F n.m.r. is due to the CF_3

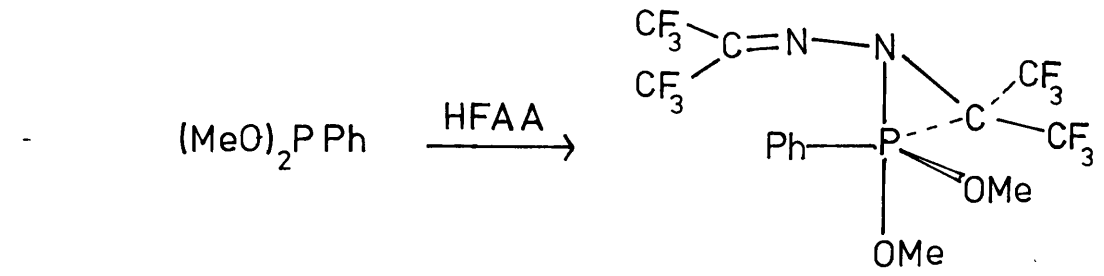
groups on the imine then the sharp singlet must be due to the CF_3 groups closest to phosphorus and part of the three-membered ring. It is surprising that the ^{19}F n.m.r. signal for these fluorine atoms is not split by coupling to phosphorus, as the two nucleii are separated by only two carbon atoms in the three-membered ring.

In the trimethyl phosphite adduct, the CF_3 groups are equivalent and only one signal would be expected in the ^{19}F n.m.r. The HFAA adduct with the cyclic phosphite (283) was therefore prepared following a similar procedure.



(283) (284)

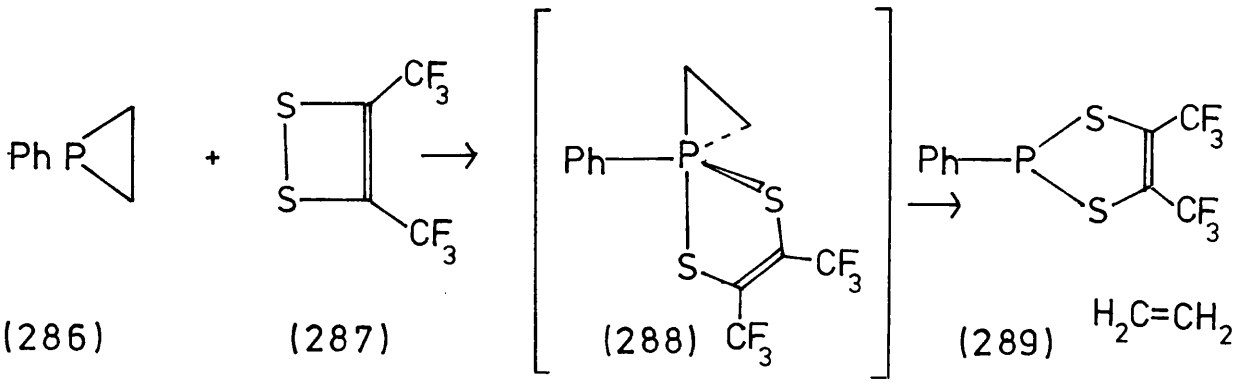
In this adduct (284), the CF_3 groups nearest to phosphorus can become equivalent only by a pseudorotation that puts the pinacol ring diequatorial and the methoxy group apical, a process known to be of high energy (20 kcal. $mol.^{-1}$). When the adduct (284) was prepared, the ^{19}F signal for these CF_3 groups was a singlet at room temperature and remained unchanged even at -118^{o}, the lower limit of the spectrometer. These CF_3 groups may become equivalent by an irregular process involving rapid reversible P-N bond breaking in the three-membered ring but it seems unlikely that this process will be rapid at -118^{o}. The CF_3 groups may be accidentally equivalent in the ^{19}F n.m.r. so the HFAA adduct (285) with dimethyl phenylphosphonite was prepared.



(285)

In this molecule, (285), the methoxy group can become equivalent only while the pseudorotation that puts phenyl and the carbon atom of the three-membered ring apical is fast on then.m.r. time-scale. In fact in the room temperature ^{1}H n.m.r. only one type of methoxy group was present and on cooling no change was observed even at -98°.

These unexpected results cast doubt on the validity of the assigned structure for these adducts. Denney[104] proposed the intermediacy of a phosphorane containing a three-membered ring in the reaction between phenylphosphiran (286) and the dithieten (287).

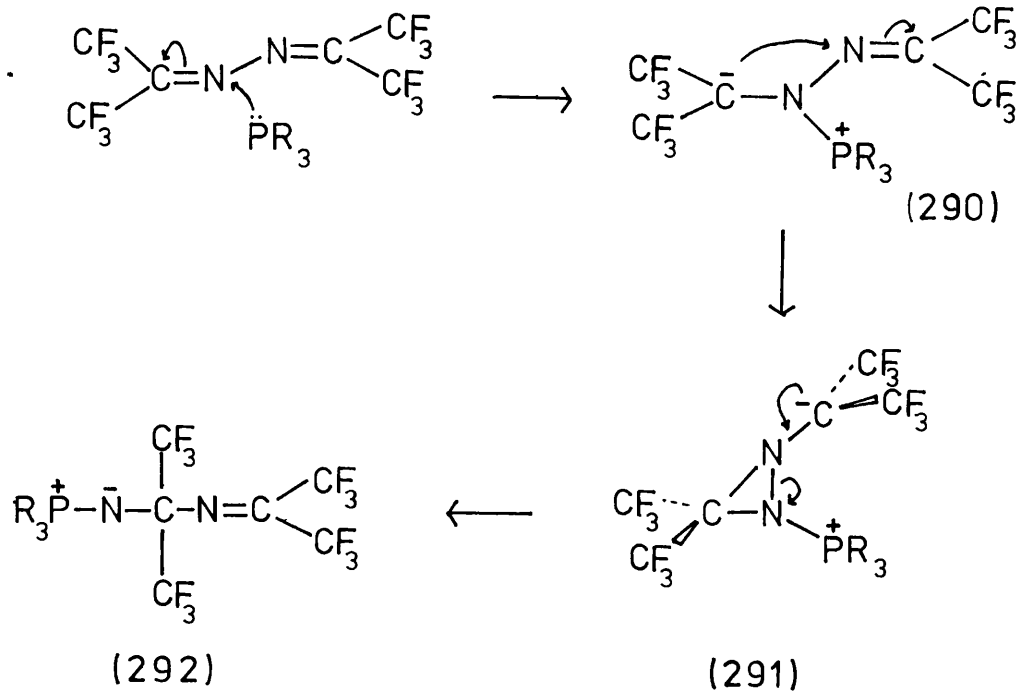


(286) (287) (288) (289)

Even when the reaction was carried out at -78° the phosphorane (288) was thermally unstable giving ethylene and the dithiaphospholen (289).

As the three-membered ring phosphorane prepared by Denney was very

thermally unstable it seemed unlikely that the very thermally stable HFAA adducts contained three-membered rings. Bearing all the acquired evidence in mind it is proposed that the 1:1 adducts of HFAA and trialkyl phosphites do not contain three-membered rings but are in fact iminophosphoranes formed by the following mechanism;



(290)

(292) (291)

Initial attack by phosphorus on the nitrogen of the azine puts a negative charge on the carbon atom; the carbanion is stabilised by the presence of two CF_3 groups (290). This negative charge attacks the nitrogen of the other imine function forming another carbanion stabilised by two CF_3 groups (291). The negative charge is now fed back to reform the imine double bond with cleavage of the N-N bond forming the iminophosphorane (292).

This structure accounts for all the original n.m.r. data described by Burger.[102] Also, the CF_3 groups closest to phosphorus are expected to be a singlet in the ^{19}F n.m.r. even in adducts (294)

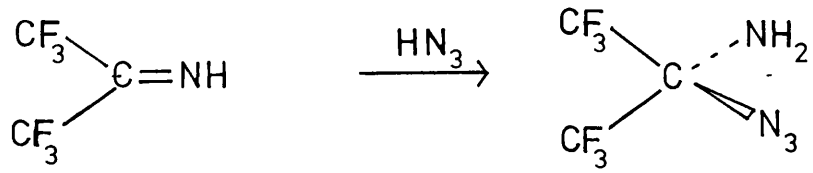
and (285) as there is a plane of symmetry passing between the CF_3 groups in these molecules. This structure accounts for the high thermal stability of the adducts and as the CF_3 groups closest to phosphorus are one atom further removed from the phosphorus than in the three-membered ring formula, coupling between fluorine and phosphorus would not be expected in the ^{19}F n.m.r. The proposed mechanism explains why other HFA imines such as $(CF_3)_2C{=}NH$ and $(CF_3)_2C{=}NMe$ would not react with trialkyl phosphites.

To try and prove this proposed structure, the trimethyl phosphite adduct was hydrolysed in the hope that the imine $H_2N\text{-}C(CF_3)_2\text{-}N{=}C(CF_3)_2$ could be isolated. The adduct proved extremely resistant to acid hydrolysis and when this was finally achieved, only HFA hydrate was isolated.

In the next attempt to prove the structure it was hoped that the molecule, if a nitrogen ylide, could be made to undergo a Wittig reaction with an aldehyde. However, no reaction occurred even with the very reactive p-nitrobenzaldehyde. The adduct was treated with HFA which is known to add to carbon ylides but no reaction occurred.

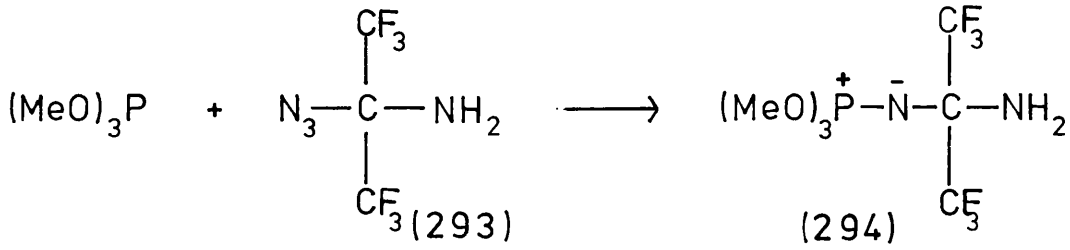
Several attempts were made to prepare solid adducts so that an X-ray structure determination could be carried out, but all the adducts prepared were liquids.

An attempt was therefore made to prepare the trimethyl phosphite adduct by an alternative route. The imine $(CF_3)_2C{=}NH$ was prepared by the method described by Middleton[105] by the reaction of HFA with ammonia followed by dehydration with phosphorus oxychloride and a tertiary base. The imine was treated with hydrazoic acid to form the aminoazide (293). This reaction is also described by Middleton.[105]

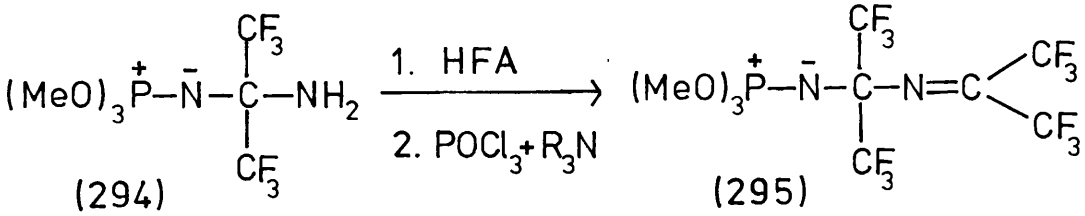


(293)

The aminoazide (293) was treated with trimethyl phosphite to form the iminophosphorane (294).



The iminophosphorane (294) was treated with HFA followed by phosphorus oxychloride in an attempt to prepare the original adduct (295). Unfortunately the nitrogen of the primary amine was not basic enough to react with HFA and although many attempts were made under various conditions, the final step of this synthesis could not be made to work, i.e.

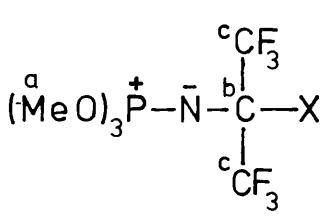


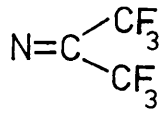
It was noted, however, that the iminophosphorane (294) had remarkably similar properties to those of the HFAA adduct (281) from trimethyl phosphite including great thermal stability and lack of reactivity of the nitrogen ylide with HFA. The ^{31}P chemical shifts were reasonably close, +4.5 p.p.m. for the iminophosphorane (294) and +12 p.p.m. for the HFAA adduct (281) relative to 85% H_3PO_4. The ^{19}F

n.m.r. chemical shifts of the CF_3 groups closest to phosphorus were also in fairly good agreement, 18.5 p.p.m. for the iminophosphorane (294) and 13.5 p.p.m. of the HFAA adduct (281) relative to $PhCF_3$ standard.

Further comparison between the iminophosphorane (294) and the trimethyl phosphite HFAA adduct (281) was obtained from a detailed study of the various coupling constants found in the ^{13}C n.m.r. spectra of these compounds. The details of this study are set out in Table Five.

TABLE FIVE



X =  I

X = NH_2 II

	a		b			c		
		J_{P-C}(Hz)		J_{P-C}	J_{F-C}		J_{P-C}	J_{PF}
I	54.6	7.5	81.7	11	31	122.4	6	241
II	54.2	8.8	73.1	4.5	31	123.9	13	288

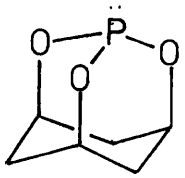
The ^{13}C n.m.r. spectra were obtained on a 22.63 MHz machine using tetramethylsilane as the internal standard.

The two spectra turned out to be remarkably similar as can be seen from Table Five. The important point to note is the coupling constant between phosphorus and carbon (b). Although this J_{P-C} value is slightly greater for the trimethyl phosphite azine adduct (281) it is much smaller than the value expected for a carbon bonded directly to pentacovalent phosphorus as in the three-membered ring structure which

would be in the region of 150 Hz.[92,106,107]

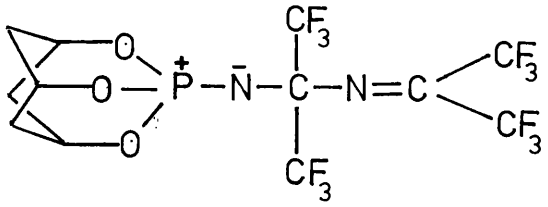
The results of these experiments confirm that the structure of the 1:1 adduct between trimethyl phosphite and hexafluoroacetone azine is an iminophosphorane (295) and not the three-membered ring phosphorane proposed by Burger.

Shortly after this work was complete Burger[108] published a second paper. The HFAA adduct with the tricyclic phosphite (296) was a crystalline solid for which an X-ray determination was made.



(296)

They reported that the structure of the adduct was not a three-membered ring phosphorane as they had first thought but was in fact the iminophosphorane (297)!



(297)

EXPERIMENTAL

Instrumentation.

Melting points were determined using a Kofler heating stage and are uncorrected. Infrared spectra were obtained from nujol mulls unless stated otherwise, and were recorded on a Perkin-Elmer 237 grating spectrometer. Mass spectra were determined with an A.E.I. MS9 instrument; in each case the molecular ion is given first unless stated otherwise, followed by peaks of structural significance. Routine proton n.m.r. spectra were recorded on a Varian T60 instrument in deuterochloroform as solvent unless otherwise stated. Variable temperature proton n.m.r. spectra were recorded on a Varian A60, Varian DA60 or a Jeol PS100 instrument. Proton shifts are relative to tetramethylsilane. Fluorine n.m.r. spectra were recorded on either a Varian DA60 or Jeol PS100 instrument with α , α , α-trifluorotoluene as internal standard. Phosphorus n.m.r. spectra were recorded on a Varian DA60 instrument. Phosphorus chemical shifts were obtained where possible by heteronuclear INDOR spectroscopy using an HD-60 heteronuclear decoupler (N.M.R. Specialities). Phosphorus chemical shifts are to high field of external 85% H_3PO_4 solution. Proton decoupled Fourier Transform ^{13}C n.m.r. spectra were obtained by the Physico-Chemical Measurements Unit, Harwell, Didcot, Berkshire on a Bruker HX90E instrument at 22·63 MHz using a pulse width of 7 s and a post delay of 4s. Carbon chemical shifts are relative to tetramethylsilane. 1-Bromonaphthalene was used as solvent for high temperature and ^{19}F n.m.r. spectra unless stated otherwise.

General.

All operations involving air or moisture sensitive compounds were

carried out under an atmosphere of dry, oxygen free, nitrogen. Solvents were dried as follows.

Diethylether, petroleum spirit, hexane, and benzene were dried over sodium wire. Methanol and ethanol were refluxed and distilled from their magnesium alkoxides. Pyridine and triethylamine were refluxed and distilled from potassium hydroxide. Dichloromethane was refluxed over and distilled from calcium hydride.

Solvents were removed under reduced pressure by a 'swirling' technique except in cases where the solution was stable to air and moisture when a rotary evaporator was used.

Small scale distillations and sublimations were carried out using a Kugelrohr and the boiling points quoted are the oven temperatures over which distillation occurred.

Liquid reagents were distilled before use. Koch-Light Celite preparation was used as a filtering aid.

Pentacovalent phosphoranes were recrystallised from anhydrous $60\text{-}80^{o}$ petroleum spirit unless stated otherwise.

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

High yields of this cyclic chlorophosphite were obtained from the addition of pinacol to phosphorus trichloride in ether using pyridine as a base, and allowing to stand for 48 hours before filtration, removal of ether, and distillation, b_{11} 80-89° [110] (88%).

Preparation of 2-Substituted-4,4,5,5-tetramethyl-1,3,2-dioxaphospholans from the 2-Chloro Compound.

General Method of Preparation.

The alcohol or thiol (0·05 mol) in 25cm^3 of ether was added to a mixture of 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholan (0·05 mol) and pyridine (0·05 mol) in ether (100cm^3) over a period of 20-30 minutes at 0°C. When addition was complete the reaction mixture was refluxed for 1 - 2 hours. Filtration and removal of the ether under reduced pressure followed by reduced pressure distillation yielded the 2-substituted-4,4,5,5-tetramethyl-1,3,2-dioxaphospholan. By this method, the following compounds were prepared.

(1) 2-Phenoxy-4,4,5,5-tetramethyl-1,3,2-dioxaphospholan

(87%); $b_{0·15}$ 80-84; τ 2.83-3.40 (5H, m), 8.60 (6H, s), and 8.75 (6H, s).

(2) 2-Phenylthio-4,4,5,5-tetramethyl-1,3,2-dioxaphospholan

(70%); b_2 135-40°; τ 2.38-2.80 (5H,m), 8.67 (6H,s) and 8.82 (6H,s).

(3) 2-(N,N-Dimethylamino)-4,4,5,5-tetramethyl-1,3,2-dioxaphospholan

For this compound, the general method was slightly modified. 0·1 Mol of dimethylamine in ether (50cm^3) was added to the 2-chloro compound with the pyridine omitted.[111]

(75%); b_{13} 82-86°; τ 3·4 (6H, d, J_{PH} 8 Hz), 8.80 (6H, s) 8.89 (6H, s).

Preparation of Tetrachloro-o-benzoquinone Adducts with 2-Substituted--4,4,5,5-tetramethyl-1,3,2-dioxaphospholans.

General Preparation.

Tetrachloro-o-benzoquinone (0·01 mol) in ether ($25cm^3$) was added to the dioxaphospholan in ether ($10cm^3$). The reaction mixture was stirred until the deep red colour of the quinone had disappeared (about 30 minutes). Solvent was removed and the residue was recrystallised from $60-80^o$ petrol. By this method, the following adducts were prepared in almost quantitative yields.

(1) 4',4',5',5'-tetramethyl-P-phenoxy-tetrachloro-1,3,2-benzodioxaphosphole-2-spiro-2'-1',3',2'-dioxaphospholan (145).

M.p. $159-160^o$; m/e 484, 486, 488, 490, 384, 386, 388, 390, 244, 246, 248, 250; τ 2.6-3.2 (5H, m), 8.6 (12H, s); coalescence temperature ($T^c/^oC$) 106^o, frequency separation $\Delta\nu$/Hz 5.6, ΔG^*/kcals.mol.$^{-1}$ 20·5; ^{31}P (THF) + 38·9 p.p.m. (Found: C, 44.6; H, 3.5; P, 6.7. $C_{18}H_{17}Cl_4O_5P$ requires C, 44.45; H, 3.5; P, 6.4%).

(2) 4',4',5',5'-tetramethyl-P-phenylthio-tetrachloro-1,3,2-benzodioxaphosphole-2-spiro-2'-1',3',2'-dioxaphospholan (146);

M.p. 150·5-151·5^o; m/e 500,502,504,506,400, 402, 404, 406, 391, 393, 395, 397; τ 2.3-2.8 (5H, m), 8.65 (6H, s), 8.75 (6H, s); $T^c > 130^o$, $\Delta\nu$ 9Hz; ^{31}P (THF) 10.5 p.p.m. (Found: C, 43.15; H, 3.45; P, 6.1. $C_{18}H_{17}Cl_4O_4PS$ requires C, 43.2; H, 3.4; P, 6.2%).

(3) 4',4',5',5'-tetramethyl-P-dimethylamino-tetrachloro-1,3,2-benzodioxaphosphole-2-spiro-2'-1',3',2'-dioxaphospholan (147);

M.p. $132-134^o$; m/e 435, 437, 439, 441, 335, 337, 339, 341, 244, 246, 248, 250; τ 7.01 (6H, d, J_{PH} 11Hz), 8.68 (12H, s); $T^c > 180^o$, $\Delta\nu$ 10Hz; ^{31}P (THF) 29.3 p.p.m. (Found: C, 38.45; H, 4.3; P, 7.15. $C_{14}H_{18}Cl_4NO_4P$ requires C, 38.45; H, 4.1; P, 7.1%).

Preparation of 2-Dimethylamino-4,4,5,5-tetrakistrifluoromethyl-1,3,2--dioxaphospholan (151).

Perfluoropinacol (0.03 mol) in benzene (25 cm^3) was added dropwise to trisdimethylaminophosphine (0.03 mol) in benzene (10 cm^3). When addition was complete the reaction mixture was gently refluxed overnight. The benzene was removed and the product distilled under reduced pressure, b_2 40-45° (60%); ν_{max} cm^{-1}(neat liquid) 2960, 2905, 1495, 1470, 1300-1200, 1110, 990, 885, 790; τ 3.75 (6H, d, J_{PH} 9Hz);

Preparation of P-Dimethylamino-4',4',5',5'-tetrakistrifluoromethyl-1,3,2--benzodioxaphosphole-2-spiro-2'-1',3',2'-dioxaphospholan (150).

This adduct was prepared by the action of o-benzoquinone on 2-dimethylamino-4,4,5,5-tetrakistrifluoromethyl-1,3,2-dioxaphospholan (151). The benzoquinone was prepared as follows. Catechol (0.02 mol) was dissolved in 25 cm^3 of ether and cooled to -35°C; tetrachloro-o-benzoquinone (0.02 mol) in 10 cm^3 of ether was added dropwise ensuring that the temperature of the reaction mixture stayed between -25 and -35°C. When addition was complete the mixture was stirred for a further hour at -25°. Filtration while still cold gave o-benzoquinone as a bright red solid (65-80%).

Freshly prepared o-benzoquinone (0.005 mol) was suspended in ether (25 cm^3) and the dioxaphospholan (151) (0.005 mol) in ether (5 cm^3) added and the reaction mixture stirred for 24 hours. After this time, unreacted or polymerised o-benzoquinone was filtered off, ether removed, and product obtained by fractional distillation, $b_{0.3}$ 125-130°; m.p. 74-77°; ν_{max} cm^{-1} 1490, 1280, 1245, 1220, 1115, 1020, 970, 870, 750; m/e 515, 496, 471, 446, 421, 375-8 meta stable; τ 3.15 (4H, s), 7.25 (6H, d, J_{PH} 11Hz); ^{19}F 6.27 (6F, m), 7.17 (6F, m) p.p.m.; ^{31}P 27.2 p.p.m.

(Found: C, 32.45; H, 2.0; $C_{14}H_{10}F_{12}NO_4P$ requires C, 32.6; H, 1.95%).

Preparation of 2-Chloro-1,3,2-benzodioxaphosphole.

This compound was prepared from catechol and phosphorus trichloride using the method described by Crofts, Markes, and Rydon[112] (78%), b_{13} 92-95°.

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

These were prepared from addition of the alcohol or thiol to 2-chloro-1,3,2-benzodioxaphosphole in ether in the presence of pyridine using the same method as for 2-substituted-4,4,5,5-tetramethyl-1,3,2--dioxaphospholans. By this method the following were prepared:

(1) 2-Phenoxy-1,3,2-benzodioxaphosphole (152);
(76%); $b_{0.2}$ 92-98°; τ 2.7-3.3;

(2) 2-Phenylthio-1,3,2-benzodioxaphosphole (153);
(64%); $b_{0.3}$ 200-205°; τ 2.8-3.6.

Preparation of P-phenoxy-4',4',5',5'-tetrakistrifluoromethyl-1,3,2--benzodioxaphosphole-2-spiro-2'-1',3',2'-dioxaphospholan (148).

This adduct was prepared using the general chlorination method.

General Chlorination Method.

A flask containing 15cm^3 of dry carbon tetrachloride was weighed, then dry chlorine gas was bubbled slowly into the flask until the weight of the flask and contents had increased by 0.71g (0.01 mol). This chlorine solution was added very carefully with cooling to 2-phenoxy--1,3,2-benzodioxaphosphole (0.01 mol) in 10 cm^3 of carbon tetrachloride. When addition was complete, solvent was removed and the residue dissolved

in dry benzene. Pyridine (0.02 mol) was added and perfluoropinacol (0.01 mol) in 25 cm^3 of benzene added dropwise with stirring and cooling. When addition was complete, the solution was refluxed for 30 mins. Filtration, removal of solvent, followed by crystallisation of the residue from 60-80° petrol gave the adduct (148) (70%); m.p. 59-60°; $\nu_{max}^{cm^{-1}}$ 1600, 1300-1200, 1120, 975, 910, 880, 810, 745, 690; m/e 564, 545, 495, 471, 421; τ 2.5-3.2; ^{19}F 5.53 (6F, m), 6.80 (6F, m). T^c 152°, $\Delta\nu$ 116 Hz, ΔG^* 20.5 kcal. mol^{-1}; ^{31}P (THF) 32.9 p.p.m. (Found: C, 38.1; H, 1.85; F, 40.1. $C_{18}H_{19}F_{12}O_5P$ requires C, 38.3; H, 1.6; F, 40.3%).

Preparation of P-phenylthio-4',4',5',5'-tetrakistrifluoromethyl-1,3,2-benzodioxaphosphole-2-spiro-2'-1',3',2'-dioxaphospholan (149).

Using the general chlorination method, the chlorine solution (0.01 mol) was added to 2-phenylthio-1,3,2-benzodioxaphosphole (153) followed by addition of perfluoropinacol in the presence of pyridine etc. but no product (149) could be isolated.

Preparation of P-Dimethylamino-4',4',5',5'-tetrakistrifluoromethyl--tetrachloro-1,3,2-benzodioxaphosphole-2-spiro-2'-1',3',2'-dioxaphospholan (158).

This adduct was prepared by the addition of tetrachloro-o-benzoquinone (0.005 mol) in ether (25 cm^3) to 2-dimethylamino-4,4,5,5-tetrakistrifluoromethyl-1,3,2-dioxaphospholan (151) (0.005 mol). The solution was stirred overnight by which time it was almost colourless. Removal of the solvent and crystallisation of the residue from 60-80° petrol gave the adduct (158) in almost quantitative yield, m.p. 124-126°;

ν_{max} cm^{-1} (hexachlorobutadiene mull) 2950, 1610, 1560, 1460, 1377, 1280-1200; m/e 651, 653, 655, 657, 659, 607, 609, 611, 613, 582, 584, 586, 588; τ 7.1 (6H, d, J_{PH} 12Hz); ^{19}F 5.73 (6F, m), 6.83 (6F, m); ^{31}P 29.8 p.p.m. (Found: C, 25.9; H, 1.0; F, 34.7. $C_{14}H_6Cl_4F_{12}NO_4P$ requires C, 25.7; H, 1.0; F, 34.9%).

Preparation of 2-Phenylthio-4,4,5,5-tetrakistrifluoromethyl-1,3,2-dioxaphospholan (159).

Phenylthiodichlorophosphite was first prepared by the addition of benzene thiol (0.33 mol) to phosphorus trichloride (0.33 mol) in the presence of pyridine (0.33 mol) and ether (200 cm^3). After addition reaction mixture was refluxed for two hours. Filtration followed by removal of the ether and reduced pressure distillation of the residue gave $PhSPCl_2$, $b_{0.3}$ 77-79° (57%).

Perfluoropinacol (0.02 mol) in benzene (25 cm^3) was added dropwise with stirring and cooling to a mixture of phenylthiodichlorophosphine (0.02 mol), pyridine (0.04 mol) and benzene (50 cm^3). When addition was complete the reaction mixture was refluxed for 30 minutes. Filtration, removal of the benzene followed by reduced pressure distillation gave 2-phenylthio-4,4,5,5-tetrakistrifluoromethyl-1,3,2-dioxaphospholan (159) b_4 120-130° (37%).

Preparation of P-Phenylthio-4',4',5',5'-tetrakistrifluoromethyl-tetrachloro-1,3,2-benzodioxaphosphole-2-spiro-2'-1',3',2'-dioxaphospholan (157).

The reaction between tetrachloro-o-benzoquinone and 2-phenylthio-4,4,5,5-tetrakistrifluoromethyl-1,3,2-dioxaphospholan (159) was carried out using the same method as for the dimethylamino analogue (151).

However, a black polymer was formed from which no product (157) could be isolated.

Preparation of P-Phenoxy-4',4',5',5'-tetrakistrifluoromethyl-tetrachloro--1,3,2-benzodioxaphosphole-2-spiro-2'-1',3',2'-dioxaphospholan (156).

Phenyl dichlorophosphite was prepared by reaction of phenol (0.5 mol) with phosphorus trichloride (0.5 mol) in ether (300 cm^3) in the presence of pyridine (0.5 mol). Filtration, removal of ether, and reduced pressure distillation of the residue gave $PhOPCl_2$, $b_{0.5}$ 59-66° (51%).

Tetrachloro-o-benzoquinone (0.01 mol) in benzene (25 cm^3) was added dropwise to phenyl dichlorophosphite in benzene (10 cm^3). When the red colour of the quinone had virtually disappeared, pyridine (0.02 mol) was added followed by a solution of perfluoropinacol (0.01 mol) in benzene (25 cm^3). When addition was complete, the mixture was refluxed for 30 minutes. Filtration, removal of the benzene followed by extraction of the residue with 60-80° petrol gave the adduct (156), b_1 160-70° (57%); m.p. 102-103°; m/e 700, 702, 704, 706, 681, 683, 685, 687, 631, 633, 635, 637, 607, 609, 611, 613; ^{19}F 5.27 (6F, m), 5.68 (6F, m), T^c 152°, $\Delta\nu$ 22Hz, ΔG^* 21.8 kcal. mol^{-1}; ^{31}P (THF) 32.9 p.p.m. (Found: C, 30.75; H, 1.0; F, 32.55. $C_{18}H_5Cl_4F_{12}O_5P$ requires C, 30.75; H, 0.7; F, 32.5%).

Attempted Preparation of P-Phenylthio-4',4',5',5'-tetrakistrifluoromethyl--tetrachloro-1,3,2-benzodioxaphosphole-2-spiro-2'-1',3',2'-dioxaphospholan (157).

Using the same method as in the preparation of the phenoxy analogue (156) tetrachloro-o-benzoquinone was reacted with $PhSPCl_2$ followed by addition of perfluoropinacol in the presence of pyridine. However.

no adduct (157) could be isolated from the reaction mixture.

Preparation of P-Phenoxy-4',4',5',5'-tetramethyl-1,3,2-benzodioxaphosphole-2-spiro-2'-1',3',2'-dioxaphospholan (162).

Using the general chlorination method described for adduct (148) the chlorine solution was added to 2-phenoxy-1,3,2-benzodioxaphosphole followed by addition of pinacol in the presence of pyridine. Extraction of the residue with 60-80° petrol gave the adduct (162) (51%); m.p. 81-81.5°; $\nu_{max}^{cm^{-1}}$ 1595, 1495, 1215, 1155, 980, 795, 752, 695, 663; m/e 348, 256, 248, 187; τ 2.6-3.25 (9H, m), 8.6 (12H, s), T^c 101°, $\Delta\nu$ 3.5Hz, ΔG^* 20.5 kcal. mol^{-1}; ^{31}P (THF) 37.2 p.p.m. This adduct was very hydrolytically unstable and a satisfactory analysis could not be obtained.

Preparation of P-Phenylthio-4',4',5',5'-tetramethyl-1,3,2-benzodioxaphosphole-2-spiro-2'-1',3',2'-dioxaphospholan (163).

Using the general chlorination method described for adduct (148) the chlorine solution was added to 2-chloro-1,3,2-benzodioxaphosphole forming the trichlorophosphorane to which was added pyridine followed by pinacol to give the chloro-spirophosphorane to which was added pyridine (0.01 mol) followed by benzenethiol (0.01 mol). The reaction mixture was refluxed for 30 minutes. Filtration, removal of the benzene, followed by extraction of the residue with 60-80° petrol gave the adduct (163) (30%); m.p. 136-7°; m/e 364, 264, 255; τ 2.5-3.4 (9H, m), 8.71 (6H, s), 8.78 (6H, s), T^c 104° $\Delta\nu$ 3.5Hz, ΔG^* 20.7 kcal. mol^{-1}; ^{31}P 12.9 p.p.m. (Found: C, 59.1; H, 5.9; P, 8.45. $C_{18}H_{21}O_4PS$ requires C, 59.35; H, 5.8; P, 8.5%).

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

High yields of this cyclic chlorophosphite were prepared from phosphorus trichloride and ethylene glycol in dichloromethane solution in the absence of tertiary amine, using the method of Lucas,[113] b_{13} 45-47°.

Preparation of 2-Substituted-1,3,2-dioxaphospholans.

These compounds were prepared by adding the alcohol or thiol to 2-chloro-1,3,2-dioxaphospholan in ether in the presence of pyridine using the same method as described for the preparation of 2-substituted-4,4,5,5-tetramethyl-1,3,2-dioxaphospholans. By this method the following were prepared.

(1) 2-Phenylthio-1,3,2-dioxaphospholan (169).

(54%); b_3 130-135°; τ 2.37 - 2.95 (5H, m), 5.6 - 4.4 (4H, m).

(2) 2-Phenoxy-1,3,2-dioxaphospholan (170).

(77%); b_{13} 130-132°; τ 2.5 - 3.2 (5H, m), 5.75 - 6.20 (4H, m).

Preparation of 5-Phenylthio-2,2,3,3-tetrakistrifluoromethyl-1,4,6,9--tetraoxa-5-phosphaspiro[4,4,]nonane (163).

General Method for the Reaction of P^{III} Compounds with HFA.

Hexafluoroacetone (HFA 0.022 mol) was condensed into a solution of the P^{III} compound (0.01 mol) in ether (30 cm^3) at -78°. After 30 minutes at -78° the solution was allowed to warm up to room temperature and allowed to stand for one hour. Evaporation, and crystallisation or distillation of the residue, gave the required adduct.

In this case the P^{III} compound was 2-phenylthio-1,3,2-dioxaphospholan (169). Treatment with HFA in the way described gave adduct (163)

in almost quantitative yield; $b_{0.7}$ 140-145°; m.p. 67-9°; ν_{max} cm^{-1} (thin film) 1575, 1470, 1440, 1300-1050, 950, 875, 850; m/e 532, 513, 463, 423, 397, 372; τ 2.0-2.7 (5H, m), 5.5-6.2 (4H, m); ^{19}F 4.24 (6F, m), 4.76 (6F, m); T^c 69°, $\Delta\nu$ 29Hz, ΔG^* 17.3 kcal. $mol.^{-1}$; ^{31}P (THF) 3.4 p.p.m. (Found: C, 31.8; H, 1.95; F, 42.9; P, 5.5. $C_{14}H_9F_{12}O_4PS$ requires C, 31.6; H, 1.7; F, 42.85; P, 5.8%).

Preparation of 5-Phenoxy-2,2,3,3-tetrakistrifluoromethyl-1,4,6,9--tetraoxa-5-phosphaspiro[4,4]nonane (167).

This adduct was prepared using the general method for the reaction of P^{III} compounds with HFA described for adduct (163). In this case the P^{III} compound was 2-phenoxy-1,3,2-dioxaphospholan (170). Reaction with HFA in this way gave two products, adduct (167) (20%) and 5-phenoxy-2,2,4,4-tetrakistrifluoromethyl-1,3,6,9-tetraoxa-5-phosphaspiro 4,4 nonane (171) (almost 80%). Fractional crystallisation gave pure adduct (171); m.p. 74.5-75°; ^{19}F 4.79 (3F, m), 5.21 (3F, m), 16.95 (3F, m), 18.05 (3F, m); ^{31}P (THF) 18.2 p.p.m. (Found: C, 32.8; H, 1.8; F, 44.2; P, 6.0. $C_{14}H_9F_{12}O_5P$ requires C, 32.6; H, 1.75; F, 44.2; P, 6.0%). Adduct (167) was not obtained completely free of (171), the ninth crystallisation gave a product containing 80% of (167) and about 20% of (171) by integration of ^{19}F signals. This sample had a m.p. 45-53°; τ 2.6 - 3.1 (5H, m), 5.5 - 6.4 (4H, m); ν_{max} cm^{-1} (thin film) 1595, 1497, 1290-1190, 1070, 780; ^{19}F (adduct 167) 5.7 (6F, m), 6.3 (6F, m); T^c 74°, $\Delta\nu$ 34Hz, ΔG^* 17.4 kcal. $mol.^{-1}$; ^{31}P (THF) (adduct 167) 31.3 p.p.m.

Preparation of Spirophosphoranes using Diethyl Azodicarboxylate (DAD).

General Preparation.

The P^{III} compound (0.005 mol) is dissolved in ether (25 cm^3) and

DAD (0.005 mol) in ether (10 cm^3), is added dropwise. When addition is complete, the 1,2- or 1,3-glycol in ether (10 cm^3) is added dropwise and the mixture is stirred for 2 - 3 hours. By this time, a white precipitate of diethyl hydrazodicarboxylate has been formed. Filtration, removal of the ether, followed by extraction of the residue with 60-80° petrol yields the adduct which may be recrystallised from petrol.

Preparation of Spirophosphoranes using N-Chlorodi-isopropylamine.

General Preparation.

The P^{III} compound (0.005 mol) is dissolved in ether (25 cm^3) and cooled down to -78°. The 1,2- or 1,3-glycol in ether (10 cm^3) is added dropwise keeping the reaction mixture at about -78°. N-Chlorodi--isopropylamine in ether (10 cm^3) is added dropwise. When addition is complete the reaction mixture is stirred at -78° for 30 minutes. After this time the reaction mixture is allowed to warm up to room temperature then allowed to stir overnight. The reaction may be complete in a shorter time in certain cases. Filtration, removal of ether followed by crystallisation of the residue from petrol gives the adduct which may be recrystallised from petrol.

Preparation of 9-Methyl-5-phenoxy-2,2,3,3-tetrakistrifluoromethyl-1,4,6--trioxa-9-aza-5-phosphaspiro[4,4]nonane (191).

This adduct was readily prepared using the N-chlorodi-isopropyl-amine method. In this case the glycol was perfluoropinacol and the P^{III} compound was 2-phenoxy-3-methyl-1,3,2-oxazaphospholan.[19] The adduct (191) was obtained in 92% yield; m.p. 113-113.5°; $\nu_{max}^{cm^{-1}}$ 1590, 1270, 1225, 1165, 965, 157, 135, 785;, m/e 529, 510, 472, 459, 436;

τ 2.65-3.25 (5H, m), 7.1 (3H, d, J_{PH} 10Hz), 6.0-7.1 (4H, m); ^{19}F 1.22 (3F, m), 2.97 (3F, m), 3.72 (3F, m), 6.59 (3F, m); T^c 150°, $\Delta\nu$ 80Hz, ΔG^* 20.7, T^c 180, $\Delta\nu$ 480, ΔG^* 20.6 kcal. mol.$^{-1}$; ^{31}P ($CDCl_3$) 41.61 p.p.m. (Found: C, 34.46; H, 2.38; P, 2.71. $C_{15}H_{12}F_{12}NO_4P$ requires C, 34.03; H, 2.27; P, 2.65%).

Preparation of 2-Chloro-1,3,2-oxathiaphospholan.

This cyclic chlorophosphite was prepared by the same method as 2-chloro-1,3,2-dioxaphospholan. 2-Mercaptoethanol was added to phosphorus trichloride in dichloromethane. b_{13} 76-78°; (30%); τ 5.29-5.71 (2H, m), 6.5-7.0 (2H, m).

Preparation of 2-Substituted-1,3,2-oxathiaphospholans.

The alcohol, thiol or amine was added to 2-chloro-1,3,2-oxathiaphospholan in the presence of pyridine in ether using the same method as described for 2-substituted-4,4,5,5-tetramethyl-1,3,2-dioxaphospholans. By this method, the following were prepared.

(1) 2-Phenoxy-1,3,2-oxathiaphospholan (198).

(77%); $b_{0.2}$ 95-98°; τ 2.60-3.25 (5H, m), 5.30-5.95 (2H, m), 3.20 (2H, t, J_{H-H} 6Hz),

(2) 2-Dimethylamino-1,3,2-oxathiaphospholan (204).

(81%); b_{13} 86-90°; τ 5.40 (2H, dt, J_{H-H} 6Hz, J_{P-H} 8Hz), 6.78 (2H, t, J_{H-H} 6Hz), 3.20 (6H, d, J 12Hz).

Reaction of 2-Phenoxy-1,3,2-oxathiaphospholan (198) with HFA.

Using the general method for the reaction of P^{III} compound with HFA described for adduct (163), the product was 5-phenoxy-2,2,4,4-tetrakistrifluoromethyl-1,3,6-trioxa-9-thia-5-phosphaspiro[4,4]nonane

(199), in almost quantitative yield; m.p. 110-2; ν_{max} cm^{-1} 1595, 1495, 1320-1150, 1100, 1080, 970, 930, 777; m/e 532, 513, 472, 463, 451, 439; τ 2.8 (5H, s), 5.4-7.5 (4H, m); ^{19}F 4.1 (6F, m), 17.1 (6F, m); ^{31}P (THF) -11 p.p.m. (Found: C, 31.67; H, 1.53; F, 43.81. $C_{14}H_9F_{12}O_4PS$ requires C, 31.58; H, 1.69; F, 43.86%).

Reaction of 2-Dimethylamino-1,3,2-oxathiaphospholan (204) with HFA.

Using the general method described for adduct (163) the product was 5-dimethylamino-2,2,3,3-tetrakistrifluoromethyl-1,4,6-trioxa-9--thia-5-phosphaspiro 4,4 nonane (205), formed in almost quantitative yield; m.p. 87-8°; ν_{max} cm^{-1} 1305-1185, 1133, 1060, 1005, 887, 819; m/e 483, 425, 414; τ 6.2-7.5 (4H, m), 7.32 (6H, d, J_{P-H} 11Hz); ^{19}F 4.33 (9F, broad m), 5.52 (3F, m); ^{31}P ($CDCl_3$) -4.75 p.p.m. (Found: C, 24.91; H, 2.01; F, 47.48. $C_{10}H_{10}F_{12}NO_3PS$ requires C, 24.84; H, 2.07; F, 47.20%).

Reaction of Adduct (205) with Hexafluoroisopropanol.

The dimethylamino adduct (205) (0.001 mol) was dissolved in hexafluoroisopropanol (0.5 cm^3) and the solution was allowed to stand overnight. It was hoped that the acidic alcohol would displace the dimethylamino group forming the hexafluoroisopropy analogue. No displacement had occurred at room temperature overnight so the solution was refluxed for 1 hour. Removal of the solvent gave an oily residue with an extremely complex ^{19}F n.m.r. which indicated that the adduct had decomposed.

Preparation of 2-Phenoxy-5,5-dimethyl-1,3,2-oxathiaphospholan (206).

2-Hydroxy-2-methyl-propanethiol, $CH_3C(OH)(CH_3)CH_2SH$ was prepared by adding mercaptoacetone (0.33 mol) in THF (100 cm^3) to methyl magnesium iodide (0.66 mol) in ether (250 cm^3) with stirring and cooling. The reaction mixture was refluxed for 6 hours. Ammonium chloride solution (0.66 mol) was added and the mixture was extracted with three 50 cm^3 portions of ether. Removal of the solvent followed by distillation gave the desired product b_{13} 60-70° (48%).

2-Chloro-5,5-dimethyl-1,3,2-oxathiaphospholan was prepared by the action of 2-hydroxy-2-methyl-propanethiol on phosphorus trichloride in dichloromethane using the method described for 2-chloro-1,3,2-dioxaphospholan. b_2 52-64° (40%). Reaction of phenol with 2-chloro-1,3,2--oxathiaphospholan in the presence of pyridine using the method for 2-substituted-4,4,5,5-tetramethyl-1,3,2-dioxaphospholans gave the oxathiaphospholan (206) (48%); $b_{0.2}$ 88-90°; τ 2.65-3.25 (5H, m), 6.33 (1H, s), 6.38 (1H, s), 8.50 (3H, s), 8.70 (3H, s).

Reaction of 2-Phenoxy-5,5-dimethyl-1,3,2-oxathiaphospholan with HFA.

Using the general method described for adduct (163) the product was 7,7-dimethyl-5-phenoxy-2,2,4,4-tetrakistrifluoromethyl-1,3,6-trioxa--9-thia-5-phosphaspiro 4,4 nonane in almost quantitative yield, m.p. 64-65°; $\nu_{max}^{cm^{-1}}$ 1595, 1494, 1310-1160, 970, 760, 640; m/e 560, 545, 541, 491, 473, 467, 433, 403; ^{19}F 4.25 (3F, m), 5.05 (3F, m), 17.37 (6F, m); ^{31}P (THF) -9.39 p.p.m. (Found: C, 34.26; H, 2.39; P, 5.27. $C_{16}H_{13}F_{12}O_4PS$ requires C, 34.3; H, 2.3; P, 5.5%).

Preparation of Monothiobenzil (208).

This compound was prepared using the method described by Saville

and Steer[93]. The sodium S-desylthiosulphate was prepared using the method described by Baker and Barkenbus[114] in 38% yield.

Reaction of Monothiobenzil with 2-Phenoxy-4,4,5,5-tetramethyl-1,3,2--dioxaphospholan.

Monothiobenzil (0.0033 mol) was generated in solution by adding sodium S-desylthiosulphate (0.0033 mol) in water (35 cm^3) to sodium hydroxide (0.04 mol) in water (35 cm^3) and 60 cm^3 of either dichloromethane or ether as a co-solvent with vigorous stirring. When addition was complete, the mixture was stirred for 10 minutes then the blue organic layer was separated, washed with water (3 x 50 cm^3 portions) and dried (Na_2SO_4).

2-Phenoxy-4,4,5,5-tetramethyl-1,3,2-dioxaphospholan (0.0033 mol) was dissolved in 10 cm^3 of ether and cooled to -78°, the dried dichloromethane solution of monothiobenzil was added dropwise with stirring. The blue colour of the monothiobenzil was immediately discharged leaving a yellow solution. The reaction mixture was allowed to warm up to room temperature. The solvent was removed and the residue crystallised from 60-80° petrol. The adduct (212) was obtained in 32% yield, m.p. 140.5-141°; $\nu_{max}^{cm^{-1}}$ 1630, 1600, 1217, 1155, 982, 787; m/e 466, 366, 256, 210; τ 2.65-3.7 (15H, broad m), 8.42 (3H, s), 8.53 (3H, s), 8.60 (3H, s), 8.65 (3H, s) (Found: C, 66.04; H, 5.94. $C_{26}H_{29}O_4PS$ requires C, 66.9; H, 5.8%).

Using a similar method, monothiobenzil was reacted with 2-dimethylamino-4,4,5,5-tetramethyl-1,3,2-dioxaphospholan to give the adduct (213) in 63% yield, m.p. 156d (ether); $\nu_{max}^{cm^{-1}}$ 1620, 1155, 995, 975, 745, 700, 640; m/e 417, 317, 290, 257, 252, 210, 207; τ 2.95 (10H, m), 7.34 (6H, d, J_{P-H} 11Hz), 8.80 (9H, s), 8.91 (3H, s), in

in 1-bromonaphthalene on the 100 MHz machine the methyl groups appear as four signals of equal intensity, 8.85, 8.93, 8.97, 9.11; ^{31}P ($CDCl_3$) 2202 p.p.m. (Found: C, 63.28; H, 6.92; N, 3.29. $C_{22}H_{28}NO_3PS$ requires C, 63.3; H, 6.7; N, 3.3%).

Preparation of 2-Phenoxy-4,4,5,5-tetrakistrifluoromethyl-1,3,2-dioxaphospholan (216).

This compound was prepared by adding perfluoropinacol to phenyldichlorophosphite in the presence of pyridine using the method described for the phenylthio analogue (159) in 75% yield, $b_{0.5}$ 70-72°, τ 2.4-3.0 (broad m).

The dioxaphospholan (216) was reacted with monothiobenzil using the method described above. Even after 24 hours at room temperature the blue colour remained. No product could be obtained from the reaction mixture.

Preparation of the Adduct between Benzil and 2-Phenoxy-4,4,5,5-tetramethyl-1,3,2-dioxaphospholan.

A solution of the dioxaphospholan (0.0033 mol) in ether (2 cm^3) was added rapidly to benzil (0.0033 mol) and the mixture was gently warmed until the benzil had dissolved. The mixture was allowed to stand overnight by which time the adduct (217) had crystallised out. Filtration followed by recrystallisation from 60-80° petrol gave the adduct (217) in 77% yield, m.p. 122.5-123.5, $\nu_{max}^{cm^{-1}}$ 1670, 1600, 1500, 1221, 1165, 790; m/e 450, 350, 274; τ 3.0 (15H, s), 8.6 (12H, s), T^c 120°, $\Delta\nu$ 4.5Hz, ΔG^* 21.4 kcal. $mol.^{-1}$; ^{31}P (CH_2Cl_2) 40.18 p.p.m. (Found: C, 69.35; H, 6.09; P, 6.86. $C_{26}H_{27}O_5P$ requires C, 69.33; H, 6.00; P, 6.80%).

Preparation of 3,4-bistrifluoromethyl-1,2-dithieten (219).

This compound was prepared by passing hexafluoro-2-butyne into a flask containing refluxing sulphur, directly distilling out the product from the reaction mixture. This is one of the preparations described by Krespan[115] for this compound. The compound was prepared in 55% yield boiling in the range 90-96° at atmospheric pressure. ^{19}F -0.83 p.p.m.

Preparation of 7,8-Bistrifluoromethyl-5-phenoxy-2,2,3,3-tetramethyl--1,4-dioxa-6,9-dithia-5-phosphaspiro[4,4]non-7-ene (221).

The dithieten (0.005 mol) (219) in dichloromethane (15 cm^3) was added dropwise to a solution of 2-phenoxy-4,4,5,5-tetramethyl-1,3,2--dioxaphospholan in dichloromethane (20 cm^3) at -78°. When addition was complete the reaction mixture was allowed to warm up to room temperature and was allowed to stir for 1 hour. Solvent was removed and the residue was crystallised from 60-80° petrol to yield adduct (221) in an almost quantitative yield. This compound showed the curious tendency to crystallise as one giant crystal. The following physical data were found for this adduct: m.p. 88-89.5; $\nu_{max}^{cm^{-1}}$ 1595, 1490, 1260, 1150, 770; m/e 467, 373, 240, 226, 182, 162, 147; τ (1-bromonaphthalene) 9.12 (6H, s), 9.18 (6H, s); T^c 136°, $\Delta\nu$ 4.5Hz, ΔG^* 22.3 kcal. $mol.^{-1}$; ^{19}F ($CDCl_3$) -8.65 (d J_{P-F} 0.5Hz); ^{31}P (CH_2Cl_2) -13.6 p.p.m. (Found: C, 41.31; H, 3.76; S, 13.84. $C_{16}H_{17}F_6O_3PS$ requires C, 41.2; H, 3.6; S, 13.7%).

Using exactly the same procedure the dimethylamino analogue (222) was prepared by the addition of the dithieten (219) to 2-dimethylamino-4,4,5,5-tetramethyl-1,3,2-dioxaphospholan. The adduct (222) was formed in almost quantitative yield; m.p. 127-8°; $\nu_{max}^{cm^{-1}}$ 1650,

1252, 1175, 1145, 905; τ 7.27 (6H, d, J_{P-H} 13Hz), 8.62 (6H, s), 8.8 (6H, s); ^{19}F ($CDCl_3$) -8.43; ^{31}P ($CDCl_3$) -10.26 p.p.m. (Found: C, 34.59; H, 4.42; N, 3.36. $C_{12}H_{18}F_6NO_2PS_2$ requires C, 34.5; H, 4.3; N, 3.36%).

Preparation of 7,8-Bistrifluoromethyl-5-phenoxy-2,2,3,3-tetramethyl--1,4,6,9-tetraoxa-5-phosphaspiro[4,4]non-7-ene (223).

Hexafluorobiacetyl used in this preparation was prepared by P.J. Whittle.[19]

Hexafluorobiacetyl (0.005 mol) was condensed into a solution of 2-phenoxy-4,4,5,5-tetramethyl-1,3,2-dioxaphospholan (0.005 mol) in ether (30 cm^3) at 0^o. After addition was complete, the reaction mixture was stirred for 30 minutes at room temperature. Removal of the ether and crystallisation from 60-80° petrol gave the adduct (223) in almost quantitative yield, m.p. 58.5-60.5; $\nu_{max}^{cm^{-1}}$ 1705, 1595, 1205, 1125, 1000, 800, 690; m/e 434, 419, 377, 361, 341, 334, 317; τ 2.67-3.35 (5H, m), 8.67 (12H, s); T^c(CCl_3Br) 134° (sealed n.m.r. tube), $\Delta\nu$ 2Hz, ΔG^* 22.9 kcal. $mol.^{-1}$; ^{19}F ($CDCl_3$) 2.6 (s); ^{31}P (ether) 37 p.p.m. (Found C, 44.31; H, 4.05; P, 7.03. $C_{16}H_{17}F_6O_5P$ requires C, 44.24; H, 3.92; P, 7.14%).

Preparation of 5-Phenoxy-2,2,3,3-tetrakistrifluoromethyl-1,4,6-trioxa-9-thia-5-phosphaspiro[4,4]nonane (197).

This adduct was prepared using the N-Chlorodi-isopropylamine method. In this case the glycol was perfluoropinacol and the P^{III} compound was 2-phenoxy-1,3,2-oxathiaphospholan. By this method the adduct (197) was prepared in 88% yield, m.p. 107.5-8°, $\nu_{max}^{cm^{-1}}$ 1590,

1275, 1225, 1117, 950, 780; m/e 532, 513, 472, 463, 439; τ 2.8 (5H, m), 6.0-7.4 (4H, broad m); ^{19}F 4.36 (3F, m), 5.31 (3F, m), 6.06 (6F, m); T^c 94°, Δν 94Hz, ΔG* 17.7 kcal. mol.$^{-1}$; ^{31}P (CH_2Cl_2) -2.7 p.p.m. (Found: C, 31.47; H, 1.69; P, 5.89. $C_{14}H_9F_{12}O_4PS$ requires C, 31.58; H, 1.69; P, 5.83%).

Preparation of monothiocatechol.[116]

o-Aminophenol (0.5 mol) in a mixture of water (300 cm^3), ice (300g), 2N HCl (100 cm^3) and conc. HCl (35 cm^3) was diazotised with a solution of sodium nitrite (0.05 mol) in water (340 cm^3) maintaining the temperature between 0-5°. The diazonium salt was added slowly to a solution of potassium ethylxanthate (4 mols) in water (375g) maintaining the temperature of the reaction mixture between 70-75°. After addition the mixture was allowed to stand overnight. Extraction with ether (3 x 100 cm^3 portions) followed by removal of the solvent gave 41% of a yellow solid. To this yellow solid was added potassium hydroxide (100g) and ethanol (250 cm^3) and the mixture was refluxed for 24 hours under an atmosphere of nitrogen. It is necessary to exclude oxygen as monothiocatechol readily oxidises to the disulphide in alkaline solution. The reaction mixture was carefully acidified with conc. HCl (200 cm^3). Most of the ethanol was pumped off and the aqueous layer was extracted with ether, dried with $MgSO_4$, ether removed and product distilled b_{13} 88-89° (32%), ν_{max} cm^{-1} (thin film) 3405, 3050, 2505, 1580, 1475, 1200, 750.

Preparation of 2-Chloro-1,3,2-benzo-oxathiaphosphole.

This compound[117] was prepared by the reaction of monothiocatechol

with phosphorus trichloride in dichloromethane using the method described for 2-chloro-1,3,2-dioxaphospholan. b_{13} 118-9° (73%).

Preparation of 2-Phenoxy-1,3,2-benzo-oxathiaphosphole.

This compound was prepared by the reaction of phenol with 2-chloro--1,3,2-benzo-oxathiaphosphole in the presence of pyridine using the method described for 2-substituted-4,4,5,5-tetramethyl-1,3,2-dioxaphospholans. $b_{0.3}$ 136-9° (75%).

Preparation of 2-Phenoxy-4',4',5',5'-tetrakistrifluoromethyl-1,3,2--benzo-oxathiaphosphole-2-spiro-2'-1',3',2'-dioxaphospholan (226).

This compound was prepared using N-chlorodi-isopropylamine. In this case the glycol was perfluoropinacol and the P^{III} compound was 2-phenoxy-1,3,2-benzo-oxathiaphosphole. By this method the adduct (226) was prepared in 83%, m.p. 93-93.5, ν_{max} cm^{-1} 1595, 1585, 1495, 1290-1210, 1117, 945, 890, 780; m/e 580, 561, 487, 437; ^{19}F 4.12 (3F, m), 4.70 (3F, m), 6.21 (6F, m); T^c 143°, $\Delta\nu$ 54Hz, ΔG^* 20.7 kcal. $mol.^{-1}$; ^{31}P 2.43 p.p.m. (Found: C, 37.34; H, 1.64; P, 5.41. $C_{18}H_{21}O_4PS$ requires C, 37.24; H, 1.55; P, 5.34%).

Preparation of 3-Mercapto-propanol.

This compound[118] was prepared in yields of greater than 90% by the following method:

sodium hydroxide (0.33 mol) was dissolved in water (80 cm^3) and ether (100 cm^3) was added. The mixture was cooled to 0° and saturated with hydrogen sulphide. A solution of 3-chloropropanol in ether (100 cm^3) was added slowly over a period of twenty minutes to the reaction mixture with vigorous stirring. The mixture was stirred

for a further two hours at room temperature. After this time, the ether layer was removed and the aqueous layer was extracted with ether (2 x 50 cm^3 portions). The ether solutions were combined and dried ($MgSO_4$). Ether was removed and product distilled b_{13} 90-92°, 91%, τ 6.32 (2H, t, J 5Hz), 6.70 (1H, s), 7.35 (2H, dt, J_{CH-H} 5Hz, J_{SH-H} 7Hz), 8.2 (2H, quintet, J 5Hz), 8.55 (1H, t, J 7Hz).

Preparation of 2-Chloro-1,3,2-oxathiaphosphorinan.

This compound was prepared by the action of 3-mercapto-propanol on phosphorus trichloride in dichloromethane using the method described for 2-chloro-1,3,2-dioxaphospholan. $b_{3.5}$ 64-70°, 27%.

Preparation of 2-Phenoxy-1,3,2-oxathiaphosphorinan.

This compound was prepared by the action of phenol on 2-chloro--1,3,2-oxathiaphosphorinan in the presence of pyridine using the method described for 2-substituted-4,4,5,5-tetramethyl-1,3,2-dioxaphospholans. $b_{0.2}$ 132-138° (45%).

Preparation of 5-Phenoxy-2,2,3,3-tetrakistrifluoromethyl-1,4,6-trioxa--10-thia-5-phosphaspiro[4.5]decane (228).

HFA was reacted with 2-phenoxy-1,3,2-oxathiaphosphorinan using the method described for adduct (163). The reaction mixture had a rather complex ^{19}F n.m.r. indicating the presence of impurities. When the crude reaction mixture was taken up in 60-80° petrol and cooled to 0° the adduct (228) crystallised out in about 30% yield, ν_{max} cm^{-1} 1590, 1490, 1300-1200, 960, 880, 770; m/e 546, 527, 488, 477, 472, 453; τ 2.8-3.2 (5H, m), 5.6-6.1 (2H, m), 6.8-7.5 (2H, m), 7.8-8.4 (2H, m); ^{19}F ($CDCl_3$)

4.46 (6F, m), 5.36 (6F, m); T^c (ether/petrol 40°) -71°, $\Delta\nu$ 67.5Hz, ΔG^* 9.7 kcal. mol.$^{-1}$; ^{31}P ($CDCl_3$) 60.9 p.p.m.

Preparation of 2,2,3,3-Tetramethyl-7,7,8,8-tetrakistrifluoromethyl--1,4,6,9-tetraoxa-5-phosphaspiro[4.4]nonane (239).

Perfluoropinacol (0.01 mol) in benzene (20 cm^3) was added to 2-dimethylamino-4,4,5,5-tetramethyl-1,3,2-dioxaphospholan in benzene (10 cm^3) and the reaction mixture was refluxed overnight. Removal of the solvent and distillation of the residue gave adduct (239) (87%); $b_{0.15}$ 100-105°; m.p. 38-40°; $\nu_{max}^{cm^{-1}}$ 2440, 1315-1110, 975, 890, 785, 725; m/e 480, 465, 461, 422, 411, 381, 329; τ (Benzene) 3.45 (1H, d, J 830Hz), 8.95 (6H, s), 9.05 (6H, s); ^{19}F 5.93 (6F, m), 6.26 (6F, m); T^c 92°$\Delta\nu$ 18Hz, ΔG^* 18.8 kcal. mol.$^{-1}$; ^{31}P (THF) 28.3 p.p.m. (Found: C, 29.9; H, 2.8; F, 47.2. $C_{12}H_{13}F_{12}O_4P$ requires C, 30.0; H, 2.7; F, 47.5%).

Preparation of 2,2,3,3,7,7,8,8-Octa(trifluoromethyl)-1,4,6,9-tetraoxa-5-phosphaspiro[4.4]nonane.

This compound was prepared by the addition of perfluoropinacol (0.02 mol) in benzene (30 cm^3) to trisdimethylaminophosphine (0.01 mol) in benzene (10 cm^3) and refluxing overnight. Removal of solvent followed by distillation of the residue gave the adduct (243), (60%), $b_{0.2}$ 80-85°, m.p. (benzene) 48-51°; $\nu_{max}^{cm^{-1}}$ 3060, 2740, 2470, 1615, 1270-1170, 960, 855, 655; τ (THF) 3.4 (s); m/e 696, 677, 627, 530, 511; ^{19}F (THF) room temperature 5.75 (d J_{P-F} 14.5Hz), -57°C 5.66 (12F, m), 6.53 (6F, m), 6.99 (6F, m); ^{31}P (THF) -88.4 p.p.m. Satisfactory analysis could not be obtained for this adduct.

Preparation of P-Chloro-4',4',5',5'-tetramethyl-tetrachloro-1,3,2--benzodioxaphosphole-2-spiro-2'-1',3',2'-dioxaphospholan (252).

Tetrachloro-o-benzoquinone (0.01 mol) in carbon tetrachloride (25 cm^3) was put into a flask and 2-chloro-4,4,5,5-tetramethyl-1,3,2--dioxaphospholan in carbon tetrachloride (25 cm^3) was added dropwise with stirring. After addition was complete the mixture was stirred until the red colour had virtually disappeared - (30 minutes). The solution was concentrated to about 8-10 cm^3 and spectral details obtained from this solution. This procedure was necessary due to the extreme hydrolytic instability of the adduct. τ (CCl_4) 9.00 (6H, s), 9.05 (6H, s); T^c (CCl_4) 51°, $\Delta\nu$ 3Hz, ΔG^* 17.8 kcal. $mol.^{-1}$; ^{31}P (CCl_4) 13.6 p.p.m.

Preparation of P-p Nitrophenoxy-4',4',5',5'-tetramethyl-tetrachloro--1,3,2-benzodioxaphosphole-2-spiro-2'-1',3',2'-dioxaphospholan (260).

This compound was made by an exactly similar procedure to the chloro analogue (252). The P^{III} compound in this case is 2-p-nitrophenoxy-4,4,5,5-tetramethyl-1,3,2-dioxaphospholan (261) which was prepared by the action of phenol on the cyclic chlorophosphite in the presence of pyridine. Filtration and removal of the solvent gave the cyclic phosphite (261). Distillation was not attempted as deoxygenation of the nitro-group was likely to occur. The adduct (260) had the following spectral data; τ (CCl_4) 1.94 (2H, d, J 9Hz), 2.9 (2H, d, J 9Hz), 8.39 (6H, s), 8.47 (6H, s); T^c 110°, $\Delta\nu$ 16Hz, ΔG^* 20.0 kcal. $mol.^{-1}$; ^{31}P 35.6p.p.m.

Preparation of 5-Phenoxy-2,2,3,3-tetramethyl-1,4,6,9-tetraoxa-5-phosphaspiro[4,4]nonane (264).

This compound was prepared using both the 'DAD' method and the N-chlorodi-isopropylamine method. In this case the glycol was ethylene glycol and the P^{III} compound was 2-phenoxy-4,4,5,5-tetramethyl--1,3,2-dioxaphospholan. The product (264) was obtained in 80%, $b_{0.2}$ 120°, $\nu_{max}^{cm^{-1}}$ 1600, 1500, 1230, 1170, 930; m/e 300, 285, 256, 207, 200, 175; τ (CCl_4) 3.0 (5H, m), 6.43 (4H, dd, J_{P-H} 14Hz, J_{H-H} 2Hz), 8.85 (12H, s); T^c (methyl signals) 41°, $\Delta\nu$ 3Hz, ΔG^* 17.4 kcal. $mol.^{-1}$, T^c (ethylene glycol protons) 147°, $\Delta\nu$ 3Hz, ΔG^* 23.3 kcal. $mol.^{-1}$; ^{31}P 37.23 p.p.m. (Found: C, 57.29; H, 7.03. $C_{14}H_{21}O_5P$ requires C, 56.0; H, 7.0%).

Preparation of 5-Dimethylamino-2,2,3,3-tetramethyl-1,4,6,9-tetraoxa--5-phosphaspiro[4,4]nonane (265).

This compound was prepared using the 'DAD' method. In this case the glycol was ethylene glycol and the P^{III} compound was 2-dimethylamino--4,4,5,5-tetramethyl-1,3,2-dioxaphospholan. Ethylene glycol is virtually insoluble in ether so it was dissolved in THF (5 cm^3) and added to the other reactants which were dissolved in ether. The adduct (265) was formed in 56%, m.p. 37-39°; $\nu_{max}^{cm^{-1}}$ 1165, 1090, 1070, 985, 922, 715; m/e 251, 207, 151, 125; τ 5.8-6.5 (4H, m), 7.3 (6H, d, J 10Hz), 8.78 (6H, s), 8.82 (6H, s); T^c 157°, $\Delta\nu$ 12Hz, ΔG^* 22.7 kcal. $mol.^{-1}$; ^{31}P 33.71 p.p.m. (Found: C, 47.05; H, 8.7; N, 5.04. $C_{10}H_{22}NO_4P$ requires C, 47.81; H, 8.76; N, 5.58%).

Preparation of 5,5-Dimethyl-2-phenyl-1,3,2-dioxaphosphorinan.

This compound was prepared in good yield by the following method:

Phenylphosphonous dichloride (0.1 mol) was put in a graduated dropping funnel and the volume made up to 100 cm^3 with ether. In a similar manner neopentyl glycol (2,2-dimethyl-1,3-propanediol) (0.1 mol) was put into a graduated dropping funnel and the volume made up to 100 cm^3 with ether. These two solutions were added simultaneously to a solution of pyridine (0.2 mol) in ether (150 cm^3) with vigorous stirring at 0°C. When addition was complete, the reaction mixture was refluxed for two hours. Filtration, removal of the ether followed by distillation gave the product in 66% yield $b_{0.2}$ 92-93°. τ (CH_2Cl_2) 2.5 (5H, s), 5.9-6.6 (4H, m), 8.58 (3H, s), 9.3 (3H, s); ^{31}P (CH_2Cl_2) -143 p.p.m.

By a similar method the following were prepared:

(1) 5,5-Dimethyl-2-methyl-1,3,2-dioxaphosphorinan.

This compound was prepared using methylphosphonous dichloride prepared by M.W. White.[92] The phosphorinan was prepared in 57% yield, b_{13} 52-56°, τ 5.9-6.8 (4H, m) 8.62 (3H, d, J 9.5 Hz), 8.80 (3H, s), 9.25 (3H, s); ^{31}P ($CDCl_3$) -164 p.p.m.

(2) 5,5-Dimethyl-2-benzyl-1,3,2-dioxaphosphorinan.

This compound was prepared using benzylphosphonous dichloride prepared by M.W. White.[92] The phosphorinan was prepared in 40% yield, $b_{0.3}$ 115-119°, τ 2.87 (5H, s), 5.9-6.7 (4H, m), 6.85 (2H, d, J 6Hz), 8.86 (3H, s), 9.25 (3H, s); ^{31}P ($CDCl_3$) -159.1 p.p.m.

Preparation of 6-Phenyl-3,3,9,9-tetramethyl-1,5,7,11-tetraoxa-6-phosphaspiro[5,5]undecane (274).

This compound was prepared using the N-chlorodi-isopropylamine method. In this case the glycol was neopentyl glycol and the P^{III}

compound was 5,5-dimethyl-2-phenyl-1,3,2-dioxaphosphorinan. The adduct (274) was formed in 83% yield, m.p. 69-72°; $\nu_{max}^{cm^{-1}}$ 1050, 800, 770, 705; m/e 312, 226, 159, 141; τ 2.1-3.9 (5H, m), 6.35 (8H, d, J 18Hz), 9.1 (12H, s); T^c ($CDCl_3$) -15°, $\Delta\nu$ 15, ΔG^* 13.2 kcal. $mol.^{-1}$; ^{31}P ($CDCl_3$) 48.37p.p.m. (Found: C, 60.36; H, 8.19. $C_{16}H_{25}O_4P$ requires C, 60.00; H, 8.3%).

Preparation of 6-Methyl-3,3,9,9-tetramethyl-1,5,7,11-tetraoxa-6-phosphaspiro 5,5 undecane (275).

This compound was prepared using the N-chlorodi-isopropylamine method. In this case the glycol was neopentyl glycol, and the P^{III} compound was 5,5-dimethyl-2-methyl-1,3,2-dioxaphosphorinan. The adduct was formed in 78% yield, an undistillable liquid at room temperature, $\nu_{max}^{cm^{-1}}$ 1300, 1160, 990, 825, 690; m/e no mass peak, 183, 165, 110, 111, 97; τ 6.35 (3H, d, J 15Hz), 8.49 (8H, d, J 17Hz), 9.05 (12H, s); T^c ($CDCl_3$) -32°, $\Delta\nu$ 8Hz, ΔG^* 12.6 kcal. $mol.^{-1}$; ^{31}P ($CDCl_3$) 40.05 p.p.m. This compound could not be purified sufficiently to obtain a satisfactory analysis.

Preparation of 6-Benzyl-3,3,9,9-tetramethyl-1,5,7,11-tetraoxa-6-phosphaspiro[5,5]undecane (276).

This compound was prepared using the N-chlorodi-isopropylamine method. In this case the glycol was neopentyl glycol and the P^{III} compound 5,5-dimethyl-2-methyl-1,3,2-dioxaphosphoranan. The adduct (276) was found in 56% yield, m.p. 61.5-63°; $\nu_{max}^{cm^{-1}}$ 1605, 1245, 1065, 825, 690; τ 6.45 (8H, d, J 15Hz), 7.00 (2H, d, J 12Hz), 9.15 (12H, s); T^c ($CDCl_3$) -35°, Δ 13Hz, ΔG^* 12.2 kcal. $mol.^{-1}$; ^{31}P ($CDCl_3$) 46.16 p.p.m. A satisfactory analysis could not be obtained for the compound.

Preparation of Hexafluoroacetone Azine (HFAA).

This compound was prepared by the method of Burger[102] in 75% boiling in the range 67-69° at atmospheric pressure.

Preparation of the 1:1 Adduct between HFAA and Trimethyl Phosphite (281).

Using the method described by Burger[102] trimethyl phosphite in hexane was added dropwise to HFAA in hexane with stirring at 0° then allowed to stand overnight. Removal of solvent followed by distillation of the residue under reduced pressure, b_{13} 85-87°; (88%); $\nu_{max}^{cm^{-1}}$ (thin film) 2950, 1720, 1455, 1420, 1315, 1210, 1040, 960, 850; τ 6.31 (d, 12Hz); ^{19}F room temperature, 1.0 (6F, broad s), 13.5 (6F, s); -74°, -6.0 (3F, q, J 8.5Hz), +7.38 (3F, q, J 8.5Hz), 13.5 (6F, s); ^{31}P ($CDCl_3$) 12.0 p.p.m.

Preparation of 2-Methoxy-4,4,5,5-tetramethyl-1,3,2-dioxaphospholan (283).

This compound was prepared by the method described for the other 2-substituted-4,4,5,5-tetramethyl-1,3,2-dioxaphospholan by the action of methanol on 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholan in the presence of pyridine, in 49% yield, b_{13} 67-70°, τ 6.6 (3H, d, J 12Hz), 8.7 (6H, s), 8.9 (6H, s).

Preparation of the 1:1 Adduct between HFAA and 2-Methoxy-4,4,5,5-tetramethyl-1,3,2-dioxaphospholan (284).

This adduct was prepared using a similar procedure to the trimethyl phosphite/HFAA adduct (281). The adduct was formed in 78%, $b_{0.3}$ 85-87°, $\nu_{max}^{cm^{-1}}$ (thin film) 2990, 1725, 1470, 1320, 1225, 1060, 970, 840; m/e 506, 491, 437, 342; τ (CCl_4) 6.3 (3H, d, J 13Hz), 8.68 (12H, s); ^{19}F (CCl_4) room temperature, 1 (6F, very broad s), 12.06 (6F, s); -99°

(ether/petrol), -4.93 (3F, m), +6.37 (3F, q, J 8Hz), 12.06 (6F, s); ^{31}P -7.4 p.p.m; a satisfactory analysis could not be obtained for this compound.

Preparation of 1:1 Adduct between HFAA and Dimethylphenylphosphonite (285).

This compound was prepared using a similar procedure to the trimethyl phosphite/HFAA adduct (281). The adduct (285) was formed in 65%, $b_{0.2}$ 123-124°, ν_{max} cm^{-1}(thin film) 2950, 1722, 1430, 1320, 1230, 1040, 965, 815; m/e no mass peak, 479, 467, 429, 334; τ 2.0-2.6 (5H, m), 6.30 (6H, d, J 12Hz) - no change on cooling to -98°; ^{19}F (Benzene) 1.49 (6F, broad s), 13.50 (6H, s); ^{31}P ($CDCl_3$) 0.0p.p.m. (Found: C, 34.50; H, 2.14; F, 45.87. $C_{14}H_{11}F_{12}N_2O_2P$ requires C, 34.23; H, 2.20; F, 45.78%).

Attempted Preparation of the TrimethylPhosphite/HFAA adduct (281) by an alternative route.

Preparation of Hexafluoroisopropylidenimine.

This compound was prepared in 60% yield using the method described by Middleton,[105] this was all used in the next step.

Preparation of 2-Aminohexafluoroisopropyl Azide (293).

This compound was prepared by the action of hydrazoic acid in dichloromethane on hexafluoroisopropylidene imine, again using the method described by Middleton.[105] The azide (293) was obtained in 35% yield boiling over a range 83-88° at atmospheric pressure.

Reaction of 2-Aminohexafluoroisopropyl Azide with Trimethyl Phosphite.

The aminoazide (0.001 mol) in benzene (5 cm^3) was added dropwise

to trimethyl phosphite (0.001 mol) in benzene (5 cm^3). When 3 - 4 silica anti-bumping granules were added, nitrogen was smoothly evolved at room temperature. After two hours the solution was refluxed for 10 minutes then the benzene was removed and the residue distilled b_{13} 110-112° to give the iminophosphorane (294) in 80% yield, $\nu_{max}^{cm^{-1}}$ (thin film) 3400, 3330, 2955, 2850, 1620, 1460, 1430, 1220, 1050, 850; τ 6.30 (9H, d, J 14Hz) 8.03 (2H, broad s); ^{19}F ($CDCl_3$) 18.5; ^{31}P 4.0 p.p.m. (Found: C, 23.84; H, 3.84; F, 35.98. $C_6H_{11}F_6N_2O_3P$ requires C, 23.68; H, 3.62; F, 36.26%).

Reaction of HFA with the iminophosphorane (294).

The iminophosphorane (0.001 mol) was treated with HFA (0.001 mol) in triethylamine (0.75g) at -30°. After 10 minutes, phosphorus oxychloride was added as a dehydrating agent and the mixture was refluxed for 30 minutes. 40-60° Petrol (10 cm^3) was added to extract the product. The extract was distilled and found to be the starting iminophosphorane (294).

The reaction was repeated using phosphorus pentoxide as the dehydrating agent but again only the iminophosphorane (294) could be isolated from the reaction mixture.

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SUMMARY.

A review of phosphorane chemistry is presented. A number of spirophosphoranes were synthesised with a view to establishing the relative apicophilicity of sulphur containing ligands. From this work it was concluded that the relative apicophilicities of phenylthio- and phenoxy- were very similar.

In order to obtain more information on strain factors in five-membered ring phosphoranes as the ring moves from an apical -equatorial position to a diequatorial position several spirophosphoranes were prepared containing various heteroatoms adjacent to phosphorus in the five-membered ring. It was found that when an oxygen or nitrogen heteroatom was replaced by sulphur the strain in the five--membered ring was lowered by about 3.5 kcal. $mol.^{-1}$

Two new methods for the preparation of spirophosphoranes were developed and used extensively for the ring strain work and also for a series of phosphoranes from which the relative apicophilicities of phenyl, methyl and benzyl were determined. From a second series of phosphoranes, the relative apicophilicity of the dimethylamino group was determined.

From other spirophosphoranes prepared, information was obtained on the relative apicophilicity of hydrogen, chlorine and p-nitrophenoxy groups.

A study was made on the structure of the 1:1 adduct between hexafluoroacetone azine and trimethyl phosphite, a compound recently described in the literature. Using data obtained by chemical and physical means, including ^{13}C n.m.r. it is proposed that the adduct is an iminophosphorane and not the three-membered ring structure proposed by the authors of the original publication.