SOME ASPECTS
OF
THE CHEMISTRY
OF
QUINQUECOVALENT PHOSPHORANES

by

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STATEMENT

The experimental work described in this thesis has been carried out by the author in the Department of Chemistry of the University of Leicester and at CIBA-GEIGY (U.K.) Limited, between October 1971 and June 1974.

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

Signed

P. J. Whittle

September 1974.

P.J. WHITTLE

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PART 1

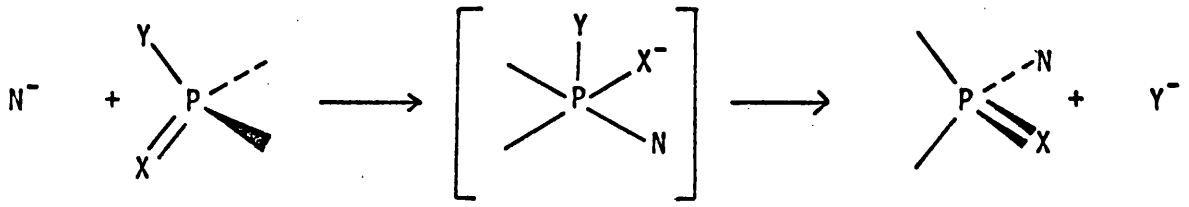
PART 1

1. PHOSPHORANES.

1.1 Structure of Phosphoranes.

The phosphoranes that will be discussed in this thesis are those compounds where the phosphorus atom is surrounded by five covalently bonded ligands. Two main classes of these compounds exist: those that are thought to be formed as metastable intermediates in substitution processes at tetraco-ordinated phosphorus, and those that are relatively stable, characterisable compounds.

Phosphoranes formed as reactive intermediates.



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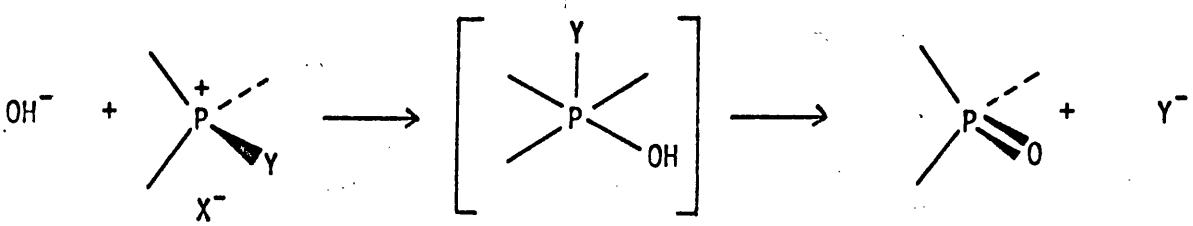


(2)

Phosphoranes of the general type (1) and (2) have been postulated as metastable intermediates in numerous substitution reactions at

tetraco-ordinated phosphorus.[1-11] Such intermediate phosphoranes have never been isolated and evidence for their existence is therefore indirect, coming mainly from kinetic or stereochemical studies of the reaction pathway.

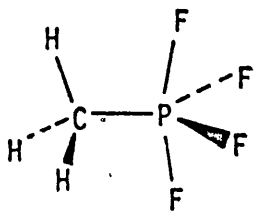
It is generally assumed that the structure and properties of phosphoranes formed as intermediates closely resemble those of the stable class and that the results of studies on stable phosphoranes are directly applicable to their metastable analogues.

Phosphoranes formed as stable, characterisable compounds.

Physical studies on a number of stable phosphoranes have shown four general points about their structure.

(a) Virtually all have essentially trigonal bipyramidal (TBP) geometry.

For acyclic phosphoranes with five identical ligands, all available data indicate adoption of the TBP geometry, e.g. an X-ray diffraction study of pentaphenylphosphorane,[12] electron diffraction[13] and infrared and Raman studies[14] of pentafluorophosphorane, and an electron diffraction study of pentachlorophosphorane.[15] There is evidence, however, that small distortions do arise when the phosphorus is asymmetrically substituted. Thus in the phosphoranes (3)[16] and (4),[17] the fluorine atoms are bent slightly away from the carbon ligand. Steric interactions are suggested to be the reason for the distortion.[16]



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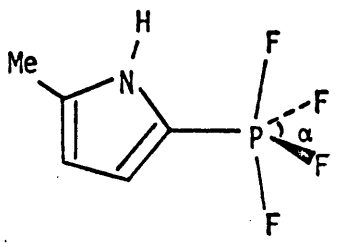
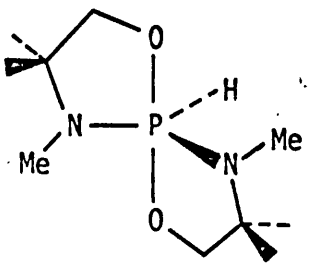


α = 108°

(4)

For cyclic phosphoranes, the constraints imposed by a small ring sometimes distort the molecule away from TBP geometry and in some cases this distortion is quite severe. The structures of the phosphoranes



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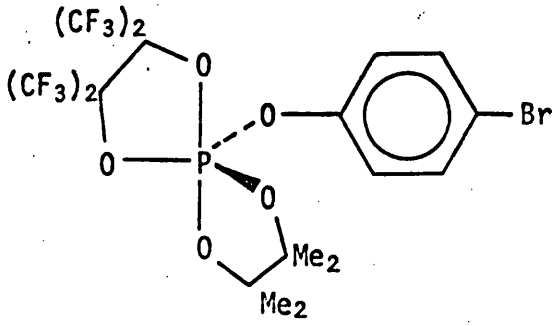

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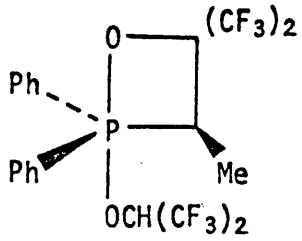

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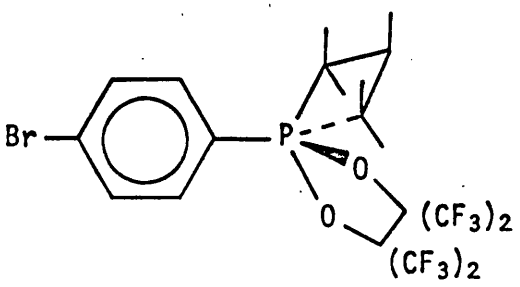


(8)

(5) - (8) have been determined by X-ray crystallography. (5)[18] and (6) (see section 4.8) are virtually perfect TBP's but in (7)[19] the oxaphosphetan ring introduces small distortions into the molecule, e.g. the Ph-C-Ph equatorial angle has decreased from 120° to 112.7°. In (8) the distortion is so severe that the molecule possesses almost square pyramidal geometry.[20]

(b) The apical bonds are longer, and therefore weaker, than the equivalent equatorial bonds.[12,13,16,17] The theoretical explanations for this difference are discussed in section 3.1. The difference in bond

lengths varies from 0.043 Å, in pentafluorophosphorane,[13] to 0.137 Å in pentaphenylphosphorane.[12] It has been suggested, at least for a series of progressively substituted fluorophosphoranes, that this variation is due to steric effects.[16,21]

(c) When the phosphorus is part of a small (four- or five-membered) ring, the ring prefers to span the apical-equatorial (ae) position of the TBP.

(d) The more electronegative elements prefer to occupy the apical positions of the TBP.

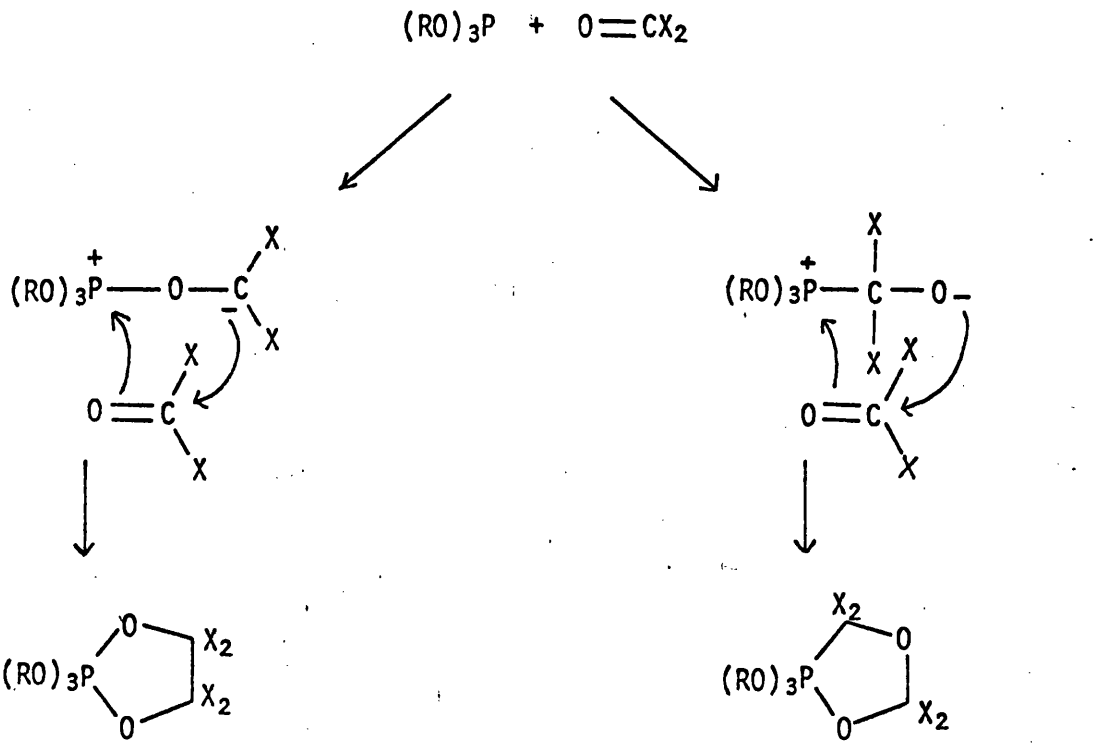
Points (c) and (d) are the 'preference rules', which were initially formulated on the basis of n.m.r. studies of fluorophosphoranes[22] and cyclic oxyphosphoranes,[23-25] and from kinetic studies of cyclic and acyclic phosphate, phosphonate and phosphinate esters.[4,26] Several X-ray structure determinations (see sections 4.2 and 4.8, and refs. 18, 19,27,28) have since confirmed point (c) but recent work, some of which is described in this thesis, suggests that point (d) is only an approximation and that electronegativity is only one of several factors (see sections 3.1 and 3.2) that may affect the preference of a ligand for a particular position in a TBP.

1.2 Synthesis of Oxyphosphoranes.

Since most of the work described in this thesis is concerned with phosphoranes which have at least one phosphorus-oxygen bond, the oxyphosphoranes, only the preparation of these is described. The most widely used methods of preparation of oxyphosphoranes are the following.

(1) Reaction of a tervalent phosphorus compound with a monofunctional carbonyl compound.

In this synthesis, two equivalents of the carbonyl compound react with one equivalent of the phosphorus compound to give a phosphorane of the general type (9) or (10). If the carbonyl compound is suitably



1,3,2-dioxaphospholan (9)

1,4,2-dioxaphospholan (10)

activated, i.e. if X is a group capable of stabilising negative charge, reaction proceeds to formation of the 2:1 adduct (9). Thus, o- and p-nitrobenzaldehyde,[29] o-phthalaldehyde,[30] hexafluoroacetone,[31] and fluorenone[32] all react with trialkyl phosphites to give 2:1 adducts of type (9). In the case of simple aliphatic aldehydes the 2:1 adduct (10) is obtained,[33] since, it is suggested,[34] location of the negative charge on the carbon of the carbonyl group is now unfavourable owing to the

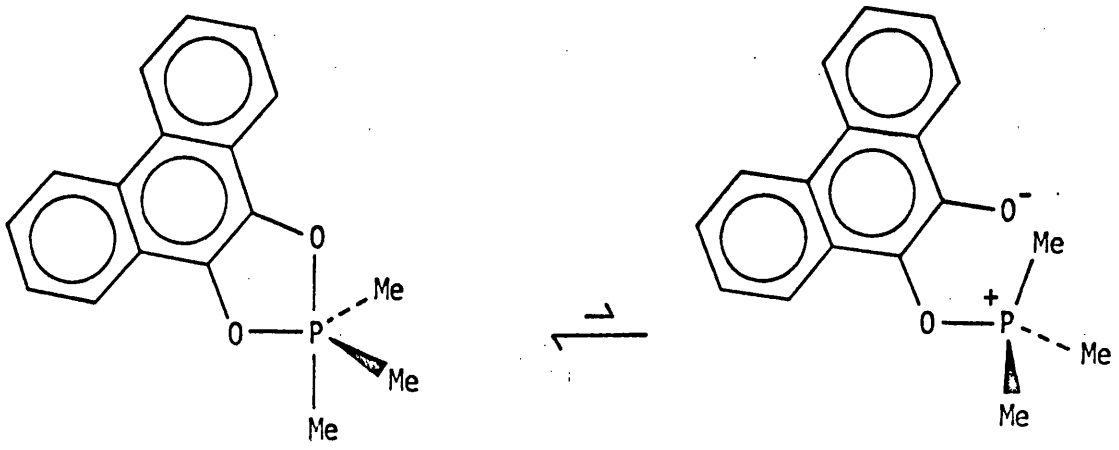
absence of any stabilising groups.

Ramirez[34] has shown that the reaction of pentafluorobenzaldehyde with triethyl phosphite leads initially to formation of the 1,4,2-dioxaphospholan which then slowly isomerises to the 1,3,2-dioxaphospholan. However, there was no compelling evidence for the intermediacy of a 1,4,2-dioxaphospholan in the preparations of other 1,3,2-dioxaphospholans.

The reaction of tervalent phosphorus compounds with hexafluoroacetone (HFA) is discussed further in section 4.1.

(2) Reaction of a tervalent phosphorus compound with an α-dicarbonyl derivative, or a similar 1,3-unsaturated system.

Tervalent phosphorus compounds react under mild conditions with a number of α-dicarbonyl systems to yield phosphoranes, e.g. (11),[35] (12),[31] and (13).[36] However, Ramirez and his co-workers have shown that the 1:1 adducts formed by reaction of some tertiary phosphines with phenanthraquinone are best described in terms of an equilibrium between quinquecovalent and dipolar structures, with the quinquecovalent structure greatly predominating, e.g. (14).[37] The equilibrium can be detected by changes in ^{31}P n.m.r. chemical shift with solvent.



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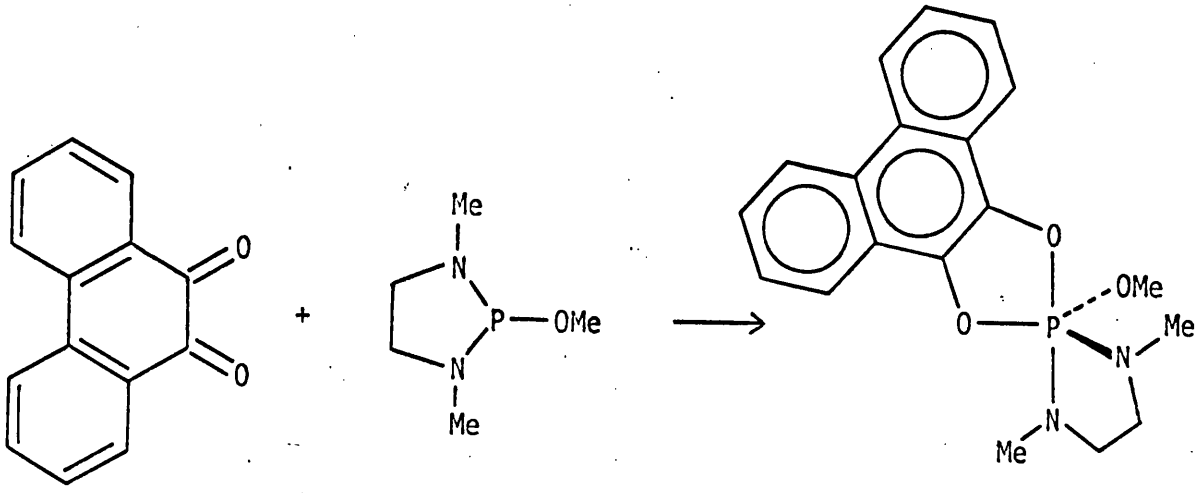

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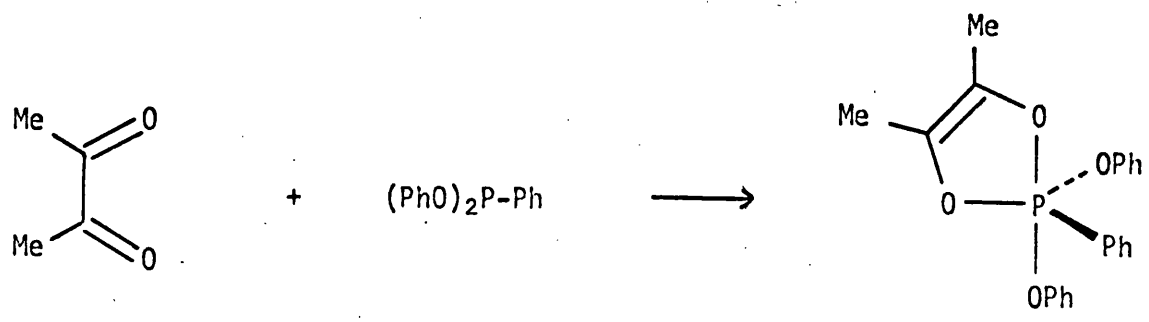

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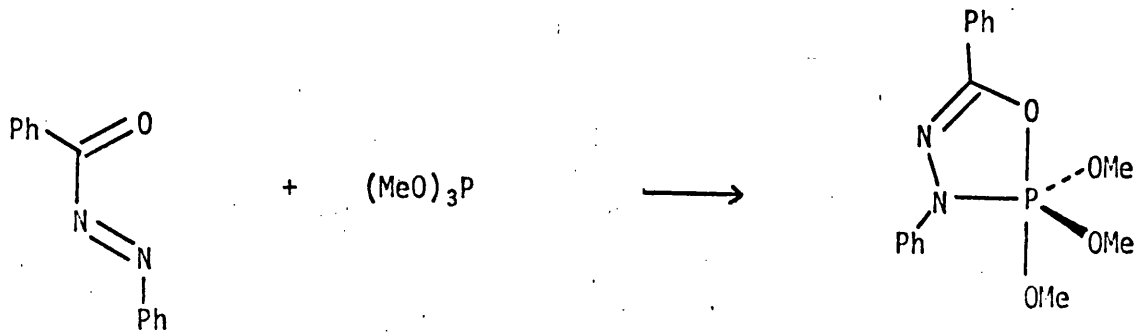
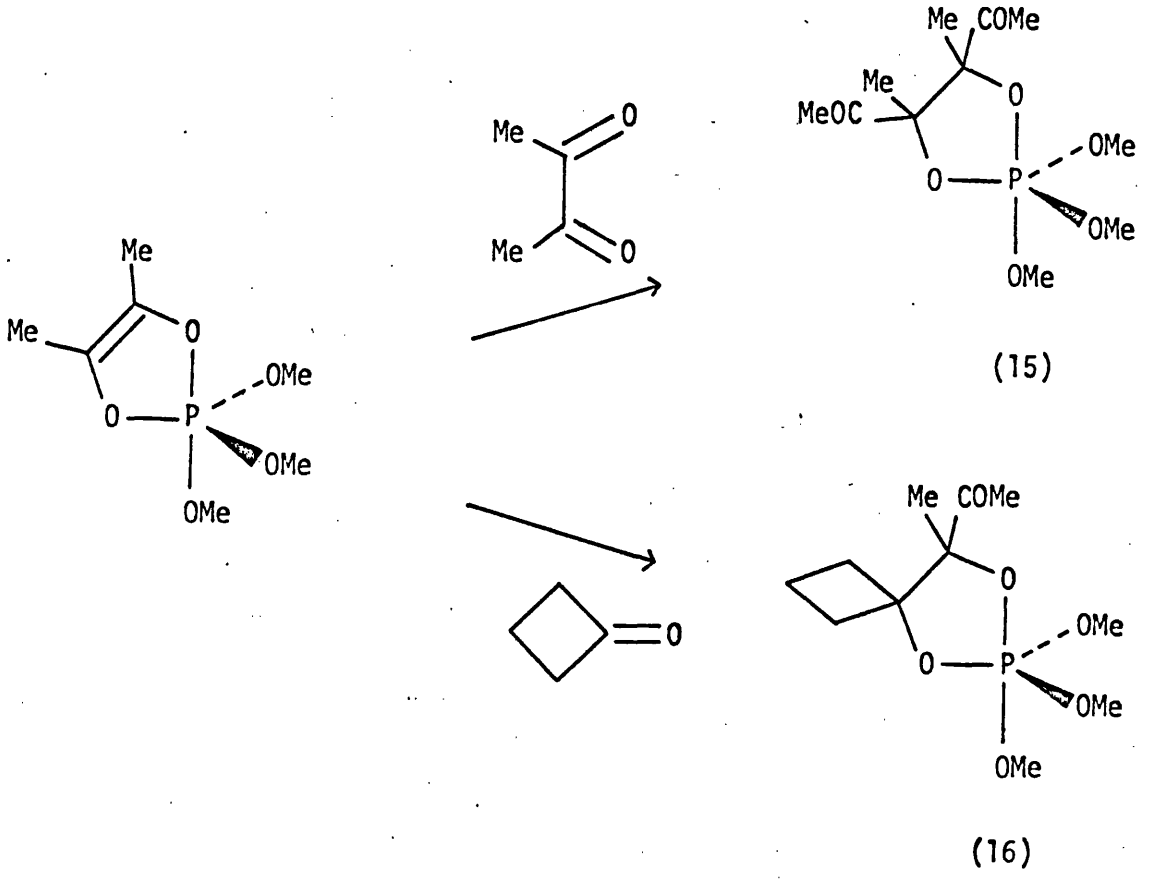


(13)

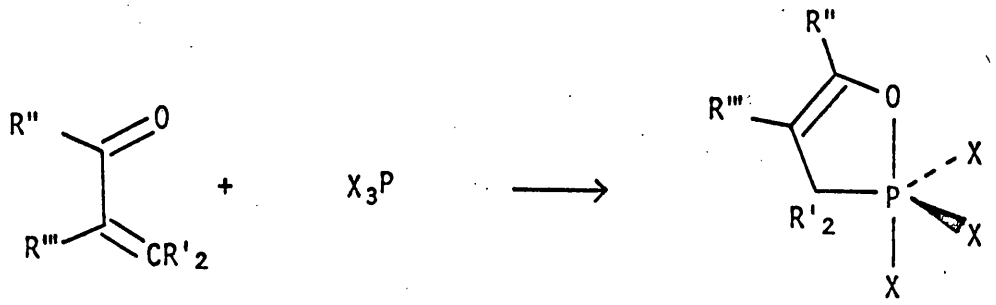
The 1,3,2-dioxaphospholen will often react further with a wide variety of carbonyl compounds to produce new 1,3,2-dioxaphospholans,[38] e.g. (15) and (16).



(3) Reaction of a tervalent phosphorus compound with an α,β-unsaturated carbonyl compound.

Phosphites, phosphonites and phosphinites, and their amino and thio analogues react with a wide range of α,β-unsaturated carbonyl compounds to yield adducts of the general formula (17).[23-25,39-41]

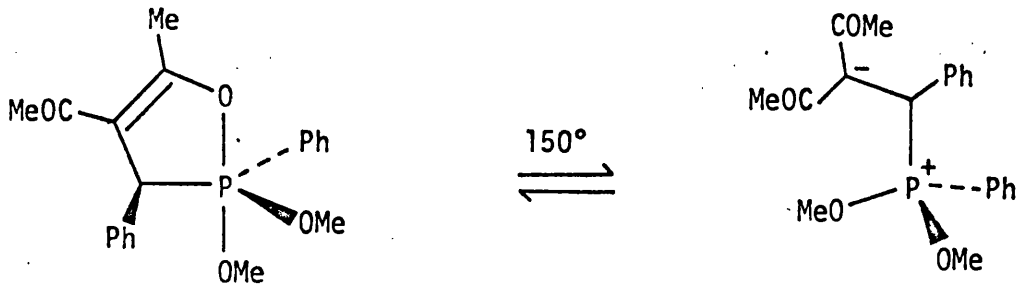
In general, the 1,2-oxaphospholens are rather less stable than the corresponding 1,3,2-dioxaphospholens and tend to undergo ionisation on heating, e.g. (18).[4] The dissociation temperature decreases as



(17)

R', R" = H, alkyl, aryl; R"' = H, alkyl, aryl, -COR, $-CO_2R$

exocyclic alkoxy groups are replaced by alkyl or aryl groups and tertiary phosphines do not, in fact, form stable phosphoranes: the 1:1 adducts exist entirely in the dipolar form at room temperature.[34,42]



(18)

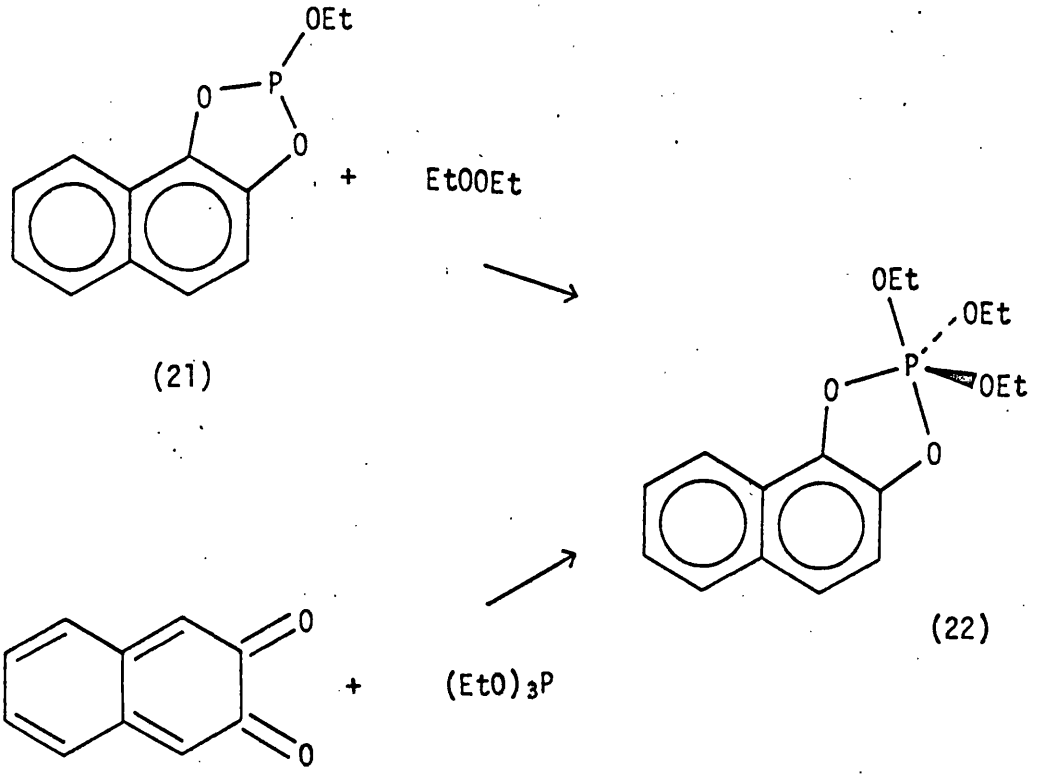
(4) Reaction of a tervalent phosphorus compound with a dialkyl peroxide.

The pentaoxyphosphoranes (19)[43] and (20)[44] have been prepared by reaction of the appropriate phosphite and dialkyl peroxide. Analogous

$$(RO)_3P + ROOR \rightarrow (RO)_5P$$

(19) R=Me; (20) R=Et

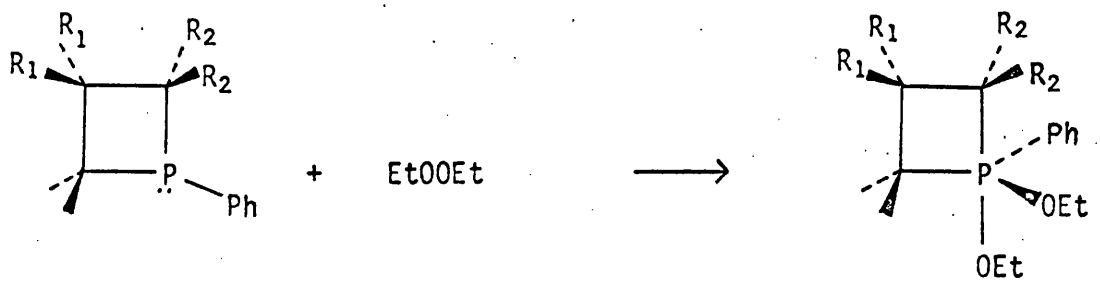
reactions take place with a number of cyclic phosphites,[45] phosphoramidites, phosphonites and phosphinites,[46] e.g. reaction of the cyclic phosphite (21)



(21)

(22)

with diethyl peroxide gave the same oxyphosphorane (22) as did the reaction of β-naphthaquinone with triethyl phosphite,[45] and reaction of the phosphines (23) and (24) with diethyl peroxide gave the quinquecovalent products (25) and (26) respectively.[47]



(23) R_1 = H; R_2 = Me

(24) R_1 = Me; R_2 = H.

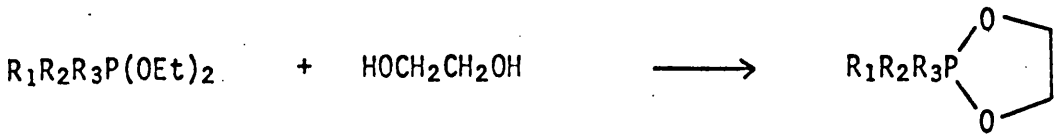
(25) R_1 = H; R_2 = Me

(26) R_1 = Me; R_2 = H.

The major disadvantage with this preparative route is that other products, mainly the oxidised tervalent phosphorus compound, are also formed. The presence of these impurities and the general hydrolytic instability of the oxyphosphoranes has precluded their isolation and complete characterisation.

(5) Reaction of oxyphosphoranes with diols.

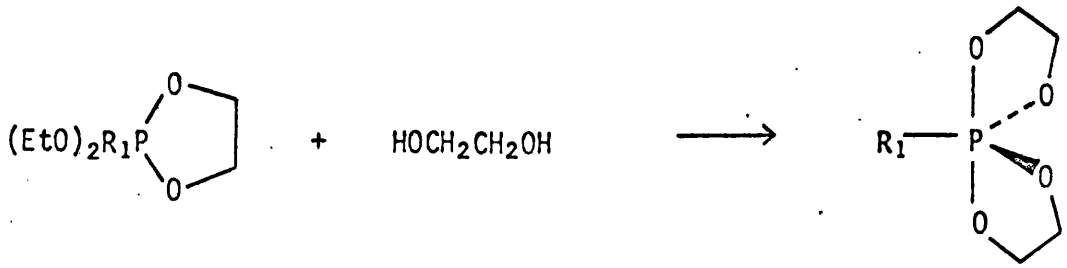
Denney and his co-workers[48] have shown that acyclic oxyphosphoranes react readily with some diols to form cyclic oxyphosphoranes. This exchange route has enabled a wide range of monocyclic and spiro-oxyphosphoranes of the general type (27) and (28) to be prepared. Similar displacements also occur with neopentyl glycol, propylene glycol, dl-2,3-butanediol and styrene glycol. Pinacol, 1,4-butanediol and 1,5-pentanediol,



(27)

R_1, R_2, R_3 = EtO, alkyl, phenyl

when $R_2 = R_3$ = EtO

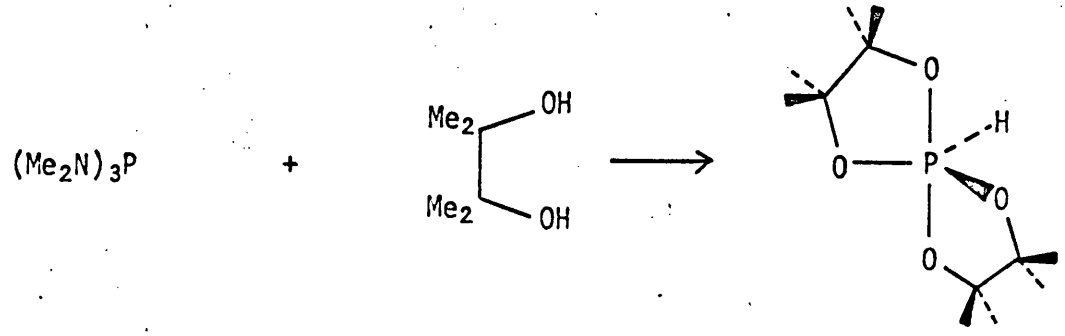


(28)

however, give only tetraco-ordinated products.

As the ethoxy groups on the phosphoranes are replaced by alkyl or phenyl groups the stability of the phosphorane decreases.

(6) Reaction of some derivatives of phosphorous acid with 1,2--diols and 2-aminoalcohols.



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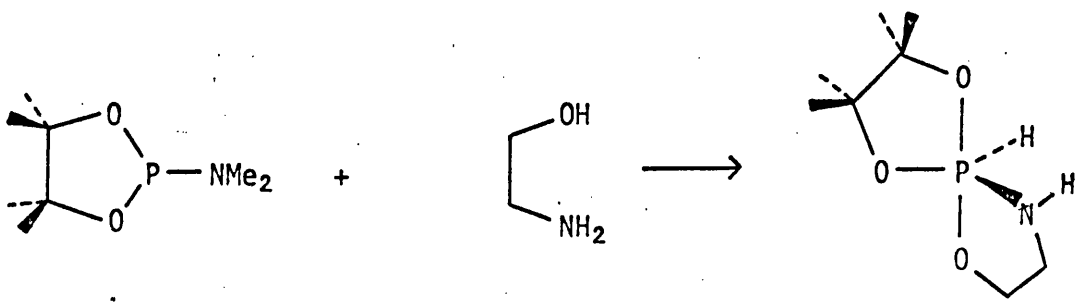

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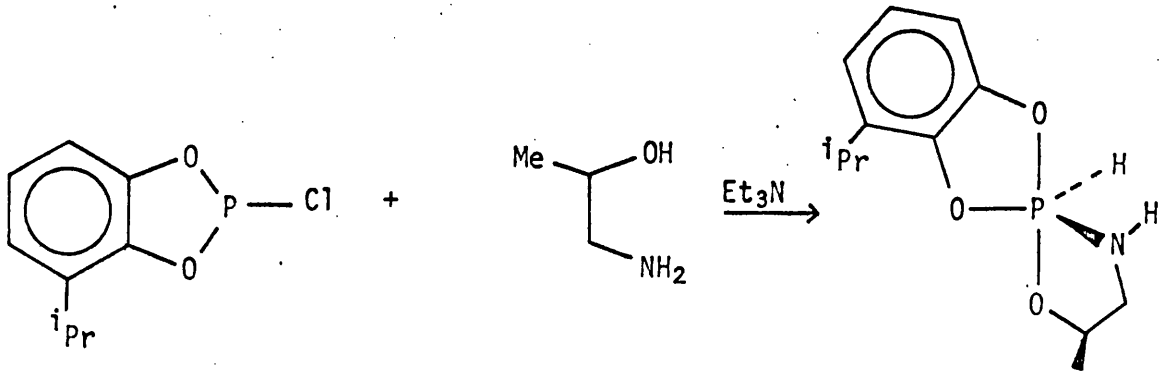
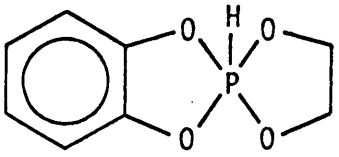


(31)

Several derivatives of phosphorous acid react with 1,2-diols and 2-aminoalcohols to yield phosphoranes containing a P-H bond,[49-51] e.g. (29), (30),[49b] and (31).[50]

The driving force for the cyclisation is presumably the relief of ring strain that accompanies formation of the quinquecovalent structure. Stabilisation in this way cannot be very large, however, since in some cases there is evidence for an equilibrium between tervalent and quinquevalent species,[49b,51] e.g. the ^{31}P n.m.r. spectrum of the phosphorane (32) shows the presence of the two phosphites (33) and (34).[51] Also, the



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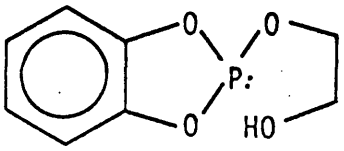

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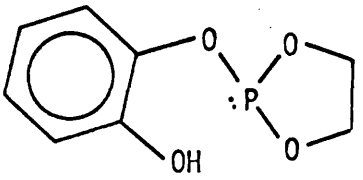
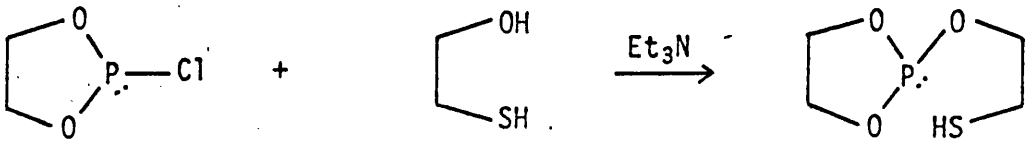


(34)

phosphite (35) exists as such and not as the trioxythiophosphorane.[52]



(35)

1.3 Stability of Phosphoranes.

The stability of a phosphorane can be judged with respect to two criteria: stability relative to ease of decomposition to a phosphonium species, kinetic stability, and the stability of a particular phosphorane relative to other phosphoranes, thermodynamic stability.

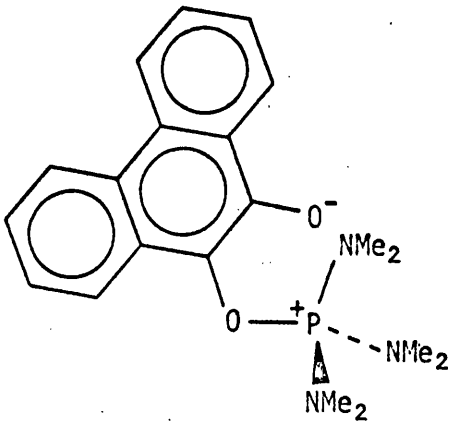
Kinetic stability.

From studies on a variety of phosphoranes there appear to be two main factors which affect the equilibrium (36).

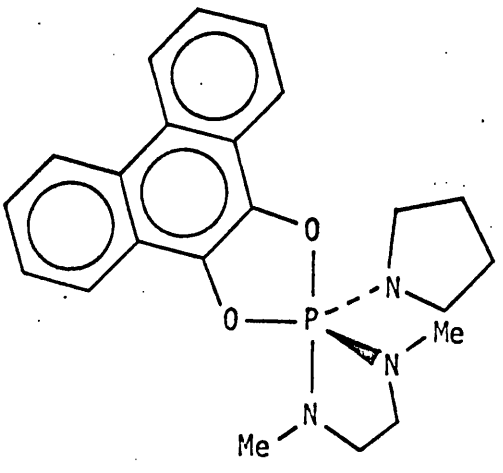
$$PX_5 \rightleftharpoons PX_4^+ + X^- \qquad (36)$$

(a) Incorporation of the phosphorus into a small ring.

From studies of X-ray diffraction data, Ramirez has concluded that a great deal of intramolecular crowding exists in phosphoranes.[19,27] If



(37)



(38)

this is so, the presence of bulky groups bonded to phosphorus will tend to decrease the phosphorane stability relative to the sterically less encumbered dipolar species. Ramirez[34] has suggested that when the phosphorus forms part of a ring, steric interactions are reduced and hence the phosphorane structure is stabilised. Thus, the reaction of phenanthraquinone with the appropriate aminophosphines gave the 1:1 adducts (37) and (38) which exist in the dipolar form and the quinquecovalent form respectively.[35,53]

Similarly, although the phosphoranes (25) and (26) exist as such,[47] (39) appears to exist in solution as an equilibrium between phosphorane and phosphonium ethoxide.[46]

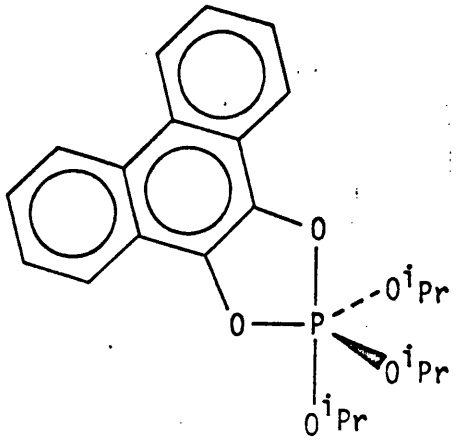
$$PhMe_2P(OEt)_2 \rightleftharpoons \underset{(39)}{PhMe_2\overset{+}{P}\text{-}OEt} + EtO^-$$

It would seem more likely, however, especially in the latter case, that the reason for the greater stability of the quinquevalent structure lies in a much lower value for ring strain in this structure than in the ionised form. Dissociation of structures (25), (26), or (38) would result in an increase in the ring angle at phosphorus from 90° to 109°: a highly unfavourable process.

(b) The electronegativity of the ligands bonded to phosphorus.

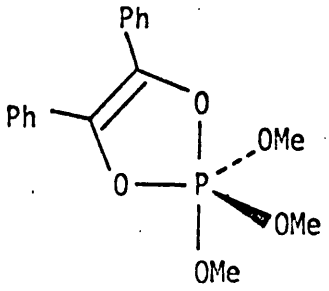
As the electronegativity of the ligands increases, the stability of the phosphonium cation would be expected to decrease and thus the equilibrium (36) will move over to favour the phosphorane structure. It seems to be a general trend in oxyphosphorane chemistry that as alkoxy groups bonded to phosphorus are replaced by amino or alkyl groups the stability of the phosphorane decreases. This is presumably due to an

increase in cationic stabilisation owing to a decrease in ligand electronegativity. Thus, the phosphorane (40) exists as such[27] but (37) exists as the dipolar species.



(40)

Likewise, (41) exists as the oxyphosphorane but (42) exists in solution as an equilibrium between quinquecovalent and dipolar forms. However, in these examples, the greater size of the dimethylamino group may also be responsible for the ready ionisation of (37) and (42).[34]



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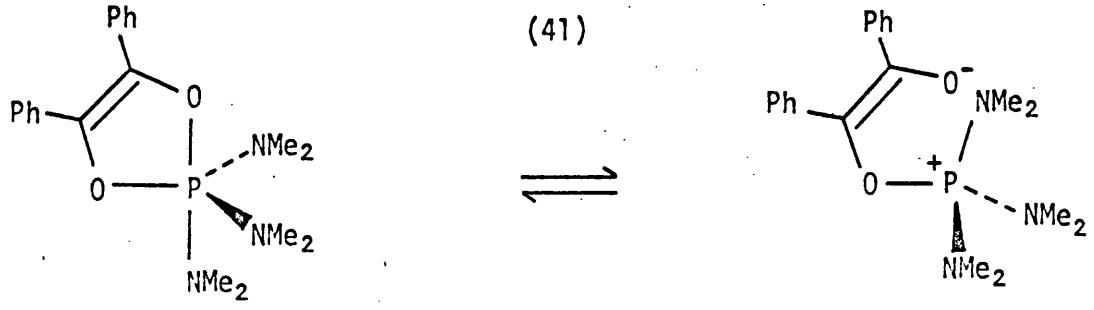


(42)

It has also been found that, while the properties of (43) are consistent with a quinquecovalent structure, (39) and (44) probably exist in solution as an equilibrium between phosphorane and phosphonium ethoxide.[46]

$PhP(OEt)_4$ $\quad$ $Ph_nPMe_m(OEt)_2 \rightleftharpoons Ph_nMe_mP\text{-}OEt + EtO^-$

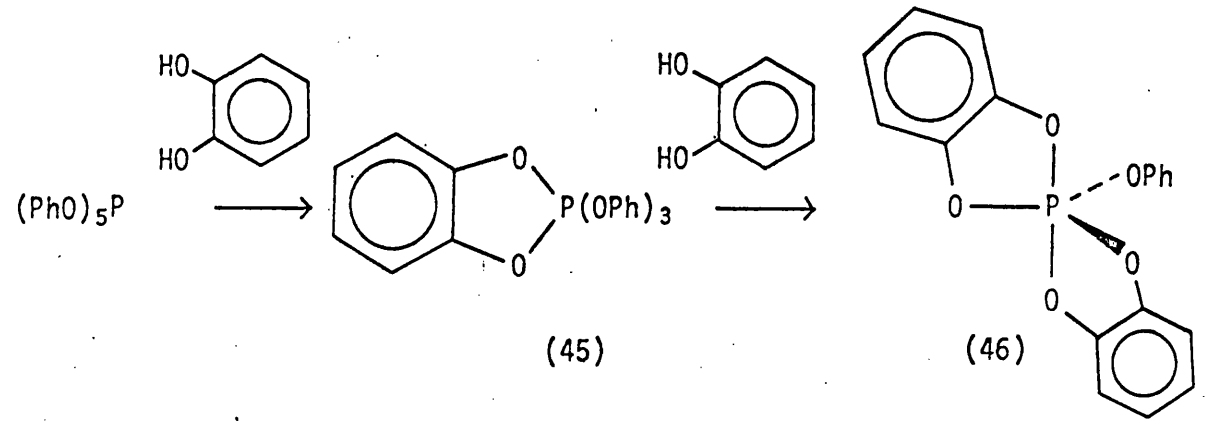
(43) $\quad$ (39) n = 1, m = 2

(44) n = 0, m = 3

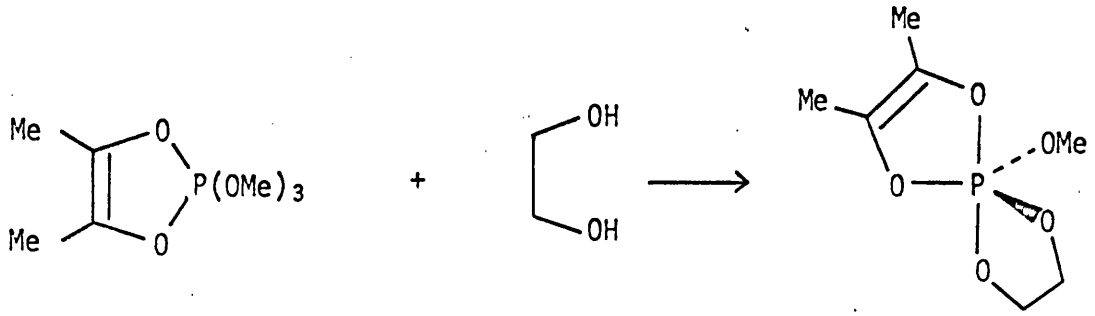
The effect of electronegativity is further illustrated by the fact that the dissociation temperature of 1,2-oxaphosph(V)olens decreases as alkoxy groups are replaced by alkyl groups.[34,42]

Thermodynamic stability.

A general property of acyclic oxyphosphoranes is that they react with several 1,2- and 1,3-diols to produce monocyclic and spirophosphoranes.



(45) $\quad$ (46)



(47) $\quad$ (48)

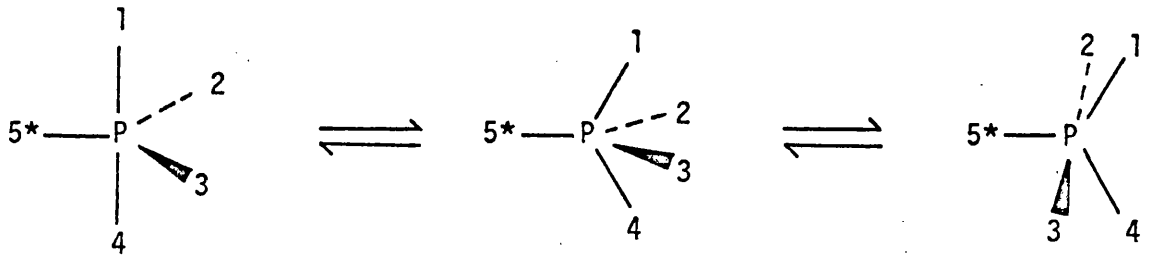
Denney's exchange route to oxyphosphoranes (see section 1.2) illustrates this reaction particularly well. Other examples include the reaction of catechol with pentaphenoxyphosphorane to yield the cyclic oxyphosphoranes (45) and (46),[54] and the formation of the spiro-oxyphosphorane (48) from the reaction of ethylene glycol with the oxyphosphorane (47).[55]

It appears, then, that incorporation of small rings into the phosphorane structure results in an increase in thermodynamic stability. Ramirez[54,55] has attributed this increase in stability to a decrease in steric crowding when the phosphorus becomes part of a ring.

2. PERMUTATIONAL ISOMERISATION OF PHOSPHORANES.

2.1 Berry Pseudorotation.

Physical studies on a number of fluorophosphoranes have shown that they all adopt essentially a TBP geometry.[13,14,17] However, in the case of pentafluorophosphorane,[56] the ^{19}F n.m.r. spectrum shows equivalence of all five fluorine atoms from room temperature to -197°, while other fluorophosphoranes also show equivalence of fluorine atoms inconsistent with a static TBP structure.[22] In 1960, Berry[57] attempted to explain the n.m.r. behaviour of pentafluorophosphorane by postulating that the positions of the fluorine atoms were rapidly equilibrated by a ligand reorganisation process that he termed 'pseudorotation'. The process is shown in scheme 1.



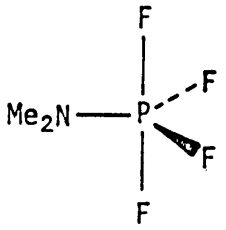
SCHEME 1

Using one of the equatorial bonds as the pivot (in this case 5*), the two apical bonds are bent towards each other and the two equatorial bonds are bent away from each other to form, as a transition state or intermediate, the square pyramid. Continuation of these ligand movements results in the formation of another TBP and, with reference to the initial TBP, it is evident that this process has exchanged ligands in a pairwise manner. The Berry pseudorotation (BPR) mechanism comprises only the two

vibrations shown: there is no relative internal rotation of ligands.

2.2 Mechanistic Alternatives: Turnstile Rotation.

Several mechanistic alternatives have been considered by Muetterties[58] but have been eliminated[59b-f] on the basis of the results of Whitesides and Mitchell.[60] They analysed the temperature-dependent ^{31}P n.m.r. spectrum of dimethylaminotetrafluorophosphorane (49) and found that, at -100° the spectrum showed a triplet of triplets, as expected for



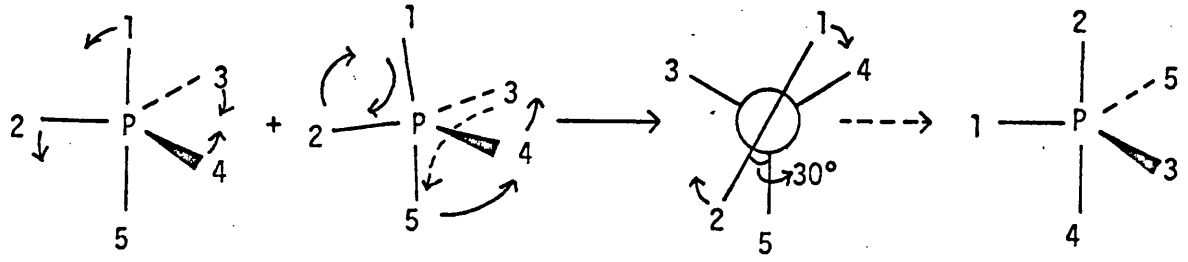
(49)

a static TBP with the dimethylamino group in an equatorial position. At -50°, however, the spectrum showed a regular quintet, consistent with coupling of the phosphorus to four equivalent fluorine atoms. By analysing the variation in line shape in the region -50° to -100° they concluded that fluorine equivalence was achieved by the simultaneous interchange of two apical with two equatorial fluorine atoms.

The Berry mechanism is consistent with this result but the alternative mechanisms of Muetterties are considered to violate it. However, the barrier to fluorine equilibration almost certainly derives from a slowing, on the n.m.r. time scale, of P-N rotation (see section 4.11) and since it may be possible that pseudorotation is still fast on the n.m.r.

time scale when P-N rotation is slow, the status of this work as a criterion of possible isomerisation mechanisms is uncertain.

An alternative to the Berry mechanism, which was not considered by Muetterties, has been suggested by Ugi, Ramirez and their co-workers. This is the 'turnstile rotation (TR)' mechanism.[59] The basic isomerisation process comprises three simultaneous movements of the ligands. These are, referring to scheme 2:



SCHEME 2

(a) a bending of ligands 1 and 2 by about 9° in the direction shown; these two ligands constitute the 'ligand pair',

(b) a bending of ligands 3 and 4 as shown, to reduce the original 120° equatorial angle to about 90°; the three orthogonal ligands 3, 4 and 5 constitute the 'ligand trio,'

and (c) an initial relative internal rotation of the ligand pair versus the ligand trio of 30°.

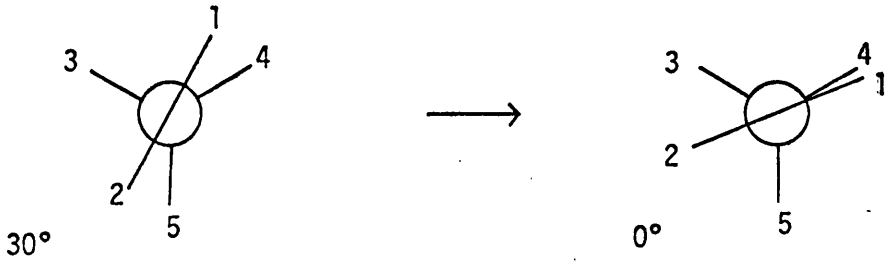
The simultaneous occurrence of these two vibrations and one rotation leads to the (30°-TR) barrier situation shown in scheme 2 as a Newman projection. A continued internal 30° relative rotation of the ligand pair versus the ligand trio and restoration of the TBP angles yields the new conformer of the original molecule. The overall process thus exchanges ligands in a pairwise manner, in accordance with the

Whitesides and Mitchell experiment.[60] The TR illustrated in scheme 2 is equivalent to a BPR with ligand 3 as the pivot.

There are four equivalent TR's for each BPR and so a TR has a higher probability. However, calculations[61] have indicated that for symmetrically substituted acyclic phosphoranes the BPR process is energetically preferred but other mechanisms may operate for less symmetrically substituted molecules or for cases where the square pyramidal structure is destabilised.

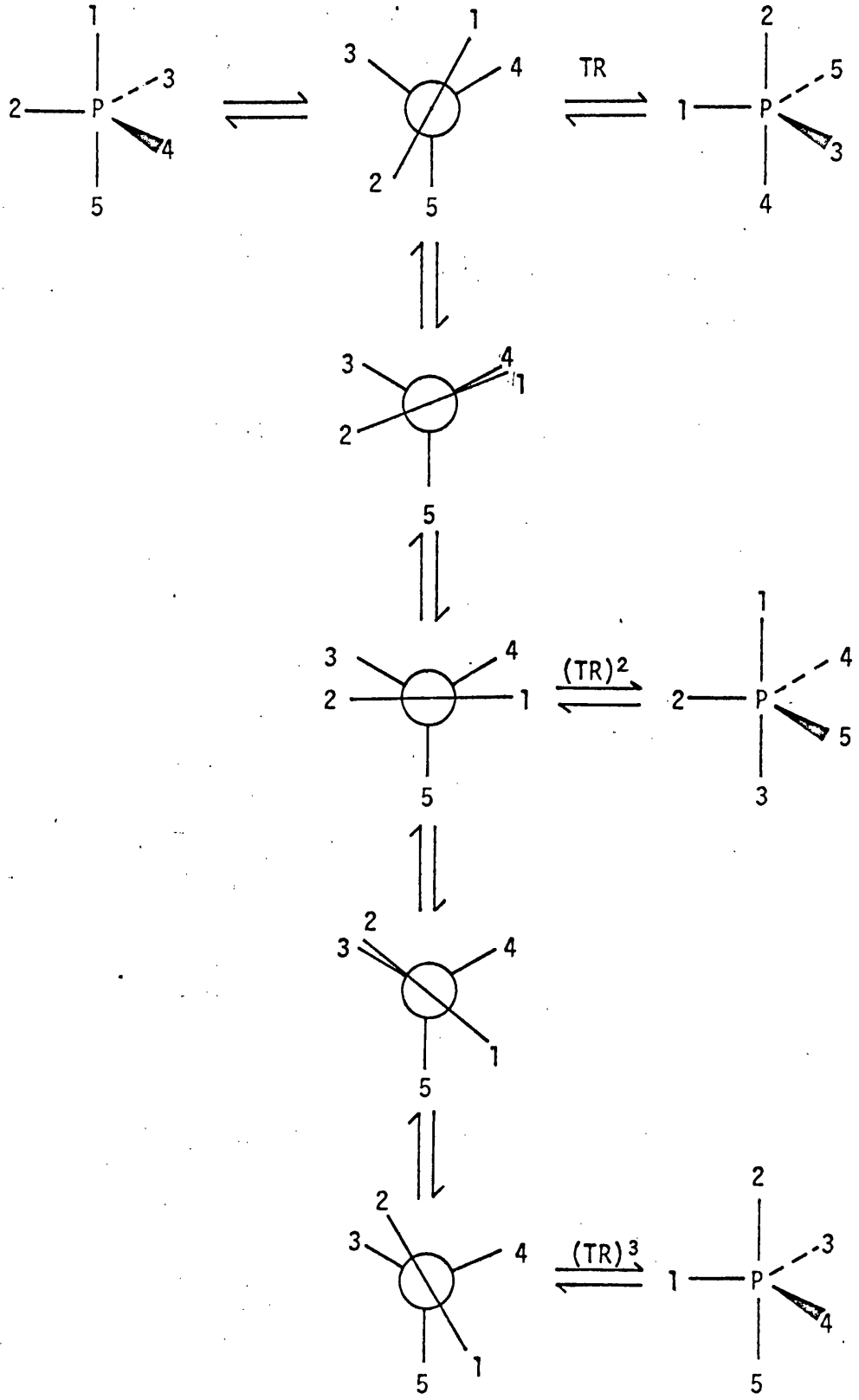
Ugi[59b-f] has suggested that operation of either mechanism is possible in acyclic phosphoranes but cyclic phosphoranes must undergo isomerisation by a TR, with the ring constituting the ligand pair.

The major departure from the Berry mechanism is that, with the TR mechanism, there is the possibility of a 'multiple TR' process occurring, i.e. once the 30° barrier situation is reached, rotation through the 0° barrier situation (50) may occur by a further rotation of 30°. The



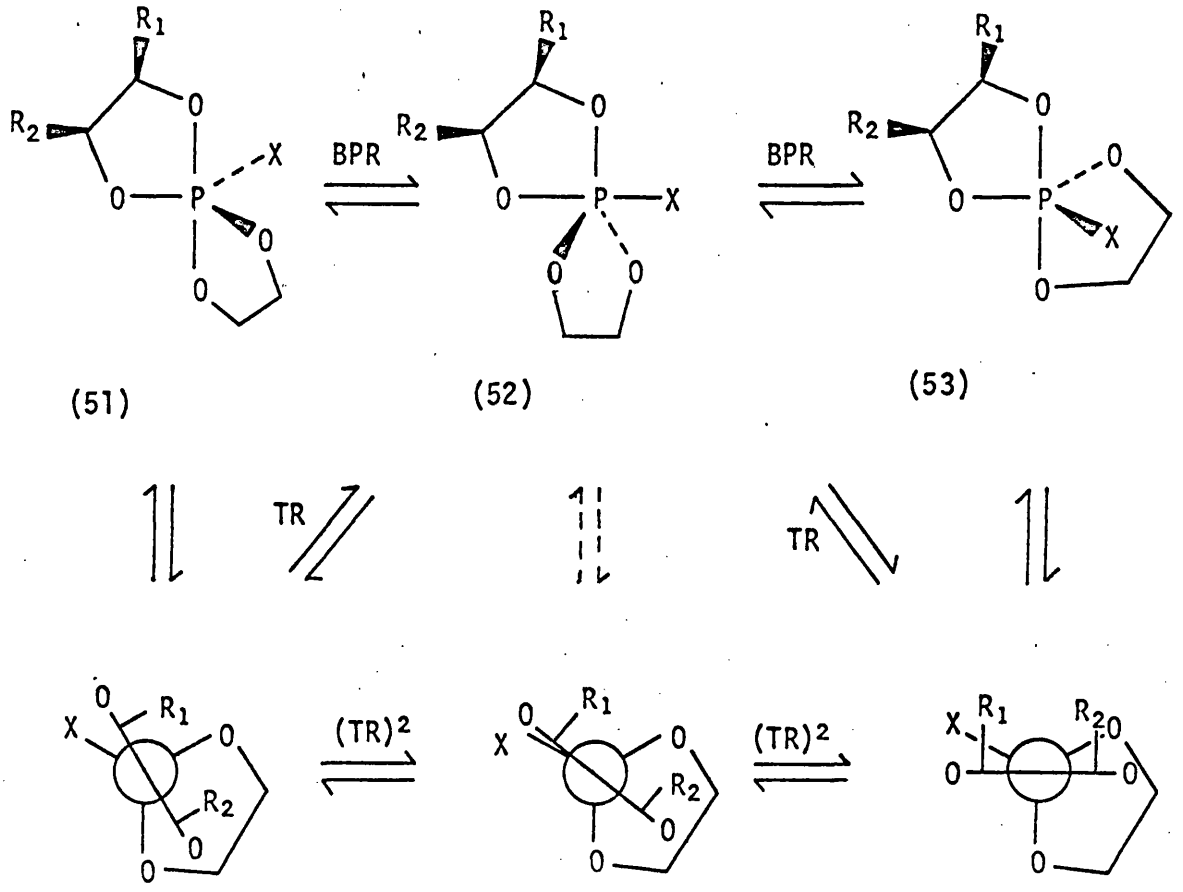
(50)

effect of a multiple TR sequence is that it allows interconversion of conformers, which are not linked by a single BPR or TR step, without the need to go through another TBP intermediate. The stereochemical consequences of single TR and multiple TR [$(TR)^2$ and $(TR)^3$] processes are shown in scheme 3.



SCHEME 3

The mechanistic significance of multiple TR's is best illustrated by considering the spirophosphorane (51). Interconversion of (51) and

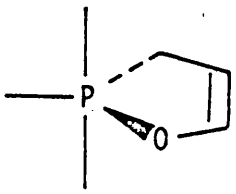


(51) (52) (53)

(53) by a BPR or TR involves formation of the highly strained TBP (52). However, this interconversion can be readily achieved by a $(TR)^2$ process without the need to form a high energy TBP.

Definite evidence for the operation of the TR mechanism seems to be rather limited and appears to consist of two main points.

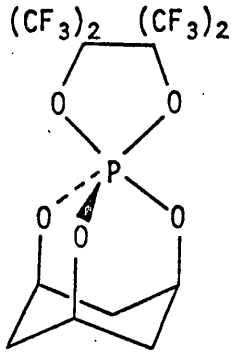
(a) In their calculations, Ugi, Ramirez and their co-workers[59d,e] estimated a value for the energy required to place the oxaphospholen ring (54) in the diequatorial (ee) position as about 40 kcal mol^{-1}. Isomerisations involving, on the BPR mechanism, formation of TBP's with



(54)

ee four- or five-membered rings were hence explained in terms of multiple TR's, where high energy intermediates such as (54) are by-passed. However, the results of several workers[25, 48, 62-64] have been explained in terms of the energy required to move small rings into the ee position but the experimental values for ring strain (10-20 kcal mol^{-2}, see section 5) are much lower than Ugi's estimate of 40 kcal mol^{-1}. If the interpretations of the experimental data are correct, it would appear that a value of 40 kcal mol^{-1} required for ee placement of the ring (54) is an overestimate.

(b) The n.m.r. spectra of the caged oxyphosphorane (55) show[59,65] that the molecule is undergoing rapid positional exchange at temperatures

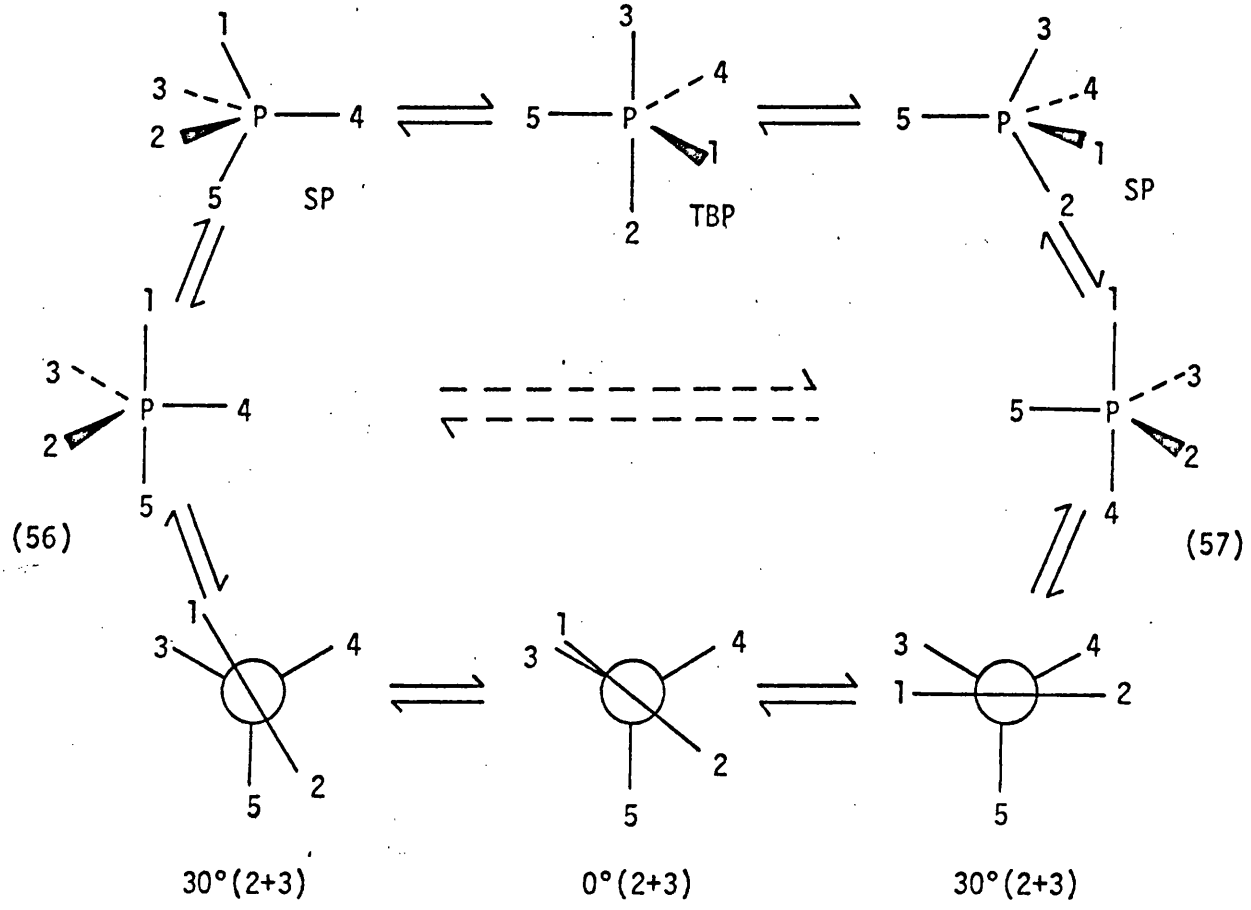


(55)

as low as -165°. By inspection of molecular models, it was concluded that it was impossible for (55) to undergo a normal BPR process owing to the restriction on motion that the adamantoid cage imposes. The rapid positional exchange was thus interpreted in terms of a TR process. In other words, interconversions through a square pyramid are of high energy but interconversions through a 30°-barrier (2+3) structure are of low energy. This seems rather unlikely since the actual difference in structure between a square pyramid and a 30° (2+3) species is exceedingly small.

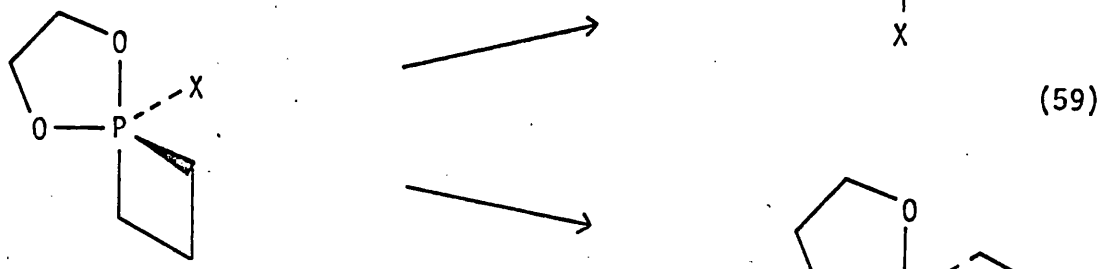
The approach to permutational isomerisation in phosphoranes that has been used in this thesis is outlined below.

Since the BPR and TR processes accomplish the same overall interconversion, passing through intermediate species of very similar structure, it is irrelevant which of these mechanisms operates.



The 30° (2+3) structure is structurally and electronically very closely related to the square pyramid, and likewise for the 0° (2+3) and TBP structures.[61] It would thus seem reasonable to suppose that the actual isomerisation of (56) to (57) proceeds *via* species which are intermediate between the limiting structures shown.

The major difference between the 0° (2+3) structure and the TBP is that the trio equatorial angle is 90°, compared with a 120° angle in the TBP. Hence, for a spirophosphorane, there is no increase in ring strain on going from the TBP (58) to the 0° (2+3) structure (59). It might be expected, therefore, that interconversion of spirophosphoranes would



(58)

(59)

(60)

proceed *via* the 0° (2+3) structure. However, it is found that isomerisations passing through structures like (59) or (60) do have appreciable energy barriers, associated with an increase in ring strain (see sections 4.5 - 4.9 and refs. 25, 48, 62-64). It is difficult to see any property which stabilises (60) at the expense of an appreciable gain in ring strain

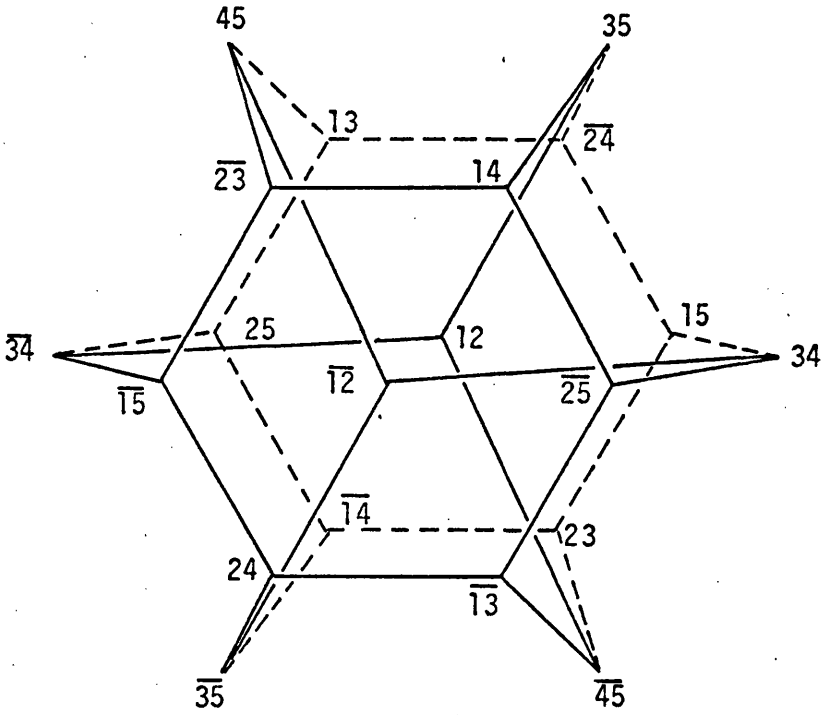
but steric effects may be important here since the 9° tilt that the ligand pair experiences brings O* nearer to X in (60), although the observed barriers to interconversion (10-20 kcal mol^{-1}) seem too high to be explained purely by this interaction.

The idea that the 0° (2+3) structure is not an energy minimum and that isomerisations pass through structures which are intermediate between a 0° (2+3) structure and a TBP also makes the occurrence of multiple TR's unreasonable since there is no energetic advantage in passing through a 0° (2+3) structure rather than through some sort of distorted TBP.

For the sake of simplicity, permutational isomerisation processes discussed in this thesis will be described formally in terms of the Berry mechanism of pseudorotation.

2.3 Topological Representations of Pseudorotation Pathways.

For a phosphorane with five different ligands there exists the possibility of three initial pseudorotations, using the three possible combinations of pairs of equatorial ligands, to form three new isomers. Pseudorotation of these isomers gives six new isomers which can also pseudorotate and this process can be extended to formation of a total of twenty isomeric phosphoranes, consisting of ten dl pairs, interconnected by thirty pseudorotation pathways. In order to aid analysis of the possible pseudorotation pathways available to specific phosphoranes, a number of topological representations have appeared,[7,25a,66-68] most of which are based on the twenty-vertex graph used by Balaban.[69] The Desargues-Levi graph (61) of Mislow[7,68] can be used to illustrate the use of these representations.



(61)

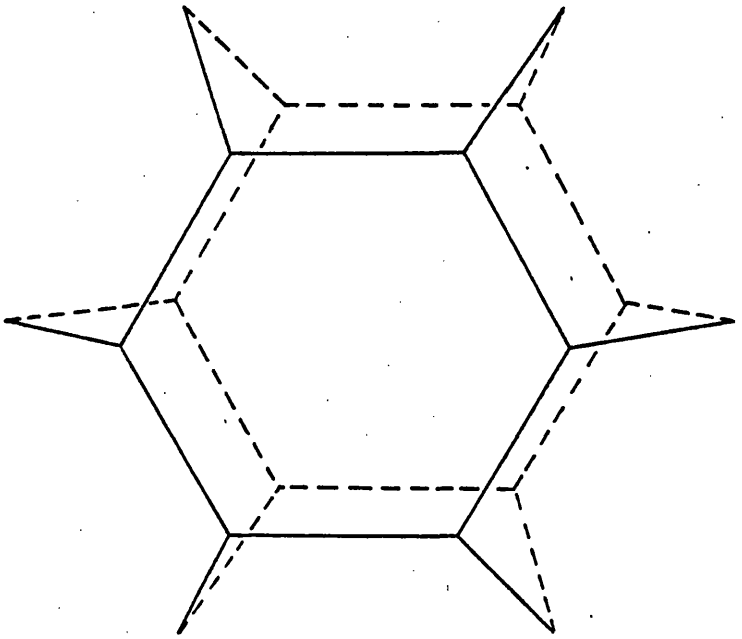
The vertices represent the twenty possible isomers while the edges represent the thirty pseudorotations. The isomers are designated by the apical ligands and the chirality of each isomer is denoted by the ascending numerical order of equatorial ligand indices: if clockwise when viewed from the apical ligand with the lower numerical index, the isomer is unbarred; if counterclockwise, barred. Thus the isomer 14 and its enantiomer $\overline{14}$ represent the two possible isomers which have ligands 1 and 4 in the apical positions.

Some of the more important points which are evident from a study of the graph are the following.

(a) For unrestricted pseudorotation processes five successive pseudorotations are required to interconvert enantiomers, which are related by the centre of symmetry of the graph.

(b) If any ligand is forbidden to occupy an apical position, only isolated pairs of isomers may interconvert, i.e., racemisation of the phosphorane cannot occur.

(c) For cyclic phosphoranes, where the ring termini are denoted by 1 and 2, (61) reduces to (62), the 'hexaasterane' graph of Mislow,[7,68] since those isomers with both ring termini in apical positions can be eliminated (except, of course, for very large rings). The 'star points' represent isomers which have a ring in the ee position.



(62)

For small rings such phosphoranes will be of high energy and so, if these are also eliminated, the graph reduces to two unconnected pseudorotation cycles. Hence, in cyclic phosphoranes, racemisation can only occur, by a BPR mechanism, via a species with the ring in the ee position.

3. LIGAND ARRANGEMENT IN PHOSPHORANES.

3.1 Bonding in Phosphoranes.

A number of different approaches to bonding in phosphoranes[16,59b-f,61,70-72] has resulted in various explanations for the experimentally observed facts that (a) apical bonds are longer than equatorial bonds and (b) the more electronegative elements prefer to occupy the apical positions of the TBP. It is generally agreed that apical ligands must be able to accommodate more negative charge than equatorial ligands and hence any property of a ligand which serves to stabilise negative charge will increase the preference of that ligand for the apical position and vice versa. The most important property in this context is probably electronegativity; the greater this is, the greater will be the preference for the apical position: hence the preference rule.

There may be other properties of the ligand which are also effective in stabilising negative charge, e.g. polarisability: the more polarisable a ligand the greater will be its preference for the apical position. This may be an important factor when comparing first and second row elements bonded to phosphorus.

π Interactions between ligand and phosphorus have also been predicted to have some bearing on the preference of a ligand for a particular position in a TBP.[59b-f,61] Ramirez, Ugi and their co-workers[59d,e] have shown from their semi-empirical calculations that phosphoranes are stabilised appreciably by donation of electron density from the ligand π-orbitals into the phosphorus d-orbitals. This π interaction is greater from an equatorial position and so apical ligands must be able to accommodate more negative charge. This again explains the

experimentally observed preference rule and the greater length of the apical bonds, since their multiple bond character is less. It also follows that the greater the π-donor ability of a ligand, the less that ligand will prefer the apical position.

This bonding model, then, predicts that d orbital interactions play a major rôle in determining ligand positions in a TBP.

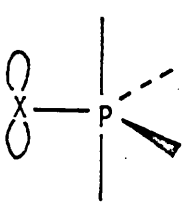
An alternative theoretical approach to bonding in phosphoranes is that of Hoffmann, Howell, and Muetterties.[61] In their M.O. treatment, they came to the same conclusions as other workers on the preference of the more electronegative elements for the apical positions but differed from Ugi[59b-f] in that the rôle of the phosphorus d orbitals in determining ligand arrangement in a TBP was considered to be much smaller. π Interactions between ligand donor orbitals and phosphorus were considered in terms of destabilising interactions between the ligand π system and the phosphorane framework σ orbitals and stabilising interactions between the ligand π system and the phosphorus d orbitals. For ligand acceptor orbitals, the only chemically significant interaction is that between the acceptor orbital and the framework σ orbitals: this is a stabilising interaction.

The main conclusions that arose are outlined below.

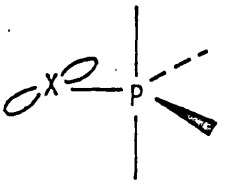
(a) Although there is probably a significant degree of p-d π-bonding in phosphoranes, the difference between apical and equatorial p-d π-bonding appears to be a smaller effect than interactions of ligand π systems with framework σ orbitals, i.e. the preference of a ligand for a particular position is determined mainly by the latter interaction.

(b) Interaction between a ligand π system and framework σ orbitals is greater for apical than for equatorial substituents. Hence, it follows that π-acceptors will prefer apical sites and π-donors equatorial sites.

Some predictions were also made concerning the preferential orientation of ligands with single π systems available for interaction with the phosphorus. It was shown that, while there is no preferential orientation of the π-orbital in an apical position, an equatorial π-acceptor will prefer to have its acceptor orbital perpendicular to the equatorial plane (63), whereas a π-donor will prefer to have its donor orbital in the equatorial plane (64).



(63)



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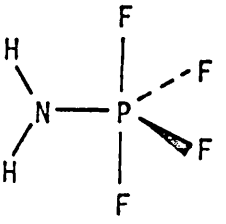


(65)

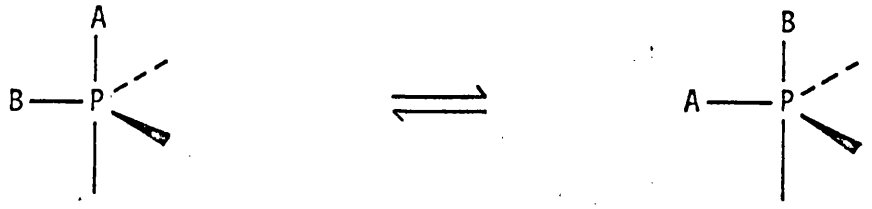
The magnitude of this differential donor-framework π-bonding effect was calculated for the amino group of (65) as between 0.28 and 0.78 e.v. Some experimental observations concerned with this effect are discussed in sections 4.2 and 4.11.

3.2 Apicophilicity Values of Ligands.

In view of the probable importance of p-d π interactions, π-σ interactions, polarisability and steric effects (see section 7) in determining the preference of a ligand for a particular position in a TBP, it seems rather naïve to use electronegativity as the only criterion of ligand arrangement in acyclic phosphoranes. In order to take into account all of the other possibly relevant factors, the use of the term

'apicophilicity' has been suggested.[59d] This means the preference of a particular ligand for the apical, as opposed to the equatorial, position. Its use avoids any preconceptions as to why a ligand prefers to occupy a particular position: it is purely an empirical term.

Apicophilicity values are always relative to other ligands since, if one ligand moves from an equatorial to an apical position, another ligand necessarily travels in the reverse direction. The energy difference between the TBP's (66) and (67) is thus a measure of the apicophilicity difference between A and B.



(66) (67)

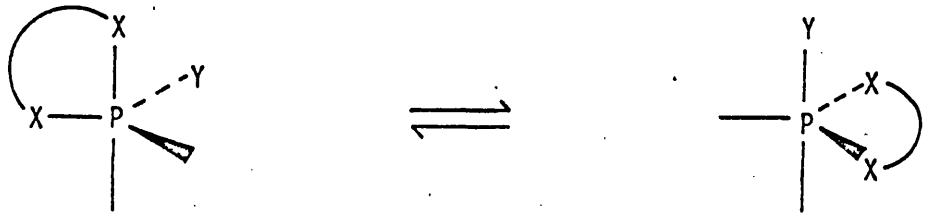
3.3 Applications and Limitations of Apicophilicity Values.

Apicophilicity values, in theory, provide a way of predicting the energetically most favourable arrangement of ligands about the phosphorus in any given acyclic phosphorane. If quantitative data on the relative apicophilicities of various ligands could be obtained, then the most stable arrangement of ligands in any given phosphorane could be predicted by reference to an 'apicophilicity scale'.

In determining an apicophilicity scale it would be expedient if the relative importance of the various factors which make up the overall apicophilicity value could also be determined since, if any of the

individual factors vary with environment, i.e. with the other groups on the phosphorus, an assessment of the effect on the overall apicophilicity value could be determined.

For cyclic phosphoranes, a knowledge of the energy required to move various rings into the ee position of the TBP is also necessary in predicting relative phosphorane stability. Small rings prefer to span the ae position of the TBP but this arrangement may sometimes conflict with apicophilicity considerations. Thus, if Y is more apicophilic than X,



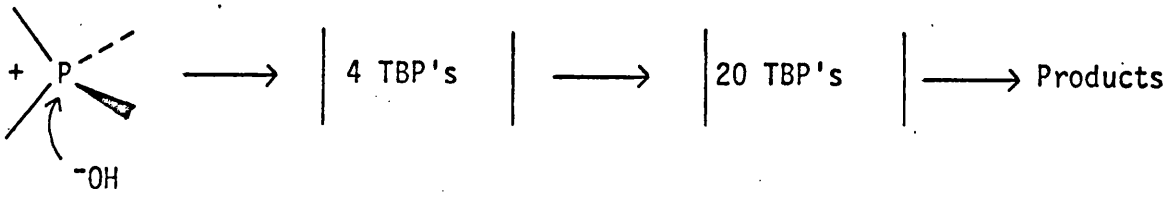
(68) (69)

(68) is favoured from ring strain considerations but apicophilicity values would predict (69) as the low energy structure. In this case, then, the preferred arrangement of ligands is dependent upon the balance of these two opposing terms and a knowledge of ring strain is required before this arrangement can be determined.

The relevance of apicophilicity and ring strain data is mainly in the field of nucleophilic substitution at tetraco-ordinated phosphorus. An assumption made by most workers in this field is that the nucleophile enters into the apical position of the TBP and the leaving group departs from the apical position.[4,7] This will also be assumed in the following discussion.

As stated in section 1.1, there is a great deal of evidence to suggest that many phosphoranes formed during substitution reactions have

a finite lifetime. If this is the case, nucleophilic attack at the faces of the tetrahedron results in the formation of a maximum of four TBP's. These initial TBP's may be sufficiently long-lived to undergo BPR to form other TBP's which may also pseudorotate and so there is the possibility of formation of up to twenty phosphoranes (scheme 4). Any

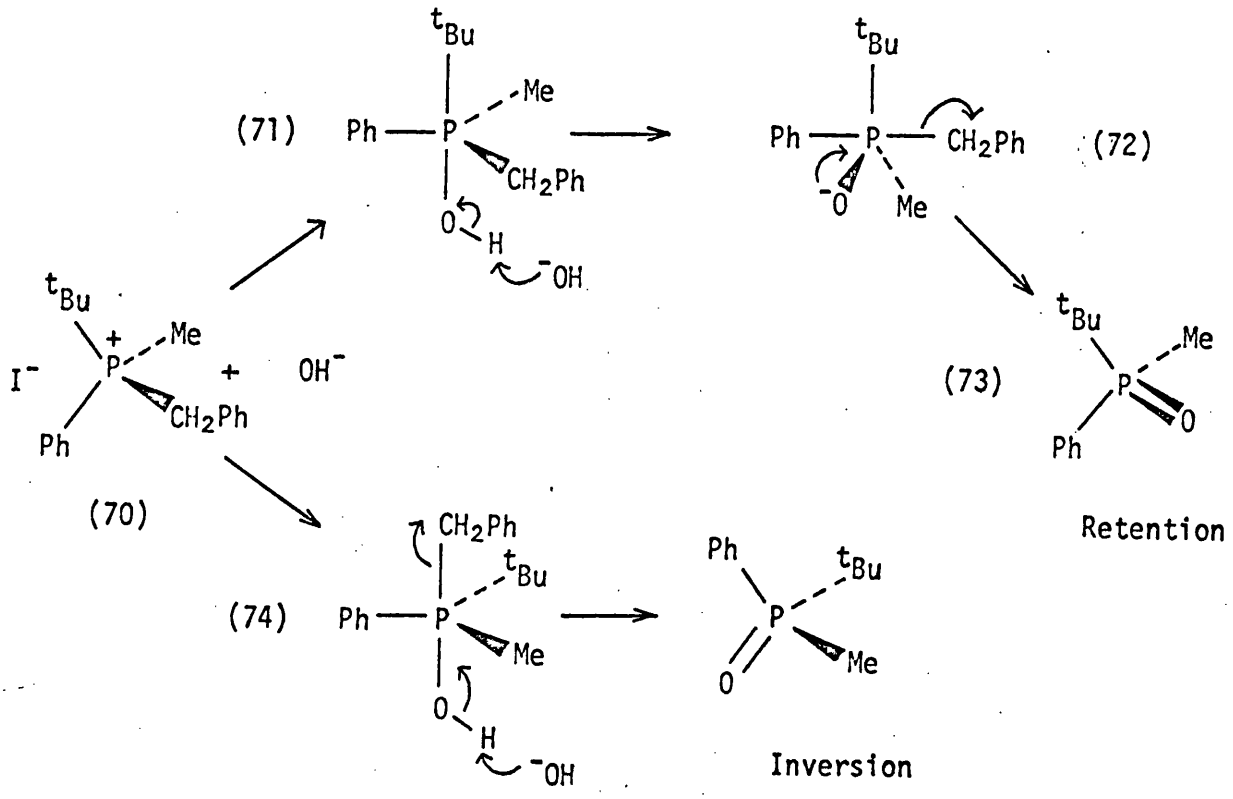


SCHEME 4

of these intermediate phosphoranes may be capable of decomposing to products and so, if the entire reaction scheme is considered, there is the possibility of the formation of a very wide range of products. In order to simplify this scheme, the main requirement is a knowledge of the relative stabilities of the phosphorane intermediates. An apicophilicity scale could possibly provide this information and hence enable the most likely reaction pathway to be determined. However, apicophilicity data provide information only on this one aspect of the reaction pathway. This information alone will enable predictions concerning substitution routes to be made only if the following two assumptions hold.

(a) Phosphorane formation is under thermodynamic and not kinetic control, i.e. the most stable phosphorane is formed the fastest. This appears to be so in most cases but there are some important exceptions, e.g. where bulky ligands are bonded to phosphorus.

De'ath and Trippett[73] have shown that the phosphonium salt (70) undergoes alkaline hydrolysis to yield (73) with predominant retention of



configuration. This was explained in terms of attack of the nucleophile opposite the t-butyl group to form the phosphorane (71). BPR of (71) to (72) and loss of the anion from (72) gives the product (73). Apicophilicity considerations would predict initial formation of (74) by attack of hydroxide directly opposite the leaving group.

In this case, then, the direction of attack is determined, not by apicophilicity considerations but by the ease of approach of the incoming nucleophile.

(b) Formation of products derives from the most stable phosphorane, i.e. relative leaving group abilities do not affect the reaction pathway. This will generally be so since the most apicophilic group is usually the best leaving group but there are some important exceptions, e.g. fluorine is more apicophilic than chlorine but is a poorer leaving group. In this case leaving group ability would be expected to play a part in determining the reaction pathway.

Therefore, in order that accurate predictions concerning reaction pathways may be made, apicophilicity data must be complemented by information on these other two aspects of the reaction pathway.

3.4 Variable Apicophilicity.

The predictive use of apicophilicity values depends to a large extent upon the degree of variation of an apicophilicity value with environment. If the variation is large, the data become virtually useless for predictive purposes since results obtained for one system do not necessarily apply to others.

The individual factors which make up the overall apicophilicity value would be expected to vary with environment, e.g. the magnitude of the steric factor will depend upon the size of the other groups bonded to phosphorus (see section 7), while inductive and mesomeric interactions between a ligand and phosphorus might also be expected to vary with the nature of the other ligands.[74,75] However, unless the relative importance of the individual factors is known, the effect of any variation on the overall apicophilicity value cannot *a priori* be determined.

3.5 Determination of Apicophilicity Values.

There exist in the literature three general methods for determination of ligand apicophilicities. These are described below.

(a) BPR rates are obviously dependent upon the energy difference between the interconverting phosphoranes and systems have been designed to enable the BPR rate to be monitored by d.n.m.r. spectroscopy[62-64,76,77] or, in the case of higher energy B.P.R.'s by 'conventional' kinetic

determinations.[78] From a knowledge of the BPR rate the energy difference between the phosphoranes can be determined and hence information on apicophilicities can be obtained.

Apicophilicity values derived from such kinetic experiments will differ slightly from the true, thermodynamic values. This point is discussed in section 3.6.

(b) From the discussion (see section 3.3) concerning the application of apicophilicity data to predictions of substitution reaction pathways, it follows that a prior knowledge of the reaction pathway may give information on relative apicophilicities. Thus a knowledge of reaction products and stereochemistry has enabled DeBruin and his co-workers[79] to build up a semi-quantitative apicophilicity (the authors actually use the term 'kinetic axiophilicity') scale for a range of common groups.

(c) A qualitative assessment of ligand apicophilicities can be made by investigating the ground state ligand arrangement of asymmetrically substituted phosphoranes.[22,80-82] This is usually accomplished by cooling the sample until all BPR's are slow on the n.m.r. time scale. The ligand arrangement in the 'frozen' structure can then be determined by analysis of the n.m.r. spectrum.

This method has led to the formation of a rather limited apicophilicity scale[81] but is not particularly useful for obtaining quantitative data.

In the work described in this thesis, apicophilicity values were determined by evaluation of BPR rates using d.n.m.r. spectroscopy. Rate data were obtained by measurement of the coalescence temperature (Tc) of signals of equal intensity and free energies of activation were derived from the coalescence temperatures by application of the Gutowsky-Holm

equation (75).[83]

$$k_c = \frac{\pi\Delta\nu}{\sqrt{2}} \qquad (75)$$

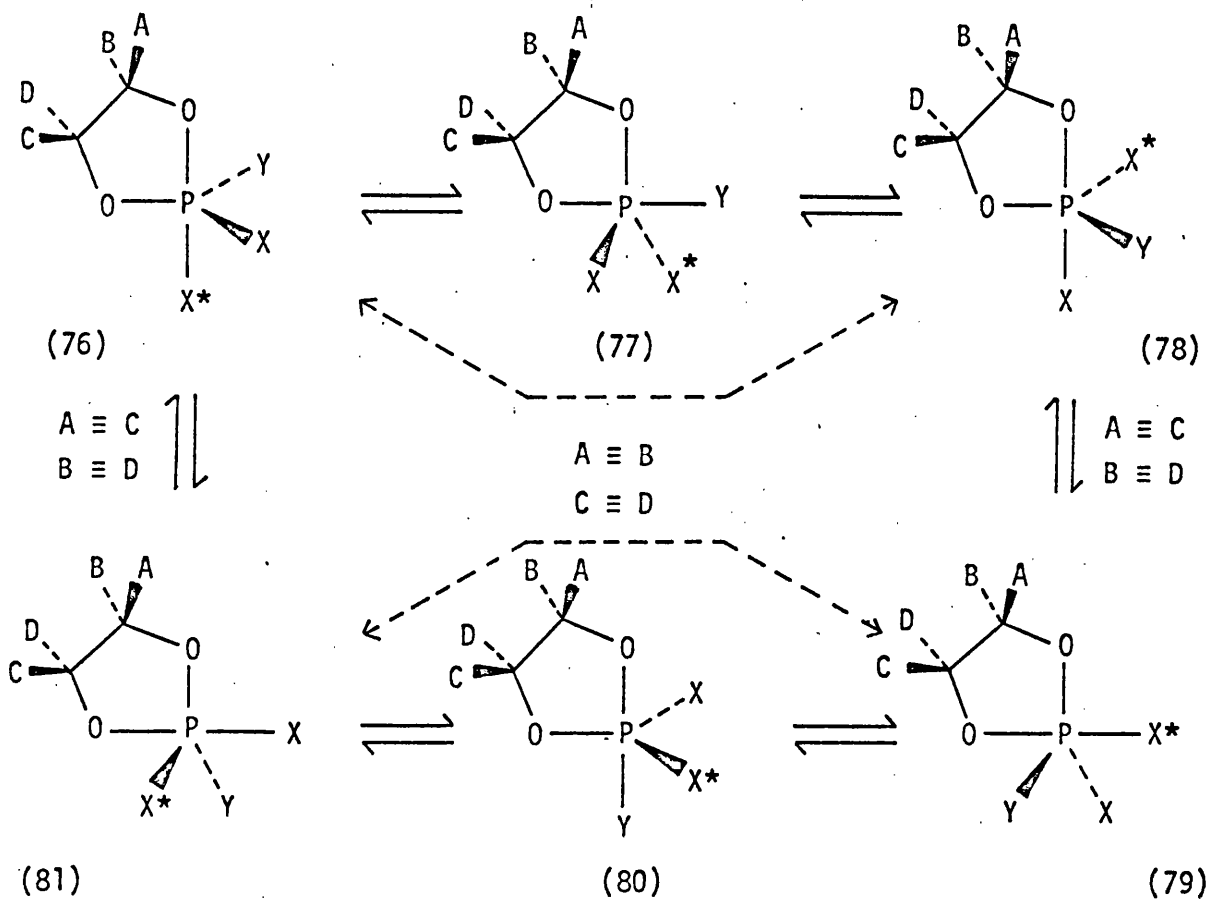
k_c = rate constant at coalescence

$\Delta\nu$ = maximum frequency separation of signals below coalescence

The comparison of ΔG^* values determined at different temperatures is valid only if the entropy of activation for a BPR process is zero. Estimates of ΔS^* values have been subject to a large experimental error but the results of Gorenstein[25b] and Wolf and his co-workers[78] do indicate that the values are very small.

3.6 Phosphorane Systems Used for D.N.M.R. Analysis.

Most of the apicophilicity data which are described in this thesis have been obtained from the following four general systems.



SCHEME 5

(1) With reference to scheme 5, A-D are the groups giving rise to the n.m.r. signals under investigation, e.g. methyl, trifluoromethyl, and X and X* are identical ligands. With the restriction that the dioxaphospholan ring remains ae, the molecule can undergo the BPR's shown. BPR's which involve placement of a small ring in the ee position without any compensating gain in the apicophilicities of the groups occupying the apical positions are known to be high energy processes[62,63] and are certainly slow, on the n.m.r. time-scale, at the temperatures used for monitoring the BPR's shown. If all the BPR's are fast, on the n.m.r. time scale, groups A-D

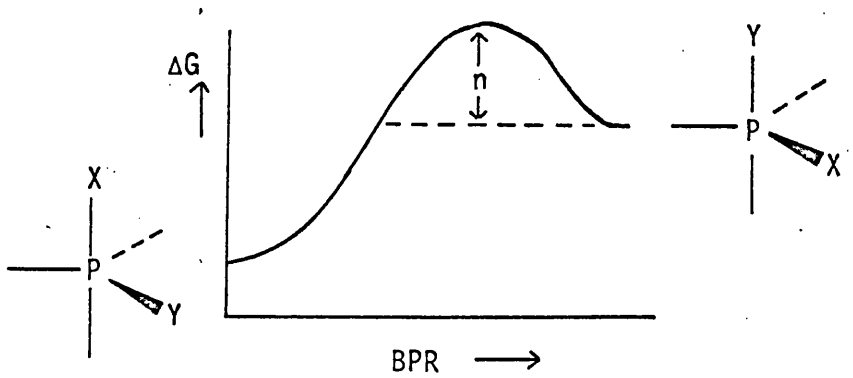
are all equivalent since the BPR's equilibrate these groups as indicated. Structures (76), (78), (79) and (81) are all identical, apart from the interchange of equivalent groups, and have identical energies, i.e. they are topomeric.[84] Direct BPR's between topomeric species have never been slowed, on the n.m.r. time scale, even at very low temperatures, and modern calculations[21,59d,e,61,72] indicate an upper limit to the BPR barrier of about 4 kcal mol^{-1}.

Considering the relative apicophilicities of groups X and Y, two situations can exist.

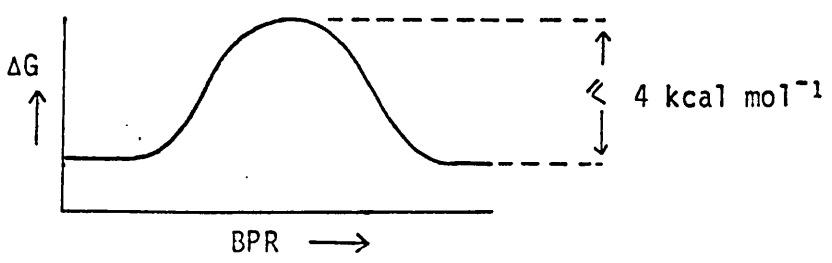
(a) X is more apicophilic than Y.

In this case (77) and (80), where Y occupies an apical position, are the high energy species. If the sample is cooled, a situation may arise where the topomeric BPR's are fast, on the n.m.r. scale, but BPR's through (77) and (80) are now slow. Thus A≡C and B≡D only, and the single absorption of the groups A-D now splits into two signals of equal intensity. From the coalescence temperature, a value of ΔG^* for the

(82)



(83)



BPR between a phosphorane with X in an apical position and a phosphorane with Y in an apical position can be determined.

This ΔG^* value overestimates the true apicophilicity difference between X and Y by n kcal mol^{-1} in (82) but since n for a topomeric BPR (83) is no greater than 4 kcal mol^{-1}, the overestimation in the case of (82) is unlikely to be more, and will probably be less, than this value.

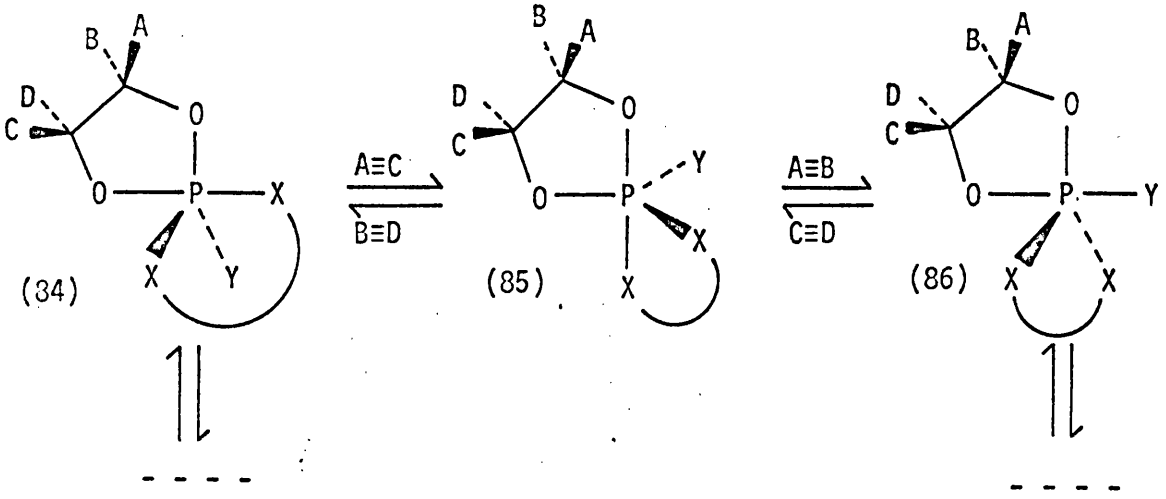
(b) Y is more apicophilic than X.

In this case (77) and (80) are the low energy structures and when the sample is cooled, BPR's which place X in an apical position may eventually become slow and the molecule will then be 'frozen' in a structure with Y in an apical position. When this happens, A≡B and C≡D only, and from the coalescence temperature a value for the apicophilicity difference between X and Y can be obtained. This value is, again, an overestimation of the true apicophilicity value.

The system may be extended by, for example, keeping X constant and varying Y. This enables a measurement of the relative apicophilicities of Y and the groups that replace Y to be made. However, in this case, the apicophilicity values are underestimated, since, for similar processes, an increase in ΔG results in a decrease in the difference between ΔG and ΔG^*.

This is a general rule for all of the systems to be discussed: an intramolecular comparison overestimates, while an intermolecular comparison underestimates, the true apicophilicity difference.

(2) The system used for spirophosphoranes is basically the same as system (1) (only half of the symmetric cycle is shown in scheme 6).



SCHEME 6

A-D are again the groups under investigation in the n.m.r. spectrum. (85) may undergo two BPR's: (84)⇌(85), which is a topomeric BPR and equilibrates A with C and B with D, and (85)⇌(86), which equilibrates A with B and C with D. The topomeric BPR is always fast, on the n.m.r. time scale, but the BPR (85)⇌(86) is likely to be of high energy since the XX ring moves into the ee position. [A BPR which places the dioxaphospholan ring in the ee position need not be considered since it has the same stereochemical consequences as the much lower energy topomeric BPR (84)⇌(85).] It is the slowing of the BPR (85)⇌(86) which can be monitored by d.n.m.r. spectroscopy and a value obtained for the difference in energy between (85) and (86). This difference is made up from two factors, (a) the apicophilicity difference between groups X and Y and (b) the energy required to move the XX ring into the ee position. If Y is now replaced by other groups, estimates of the relative apicophilicities of these groups can be obtained since the strain factor remains essentially constant.

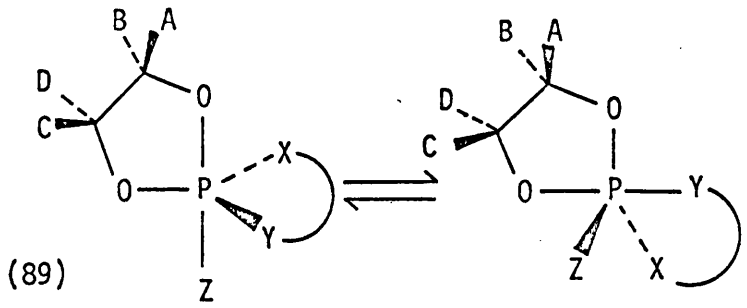
For the special case where Y = X, there is no apicophilicity change involved in the BPR and hence a value for the ring strain energy can be obtained.

(3) In this system, in order to equilibrate fully groups A-D both rings must be moved, in turn, into the ee position. The BPR's necessary for complete equilibration are shown in scheme 7.

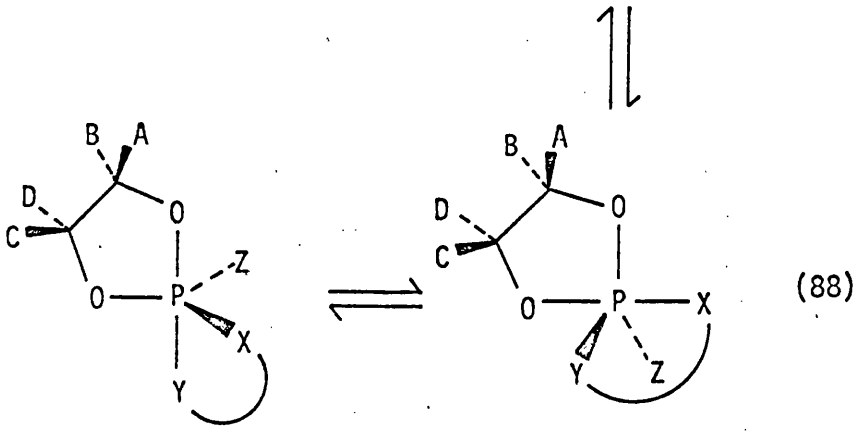
If Y is more apicophilic than X, (87), (90), and (93) are the low energy topomers and (89) and (91) are the high energy species since they each have a ring in the ee position. If BPR's through (89) and (91) are slow, on the n.m.r. time scale, none of the groups A-D are equivalent and the n.m.r. spectrum will therefore show four absorptions of equal intensity. If BPR through either (89) or (91) becomes fast, coalescence to two signals will be observed, and when BPR's through both high energy structures are fast, the n.m.r. spectrum of A-D will consist of a single absorption.

It is not usually possible to tell, merely from the n.m.r. spectrum, whether the coalescence of four to two absorptions is due to fast BPR through (89) or (91). In practice, however, the molecule is designed such that the energy required to place a ring in the ee position differs considerably for each ring. In this way the 'four to two' and the 'two to one' coalescences can be ascribed to the appropriate rings with a high degree of certainty.

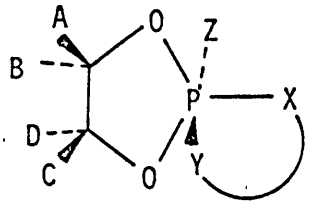
As with system (2), replacement of Z by other groups allows a series of relative apicophilicity values to be built up and for the special case where Z = Y, the energy required to move the XY ring into the ee position can be obtained from the appropriate coalescence temperature.



(89) (90)



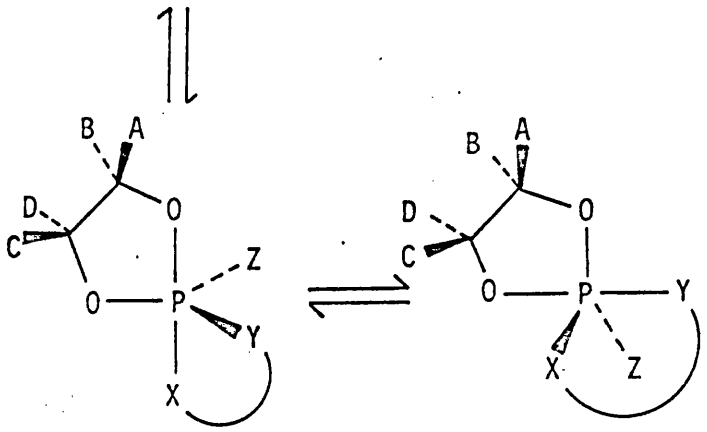
(87) (88)



(91)

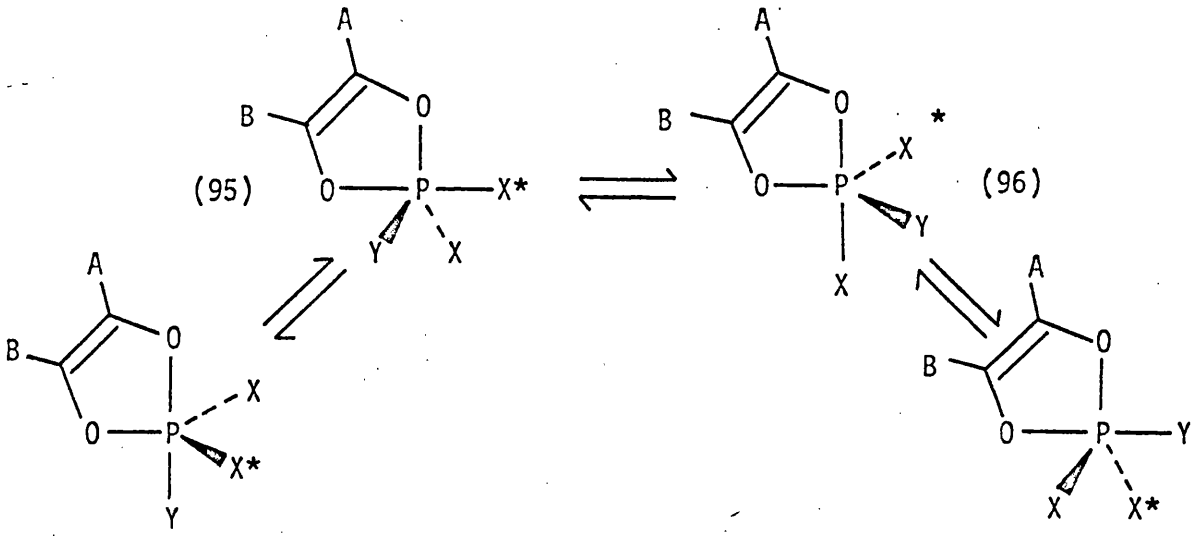
(87) $\overset{A \equiv D}{\underset{B \equiv C}{\rightleftharpoons}}$ (90)

(87) $\overset{A \equiv C}{\underset{B \equiv D}{\rightleftharpoons}}$ (93)



(92) (93)

SCHEME 7



(94) (97)

SCHEME 8

(4) For this system, A and B are the groups giving rise to the signal under investigation in the n.m.r. spectrum.

If Y is more apicophilic than X, the topomeric species (94) and (97) are the low energy TBP's and equilibration of A with B proceeds by the route shown in scheme 8, each X group being placed, in turn, in the apical position. (95) and (96) are the high energy TBP's and as the sample is cooled, the equilibration process via these species may eventually become slow. When this happens, the single absorption due to A and B will split out into two signals of equal intensity and from the coalescence temperature, the relative apicophilicities of X and Y can be determined. As before, this system can be extended by varying X or Y to enable a series of relative apicophilicity values to be constructed.

For the situation where X is more apicophilic than Y, (95) and (96) are the low energy species and A and B are equilibrated by the topomeric

BPR connecting (95) and (96). The system is therefore useless for d.n.m.r. study since equilibration of A with B requires no change of groups in the apical position.

3.7 Accuracy and Limitations of the D.N.M.R. Method for Determination of Ligand Apicophilicity Values.

Accuracy.

This will depend mainly upon the following factors.

(a) The accuracy of the Gutowsky-Holm equation in deriving ΔG^* values from coalescence temperatures.

The use of this equation is unlikely to introduce any significant error into the results since, for systems where coalescence of signals of equal intensity is observed, the Gutowsky-Holm equation has been shown[85] to be almost as accurate as a complete line shape analysis procedure.

(b) The accuracy of the temperature measurement.

The total error in the measurement of a coalescence temperature is ±5°, which corresponds to an error in the ΔG^* value of ±0.3 kcal mol^{-1}.

(c) The accuracy with which the maximum frequency separation of the exchanging groups can be determined.

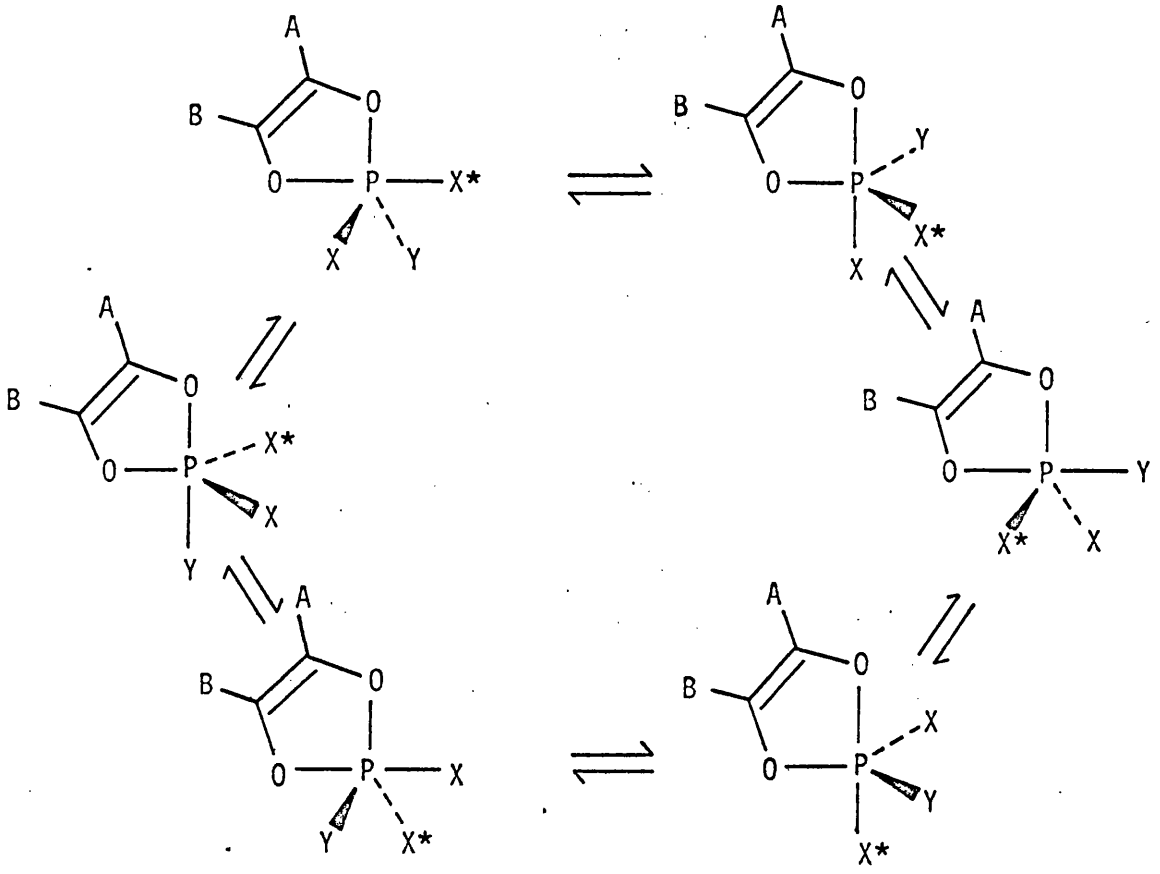
Errors may be introduced into the results in cases where it is impossible to measure the maximum frequency separation of exchanging groups. This sometimes occurs when the coalescence temperature is near to the lower limit of operation of the n.m.r. spectrometer but is only a very minor source of error since even an inaccuracy of 50% in the frequency separation value leads to an error of only about 0.2 kcal mol^{-1} in the ΔG^* value.

(d) The deviation of the ΔG^* value from the true, thermodynamic apicophilicity value.

Since the measured ΔG^* value is always an under- or overestimate of the true apicophilicity value this does introduce errors into the results. However, as stated in section 3.6, these errors are likely to be small and in many cases can be determined by using two different n.m.r. systems to encompass the true apicophilicity value.

(e) The accuracy with which a ΔG^* value can be assigned to a specific BPR.

In many cases, equilibration of groups can be achieved by several BPR routes. Some of these pathways may be of much higher energy than others and so can be neglected but, because of the circular nature of



SCHEME 9

most interconversion pathways, equilibration can occur by at least two routes of identical energy, e.g. in scheme 9, equilibration of A with B can take place by the two equivalent pathways shown. Hence, if apicophilicity values are calculated using only one interconversion pathway, the ΔG^* value will be in error by an amount equivalent to a factor of two in the measured rate constant, i.e. about 0.24-0.6 kcal mol^{-1} depending upon the coalescence temperature.

For the results described in the following sections, each ΔG^* value has been corrected for the multiplicity of the lowest energy interconversion pathway. Further correction for pathways of higher energy is not possible unless assumptions are made concerning the relative energies of the pathways.

Limitations.

The major limitation of the d.n.m.r. method is that there is always the possibility that the n.m.r. changes are not due to a slowing of a BPR process but to some other phenomenon. The more likely alternative mechanisms are described below.

(a) Coalescence may be due to an accidental magnetic equivalence of the groups giving rise to the n.m.r. spectrum. In order to distinguish this from a coalescence due to a rate process it is necessary to measure the line widths of the signals as coalescence is approached. If a true rate process, the line widths will greatly increase whereas there should be no variation for accidentally equivalent peaks.

(b) Perhaps the most likely alternative mechanism is an irregular isomerisation of the phosphorane.

A regular isomerisation process takes place with no bond rupture and with no change in co-ordination number at the phosphorus; an irregular isomerisation process does not.

The possibility of isomerisation by an irregular process involving a hexaco-ordinated phosphorus atom has been suggested by Musher[86] but there are no reported examples of the occurrence of such a mechanism other than in some fluorophosphoranes.[87,88] However, several irregular rearrangement processes, where the phosphorane dissociates into ions, have been reported.[11,37,42] The method used by Ramirez[11,37,42] to detect the presence of ionic species is to examine the variation in ^{31}P n.m.r. chemical shift with solvent. If the equilibrium (98)$\rightleftharpoons$(99) does exist, increase in solvent polarity would be

$$\underset{(98)}{PX_5} \rightleftharpoons \underset{(99)}{PX_4^+ + X^-}$$

expected to favour the ionic form (99) and so the ^{31}P n.m.r. chemical shift in the acidic hexafluoroisopropanol, for example, will show a downfield shift relative to the ^{31}P n.m.r. chemical shift in a non-polar solvent. However, even if virtually all of the compound exists in the quinquecovalent form (98), if the equilibrium with the ionised form (99) is fast, on the n.m.r. time scale, the n.m.r. spectrum of the phosphorane will show equivalence of groups due to this irregular mechanism.

In the results described in later sections, the approach to this problem has been that the ^{31}P n.m.r. spectra of phosphoranes which are stable to hydrolysis have been determined in different solvents, including hexafluoroisopropanol. Where this was not possible, the coalescence temperature data have been interpreted in terms of a regular (BPR) mechanism where the results of a series of related compounds form a regular pattern. With the accumulation of apicophilicity data, it doubtless will become easier to decide whether a result is meaningful, in

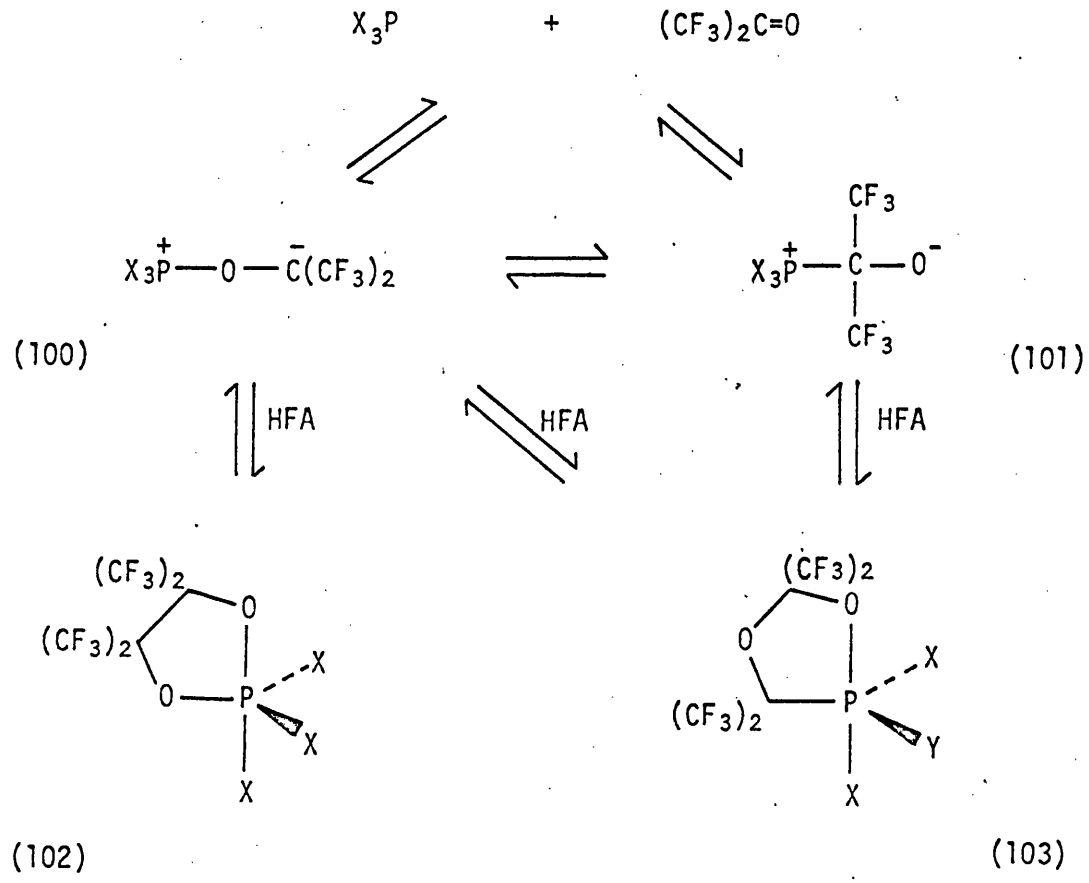
apicophilicity terms, or not.

(c) Coalescence may also be due to slow rotation around a P-N or P-S bond (see section 4.11). In phosphoranes which contain a P-S or P-N bond it is sometimes difficult to decide whether the spectral changes are due to a BPR process or a slowing of P-N(S) rotation. This confusion arises only when the energies of the two processes are similar and ambiguous results can normally be checked by recourse to other systems where the energies of the two processes are substantially different.

4. D.N.M.R. STUDIES OF SOME OXYPHOSPHORANES.

4.1 Reaction of Hexafluoroacetone with Tervalent Phosphorus Compounds.

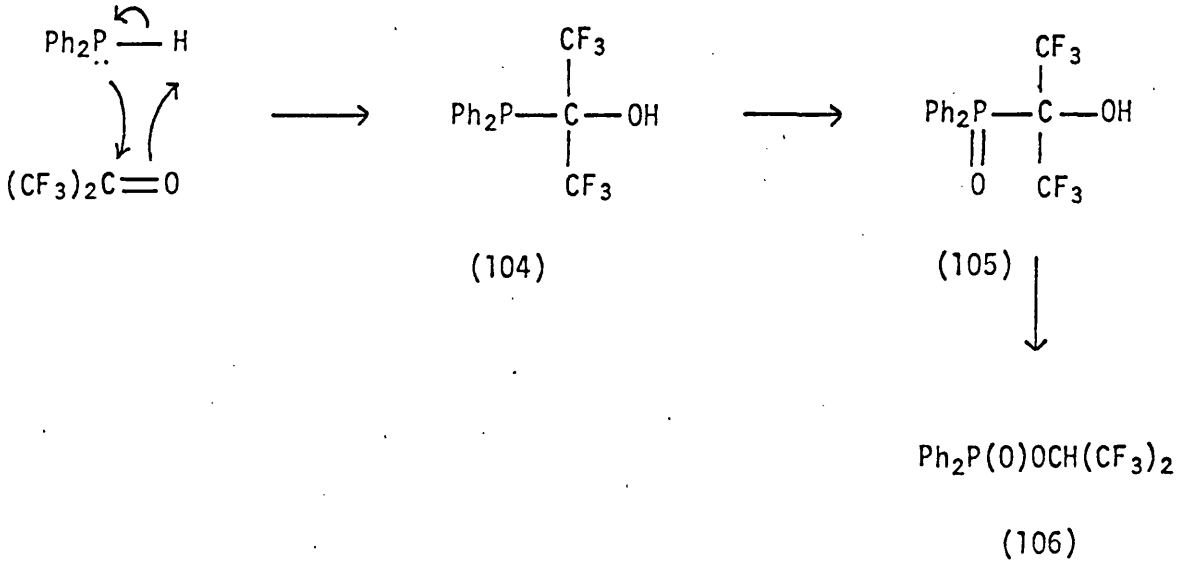
Most of the phosphoranes to be described were prepared by the reaction of two equivalents of HFA with one equivalent of the tervalent phosphorus compound. The phosphoranes so formed have either the 1,3,2-dioxaphospholan (102) or the 1,4,2-dioxaphospholan (103) structure (other products are obtained when the tervalent phosphorus compound contains an α-hydrogen atom or a group susceptible to nucleophilic attack; see sections 4.9 and 4.12). These two products can arise by the routes shown in scheme 10.



SCHEME 10

Ramirez[37] has suggested that the reaction to form (102) proceeds *via* the betaine (100) but it is not known whether this is formed directly from reactants or by isomerisation of (101).

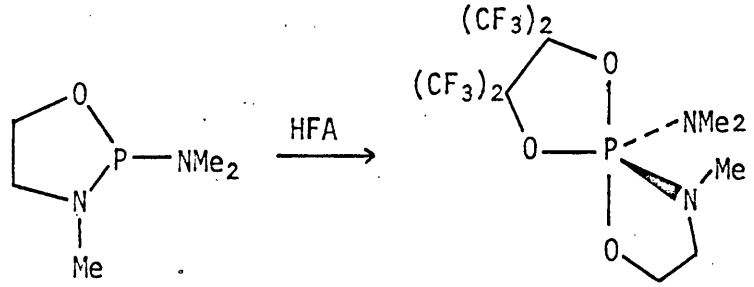
Janzen and Vaidya[89] have investigated the reaction of HFA with diphenylphosphine and concluded that attack of the phosphorus occurs at the carbonyl carbon, since spectral evidence indicated initial formation of the phosphine (104). (104) was readily oxidised to (105), which



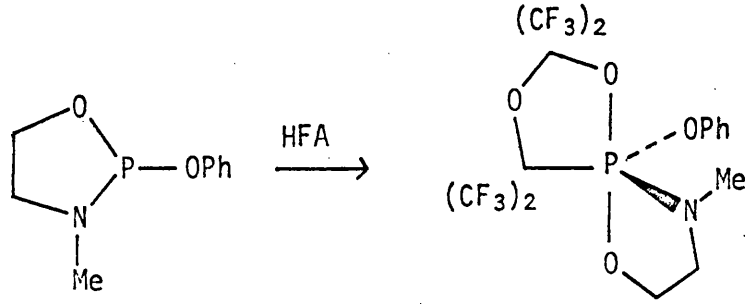
(104) (105) $Ph_2P(O)OCH(CF_3)_2$ (106)

rearranged in the presence of tetrahydrofuran to (106). (104) was stable under the reaction conditions and this could be construed as evidence against the formation of (100) *via* (101). This comparison is not strictly valid, however, because isomerisation in the betaine form (101), as opposed to the uncharged form (104), may very well be easier.

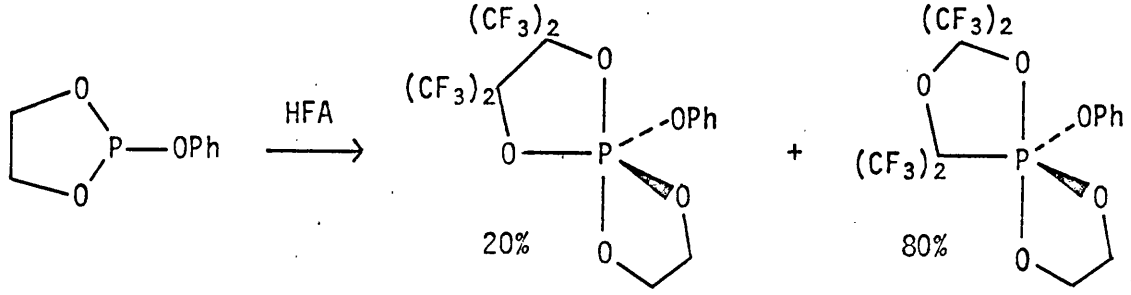
The 1,3,2-dioxaphospholan (102) is the product usually obtained but initial formation of (103) is often indicated by precipitation of a white solid which rapidly redissolves. Conversion of (103) to (102) presumably occurs by dissociation of (103) to (100) or (101) and subsequent recyclisation.



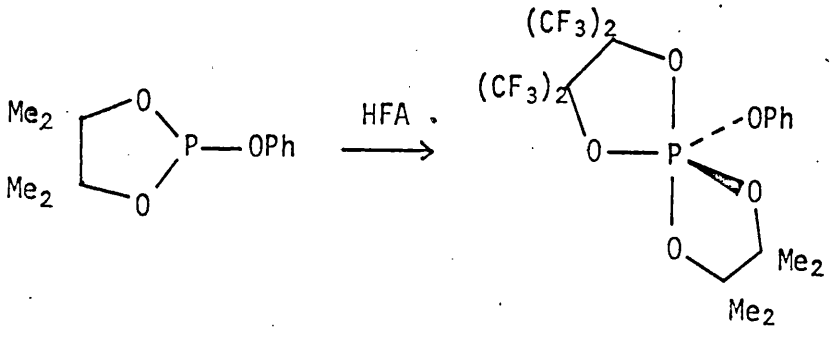
(107)



(108)



(109)



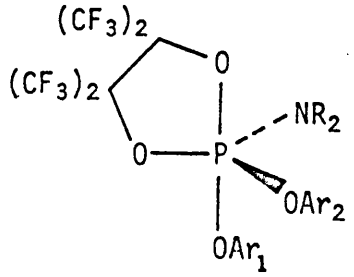
(110)

In some cases, (103) is obtained as a stable product, either by itself, as for (108) or as a mixture with (102), e.g. (109).[90]

It is difficult to see any controlling factors that decide which phosphorane shall be formed but a steric effect may be important here because both (108) and (109) have a very bulky carbon ligand bonded to phosphorus and would thus be expected to become destabilised, relative to the alternative 1,3,2-dioxaphospholan structure, as the size of the other groups on the phosphorus increases. This appears to be so from comparison of (107) with (108) and (109) with (110).

4.2 Reaction of Some Diaryl Phosphoramidites with Hexafluoroacetone.

The phosphoranes (112)-(118), of general formula (111) were prepared by reaction of two equivalents of HFA with one equivalent of the phosphoramidite at -78°.



(111)

	(112)	(113)	(114)	(115)	(116)	(117)	(118)
NR_2	Me_2N	Me_2N	Me_2N	$[CH_2]_4N$	$(^iPr)_2N$	MePhN	Ph_2N
Ar_1	Ph	Ph	p-Br-Ph	Ph	Ph	Ph	Ph
Ar_2	Ph	p-Br-Ph	p-Br-Ph	Ph	Ph	Ph	Ph

Adduct	^{19}F Tc/°C	$\Delta\nu$/Hz[c]	ΔG^*/kcal mol^{-1}[d]	^{31}P δ[e]
(112)	-58[a]	156	9.7	+54.5
	< -110		< 7	
(113)	-58[b]	185	9.6	+54.5
(114)	-57[b]	174	9.7	+54[f]
(115)	-8[a]	186	11.9	+56[a]
	-100	127	7.8	
(116)	-31[a]	188	10.9	+51
	-62	94	9.7	
(117)	-42[a]	156	10.4	+57
	-51	56	10.5	
(118)	-43[b]	195	10.3	+60
	-94	130	8.1	

[a] In toluene. [b] In ether-light petroleum. [c] Maximum frequency separation below coalescence. [d] Corrected for multiplicity of lowest energy interconversion pathway. [e] P.p.m. relative to 85% H_3PO_4; in $CDCl_3$ unless otherwise stated. [f] In carbon tetrachloride.

TABLE 1

The phosphoranes correspond to an 'n.m.r. system type 1(a)' molecule and the d.n.m.r. data are explained on the basis that oxygen ligands are more apicophilic than nitrogen ligands. This is to be

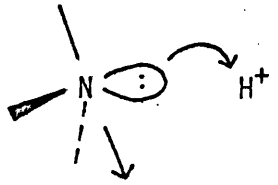
expected[59b-f,61] on the grounds (a) that oxygen is more electronegative than nitrogen and (b) that the π-donor ability of the amino group is greater, and the work of Trippett[63] and DeBruin[79] indicates that this is indeed the case. The X-ray analysis of the phosphorane (5)[18] also shows that oxygen is more apicophilic than nitrogen, at least for compounds where the relevant ligands form part of a ring. The energy barrier to the BPR that places the amino group in an apical position was investigated by d.n.m.r. spectroscopy and the data are shown in table 1.

Considering the ΔG* values from the higher energy coalescence temperatures (the additional spectral changes observed for some of the compounds are explained later in this section), the points that are evident from the data are the following.

(a) The oxygen ligands are more apicophilic than the nitrogen ligands by 10-12 kcal mol^{-1} but since this intramolecular comparison overestimates the true apicophilicity value by a small amount, the results seem to be in agreement with those of Oram and Trippett[63] who obtained an underestimated value of 7-8 kcal mol^{-1} for the difference in apicophilicity between the phenoxy and dimethylamino groups. As was stated earlier, this rather large difference in apicophilicity is probably a consequence of the lower electronegativity and greater π-donor ability of nitrogen. However, the data give no indication of the relative importance of these two effects.

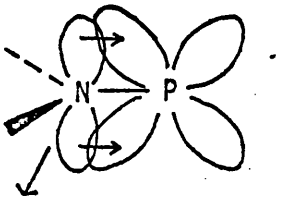
(b) The ΔG* values are virtually independent of any variation in substitution at the nitrogen or in the aromatic ring. Comparing (115) and (116), steric effects do not appear to be particularly important, while, comparing the results as a whole, there seems to be no correlation between the apicophilicity of an amino group and the basicity of the corresponding secondary amine, e.g. there is a difference between the ΔG*

values for (112) and (118) of only 0.6 kcal mol^{-1} although the pKa values for the corresponding secondary amines differ by almost 10.[91] It was expected that an increase in the basicity of the amino group would increase its p-d π-donor ability and hence decrease its apicophilicity. While it is true that donation of the nitrogen lone pair to a proton (119) and donation into a phosphorus d orbital (120) may not be strictly comparable processes, nevertheless this lack of correlation was surprising.



sp³

(119)



sp²

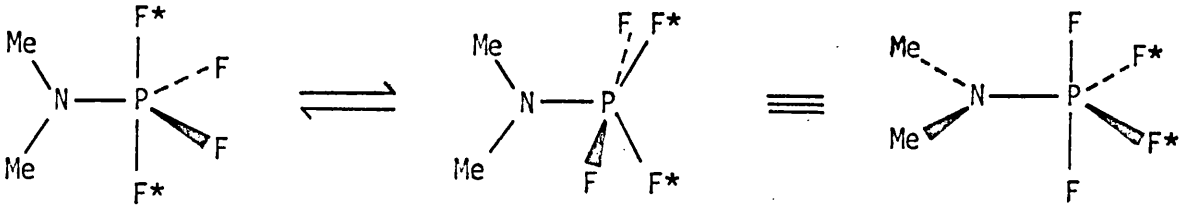
(120)

The insensitivity of apicophilicity values to substitution in a phenyl ring has also been observed by Oram and Trippett,[63] where the lack of variation is even more remarkable because the phenyl ring is bonded directly to the phosphorus.

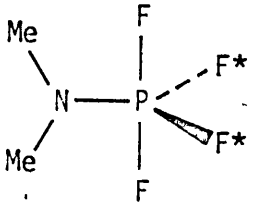
The adducts are all relatively stable, crystalline compounds and can be recrystallised from ethanol. The ^{31}P n.m.r. chemical shifts were measured in the solvents shown and also, for several of the compounds, in hexafluoroisopropanol. The shifts were virtually independent of solvent and this, together with their hydrolytic stability, suggests that the n.m.r. changes are not due to an irregular isomerisation process. The ^{19}F d.n.m.r. behaviour of (117) was also independent of concentration and virtually unaffected by addition of hexafluoroisopropanol. This again indicates that an irregular process is not occurring.

The lack of variation in the coalescence temperature of (117) on addition of hexafluoroisopropanol also suggests that the nitrogen is only very weakly basic, since protonation by the acidic alcohol would give an ammonium ligand which would be expected to be appreciably more apicophilic than the amino group. This low basicity is presumably a consequence of substantial electron donation from the lone pair of the amino group into the phosphorus d orbitals.

The positive values for the ^{31}P n.m.r. chemical shifts indicate quinquecovalent character[34] but no further attempt has been made to correlate shifts with the electronic properties of the ligands since the actual effect of ligand electronic interactions with phosphorus, in terms of a ^{31}P n.m.r. chemical shift, seems to be uncertain. It appears to be undecided, for instance, whether inductive or mesomeric electron withdrawal by a ligand leads to a higher[92] or lower[93] ^{31}P n.m.r. chemical shift. Even if these basic problems are solved, the use of ^{31}P n.m.r. chemical



(49a) (49b)

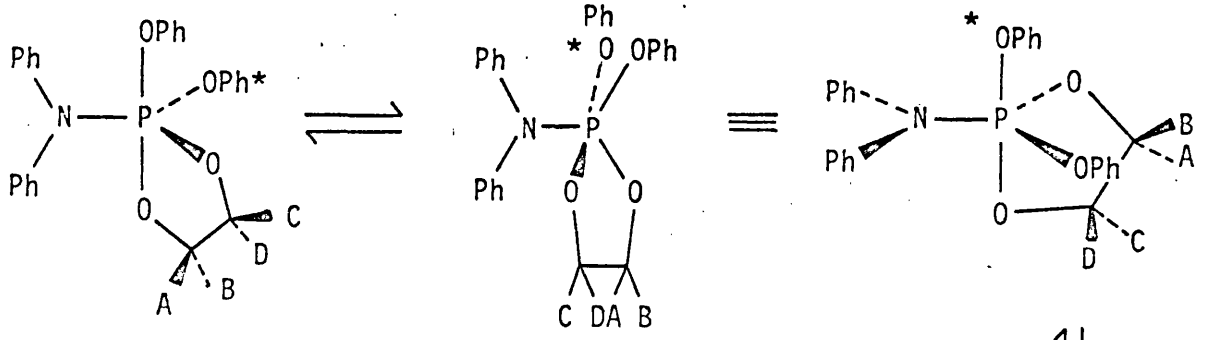


(49c)

shift data in apicophilicity determinations will still be very limited unless the properties of a ligand which make up its apicophilicity value combine together in the same sense to give a ^{31}P n.m.r. chemical shift value.

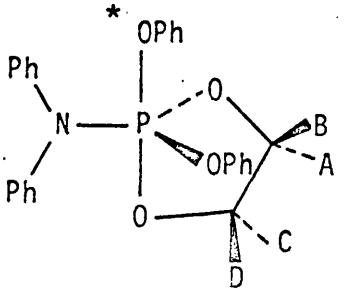
Further lowering of the temperature resulted in additional spectral changes for adducts (115)-(118), which are attributed to a slowing, on the n.m.r. time scale, of the equatorial P-N rotation. The effect of slow P-N rotation can best be illustrated by firstly considering a simpler case, the dimethylaminotetrafluorophosphorane molecule (49).

In order to equilibrate the fluorine atoms it is necessary to perform a BPR and a P-N rotation. (49a) and (49c) are topomers but (49b) is of higher energy owing to the unfavourable[61] alignment of the amino group.



(118a) (118b)

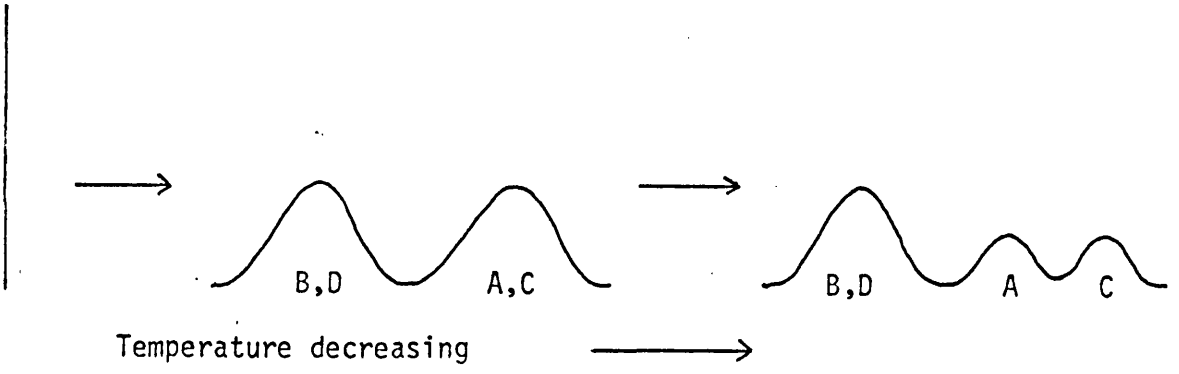
A - D = CF_3



(118c)

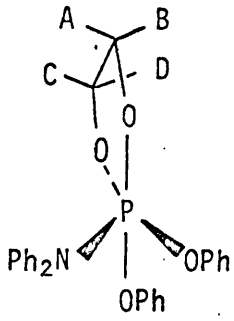
(49b) can be reached by a BPR or a P-N rotation from the lower energy conformers. When one or both of these processes becomes slow, non-equivalence of the fluorines is observed.

If the same reasoning is applied to the adduct (118), in order to equilibrate A with C and B with D (no further equilibration is possible since the BPR which places the amino group in an apical position is already slow on the n.m.r. time scale) it is necessary to perform a BPR and a P-N rotation. (118a) and (118c) are topomers and (118b) is the higher energy species, with the amino group in an unfavourable alignment. Thus, when P-N rotation becomes slow, none of the groups A-D are equivalent and the ^{19}F n.m.r. spectrum would be expected to show four signals of equal intensity. In fact, only one absorption splits out further on lowering the temperature (scheme 11). This can be explained by reference to (121),



SCHEME 11

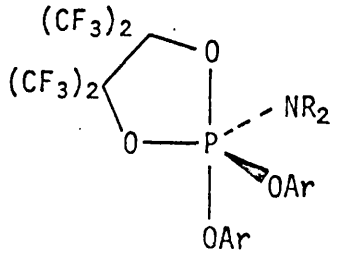
where the adduct is viewed opposite the equatorial ring P-O bond. Groups A and C are always on the same side of the molecule as the amino group and B and D are always on the opposite side. Since groups B and D are far away from the amino group, they are affected very little by its orientation and remain magnetically equivalent when P-N rotation slows. Groups A and C, however, are likely to be affected much more by the amino group



(121)

orientation and do show a distinct chemical shift difference at the onset of slow P-N rotation.

In order to test the validity of the spectral assignments, the phosphoranes (122)-(124) were prepared, so that the temperature at which the p-fluorophenoxy groups became non-equivalent could be found.



	(122)	(123)	(124)
R_2N	Me_2N-	$[CH_2]_4N$	MePhN

Ar = p-fluorophenyl

On the suggested interpretation, the p-fluorophenoxy groups remain equivalent after the BPR which places the amino group in an apical position has slowed but become non-equivalent at the onset of slow P-N rotation.

Adduct	^{19}F Tc/°C		$\Delta\nu$/Hz[c]		ΔG^*/kcal mol^{-1}[d]		^{31}P δ[e]
	CF_3	p-F	CF_3	p-F	CF_3	p-F	
(122)	-65[a]	-	182.5	-	9.3	-	+53.5[f]
(123)	-15[a]	-100	171.5	127	11.6	7.8	+60[b]
	-102		123.5		7.7		
(124)	-41[b]	-40	157	89	10.5	10.8	+58.5[f]
	-60		57		10.0		

[a] In light petroleum. [b] In ether. [c] Maximum frequency separation below coalescence. [d] Corrected for multiplicity of lowest energy interconversion pathway. [e] P.p.m. relative to 85% H_3PO_4. [f] In carbon tetrachloride.

TABLE 2

The experimental data (see Table 2) seem to confirm this, since, for (123), the ΔG^* value for equilibration of the p-fluorophenoxy groups corresponds to the lower energy equilibration process of the trifluoromethyl groups, i.e. the ΔG^* value for P-N rotation. For (124), the ΔG^* values for the trifluoromethyl groups are too close together to enable the ΔG^* value for the p-fluorophenoxy groups to be confidently assigned to either, and for (122), which shows no spectral changes due to slow P-N rotation on lowering the temperature, the p-fluorophenoxy groups remain equivalent, as they should do if the suggested interpretation is correct.

An additional splitting out of the ^{19}F n.m.r. spectrum was observed for (117) at very low temperature but this was found to be due to variations in chemical shift with temperature and not to a slowing of a

rate process.

It is not clear why the ^{19}F n.m.r. spectra of the adducts (112)-(114) and (122) show no changes associated with hindered rotation of the dimethylamino group. It may be that the methyl groups bonded to the nitrogen are not sufficiently large to exert an influence on the trifluoromethyl groups but this seems rather unlikely since these groups are affected by the orientation of the pyrrolidine group which is no larger than the dimethylamino group.

The ^{1}H n.m.r. spectrum of the adduct (114) was unchanged from room temperature to -110°. This again indicates that rotation about the P-N bond is still fast even at low temperatures, since 'freezing' of the dimethylamino group would leave the methyl groups in distinctly different environments.

The low-temperature ^{1}H n.m.r. spectrum of (116) showed changes in the isopropyl absorption around -60°, presumably due to slow P-N rotation but it was not possible to quantify these changes.

Considering the adducts (112)-(118) and (122)-(124), there appears to be no correlation between energy barriers to P-N rotation and the basicity of the amino group. It might be expected that there would be some correlation if the rotational barriers are due to orientation-dependent p-d π-bonding or p-σ interactions. The lack of such correlation, therefore, suggests either that the rotation barrier is not due to p-d π-bonding or p-σ interactions, or that these interactions are so large that the other substituents on the nitrogen make virtually no difference to their overall values. The following points indicate that the latter interpretation is probably correct.

(a) Calculations indicate a high degree of ligand-phosphorus π[59d,e] or σ[61] interaction.

(b) The nitrogen atom in the adducts appears to be only feebly basic, as evidenced by the unchanged ^{31}P n.m.r. and ^{19}F n.m.r. spectra on addition of hexafluoroisopropanol and by the lack of reaction of the adducts with methyl iodide.

A high degree of electron withdrawal from the nitrogen is also indicated by the results of a study of aminotetrafluorophosphorane,[94] which suggest, from the ^{15}N - ^{1}H coupling constant, that the nitrogen is sp^2 hybridised. This conclusion was also reached from studies of the frequency of the fundamental N-H stretching transition in spirophosphoranes containing one or two such groups.[95]

In order to investigate the general structure of the adducts and, in particular, the orientation of the amino group and the hybridisation of the nitrogen, an X-ray analysis of (114) was undertaken. The results are shown on pages 67 and 68.

The more notable points about the structure are:

(a) the molecule is a virtually perfect TBP;

(b) the dimethylamino group resides in an equatorial position, in accord with the expected relative apicophilicities of nitrogen and oxygen ligands;

(c) the dimethylamino group and the equatorial phenoxy group are aligned with their donor orbitals essentially in the equatorial plane, as predicted by Hoffmann;[61]

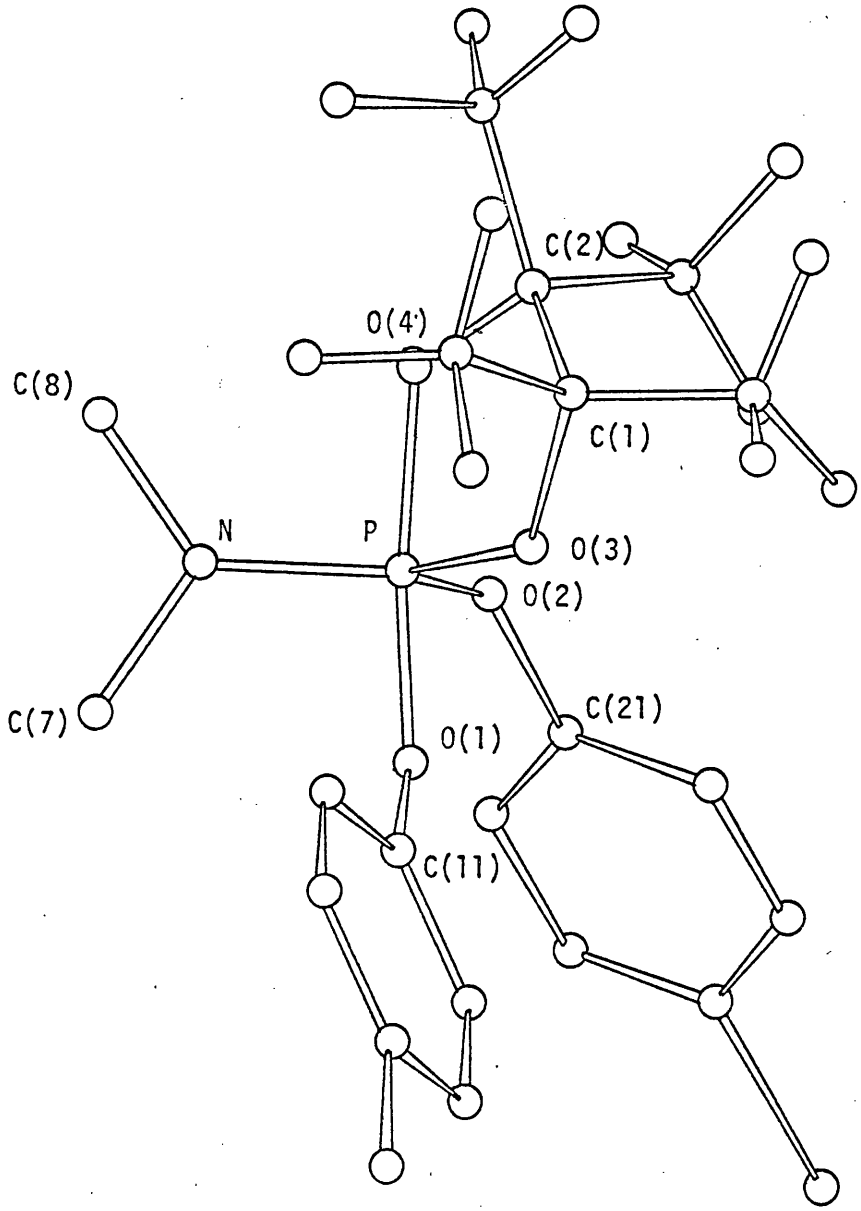
and (d) the nitrogen and the four oxygen atoms are all approximately sp^2 hybridised; this is indicative of a high degree of ligand-phosphorus p-d π-donation.

Interatomic Distances (Å) and E.S.D.'s in the Phosphorane (114).

P - O(1)	1.629 (0.01)	O(2) - C(21)	1.379 (0.013)
P - O(2)	1.590 (0.011)	O(3) - C(1)	1.371 (0.019)
P - O(3)	1.662 (0.012)	O(4) - C(2)	1.381 (0.02)
P - O(4)	1.707 (0.01)	N - C(7)	1.442 (0.023)
P - N	1.653 (0.014)	N - C(8)	1.474 (0.022)
O(1) - C(11)	1.346 (0.014)	C(1) - C(2)	1.554 (0.024)

Interatomic Angles (°) and E.S.D.'s in the Phosphorane (114).

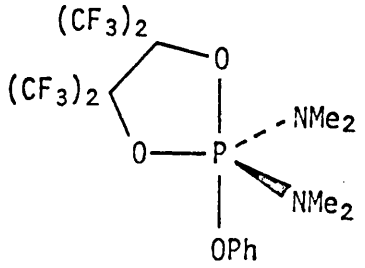
O(1) - P - O(2)	91.42 (0.52)	P - O(1) - C(11)	131.85 (0.86)
O(1) - P-O(3)	87.40 (0.54)	P - O(2) - C(21)	128.71 (0.88)
O(1) - P - N	94.89 (0.60)	P - O(3) - C(1)	118.96 (1.00)
O(4) - P - O(2)	88.75 (0.52)	P - O(4) - C(2)	118.23 (0.94)
O(4) - P - O(3)	86.79 (0.53)	P - N - C(7)	122.05 (1.12)
O(4) - P - N	90.60 (0.58)	P - N - C(8)	122.57 (1.11)
O(4) - P - O(1)	173.71 (0.60)	O(3) - C(1) - C(2)	105.97 (1.36)
O(2) - P - O(3)	113.93 (0.56)	O(4) - C(2) - C(1)	102.50 (1.25)
O(2) - P - N	117.61 (0.67)	C(7) - N - C(8)	110.42 (1.36)
O(3) - P - N	128.31 (0.64)		



(114)

4.3 Reaction of Phenyl NNN'N'-Tetramethylphosphorodiamidite with Hexafluoroacetone.

The adduct (125) was prepared in order to see whether the value obtained for the apicophilicity difference between the phenoxy and dimethylamino groups would be the same as for the adduct (112). (125)



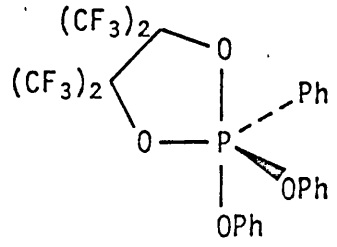
(125)

corresponds to an n.m.r. system type 1(b) molecule, where the BPR which places a dimethylamino group in an apical position is monitored by ^{19}F d.n.m.r. spectroscopy. The ΔG^* value obtained was expected to correspond to the value obtained for (112) but, in fact, the ^{19}F n.m.r. spectrum of (125) remained a singlet even at -130°. The two most likely reasons for this unexpected n.m.r. behaviour are (a) that an irregular mechanism, involving ionisation of the phosphorane is operating; this is more likely for (125) than for (112) since phosphoranes are known to become more prone to dissociation as alkoxy groups are replaced by amino or alkyl groups (see section 1.3) or (b) that replacement of a phenoxy by a dimethylamino group results in an increase in the apicophilicity of the latter; this seems quite likely because the presence of two highly efficient π-donors bonded to phosphorus would be expected to reduce the degree of back-bonding that each experiences and hence cause an increase in apicophilicity.

4.4 Reaction of Diphenyl Phenylphosphonite and Phenyl Diphenylphosphinite with Hexafluoroacetone.

The basic phosphorane system (111) may be extended by, for example, replacing the dimethylamino group by other groups but the system is rather limited because there has to be an apicophilicity difference between the groups on the phosphorus of greater than about 6 kcal mol^{-1} in order that the coalescence temperature may be brought into the experimentally observable range.

For the adduct (126), an n.m.r. system type 1(a) molecule, a value of 7.9 kcal mol^{-1} was obtained for the apicophilicity difference between the phenyl and phenoxy groups (see table 3). This means that the phenyl group in this system is more apicophilic than is indicated by the work of Trippett[63] and Denney.[47]



(126)

Adduct	^{1}H Tc/°C	Δν/Hz	ΔG*/kcal mol^{-1}	^{31}P δ
(126)	-105[a]	82[b]	7.7[c]	+ 40[d]

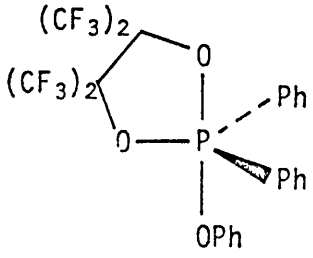
[a] In toluene. [b] Maximum frequency separation below coalescence.
[c] Corrected for multiplicity of lowest energy interconversion pathway.
[d] P.p.m. relative to 85% H_3PO_4; in toluene.

TABLE 3

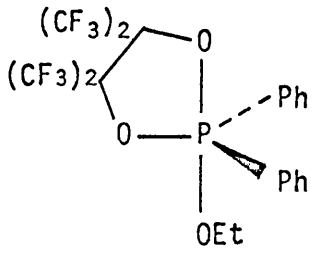
It is possible that the low coalescence temperature is due to the operation of an irregular isomerisation process. However, the ^{31}P n.m.r. chemical shift of (126) is the same with toluene or hexafluoroisopropanol as solvent and this indicates, but does not prove conclusively, that ionisation of the phosphorane is not responsible for the ^{19}F n.m.r. behaviour.

It may be that, in the case of (126), the presence of two relatively efficient π-donors, the two phenoxy groups, inhibits the back-bonding capability of the phenyl group, thus making it more apicophilic than in those adducts where its π-donor properties are likely to be more heavily used.

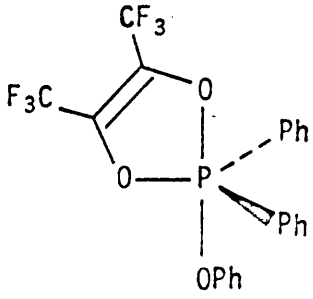
The adduct (127) was prepared in order to gain more information on the apicophilicity difference between the phenyl and phenoxy groups. (127) was rather susceptible to hydrolysis and decomposed, on warming in ethanol, to give the adduct (128) which was relatively stable.



(127)



(128)



(129)

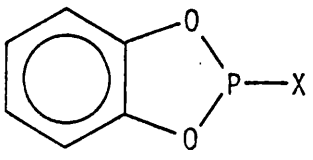
The ^{19}F n.m.r. spectra of (127) and (128) remained singlets down to -130° and it is difficult to see any reason for this other than an irregular isomerisation process. (127) and (128) are both n.m.r. system type 1(b) molecules which show the same d.n.m.r. behaviour as n.m.r. system type 4 molecules. Thus the fact that the singlet in the room temperature ^{19}F n.m.r. spectrum of (129)[96] splits out at -8° seems good

evidence for the operation of an irregular isomerisation mechanism in the case of (127) and (128).

The ^{31}P n.m.r. chemical shifts of (127) and (128) were independent of solvent polarity and this illustrates the inadequacy of this method for detecting the presence of small quantities of dipolar species.

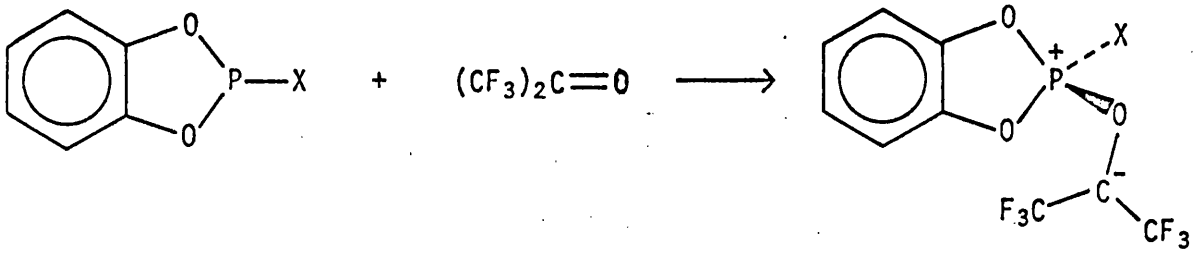
The results of sections 4.3 and 4.4, as a whole, show that it is unwise to assume that similar systems will produce similar results in terms of apicophilicity values. Unfortunately, it is not usually possible to tell whether the differences between similar systems are due to variations in ligand apicophilicities or to the operation of an irregular isomerisation mechanism.

4.5 Reaction of Some o-Phenylene Derivatives of Phosphorous Acid with Hexafluoroacetone.

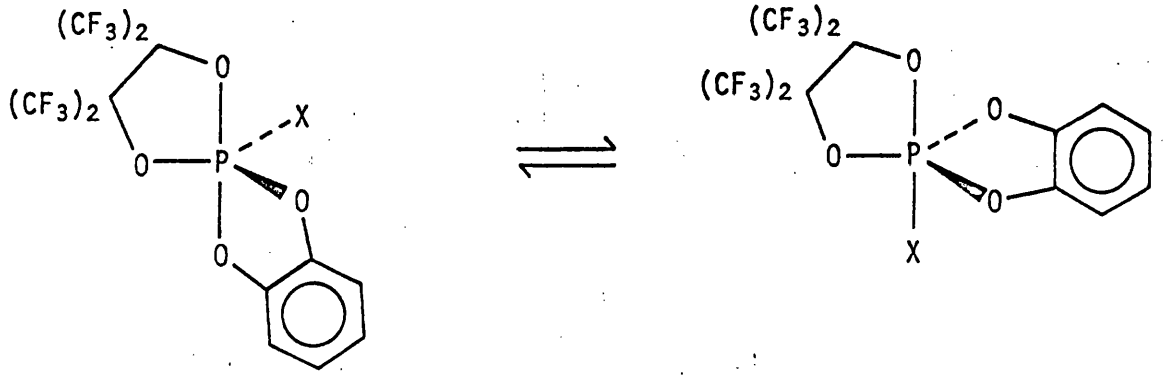


(130)	(131)	(132)
NMe_2	OPh	SPh

When the compounds (130) - (132) were treated with HFA in the usual way there was no reaction. Extension of the reaction period to one month at -40° did result in quantitative formation of (134) but there was no reaction with (131) or (132) even after an extended reaction time and, in the case of the former, even after ampouling with excess HFA and setting aside at room temperature for two months.



(133)



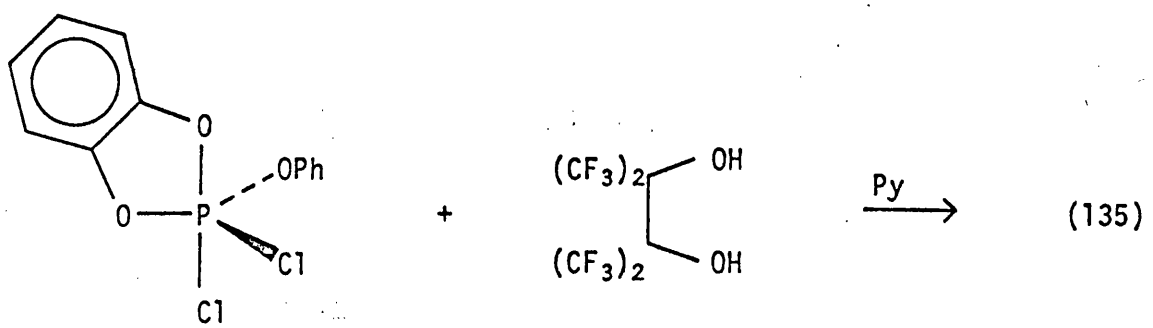
(a) (b)

(134) (135)

X = NMe_2 OPh

The lack of reaction is presumably due to a combination of the low basicity of the phosphorus and a high degree of ring strain associated with formation of the intermediate betaine (133).

Bone[90] has since prepared the phosphorane (135) by treatment of the dichlorophosphorane (136) with perfluoropinacol in the presence of pyridine.



(136)

The phosphoranes (134) and (135) are n.m.r. system type 2 molecules and so the process that is monitored by ^{19}F d.n.m.r. spectroscopy is the interconversion of (134(5)a) and (134(5)b). The difference in energy between these two structures can be written as:

$$\Delta G(b\text{-}a) = A(X\text{-}O) + S^5_{00}$$

where A(X-O) = the difference in apicophilicity between X and O,

and S^5_{00} = the energy required to move the dioxaphospholen ring into the ee position.

Since (134(5)b) is very unfavourable in terms of ring strain, unless X is a highly apicophilic group, (134(5)a) will be the low energy structure.

The ^{19}F n.m.r. spectrum of (134) showed two multiplets of equal intensity at room temperature and up to 180°, so

$$S^5_{00} + A(N\text{-}O) > 23 \text{ kcal mol}^{-1}$$

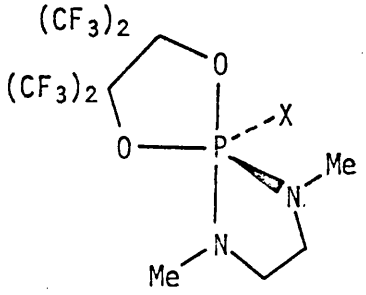
From the ^{19}F d.n.m.r. spectra of (135) the S^5_{00} term was calculated[90] as 20.5 kcal mol^{-1} and so

$$A(N\text{-}O) > 2.5 \text{ kcal mol}^{-1}$$

The ^{19}F d.n.m.r. data of adducts (134) and (135), then, again confirm that oxygen ligands are more apicophilic than nitrogen ligands although only a minimum value for the difference could be ascertained.

4.6 Reaction of Some Diazaphospholan Derivatives with Hexafluoroacetone.

The phosphoranes (137) - (139) were prepared by the reaction of HFA with the appropriate tervalent phosphorus compounds. The ^{19}F d.n.m.r. data for these adducts are shown in table 4



	(137)	(138)	(139)	(140)
X =	OPh	SPh	NMe_2	$OCH(CF_3)_2$

Adduct	^{19}F Tc/°C	Δν/Hz [c]	ΔG*/kcal mol^{-1} [d]	^{31}P δ [e]
(137)	152 [a]	158.5	19.6	+36.5
(138)	115 [a]	46	18.9	+13.5
(139)	0 [b]	30	13.3	+29.5
(140)	155 [a]	152	19.8	+36

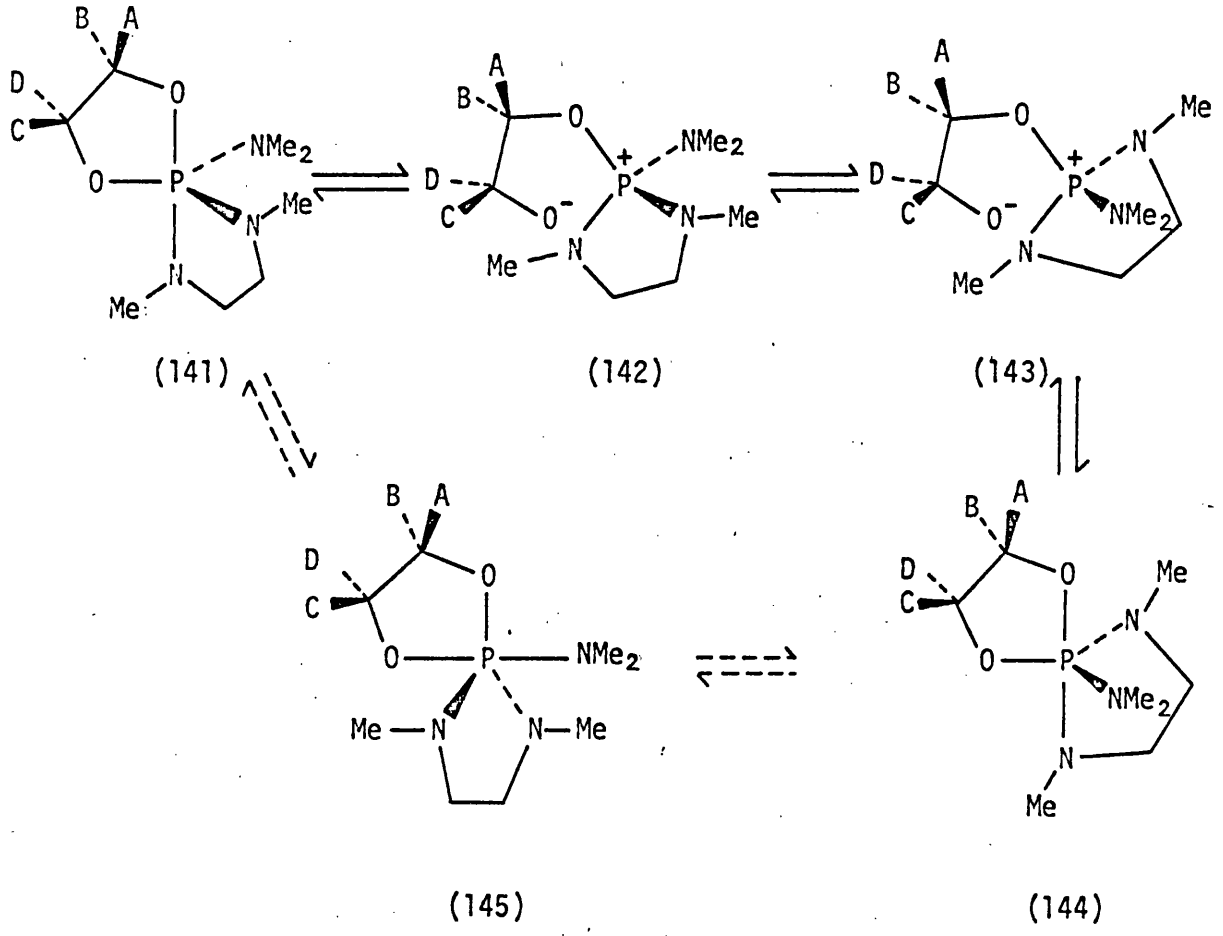
[a] In 1-bromonaphthalene. [b] In ether. [c] Maximum frequency separation below coalescence. [d] Corrected for multiplicity of lowest energy interconversion pathway. [e] P.p.m. relative to 85% H_3PO_4; in $CDCl_3$.

TABLE 4

The phosphoranes correspond to an n.m.r. system type 2 molecule and the ΔG* values thus decrease as the apicophilicity of the X group increases.

The data of table 4 imply that the dimethylamino group is 6.3 kcal mol^{-1} more apicophilic than the phenoxy group. This is in total disagreement with the results of sections 4.2 and 4.5.

It may be that in the case of (139), equilibration of the trifluoromethyl groups is achieved by an irregular isomerisation process



SCHEME 12

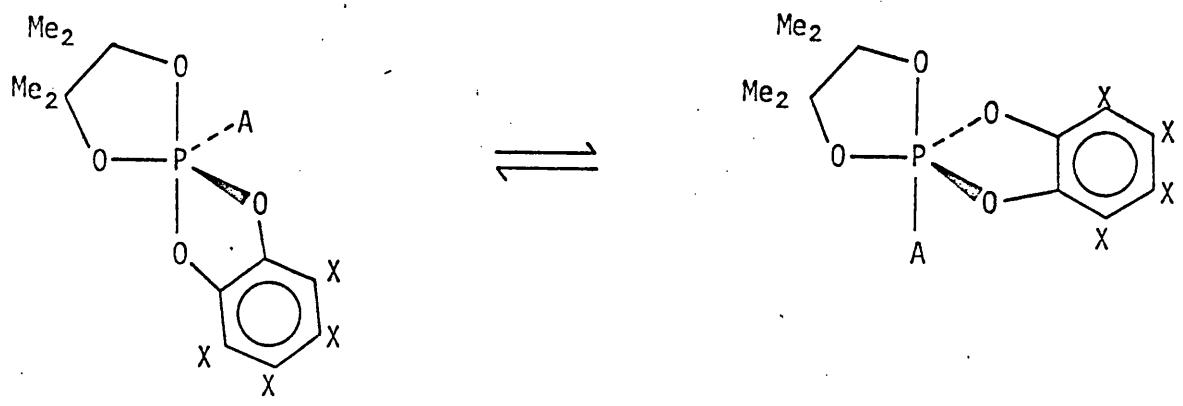
as outlined in scheme 12. Equilibration of A with B and C with D can be achieved by dissociation of (141) to give the betaine (142), followed by bond rotation to give (143) and ring closure to form (144). The same equilibration can be accomplished by a BPR process but this necessitates formation of the high energy intermediate (145). The irregular mechanism by-passes this high energy intermediate and so the ΔG^* value for the equilibration is lower.

In order to obtain further evidence for the operation of an irregular mechanism, the adduct (139) was dissolved in hexafluoroisopropanol so that its ^{31}P n.m.r. chemical shift in this solvent could be compared with the value obtained with chloroform as solvent. An instantaneous reaction occurred which resulted in quantitative formation of the adduct (140). This could be construed as evidence for the ready ionisation of (139) if it is assumed that the substitution reaction proceeds <u>via</u> the betaine (142).

The ^{31}P n.m.r. chemical shifts of the adducts (137) and (138) were the same in hexafluoroisopropanol and in chloroform and so the d.n.m.r. data for these compounds are probably valid.

4.7 <u>The Relative Apicophilicities of Oxygen and Sulphur Ligands.</u>

From the d.n.m.r. data for the adducts (137) and (138) it appears that sulphur is slightly more apicophilic than oxygen. This result is also obtained for the system discussed in section 4.8. However, Bone[90] has found that in the system (146) oxygen is more apicophilic than sulphur,

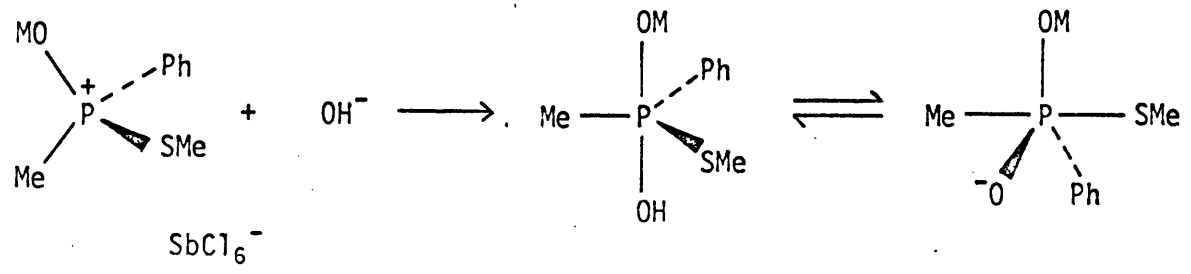


system (146); X = Cl
system (147); X = H

	System (146)		System (147)	
A	OPh	SPh	OPh	SPh
^{19}F Tc/°C	106	dec.> 130	101	104
$\Delta\nu$/Hz	5.6		3.5	3.5
ΔG^*/kcal mol^{-1}	20.5		20.5	20.7

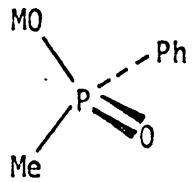
although decomposition at high temperature precluded the determination of an accurate value for the difference. The work of Bone[90] has also shown that, in system (147), sulphur and oxygen have very similar apicophilicities.

From these results it appears that, although there are small variations either way depending upon the actual system used, oxygen and sulphur have very similar apicophilicities. This conclusion is also indicated from studies of various substitution reactions at tetraco-ordinated phosphorus.



(148) (149) (150)

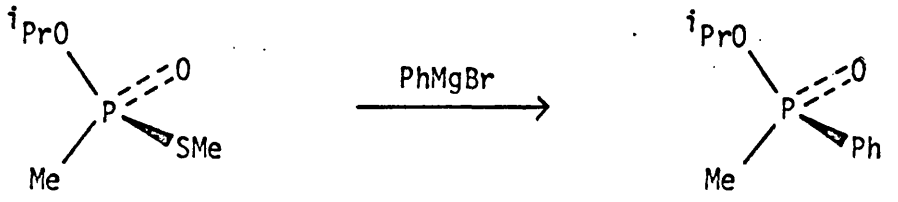
M = (-)-menthyl



(151)

From studies of the products of alkaline hydrolysis of 1-X-1--alkoxy-2,2,3,4,4-pentamethylphosphetanium salts, DeBruin and his co-workers[79] have concluded that the methylthio group is more apicophilic than certain alkoxy groups. However, in other systems sulphur appears to be less apicophilic than oxygen, e.g. Trippett and his co-workers[97] have shown that the salt (148) is hydrolysed with retention of configuration at phosphorus presumably by initial formation of the phosphorane (149), BPR to (150) and loss of the anion to give the product (151).

Benschop[98] has proposed a similar mechanism to explain the formation of (153), from the reaction of phenylmagnesium bromide with (152), with retention of configuration.



(152) (153)

In these two examples, initial formation of the phosphorane with the oxygen, as opposed to the sulphur, ligand in an apical position is preferred.

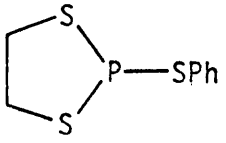
This similarity between oxygen and sulphur seems rather surprising in view of the lower electronegativity of sulphur and also because the barrier to rotation about a P-S bond is higher than that about a P-O bond (see section 4.11): this indicates greater ligand-phosphorus p-d π or p-σ interaction in the case of sulphur. There are, however, two properties which may serve to make sulphur more apicophilic than would be expected from electronegativity and back-bonding considerations.

(a) Sulphur has empty d orbitals which may be available to act as π-acceptors. This may counteract to some extent the π-donor property of sulphur and hence increase its apicophilicity. The balance of donor-acceptor properties would be expected to vary with the nature of the other groups bonded to phosphorus and this would explain the slight variation in apicophilicity; an increase in the π-donor ability of the other groups would be expected to increase the apicophilicity of sulphur and, from a comparison of adducts (137) and (138), and (159) and (161), with systems (146) and (147), this appears to be the case.

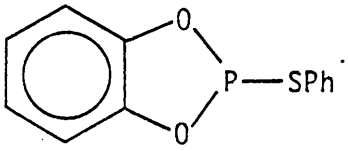
(b) Sulphur is more polarisable than oxygen and this also may lead to a higher apicophilicity value than would be otherwise expected.

Chlorine has been found to have a similar apicophilicity to oxygen[90,96] although it is less electronegative and this may be due again to its π-acceptor ability and greater polarisability.

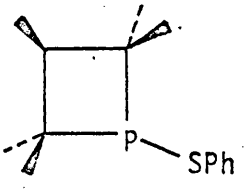
The accumulation of data on the apicophilicity of sulphur in various environments is hampered by the fact that tervalent phosphorus compounds containing sulphur ligands are usually so weakly basic that reaction with carbonyl compounds is very slow, if at all, e.g. (154) and (132) failed to react with HFA; reaction of (155) with HFA gave, after ampouling and setting aside for ten days, diphenyl disulphide as the only isolated product;[63] and (156) failed to react with hexafluorobiacetyl[99]



(154)



(132)

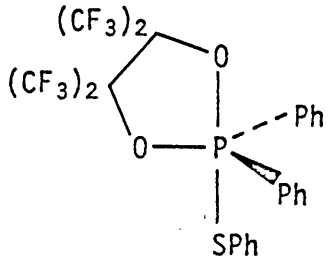


(155)

Ph_2P—SPh

(156)

and hexafluoroacetone under normal reaction conditions, but after an extended reaction period with the latter, the spectral characteristics of the crude product did indicate formation of a small amount of (157).



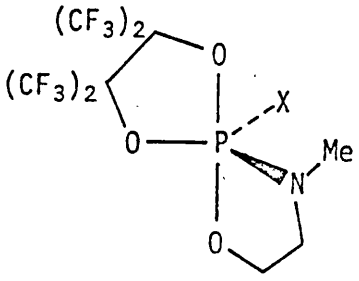
(157)

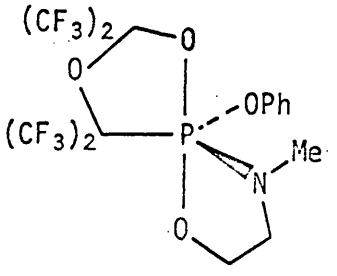
The ^{19}F n.m.r. spectrum of (157) was a singlet from room temperature to -130°. This behaviour is due, presumably, to the operation of an irregular isomerisation mechanism, as for (127) and (128).

The thiophosphoranes, once formed, are not as stable as the analogous oxyphosphoranes[100] and tend to decompose at lower temperatures.[41,100]

4.8 Reaction of Some Oxazaphospholan Derivatives with Hexafluoroacetone.

The 1,3,2-dioxaphospholans (158) and (159) and the 1,4,2-dioxaphospholan (160) were prepared by reaction of the appropriate tervalent phosphorus compounds with HFA.



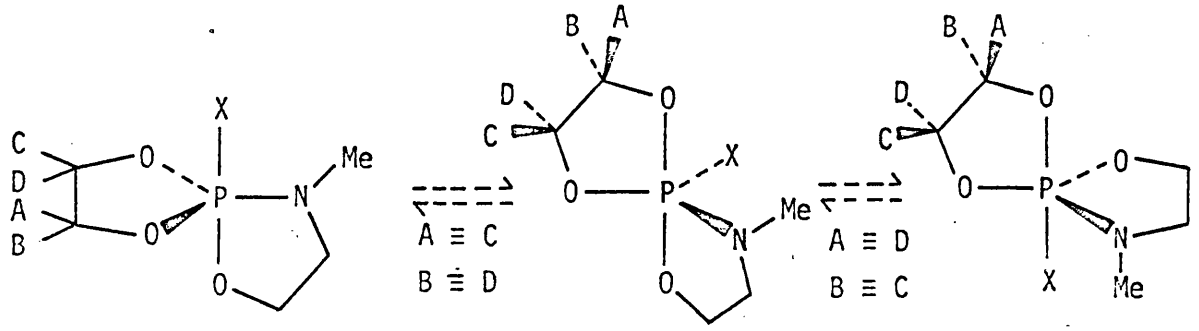


(158) (159) (161) (160)

X = NMe_2 SPh $OCH(CF_3)_2$

(158) was stable in hexafluoroisopropanol at room temperature for several hours but after refluxing for 24 hours, removal of excess alcohol and recrystallisation of the residue gave the adduct (161) in 61% yield.

The adducts (158), (159), and (161) are n.m.r. system type 3 molecules and the high energy species in the equilibration processes are (162) and (163)



(162) (163)

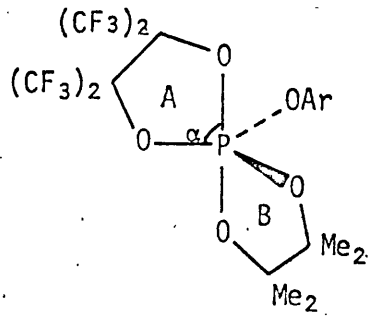
The ^{19}F d.n.m.r. data for the adducts are shown in table 5.

Adduct	^{19}F Tc/°C [a]	Δν/Hz [b]	ΔG* kcal mol^{-1} [c]	^{31}P δ [d]
(158)	ca. 170	33.8	ca. 23	+33
(159)	138	188	18.8	+17.5
(161)	165	135, 146 } 140	20.4	+41.5

[a] In 1-bromonaphthalene. [b] Maximum frequency separation below coalescence.
[c] Corrected for multiplicity of lowest energy interconversion pathway.
[d] P.p.m. relative to 85% H_3PO_4; in $CDCl_3$.

TABLE 5

For compounds (158) and (159), the ^{19}F n.m.r. spectrum at room temperature showed two multiplets in the ratio 3:1. This in interpreted as arising from a 'frozen' phosphorane molecule where both high energy equilibrations are slow on the n.m.r. time scale. This should theoretically give a ^{19}F n.m.r. spectrum consisting of four absorptions of equal intensity and the observed spectrum is presumably a consequence of accidental magnetic equivalence of three of the trifluoromethyl groups. As the temperature was raised, the two absorptions began to move together and for (159), the coalescence temperature for this process was measured. This coalescence is associated with a speeding up, on the n.m.r. time scale, of equilibration *via* (163). Evidence that coalescence is not due to equilibration *via* (162) comes from the d.n.m.r. behaviour of the adduct (164).



(164) (165)

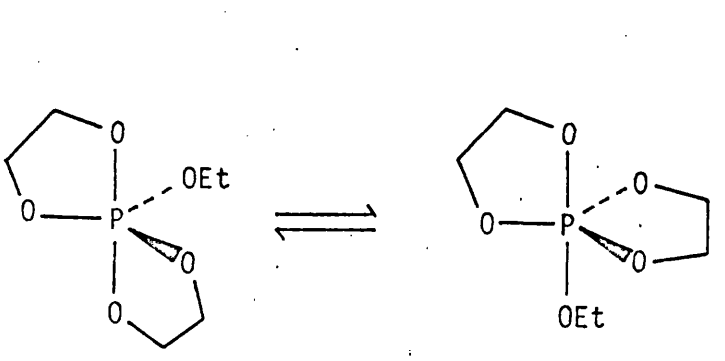
Ar = Ph p-Br-Ph

Although equilibration of the trifluoromethyl groups by *ee* placement of the ring (B) is fast on the n.m.r. time scale at -100°, complete equilibration of the methyl groups is not achieved even at 180°. This implies that the ring (A) requires substantially more energy to place it in the *ee* position than does the corresponding unfluorinated ring (B). The reason for the much higher strain in ring (A) is unknown. It was

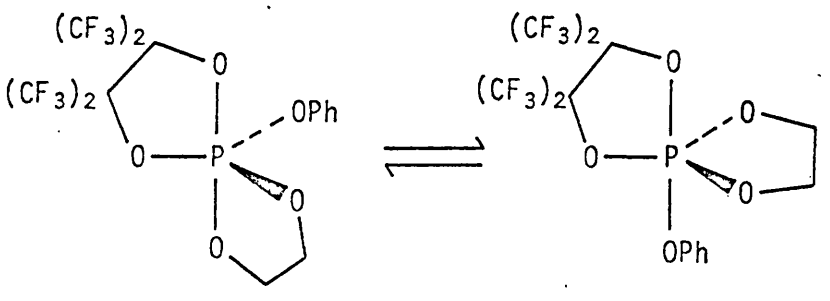
thought that the presence of the highly electronegative trifluoromethyl groups might distort the geometry of the phosphorane in such a way that the ring angle (α) becomes smaller. This would lead to a higher value of ring strain when the (A) ring is placed in the ee position.

An X-ray analysis of the adduct (165) was undertaken with the expectation that the molecule would turn out to be a distorted TBP. In fact the molecule is a virtually perfect TBP and so the excessive strain in ring (A) cannot be due to any structural distortions.

[The strain associated with placing the ring (B) in the ee position is in fact lower than would be expected from other results,



(166)



(167)

e.g. (166)[48] and (167);[90] the corresponding strain energy for ring (B) is < 8 kcal mol^{-1}, but nevertheless, even in comparison with (166) and

(167), the value of > 24 kcal mol^{-1} for the strain energy in ring (A) is still large].

The coalescence observed for the adduct (159) is almost certainly due to a rate process and not to accidental equivalence of signals because the line widths of the two absorptions greatly increase as coalescence is approached. For the adduct (158), although the two absorptions did coalesce at about 170° it was impossible to determine an accurate value for the coalescence temperature because of the close proximity of the signals. It was also impossible to tell whether the coalescence was due to accidental equivalence or a rate process but on the basis of other data (see section 4.2 and ref. 63) the ΔG^* value for (158), in comparison with that for (161), would be expected to be much higher and so the coalescence observed for (158) is probably due to accidental equivalence or the operation of an irregular isomerisation mechanism.

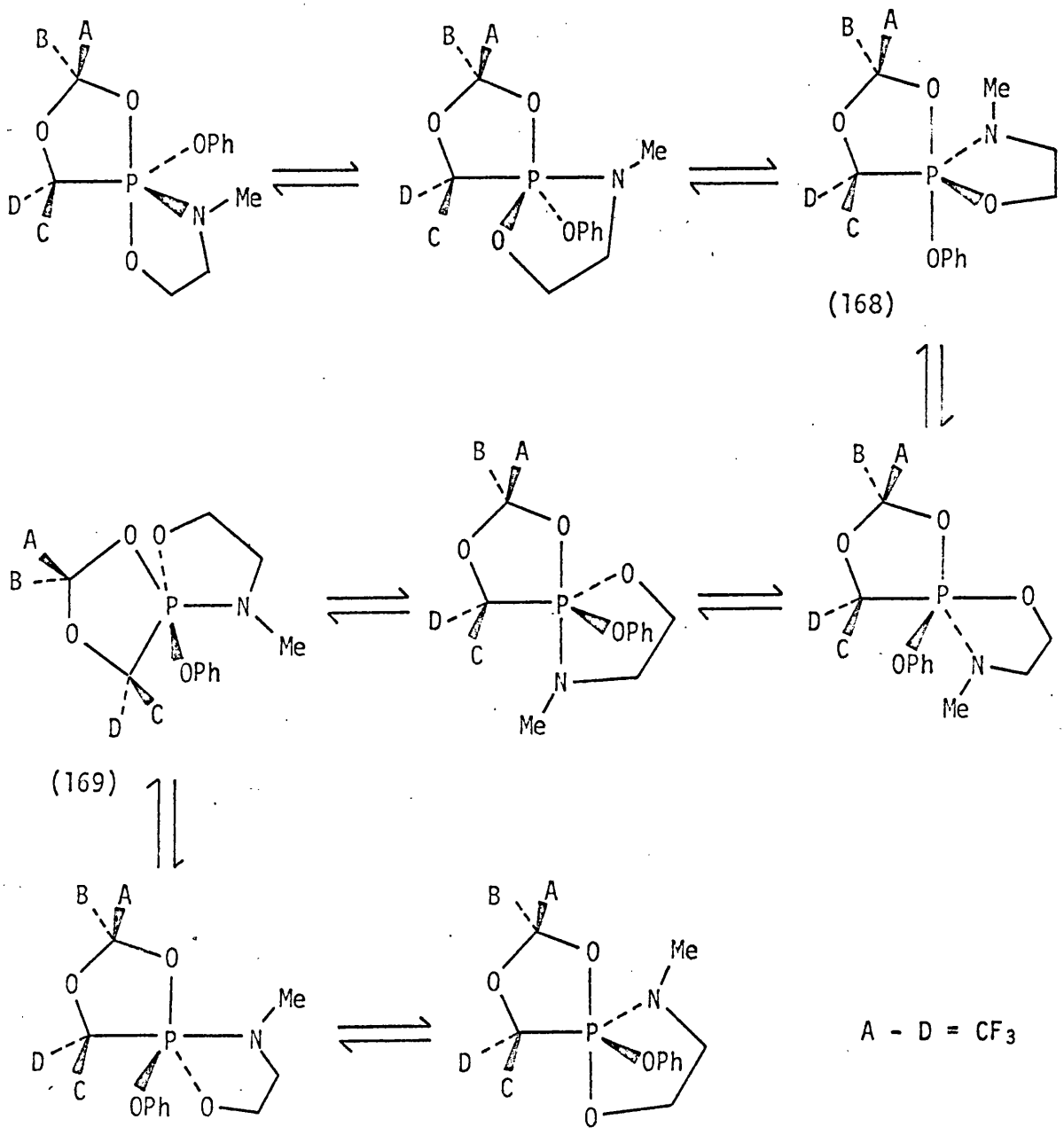
The ^{19}F n.m.r. spectrum of (161) at room temperature showed three absorptions, due to the trifluoromethyl groups on the ring carbon atoms, in the ratio 1:2:1. At higher temperatures the spectrum simplified to two signals of equal intensity and this is interpreted in terms of a speeding up, on the n.m.r. time scale, of the equilibration process via (163). The $\Delta\nu$ value quoted in table 5 is the average value for the two pairs of multiplets. The difference in $\Delta\nu$ between the two pairs of signals was small and no difference in coalescence temperature was observed.

From the d.n.m.r. data of (159) and (161) sulphur appears to be slightly more apicophilic than oxygen, presumably for the same reasons that were discussed in the previous section.

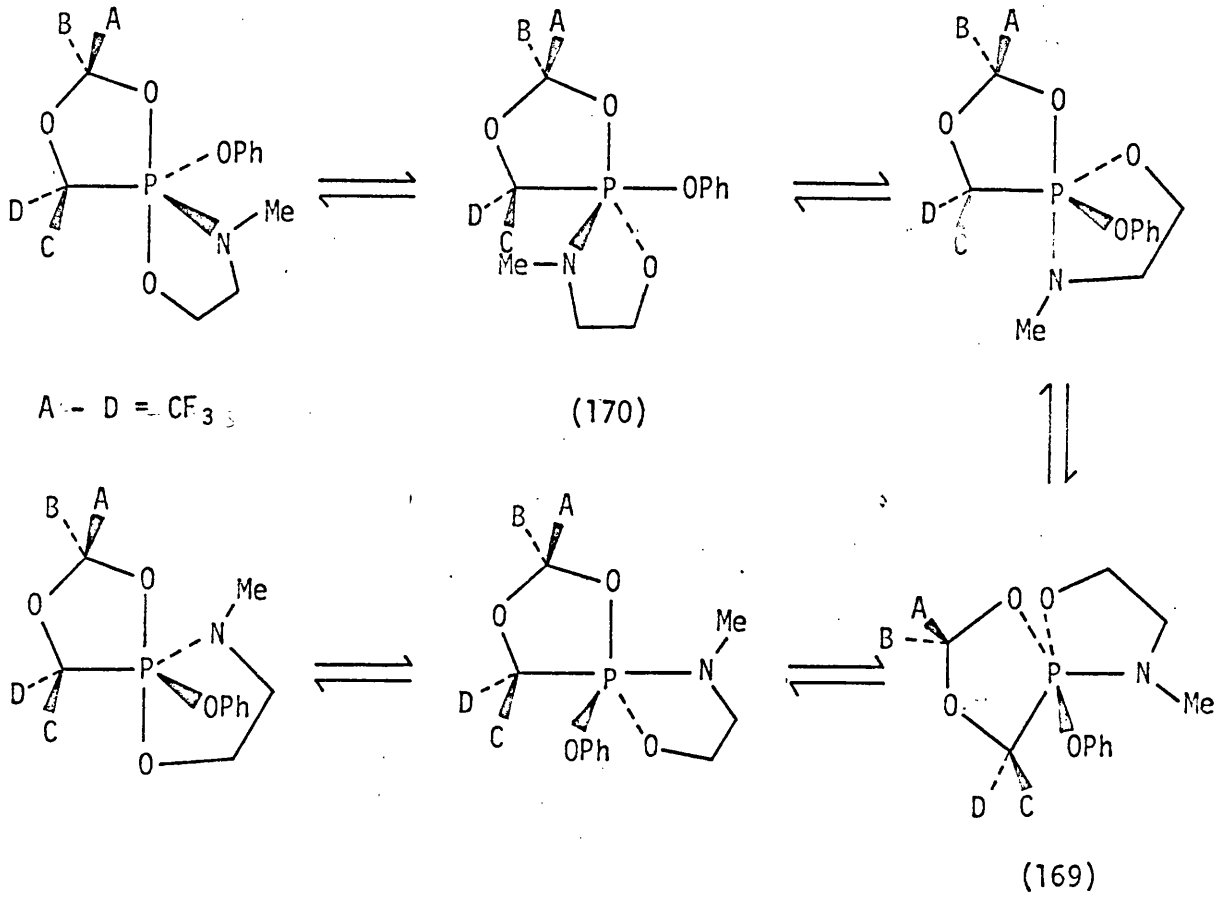
The 2:1 adduct formed from the reaction of 3-methyl-2-phenoxy-1,3,2--oxazaphospholan with HFA is formulated as the 1,4,2-dioxaphospholan (160) on the basis of the ^{19}F n.m.r. spectrum which shows four signals of equal

intensity. Two of the signals are at chemical shifts higher than is found in 1,3,2-dioxaphospholans and these signals show a larger J_{P-F} value which is also consistent with the 1,4,2-dioxaphospholan structure.

Partial equilibration of the trifluoromethyl groups can be achieved through the BPR routes shown in schemes 13 and 14.



SCHEME 13

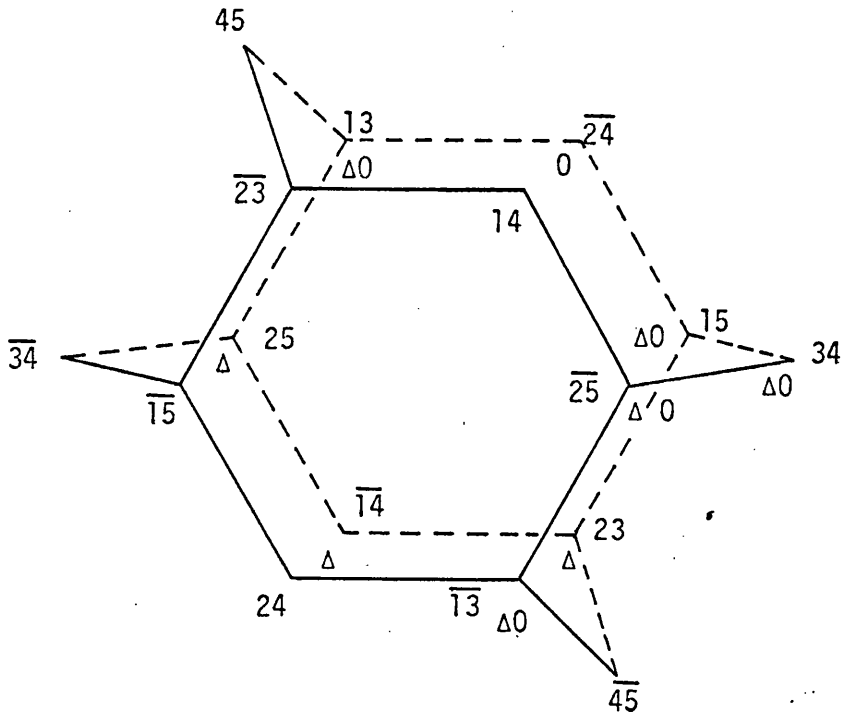


SCHEME 14

These two BPR routes are also shown on the graph (171), which is Mislow's Desargues-Levi graph[7,68] but with the vertices corresponding to TBP's with either of the rings in an aa placement removed.

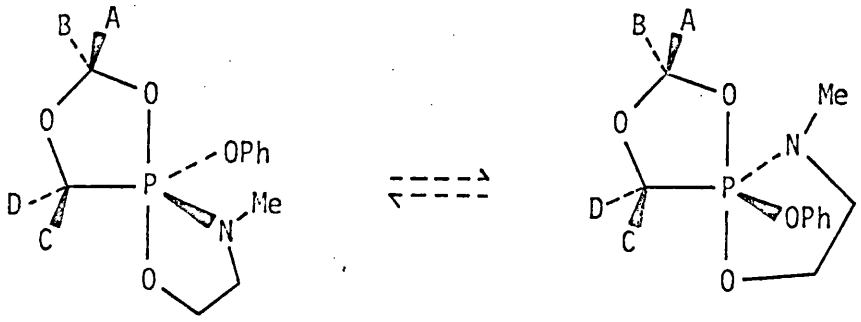
The two high energy intermediates formed in the seven-BPR pathway are (168) and (169) and in the five-BPR pathway (169) and (170). (168) is of lower energy than (170) since oxygen is in an apical position in (168) and carbon in (170),[4,63] and so, if (169) is of lower energy than (168) and (170) the seven-BPR pathway would be expected to be the preferred equilibration route.

BPR's via (168) should be of similar energy to BPR's via (163, X = $OCH(CF_3)_2$) [assuming that the phenoxy and hexafluoroisopropoxy groups have similar apicophilicities, as is indicated from the d.n.m.r. data for



Δ = 7-BPR route

O = 5-BPR route



13 $\overline{13}$

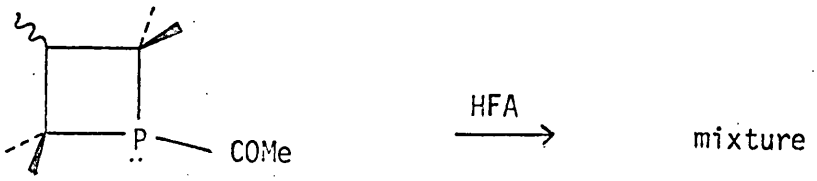
(171)

adducts (137) and (140)] but the ^{19}F n.m.r. spectrum of (160) is unchanged from room temperature to 160°, unlike that of (161). This suggests that (169) is the high energy intermediate and that the energy required to place the 1,4,2-dioxaphospholan ring in the ee position is greater than that required to place the oxazaphospholan ring in the ee position. Although the reverse would probably be predicted (see section 5), the high

strain energy in the 1,4,2-dioxaphospholan ring may be due to the presence of two bulky trifluoromethyl groups on the α-carbon atom (see section 5) or to the same (unknown) factor that is responsible for the high strain energy in the 4,4,5,5-tetrakis(trifluoromethyl)-1,3,2-dioxaphospholan ring.

4.9 The Apicophilicity of the Benzoyl Group.

There have been very few reports of the preparation of a phosphorane with an acyl group bonded to phosphorus.[101,102] This may be because the usual methods of preparation of phosphoranes, i.e. reaction of a quinone or ketone with a tervalent phosphorus compound, do not appear to be successful in the case of acyl phosphines, e.g. the phosphine (172),

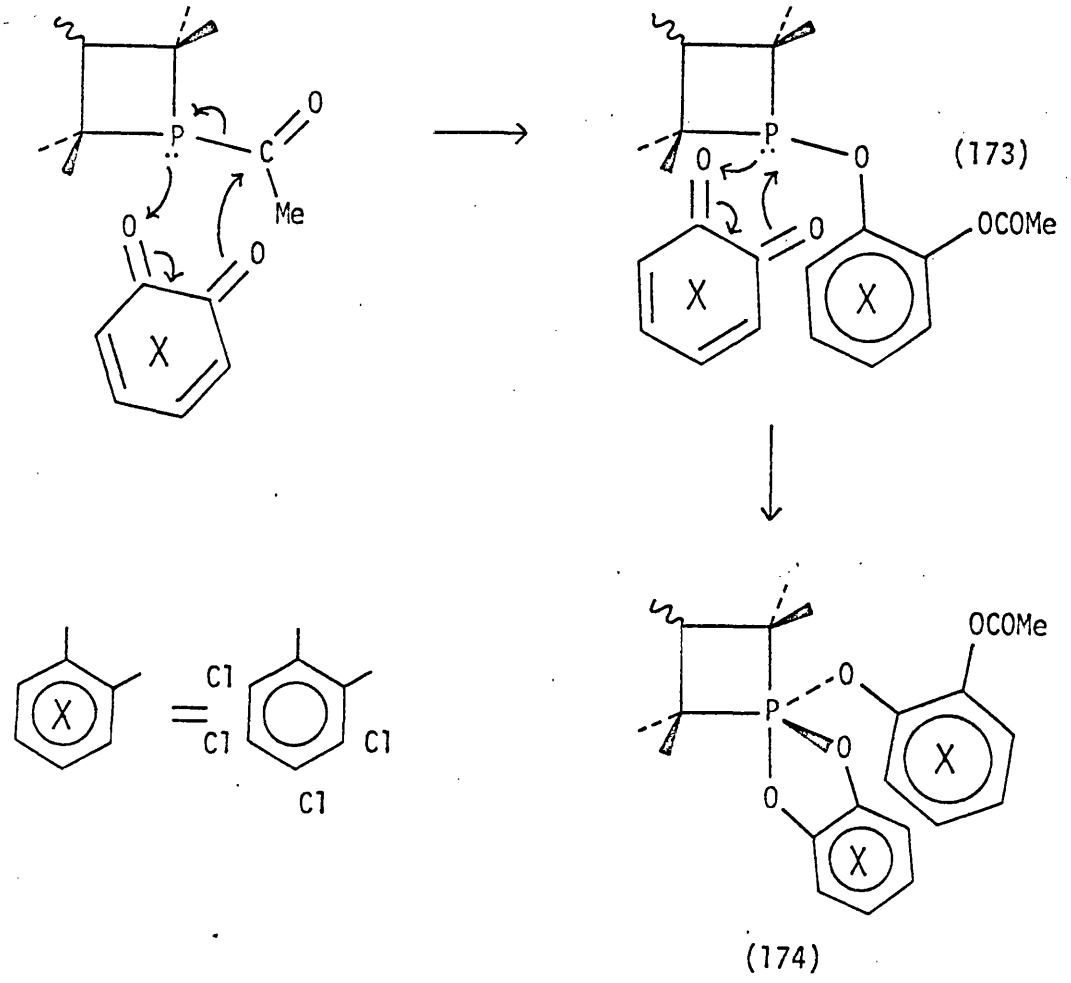


(172)

when treated with HFA in the usual way, gave a complex mixture of products from which no pure substance could be isolated. The doublet in the ^1H n.m.r. spectrum due to the acetyl group had virtually disappeared in the product, to be replaced by a singlet. This loss of coupling could indicate transfer of the acetyl group from the phosphorus.

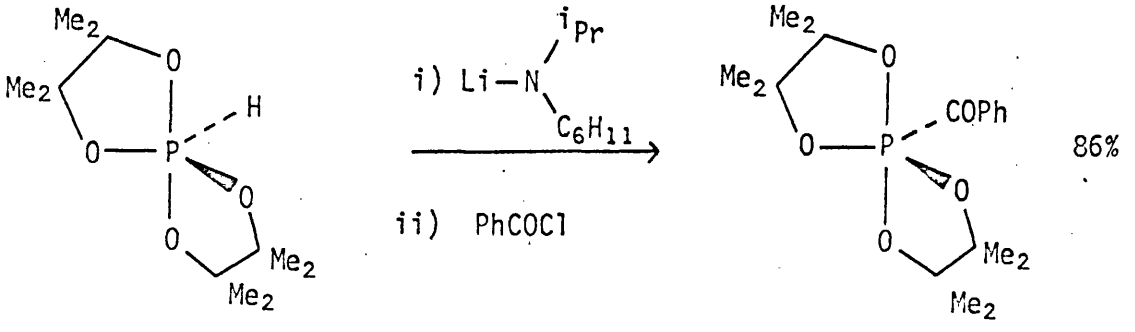
Reaction of (172) with tetrachloro-o-benzoquinone gave the phosphorane (174), presumably by attack of the phosphorus lone pair on the

quinone oxygen and transfer of the acetyl group as is indicated to form



the phosphinite (173). This then reacts with a second molecule of the quinone in the 'normal' way to give the product.

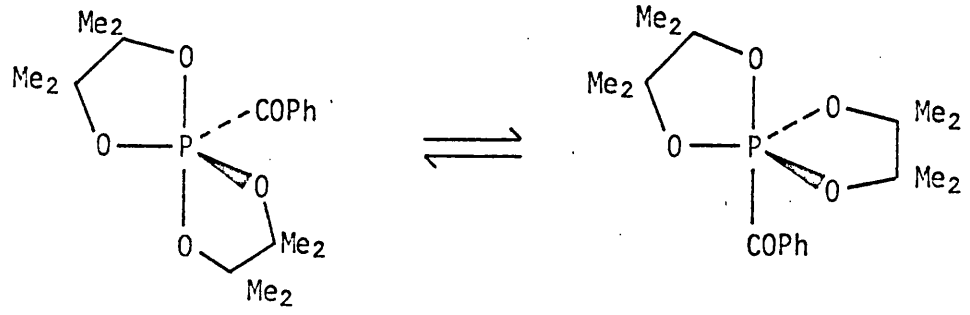
The acyl phosphorane (175) was prepared by treatment of the



(29) (175)

phosphorane (29) with the non-nucleophilic base, lithium cyclohexylisopropylamide, and then with benzoyl chloride.

(175) corresponds to an n.m.r. system type 2 molecule. The ^1H n.m.r. spectrum at room temperature showed two singlets of equal intensity for the methyl groups, implying that the BPR (175a) $\rightleftharpoons$ (175b) is slow on the n.m.r. time scale. Coalescence was observed at a higher temperature and the d.n.m.r. data are shown in table 6.



(a) (b)

Adduct	^1H Tc/°C	Δν/Hz	ΔG*/kcal mol^{-1}	^{31}P δ
(184)	140[a]	16[b]	20.9[c]	+39[d]

[a] In 1-bromonaphthalene. [b] Maximum frequency separation below coalescence. [c] Corrected for multiplicity of lowest energy interconversion pathway. [d] P.p.m. relative to 85% H_3PO_4; in dichloromethane.

TABLE 6

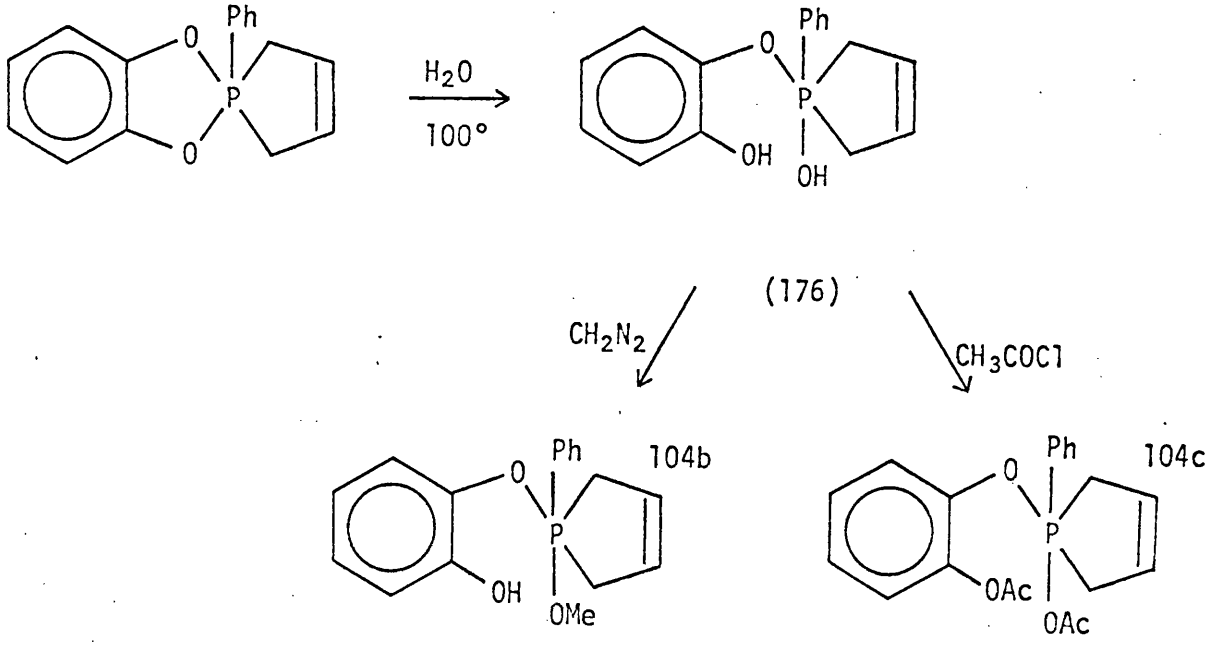
The ΔG* value of 20.9 kcal mol^{-1}, when compared with a value of about 22 kcal mol^{-1} for the analogous BPR of the phosphorane (166), indicates that the benzoyl and ethoxy groups have very similar apicophilicities.

This relatively high apicophilicity value for the benzoyl group may simply be a consequence of its high electronegativity[103b] or it may be due to the fact that the benzoyl group is able to act as a π-acceptor. Unfortunately, the experimental result gives no information on this point.

4.10 Hydroxyphosphoranes.

The apicophilicity of the hydroxy group would be an extremely useful piece of information, since phosphonium salt hydrolyses[1,7,9] and numerous substitution reactions[2-8,10,11] at phosphoryl centres are considered to proceed via a hydroxyphosphorane or its conjugate base.

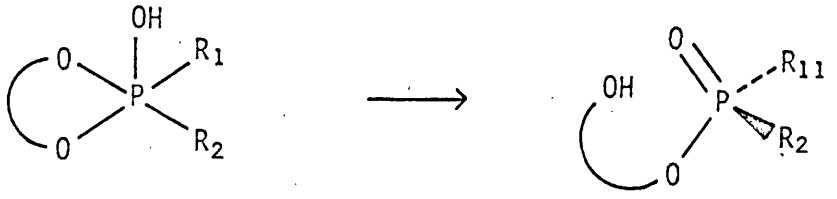
A number of compounds which have been formulated as hydroxyphosphoranes have been reported,[104] e.g. (176), but no ^{31}P n.m.r. chemical shifts were given and the ^{1}H n.m.r. absorption of the methoxy group in (177) was



(177)

reported[104b] as a singlet. Until fuller spectral characteristics are reported these results must be regarded with a certain amount of scepticism.

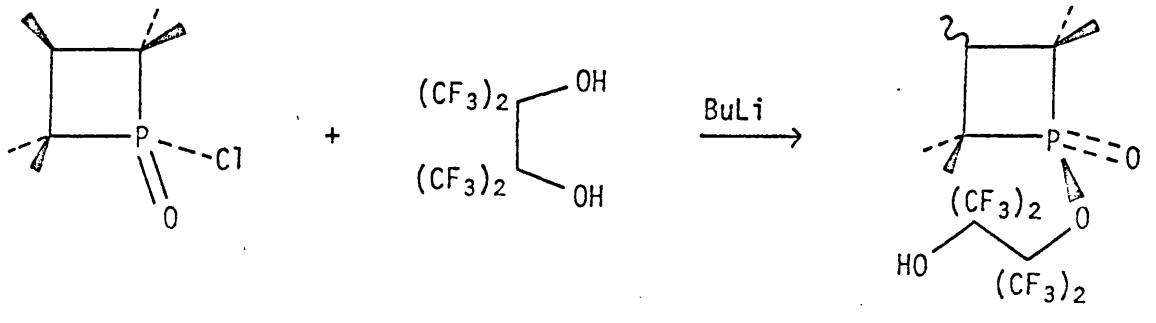
Considering the equilibrium between the hydroxyphosphorane (178) and the phosphoryl (179) structures, the factors which are known to



(178) (179)

stabilise phosphoranes (see section 1.3) should presumably help to push the equilibrium over to the left and in particular, if the phosphorus is part of a highly strained ring, ring strain considerations should favour the hydroxyphosphorane structure quite appreciably.

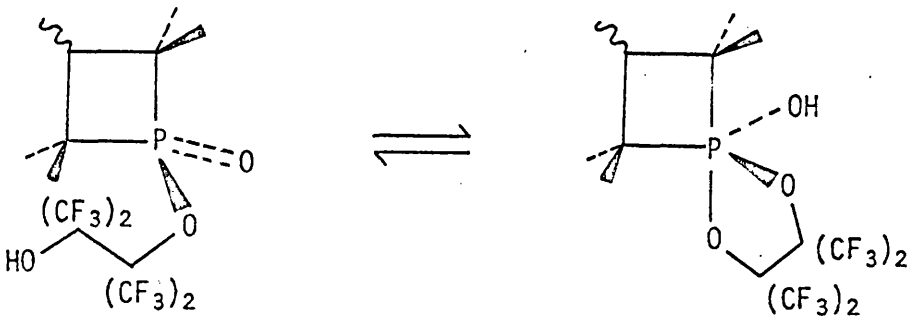
Reaction of the pure <u>trans</u> isomer of the acid chloride (180) with the lithium salt of perfluoropinacol gave the phosphinate (181) as a mixture of isomers in 60% yield.



(180) (181)

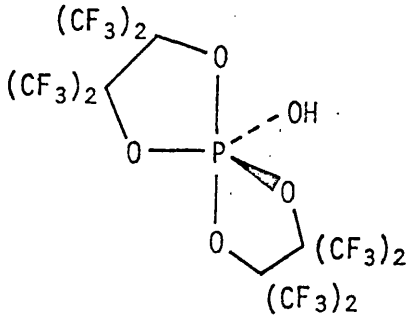
(181) is formulated as the phosphinate and not the hydroxyphosphorane (182) because both isomers show distinctly negative ^{31}P n.m.r. chemical

shifts: -83p.p.m. (major) and -63.5 (minor) p.p.m..



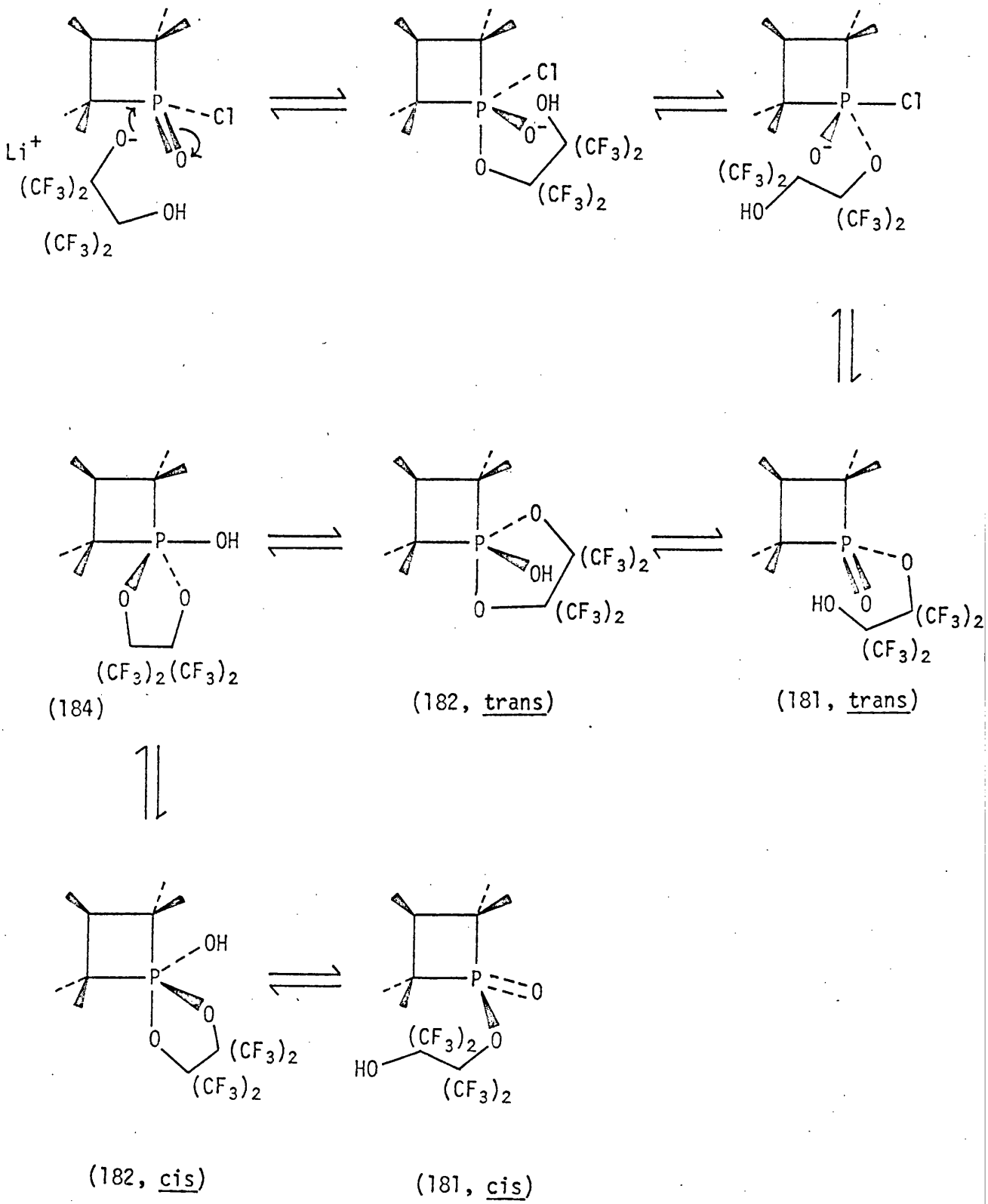
(181) (182)

The fact that, despite the tremendous increase in ring strain, the equilibrium still lies in favour of (181) suggests that very few, if any, hydroxyphosphoranes are likely to be stable species. Increase in the electronegativity of the groups bonded to phosphorus, as well as a high ring strain, may possibly swing the equilibrium over to the left and the hydroxyphosphorane (183), which combines these two properties, seems to be the most likely compound to exist as such.



(183)

The fact that the phosphinate (181) was obtained as a mixture of isomers suggests that the hydroxyphosphorane (182) is formed as a metastable imtermediate. The acid chloride (180) is known to undergo substitution with retention of configuration at phosphorus[5,6] and so the initial product



(184)

(182, trans)

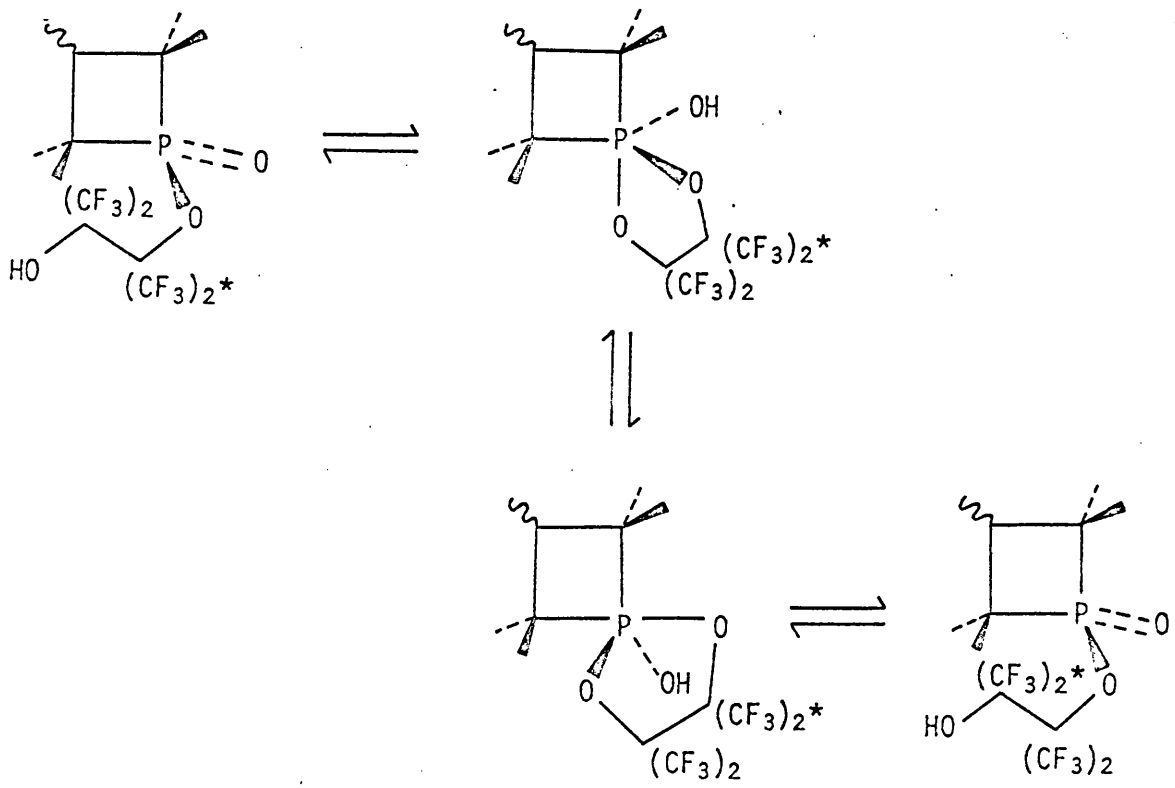
(181, trans)

(182, cis)

(181, cis)

of the reaction is presumably the pure trans isomer of the phosphinate (181). Isomerisation to the hydroxyphosphorane (182, trans) and subsequent BPR via (184), where the dioxaphospholan ring is placed in the ee position, results in the formation of the cis isomer of (181).

Further evidence for formation of the hydroxyphosphorane (182) comes from the ^{19}F n.m.r. spectrum of (181). At room temperature the spectrum consists of one singlet, consistent with formation of the hydroxyphosphorane and subsequent equilibration as shown in scheme 15.



SCHEME 15

As the temperature was lowered broadening occurred and at -100° the spectrum consisted of two absorptions of equal intensity. The spectral data associated with the coalescence are shown in table 7.

Compound	^{19}F Tc/°C	Δν/Hz	ΔG*/kcal mol^{-1}
(181)	-87[a]	139[b]	8.6

[a] In ether. [b] Maximum frequency separation below coalescence.

TABLE 7

The process that becomes slow on the n.m.r. time scale is presumably the isomerisation between the tetra- and pentaco-ordinate structures since the topomeric BPR would be expected to have a much lower activation energy.

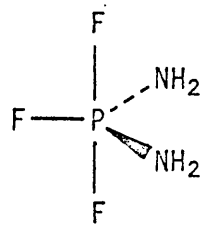
4.11 Hindered Rotation in Phosphoranes.

The calculations of Hoffmann, Howell, and Muetterties[61] have indicated certain specific, favoured orientations for equatorial ligands with single π systems available for interaction with the phosphorus. They have also indicated that the barrier to free rotation may be quite considerable. Some of the experimental data that have been interpreted in terms of hindered rotation and preferential orientation of ligands are described below.

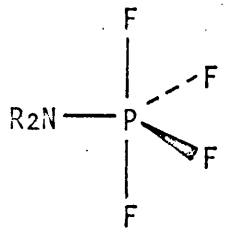
P-N Rotation.

The predicted high barrier to P-N rotation has been confirmed by several studies: values of 5 - 12 kcal mol^{-1} have been reported,[60,105-108] e.g. the P-N rotation barrier in (185) has been determined as 11.15 kcal mol^{-1}.[108]

The phosphoranes of general formula (186)[60,105] show ^{19}F or ^{31}P



(185)

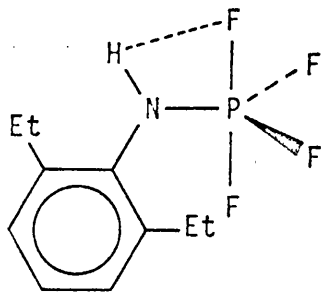


R = Ph, Me, Et.

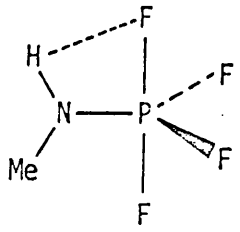
(186)

d.n.m.r. spectra consistent with four equivalent fluorine atoms at room temperature but at temperatures between -50° and -100° the spectra indicate two sets of non-equivalent fluorine atoms. As explained in section 4.2, these spectral changes can be interpreted in terms of a slowing of P-N rotation and/or a slowing of BPR. These two processes may be distinct, with different ΔG^* values, or they may be coupled.[105a,108]

The above experiments do not give any information on the preferred orientation of the amino group but the predictions of Hoffmann appear to be confirmed by the ^{19}F d.n.m.r. studies of (187)[106] and (188).[107] The apical fluorine atoms become non- equivalent on cooling but the equatorial fluorine atoms do not. This suggests that the amino group is aligned with



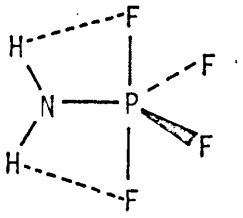
(187)



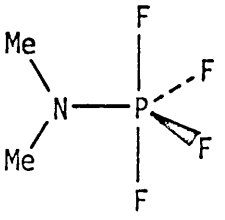
(188)

its donor orbital in the equatorial plane but there is the possibility that

this orientation is due to a hydrogen-bond interaction between the amino hydrogen and the apical fluorine and not to a ligand-phosphorus π interaction. This seems highly likely in view of the fact that the ΔG^* value for fluorine equilibration in (65)[94] is about 6kcal mol^{-1} higher than in



(65)

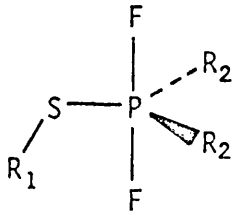


(49)

(49).[60,108] For the adduct (114), where the possibility of any hydrogen-bonding affecting the orientation of the dimethylamino group is highly unlikely, the X-ray analysis (see section 4.2) has shown conclusively that the dimethylamino group is aligned in the predicted orientation for a π-donor.

Schmutzler and his co-workers[109] have suggested that steric interactions may also be important in determining the preferred orientation of the amino group.

P-S Rotation.



R_1 = Me, Et, Ph.

R_2 = F, Me, Ph.

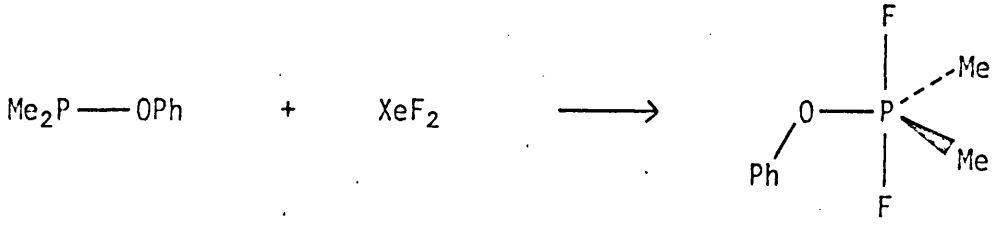
(189)

The same sort of evidence as for the amino group has shown that sulphur acts as a π-donor and prefers to align itself with its donor orbital in the equatorial plane.[110] The phosphoranes of general formula (189) show non-equivalence of the apical fluorine atoms in their low-temperature ^{19}F n.m.r. spectra consistent with the R_1 group lying in an apical plane. From the observed temperatures of non-equivalence the barrier to P-S rotation appears to be of the same magnitude as the P-N rotation barrier.

P-O Rotation.

An accurate P-O rotation barrier has not as yet been determined but the results of Schmutzler[111] and Riess[112] indicate that the barrier is less than about 8kcal mol^{-1}.

In order to obtain a definite value for the P-O rotation barrier, the phosphorane (190) was synthesised by treatment of phenyl dimethylphosphinite with xenon difluoride. The ^{19}F n.m.r. spectrum of (190), as a solution in trichlorofluoromethane, was investigated at low temperatures



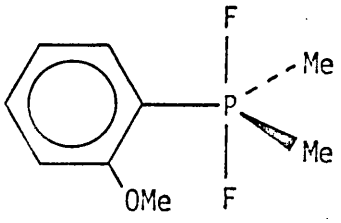
(190)

to see whether non-equivalence of the fluorine atoms due to slow rotation could be observed. The spectrum at -100° did show considerable broadening but this was probably due to changes in resolution and not to the onset of slow P-O rotation.

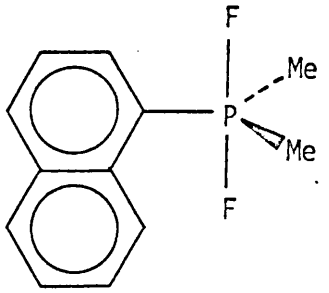
The only conclusion that can be reached, then, is that the P-O rotation barrier is less than about 8 kcal mol^{-1}.

P-C Rotation.

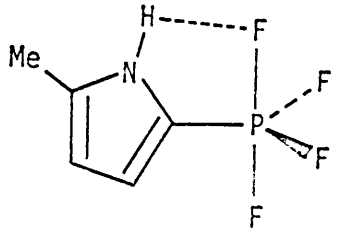
Oram and Trippett[63] have suggested that the low apicophilicity of the phenyl group compared with alkyl groups is due to its ability to 'back-bond' into the phosphorus d orbitals. If this interaction were substantial it might be detectable in the same way as for hindered rotation about a P-N or P-S bond. Accordingly, the authors investigated the low-temperature ^{19}F n.m.r. and ^{1}H n.m.r. spectra of the phosphoranes (191) and (192) but were unable to find any evidence for slow P-C rotation.



(191)



(192)



(4)

Slow rotation about the P-C bond in (4)[17] is apparent from the ^{19}F n.m.r. spectrum at -50° because the apical fluorine atoms become non-equivalent at this temperature. However, it may be that a hydrogen-bond interaction between the amino hydrogen and an apical fluorine is responsible for the observed barrier to rotation and the alignment of the pyrrole group.

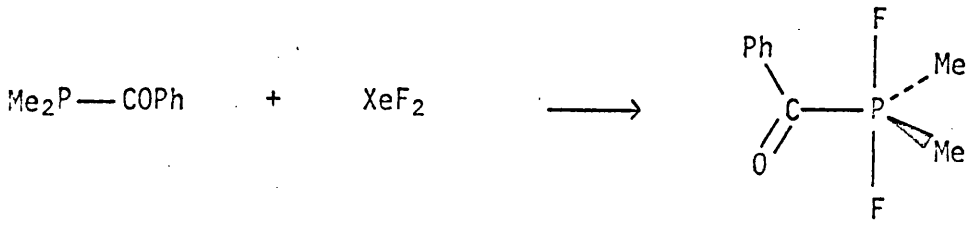
π-Acceptor Ligands.

Hoffmann's prediction[61] concerning the preferred orientation of equatorial π-acceptor ligands has not as yet been confirmed by any

experimental examples.

The ^1H d.n.m.r. data for the phosphorane (175) imply a relatively high apicophilicity value for the benzoyl group which may result from its π-acceptor properties. As the temperature was lowered considerable broadening of the two singlets due to the methyl groups occurred which may be a consequence of slow P-C rotation but the n.m.r. changes could not be quantified.

In order to gain information on the barrier to P-C rotation and on the preferred orientation of the benzoyl group, the phosphorane (193) was prepared by treatment of benzoyldimethylphosphine with xenon difluoride.



(193)

If a slowing of rotation about the P-C bond occurs at low temperature this should be apparent by non-equivalence of either the fluorine atoms or the methyl groups, depending upon the preferred orientation of the benzoyl group.

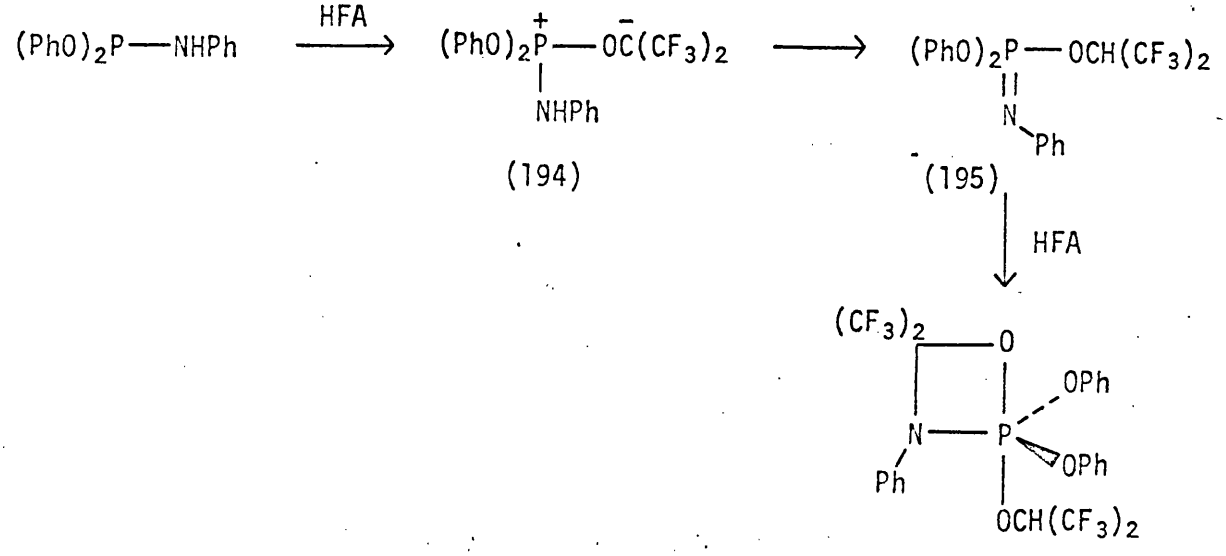
The ^{19}F n.m.r. spectrum was essentially unchanged from room temperature to -100° and was consistent with equivalent fluorine atoms. This indicates that if the benzoyl group acts as a π-donor the P-C rotation barrier is less than about 8 kcal mol^{-1}.

The ^1H n.m.r. spectrum of (193) did show broadening at about -100° but it is not definitely certain whether this is due to a 'freezing' of

the benzoyl group as a π-acceptor, with the acceptor orbital perpendicular to the equatorial plane, or to a change in resolution. However, the fact that the phosphorane (175) also showed spectral changes as the temperature was lowered, which were not due to a change in resolution, does indicate that there is a barrier of about 7 kcal mol^{-1} to P-C rotation and that the benzoyl group has the preferred alignment predicted[61] for π-acceptors.

4.12 Reaction of Diphenyl N-Phenylphosphoramidite with Hexafluoroacetone.

Reaction of diphenyl N-phenylphosphoramidite with HFA in the usual way gave the phosphorane (196). This is thought to be formed by attack of the phosphoramidite on the carbonyl oxygen of an HFA molecule to form



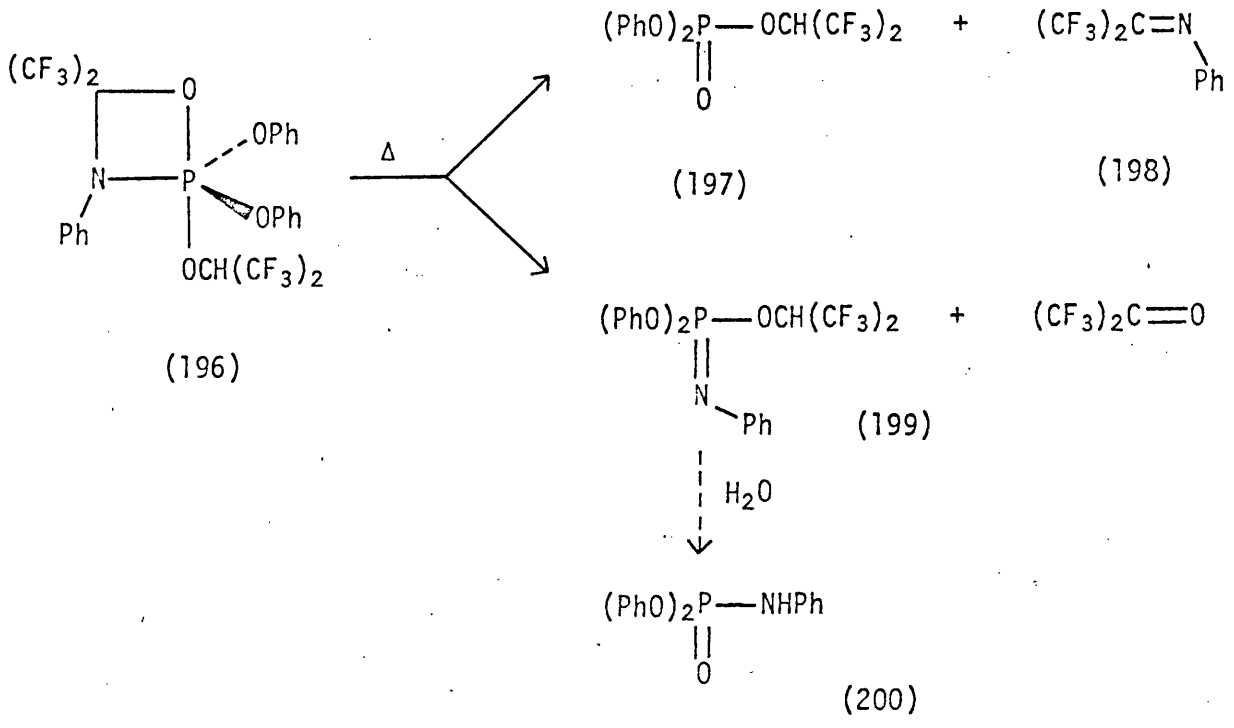
the betaine (194), followed by proton transfer to give the phosphorimidate (195). Addition of a second molecule of HFA to (195) then occurs to form the oxazaphosphetan (196).

Proton abstraction from an α-carbon atom and subsequent formation of a 1,2-oxaphosphetan is a well established reaction and is believed to proceed by an analogous mechanism.[19,63,113]

Thermolysis of the oxazaphosphetan (196).

From the generally accepted mechanism for their formation, 1,2-oxaphosphetans may be regarded as being analogous to the proposed intermediate in the 'Wittig olefin synthesis'.[114] In accord with this, 1,2-oxaphosphetans have been shown to undergo the final stage of the Wittig reaction on heating, to form phosphine oxide and olefin.[19,63,113] The oxazaphosphetan (196) is also a potential Wittig intermediate and it was therefore of interest to see whether it would undergo an analogous thermal decomposition.

The oxazaphosphetan (196) was heated for one hour at 150°. The resulting products were the phosphate (197), the imine (198), and the phosphoramidate (200). These are thought to arise by the routes shown in scheme 16.



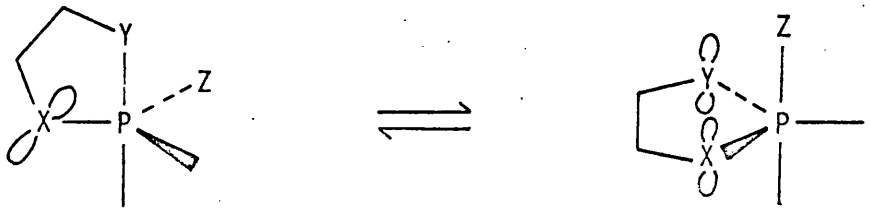
SCHEME 16

The crude thermolysis residue showed the presence of (197) and (199) in the ratio 1:1 (by ^{19}F n.m.r. integration). Formation of (199) was also apparent from the mass spectrum of the crude product but hydrolysis to (200) occurred on chromatography.

The 1:1 ratio of (197) to (199) indicates that the two thermolysis pathways are equally favoured, in contrast to the exclusive formation of phosphine oxide and olefin in the thermolysis of 1,2-oxaphosphetans.

5. RING STRAIN ENERGIES IN CYCLIC PHOSPHORANES.

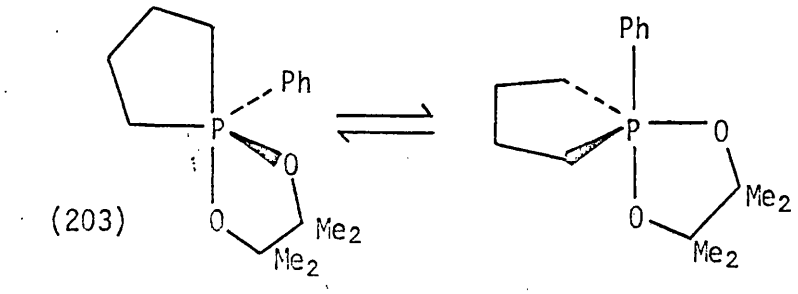
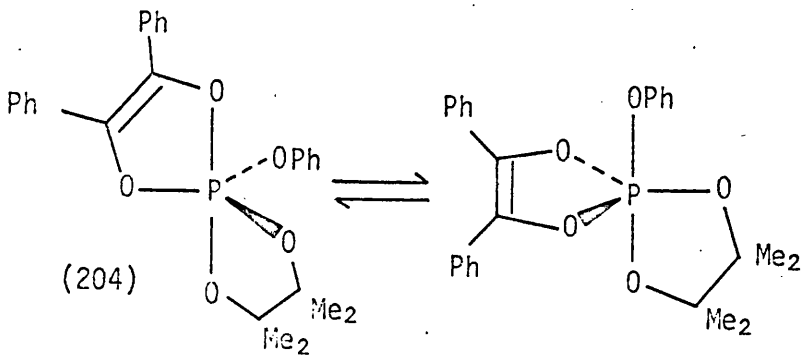
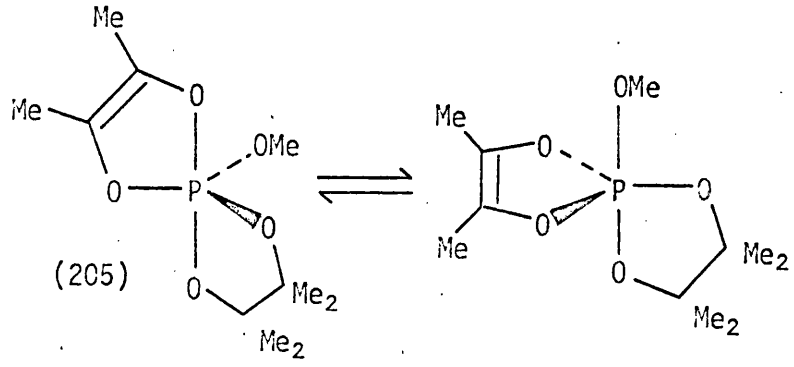
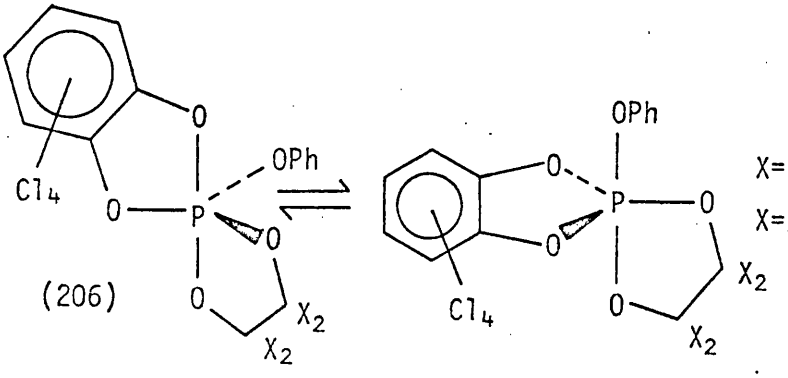
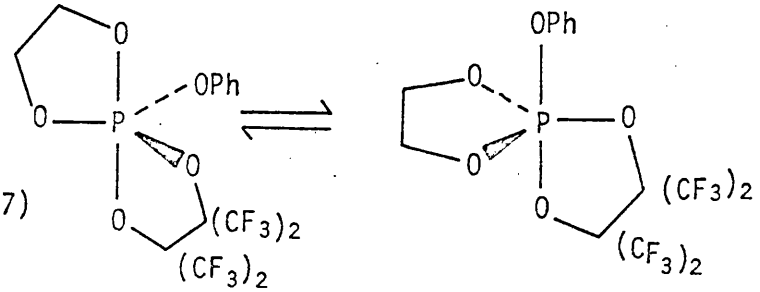
From studies on a number of five-membered cyclic phosphoranes it became apparent that the energy required to move the ring into the ee position varies enormously with the nature of the endocyclic atoms bonded to phosphorus. In all cases studied, the energy required to place a five-membered ring containing heteroatoms bonded to phosphorus in the ee position is greater than is needed for the phospholan ring.



(201) (202)

With reference to table 8 it is evident that the energy difference between (201) and (202) depends not only upon the nature of Y; this would be expected since the interconversion of (201) and (202) involves an apicophilicity term dependent upon Y, but also upon the nature of X. Even when any apicophilicity differences are taken into account, the ring strain energies still vary considerably with the nature of both X and Y.

In order to explain these variations it is necessary to look at the changes in orientation of the donor orbitals of the heteroatoms of the ring in (201) and (202). For (201) the donor orbital of X is aligned in the equatorial plane, the favoured orientation for a π-donor. Since there is no preferred orientation for a π-donor in an apical position the orientation of the donor orbital of Y need not be considered. When the ring is

Pseudorotation.	ΔG*	ΔG*-ΔA	ΔG* (calc.
	kcal mol^{-1}		
 (203)	8.9	8	9
 (204)	14.1	15	14
 (205)	21.2	21	20
 (206)	X=F: 21.8 X=H: 20.5	22 21	20
 (207)	17.4	18	17

[cont'd]

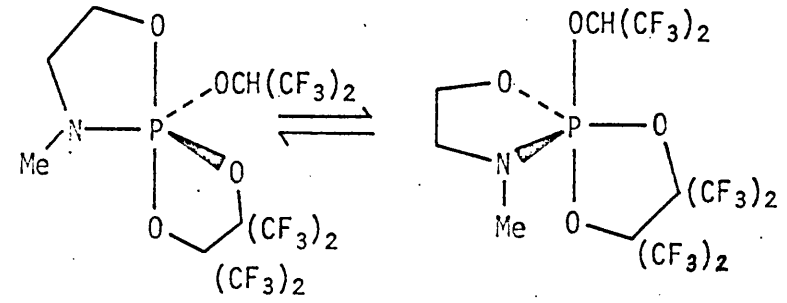
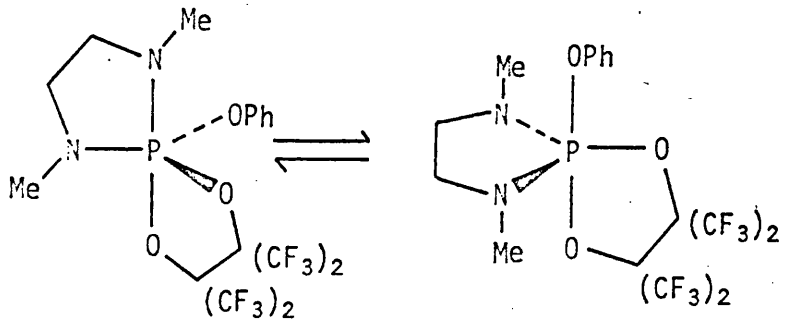
Pseudorotation.	ΔG*	ΔG*-ΔA	ΔG*(calc.)
(208) 	21.0	22	22
(209) 	20.4	29	20

TABLE 8

Compounds (203) - (205) were prepared by M. White; compounds (206) and (207) were prepared by S. Bone.

placed in the ee position, as in (202), the donor orbitals of both X and Y are aligned perpendicular to the equatorial plane, the unfavoured alignment for a π-donor. The energy difference between (201) and (202) can thus be written as:

$$\Delta G\ (202\text{-}201) = A\ (Z\text{-}Y) + S^5 + R^X + R^Y \qquad (210)$$

where A (Z-Y) = the normal apicophilicity difference between Z and Y;

S^5 = the angle strain associated with moving the five-membered ring into the ee position;

R^X = a rotational term due to X, since the donor orbital of X has moved from a favourable to an unfavourable alignment;

and R^Y = a rotational term due to Y, because the A (Z-Y) term uses the normal apicophilicity value of Y, when its donor orbital is free to align itself in the equatorial plane, as in acyclic systems. In this case it is not free to so align itself and the apicophilicity value of Y is therefore greater than the 'normal' value by the rotational term R^Y.

When X and Y are nitrogen or sulphur, the rotational terms can be as large as 10 kcal mol^{-1} and so the presence of heteroatoms in the ring will affect the overall ring strain energy quite appreciably.

Using the values shown in table 9, which are all experimentally

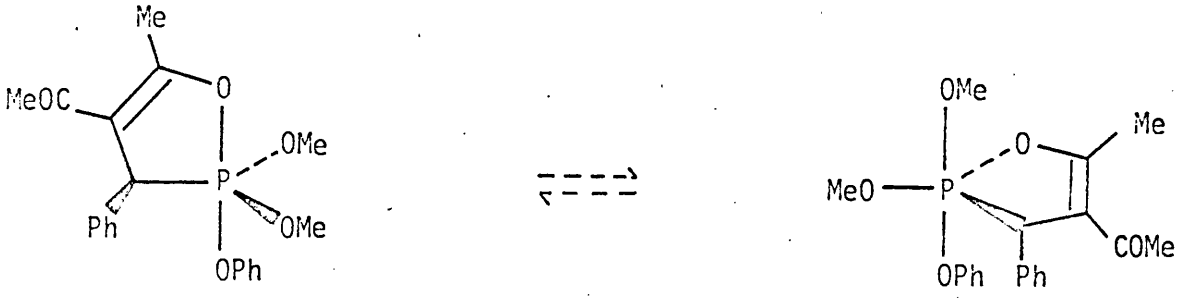
A (N-O)	= 9	kcal mol^{-1}	(see section 4.2 and ref. 63)
A (AlkO-PhO)	= 1	"	90,115
P-N rotation term	= 10	"	(see section 4.11)
P-O rotation term	= 5	"	(see section 4.11)
$S^{phospholan}$	= 8	"	[from (203)]
$S^{phospholen}$	= 10	"	115

TABLE 9

determined, with the exception of the P-O rotation barrier, the free energies predicted from equation (210) correlate extremely well with the observed values (compare columns one and three of table 8).

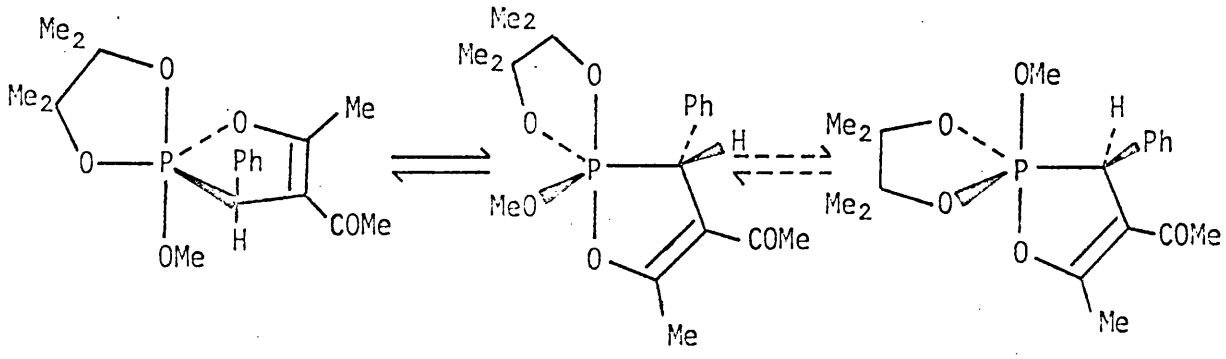
Deviations from the expected strain energies do occur when the ring contains substituents on an α-carbon atom. This is evident from the work of Gorenstein[25b] who investigated the ^1H d.n.m.r. behaviour of

a number of monocyclic phosphoranes, e.g. (211). In this case the energy required to place the oxaphospholen ring in the ee position was



(211)

found to be about 22 kcal mol^{-1}, whereas a theoretical estimate would put the strain factor at 15 kcal mol^{-1}. Nevertheless, the effect of heteroatoms in the ring is still apparent, even in sterically hindered systems, e.g. the BPR (212) (213) has a ΔG^* value of 17 kcal mol^{-1} (calculated value 15 kcal mol^{-1}) but the BPR (213) (214) is slow on the n.m.r. scale at 170° ($\Delta G^* > 23$ kcal mol^{-1}).[116]

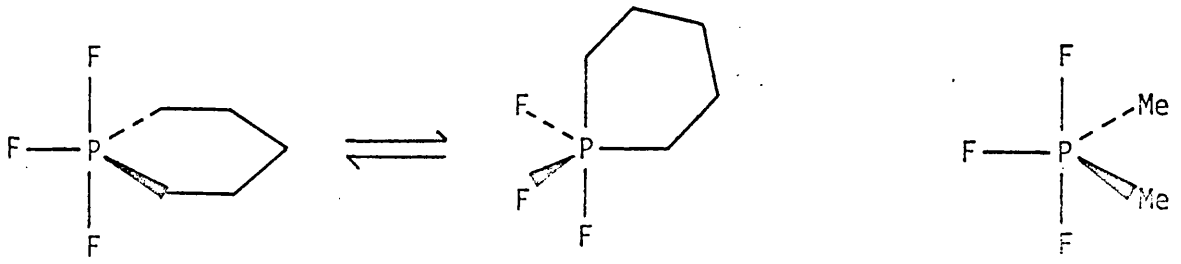


(212) (213) (214)

6. SIX-MEMBERED CYCLIC PHOSPHORANES.

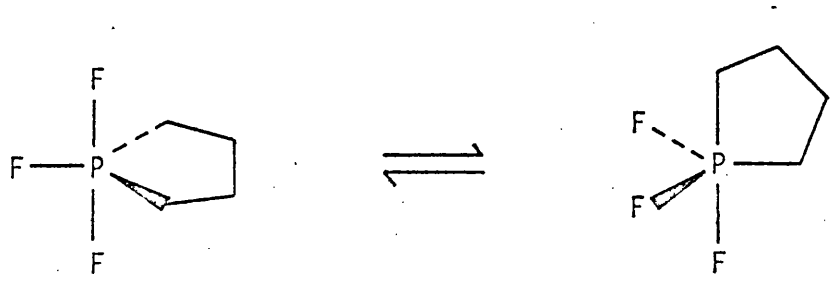
There is ample experimental evidence to support the idea that in four- or five-membered cyclic phosphoranes the ring prefers to span the ae position of the TBP (see section 1.1). When the phosphorus is part of a six-membered ring the situation is less clear. The calculations of Ugi[59d,e] have indicated a preference of the phosphorinane ring for the ee position although this has not as yet been definitely confirmed in practice. No indication of the magnitude of this preference was given.

The fluorine atoms in the phosphorane (215)[22] remain non-equivalent at all temperatures up to 100° and so the ΔG^* value for fluorine equilibration via (216) is greater than 15-16 kcal mol^{-1}. Unfortunately a direct comparison with (217), the acyclic analogue of (215), is meaningless because the fluorine equilibration in (217) has been shown to



(215) (216) (217)

proceed by an intermolecular process.[87] However, the ΔG^* value for fluorine equilibration in the phosphorane (218)[22] has been determined as 7-8 kcal mol^{-1}. The difference, therefore, between the ΔG^* values for (215) $\rightleftharpoons$ (216) and (218) $\rightleftharpoons$ (219) reflects the difference in strain energy between the phosphorinane and phospholan rings.



(218) (219)

The energy required to move a phospholan ring into the ee position has been determined as 8-9 kcal mol^{-1}[115] and since the strain in the phosphorinane ring is at least 8 kcal mol^{-1} less than this, it follows that any preference that the phosphorinane ring may have for the ae position is very small. However, no estimate can be made of the preference, if any, for the ee position.

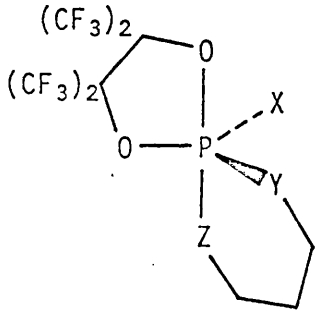
It may very well be, then, that the phosphorinane ring does prefer the ee position but if the ideas discussed in section 5 are applicable to six-membered rings, the presence of heteroatoms in the ring would be expected to destabilise the ee placement, since the donor orbitals of the heteroatoms would be aligned in an unfavourable orientation. In accord with this, the studies of Denney and his co-workers[48] on phosphoranes containing a 1,3,2-dioxaphosphorinane ring indicate that the six-membered ring does prefer to occupy the ae position of the TBP.

The situation for six-membered rings is, however, rather more complex than for five-membered rings since the six-membered ring is not planar. By inspection of a molecular model of a phosphorane with a six--membered ring in the ae position, it appears that in order to put the donor orbital of the equatorial heteroatom in the equatorial plane, the six-membered ring must adopt the 'boat' conformation. Hence, the rotational term for the equatorial heteroatom might be expected to be less

than the equivalent term in a five-membered ring by the difference in energy between the 'boat' and the 'chair' conformations.

Models also indicate that a six-membered ring is more flexible when in the ee position than is the corresponding five-membered ring. Hence it may be possible for the six-membered ring to adopt a conformation where the donor orbitals of the heteroatoms are not lying directly in an apical plane. This would also have the effect of diminishing the rotational terms for the heteroatoms of six-membered, compared with five-membered, rings.

In order to gain information on strain factors in six-membered rings, the adducts (220)-(223) were prepared.



	(220)	(221)	(222)	(223)
X	NMe_2	OPh	OPh	OPh
Y	O	O	NMe	NMe
Z	O	O	O	NMe

The ^{19}F d.n.m.r. data for the adducts are shown in table 10.

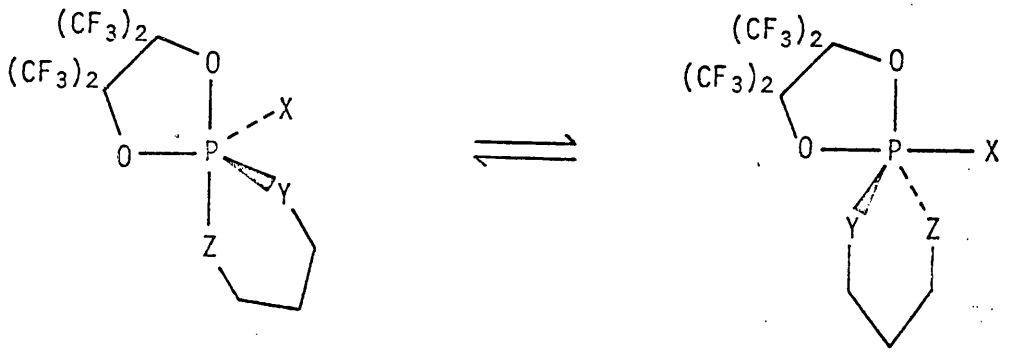
Adduct	^{19}F Tc/°C [a]	Δν/Hz [b]	ΔG*/kcal mol^{-1} [c]	^{31}P δ [d]
(220)	-63	162.5	9.4	+ 44
(221)	-140	100	5.9	+ 68
(222)	- 70	102.5	9.2	+ 58
(223)	< -140		< 6	+ 37

[cont']

[a] In ether-light petroleum. [b] Maximum frequency separation below coalescence. [c] Corrected for multiplicity of lowest energy interconversion pathway. [d] P.p.m. relative to 85% H_3PO_4; in $CDCl_3$.

TABLE 10

Adducts (220), (221) and (223) are n.m.r. system type 2 molecules and (222) is an n.m.r. system type 3 molecule. The ΔG* values in



(224) (225)

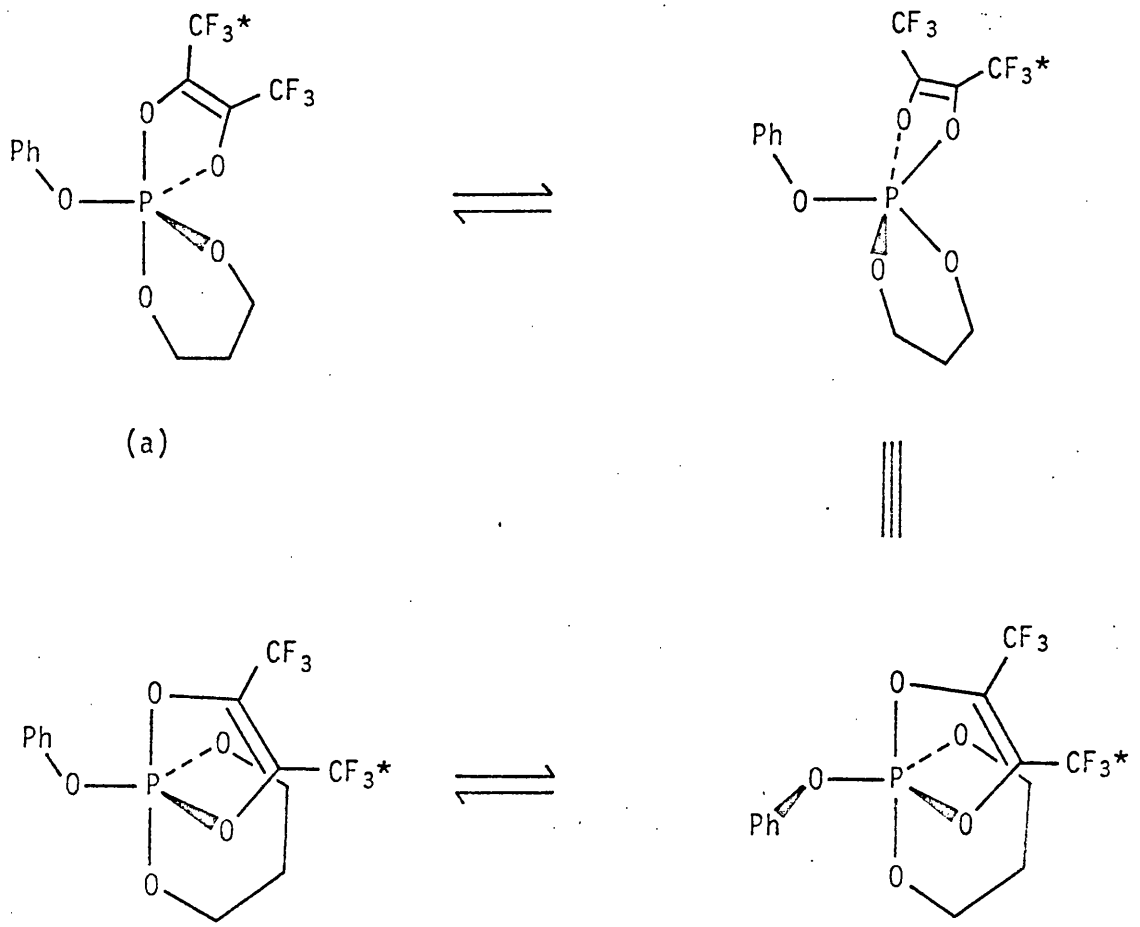
table 10 correspond to the energy difference between structures (224) and (225).

Since no quantitative data are available for the preference of the phosphorinane ring for a particular position in the TBP it would be unwise to draw any definite conclusions about the magnitudes of the rotation terms in six-membered rings from the data shown in table 10. The results do indicate, however, that six-membered rings with oxygen and/or nitrogen bonded to phosphorus have a preference for the ae position of the TBP. [However, the difference in ΔG* values for (220) and (221) is much smaller than would have been expected on the basis of a difference in apicophilicity between nitrogen and oxygen of about 9 kcal mol^{-1}. The

reason for this disparity is not known. The low ΔG* value for (220) may be due to an irregular isomerisation process but this seems unlikely since the ^{31}P n.m.r. chemical shift of (220) is the same in chloroform and in hexafluoroisopropanol.]

It is also evident, by comparison of (221) and (222), that rotation terms for the heteroatoms still affect the overall ring strain in the same way as in five-membered cyclic systems: replacement of an equatorial oxygen by nitrogen increases the energy required to place the six-membered ring in the ee position by 3.3 kcal mol^{-1}.

The ΔG* value for the adduct (221) is close to the predicted energy barrier for P-O rotation. A slowing of P-O rotation also leads to non-equivalence of the trifluoromethyl groups and so, in order to determine



(226)

whether the observed coalescence is due to the slowing of a BPR or P-O rotation, the phosphorane (226) was synthesised, by reaction of equimolar quantities of 2-phenoxy-1,3,2-dioxaphosphorinane and hexafluorobiacetyl.

The topomeric BPR (a) (c) is fast on the n.m.r. time scale even at very low temperatures and so the trifluoromethyl groups will remain equivalent until P-O rotation becomes slow. When this happens equilibration of the trifluoromethyl groups is not possible, even by a BPR process involving ee placement of the six-membered ring.

The ^{19}F n.m.r. spectrum of (226) remained a singlet from room temperature to -145°. This implies that the coalescence observed in (221) is due to a slowing of a BPR and not to a slowing of P-O rotation.

7. STERIC EFFECTS IN PHOSPHORANES.

7.1 Reaction of Some Phenyl Dialkylphosphinites with Hexafluorobiacetyl.

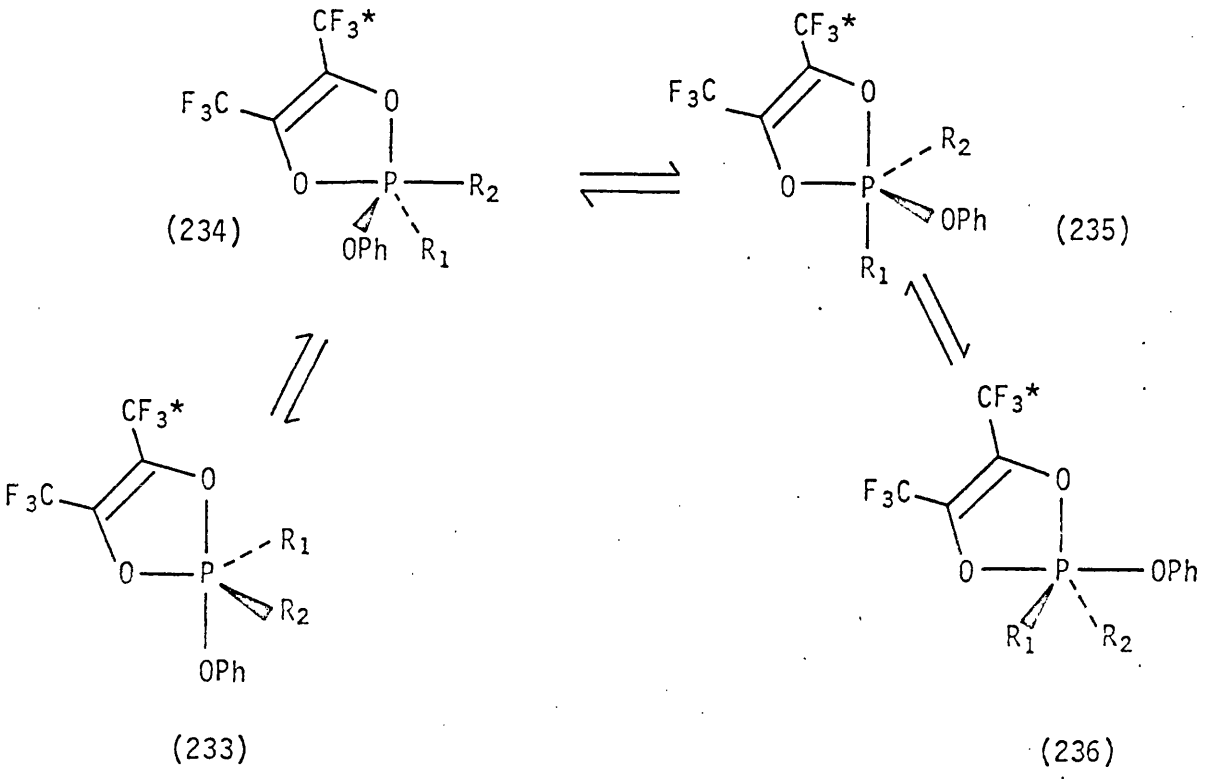
Since there are two sets of non-equivalent positions about the phosphorus in a TBP and therefore, presumably, two different steric environments it might be expected that the size of a ligand may have a bearing on its preference for a particular position. It has often been stated[25b, 59f,113,117] that steric effects do play a part in determining the apicophilicity of a ligand but no definitive data have been reported. Several workers[59f,118] have assumed that the apical position in a TBP is the more hindered although it is by no means obvious why this should be so. Although an apical ligand experiences three 90° interactions whereas an equatorial ligand only experiences two, the apical bonds are slightly longer and so crowding about the apical position will be reduced.

The work which is described in this section was designed to gain information on two main points:

(a) to determine the more hindered position in a TBP;

and (b) to determine the magnitude of the steric factor for different alkyl groups bonded directly to phosphorus; there are indications (see section 4.2 and ref. 9) that steric effects are very small unless the bulky groups are attached directly to phosphorus.

The phosphoranes (227) - (232) were prepared by treatment of one equivalent of the appropriate phosphinite with one equivalent of hexafluorobiacetyl. The adducts are all n.m.r. system type 4 molecules: (233) and (236) are the low energy topomers, since oxygen ligands are more apicophilic than carbon ligands[4,48,63] and equilibration of the trifluoromethyl groups proceeds by BPR's which place R_1 and R_2, in turn, in the apical position.



(234) (235) (233) (236)

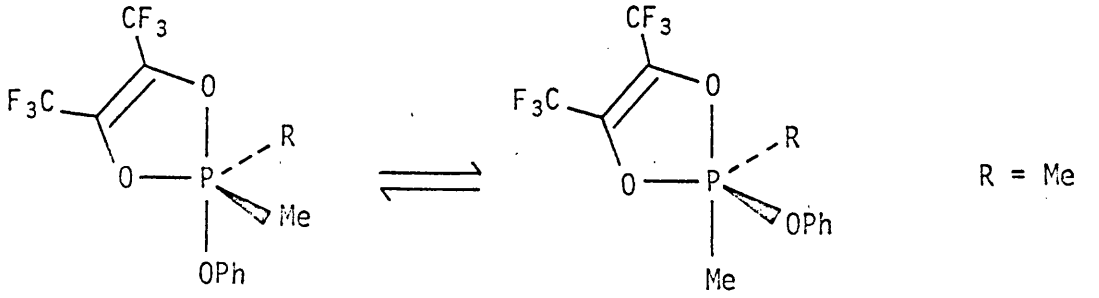
	R_1	R_2
(227)	Me	Me
(228)	Et	Et
(229)	^{i}Pr	^{i}Pr
(230)	^{t}Bu	^{t}Bu
(231)	^{t}Bu	Me
(232)	Ph	Me

As the alkyl groups become more apicophilic so the ΔG^* value for the equilibration process decreases. The ^{19}F d.n.m.r. data for the phosphoranes (227) - (232) are shown in table 11.

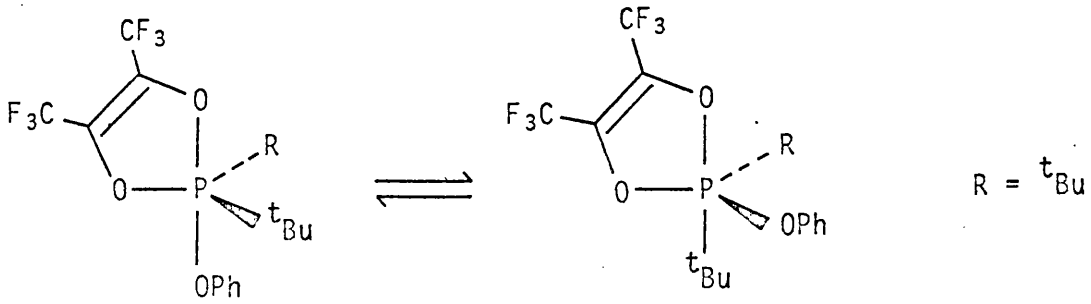
By comparing the results of adducts (227) - (230) it is evident that the ΔG^* values increase as the size of the alkyl groups increases. If the assumption is made that the electronegativities of the alkyl groups

are essentially the same,[103a] this implies that, for this system, the apical position is the more hindered.

The limitation of the data of adducts (227) - (230) is that both alkyl groups are varied along the series. This leads to inaacuracies in comparing the relative apicophilicities of the alkyl groups since, for (227), the equatorial alkyl group is methyl whereas for (230), it is



(227)



(230)

t-butyl. In order to obtain a more accurate apicophilicity scale it is necessary to keep the equatorial alkyl group constant.

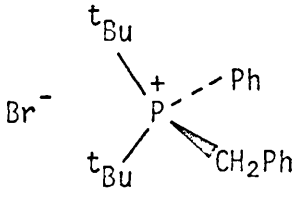
A comparison of the ΔG^* value for (231) with those for (227) and (230) illustrates the effect that a variation in the equatorial R group has on the relative apicophilicities of the alkyl groups. It can be seen that the apicophilicity difference between the methyl and t-butyl groups is much greater when R = t-butyl (t-butyl 3.2 kcal mol^{-1} less apicophilic) than when R = methyl (t-butyl 1.1 kcal mol^{-1} less apicophilic).

This is easily explicable on steric grounds because in (231) there is no longer the 90° t-butyl - t-butyl interaction that is present in (230).

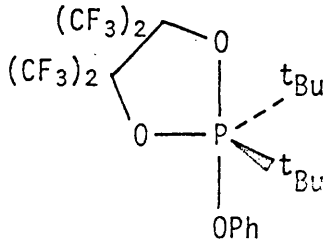
The results, then, of adducts (227) - (231) indicate that:

(a) the apical position is the more hindered position;

and (b) steric effects in the TBP are of relatively small magnitude unless there are at least two bulky groups attached to the phosphorus. This latter point is in agreement with the results of Trippett and his co-workers on the relative rates of alkaline hydrolysis of sterically hindered phosphonium salts[73] and phosphonate and phosphinate esters[119] but the agreement is probably only fortuitous since it is likely that the rate differences arise mainly from an inhibition of the rate of nucleophilic attack at phosphorus and not from any crowding in the TBP intermediates. In particular, the extreme hydrolytic stability of (233)[73] cannot be due to the reluctance of the TBP to accommodate two t-butyl groups since the rate of reaction of hexafluorobiacetyl with phenyl di-t-butylphosphinite is only slightly slower than the rate of reaction with phenyl dimethyl phosphinite.



(233)



(234)

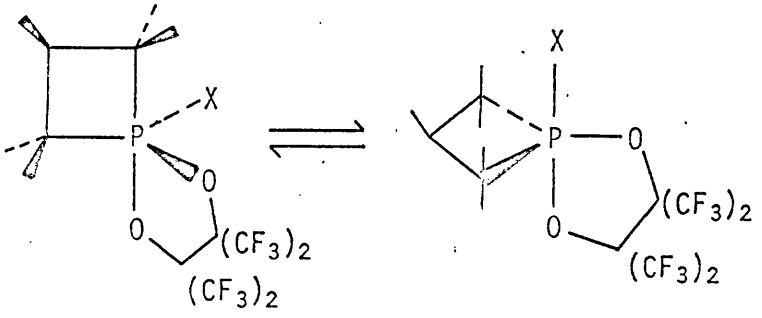
Also, the phosphorane (234) can be prepared very easily by reaction of phenyl di-t-butylphosphinite with HFA in the usual way, without the need for an extended reaction time.

[The phosphorane (234) was prepared in order to gain more information

on the difference in apicophilicity between the phenoxy and t-butyl groups. (234) is an n.m.r. system type 1(b) molecule and would be expected to show the same variable-temperature n.m.r. behaviour as the phosphorane (230). In fact, the ^{19}F n.m.r. spectrum of (234) consists of one singlet from room temperature to -120°. An irregular isomerisation mechanism is presumably responsible for this result, even though the ^{31}P n.m.r. chemical shift of (234) was the same with chloroform or hexafluoro-isopropanol as solvent.]

7.2 The Relative Apicophilicities of Phenyl and Alkyl Groups.

The adduct (232) was prepared in order to determine the relative apicophilicity of the phenyl group. The results indicate that, for this system, the phenyl group is as apicophilic as an alkyl group. This is presumably because the effect of the greater electronegativity of the phenyl group is cancelled out by its π-donor properties. This is not the case in other systems: Oram and Trippett[63] have shown that for the system (235), the phenyl group is appreciably less apicophilic than the methyl



X	ΔG*
Me	16.9
^{i}Pr	17.8
Ph	> 22

(235)

or isopropyl groups. The reason for this variation between systems is not clear but it may be that π-donation from the phenyl group in (235)

is larger than in (232) because there are fewer oxygen ligands in (235) to act as competitive π-donors (see section 4.4).

8. NUCLEOPHILIC SUBSTITUTION AT QUINQUECOVALENT PHOSPHORUS.

8.1 Base-catalysed Substitution at Quinquecovalent Phosphorus.

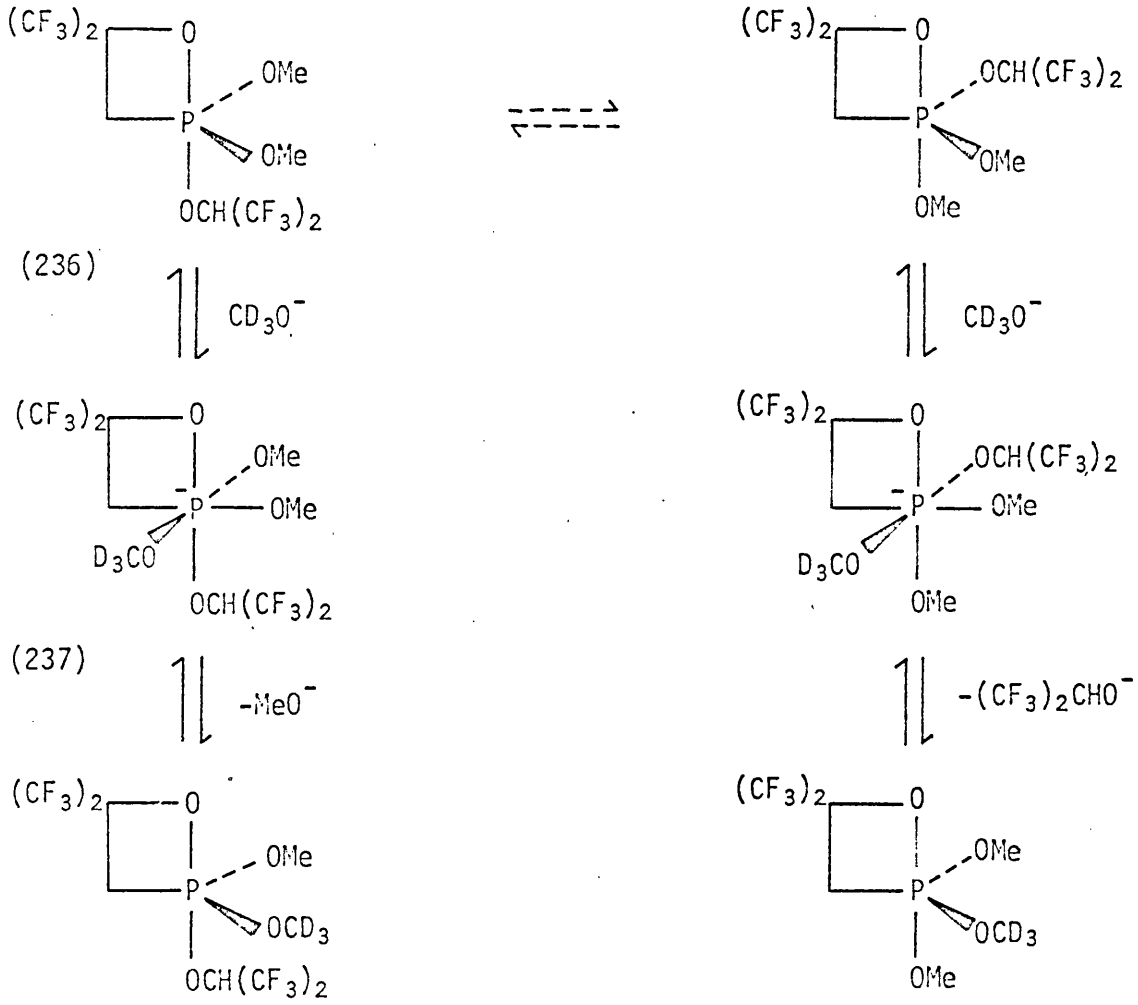
Nucleophilic substitution at the phosphorus of oxyphosphoranes is a well documented reaction both in cyclic and acyclic systems (see sections 1.2 and 1.3 and refs. 120 and 121). Ramirez[120] has shown that the exchange of alkoxy groups when oxyphosphoranes are treated with alcohols is base-catalysed and has suggested that the reaction proceeds *via* a hexaco-ordinate transition state or intermediate.

Westheimer,[121] from a study of the kinetics of hydrolysis of a series of penta-aryloxyphosphoranes, has also concluded that substitution proceeds *via* a hexaco-ordinate species.

Ramirez[120] has further shown that when the oxaphosphetan (236) is treated with CD_3OD in the presence of triethylamine the methoxy group is displaced in preference to the hexafluoroiospropoxy group in spite of the greater anionic stability of the latter.

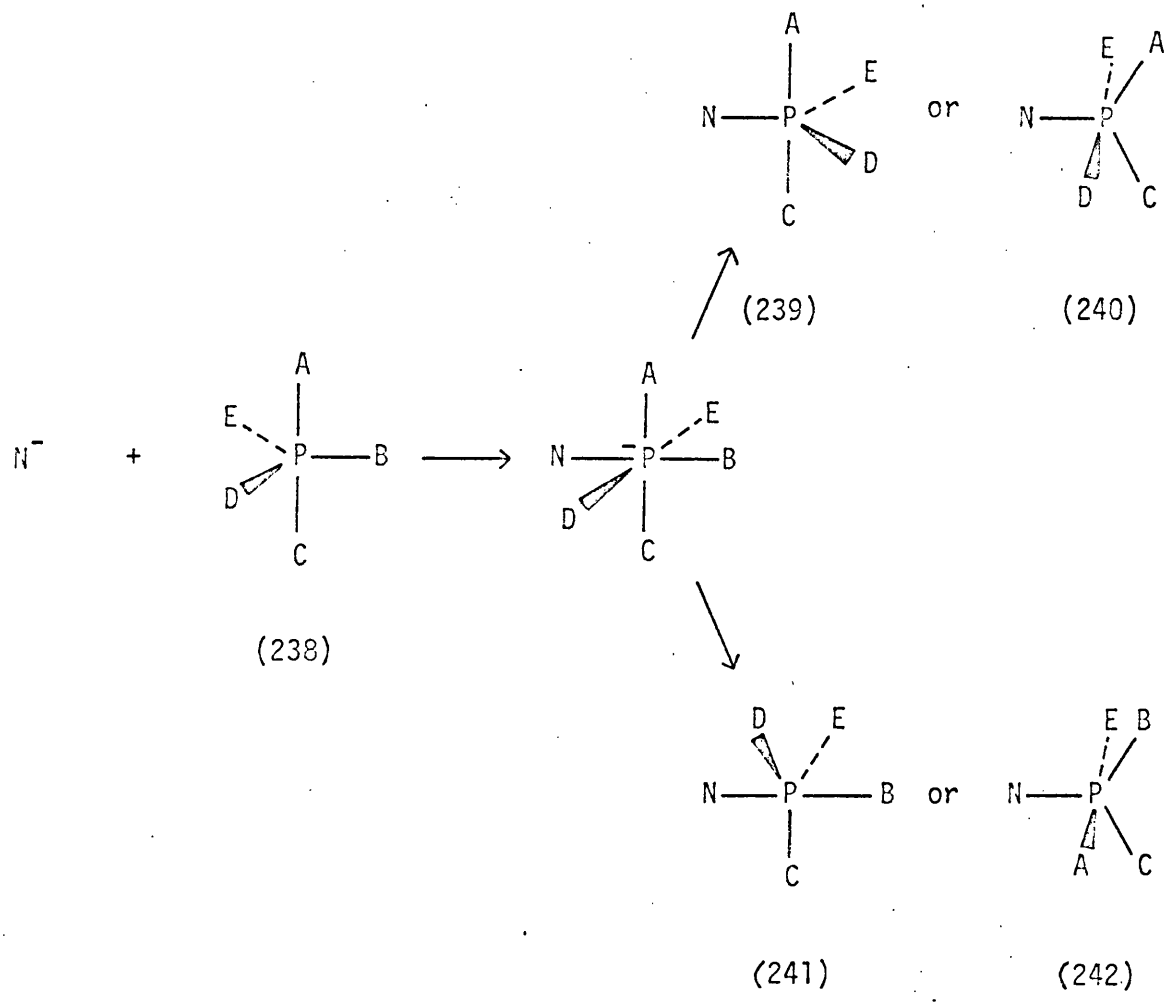
The suggested mechanism, involving nucleophilic attack in the equatorial plane directly opposite the leaving group, is shown in scheme 17.

One of the conclusions from this result was that only equatorial groups are replaceable. Although this would be expected if substitution proceeds *via* a hexaco-ordinate species where the entering and leaving groups are colinear, it may not be a general rule for all nucleophilic substitution processes at quinquecovalent phosphorus. Once the octahedral transition state or intermediate has been formed it would seem reasonable to suppose that decomposition may occur by loss of any of the six ligands.



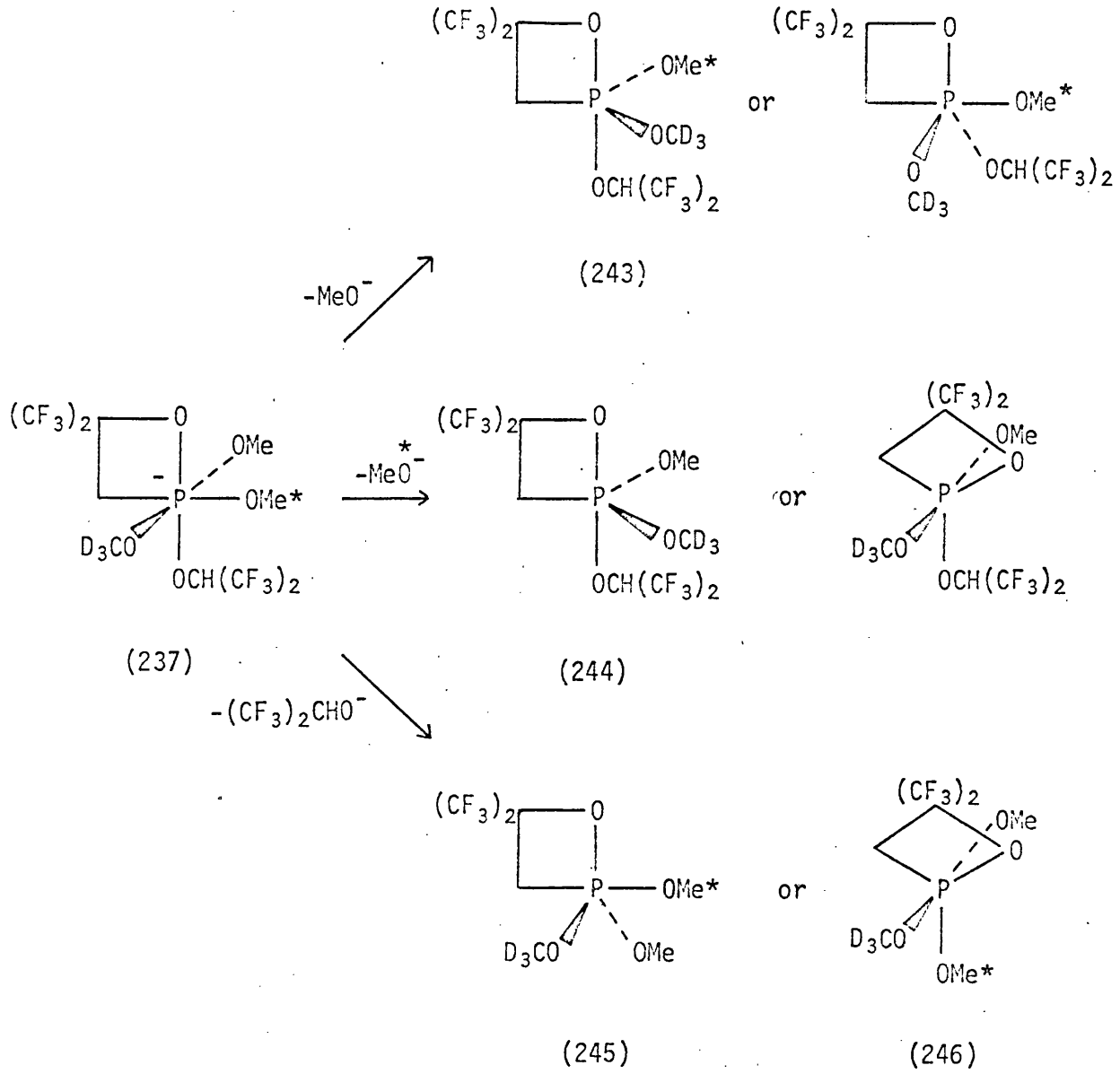
SCHEME 17

With reference to scheme 18, if B is lost from (238) either A and C or D and E must become the new apical ligands. Likewise, if A is lost, groups N and B or D and E must become the new apical ligands. It is the relative stability of the phosphoranes (239) - (242) that decides which group shall be lost. Thus, for the example shown in scheme 17, loss of a methoxy group from (237) can lead to the formation of the low energy phosphoranes (243) or (244) (see scheme 10), but loss of the hexafluoroisopropoxy group leads to phosphoranes (245) and (246),



SCHEME 18

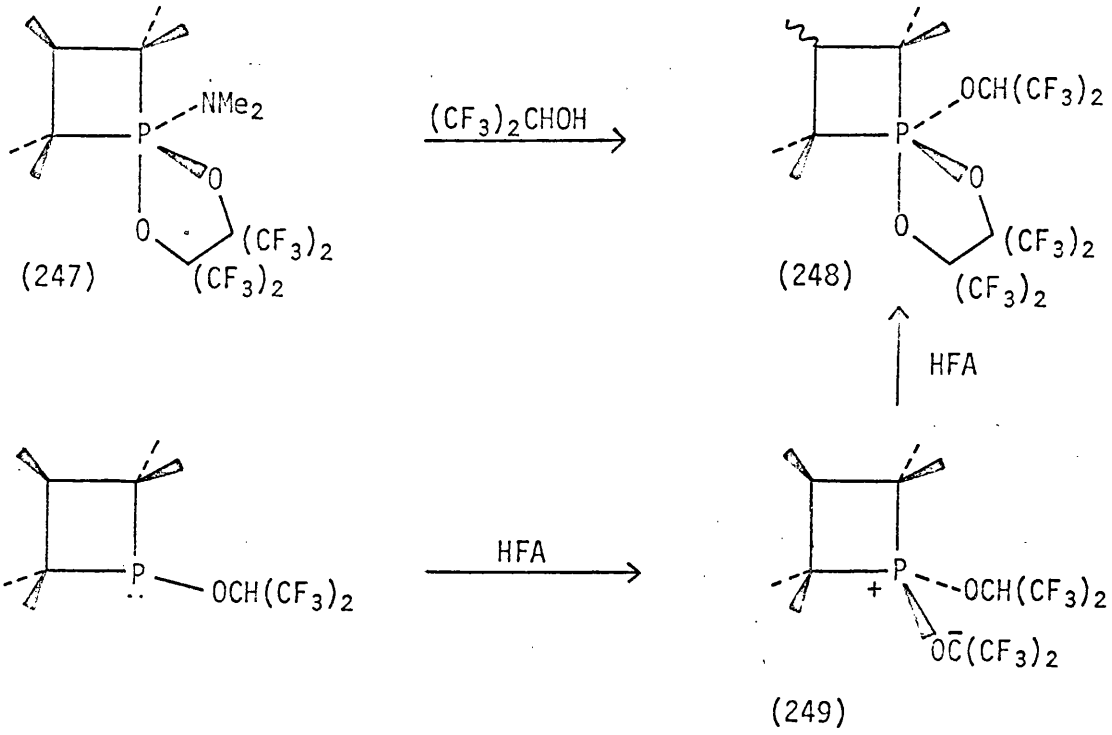
both of which are of higher energy than (243) or (244): (245) has carbon, as opposed to oxygen, in an apical position and (246) has the ring in the ee position. Hence, the loss of the hexafluoroisopropoxy group would be expected to be disfavoured over loss of a methoxy group, as is indeed observed.



SCHEME 19

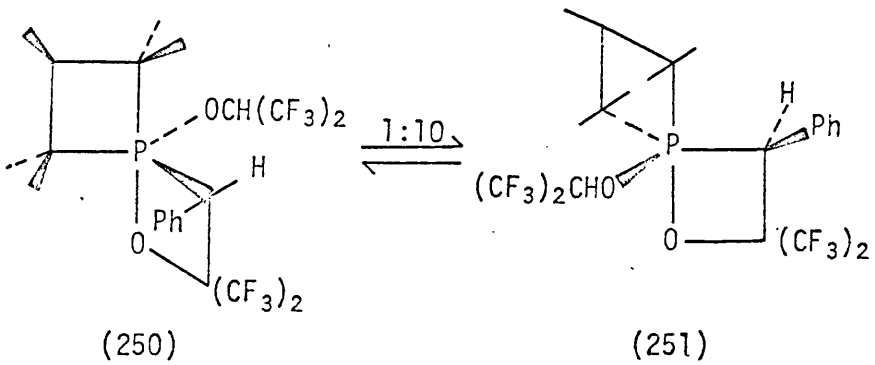
8.2 Stereochemistry of Substitution.

There are very few examples of substitution processes at quinquecovalent phosphorus where the stereochemistry of such a reaction has been determined. Oram and Trippett[63] found that the pure trans isomer of the adduct (247) reacted with hexafluoroisopropanol to give a single isomer of the adduct (248). However, owing to the possibility of proton



transfer in the intermediate (249), it was not possible to determine the stereochemistry of the substitution by comparison of (248) with an isomer of known composition.

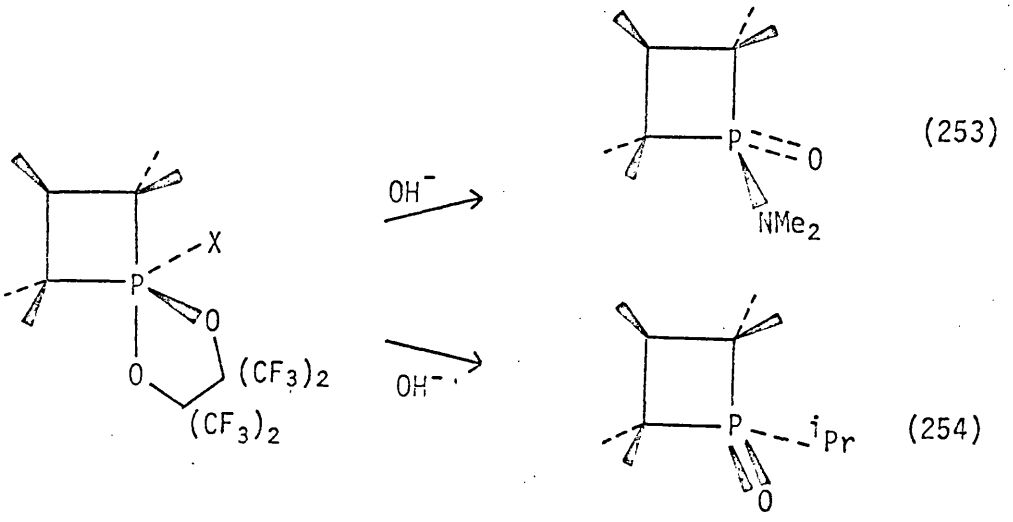
These authors[63] also found that the adduct (250), when treated with two equivalents of hexafluoroisopropanol, slowly isomerised and after



18 hours, equilibrium was established with (251) in the ratio of 1:10. Thus, for this example, substitution proceeds with inversion of configuration

at phosphorus and, if it is assumed that the equilibration proceeds *via* a hexaco-ordinate species and not by an ionisation mechanism, this can only occur by attack of the nucleophile directly opposite the leaving group.

Hydrolysis of the *trans* isomer of the phosphorane (247) yielded



(253)

(254)

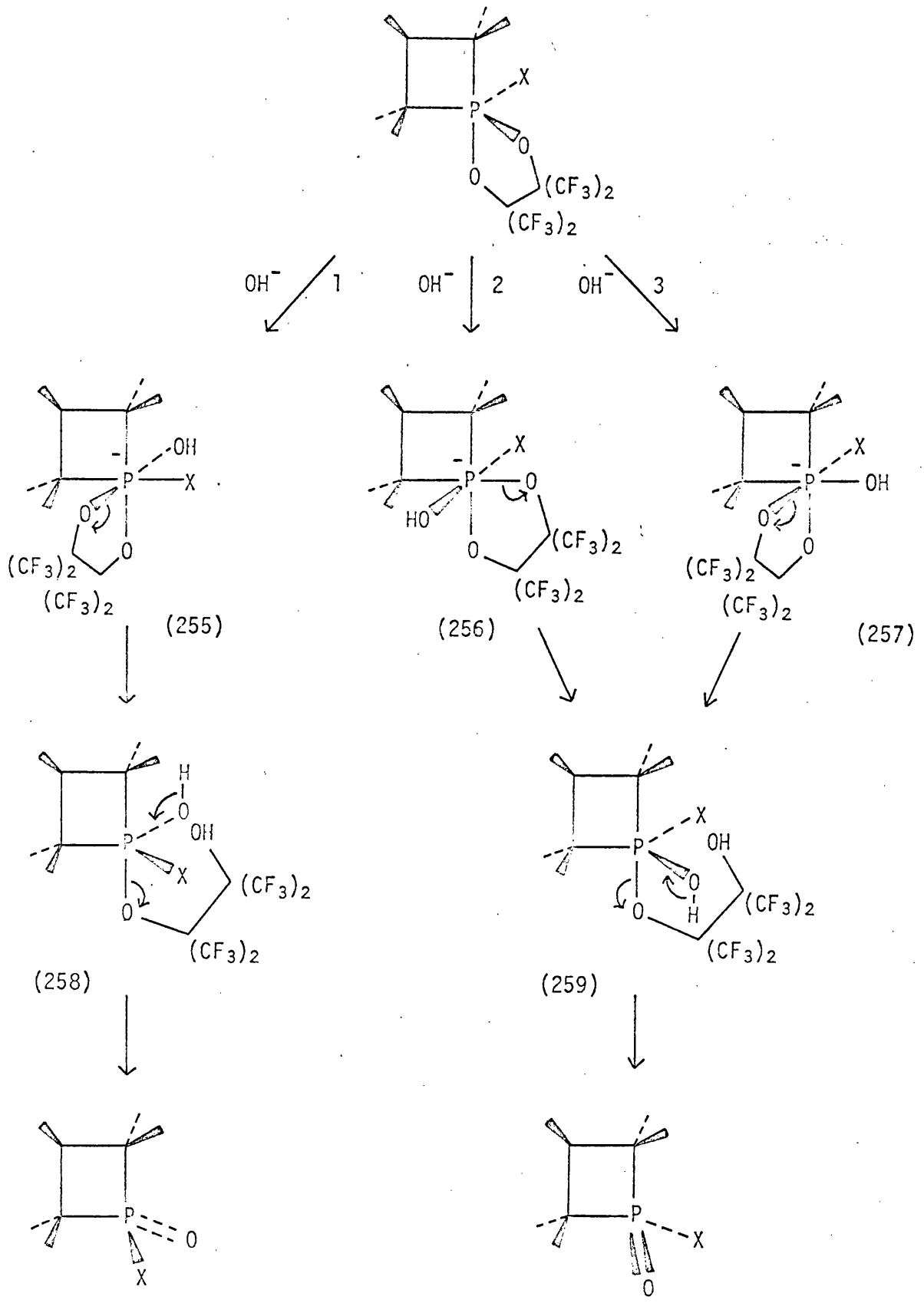
X = NMe_2 (247)

X = ^iPr (252)

only the *cis* isomer of the amide (253). Conversely, hydrolysis of the *trans* isomer of the phosphorane (252) gave only the *trans* isomer of the oxide (254). If it is assumed that these substitutions proceed *via* hexaco-ordinate species, the possible reaction pathways are shown in scheme 20.

Attack of the nucleophile can occur opposite any of the equatorial ligands to give three possible hexaco-ordinate species, (255) - (257). Loss of alkoxide as indicated gives the hydroxyphosphoranes (258) and (259) and loss of the diol then gives either the *cis* or the *trans* oxide. [The stereochemical consequences of the reaction pathways are the same if the other ring P-O bond in the hexaco-ordinate species is broken.].

Route 1 involves attack of the nucleophile directly opposite the



SCHEME 20

the leaving group and the substitution involves inversion of configuration at quinquecovalent phosphorus. Routes 2 and 3 involve attack of the nucleophile opposite each of the other equatorial ligands and the substitution at the phosphorane in these cases proceeds with retention of configuration.

The hydrolysis of the adduct (247), then, proceeds by route 1 to give the cis amide (253). The hydrolysis of the adduct (252) can occur by routes 2 or 3 to give the trans oxide (254).

The stereochemistry of the hydrolysis of (252) shows that a colinear relationship between entering and leaving groups is not a necessary prerequisite for nucleophilic substitution at quinquecovalent phosphorus.

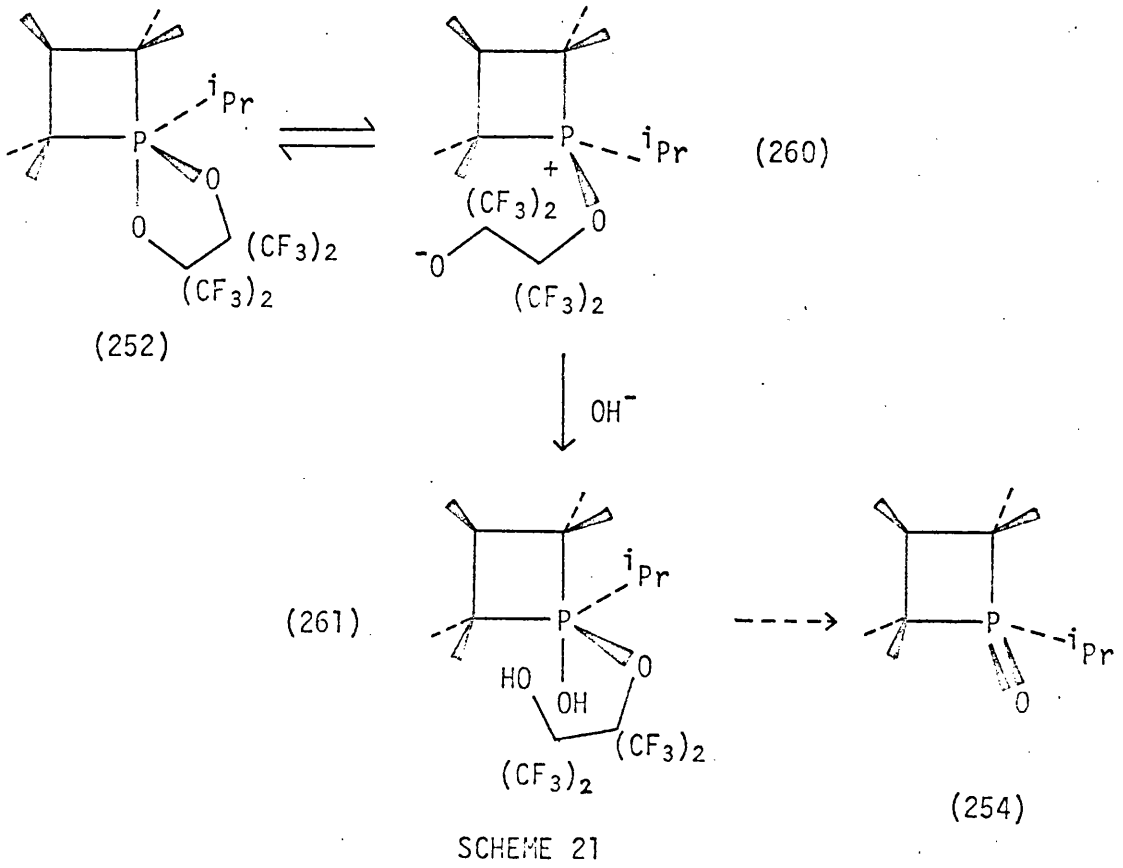
No information on whether the hexaco-ordinate species are transition states or intermediates can be obtained from the hydrolysis results but the involvement of hexaco-ordinate intermediates in at least some substitution reactions seems highly likely in view of the rapidly increasing number of stable hexaco-ordinate phosphorus compounds that are being reported.[122-126]

It is not clear why the adducts (247) and (252) hydrolyse by different pathways. Little seems to be known about the stereoelectronic requirements of an octahedron and it would be unwise to formulate any definite theory on the basis of two experiments but, if π interactions between the ligands and the phosphorus in an octahedron are important in determining the position of initial nucleophilic attack, π-donation from the dimethylamino group, which is absent for the isopropyl group, presumably controls the reaction pathway in some way.

Studies of the stable class of hexaco-ordinate compounds may enable the factors affecting ligand arrangement in an octahedron to be determined. These should enable substitution pathways at quinquecovalent phosphorus to be rationalised and may also be of use in the field of nucleophilic substitution at tetraco-ordinated phosphorus since there have

been suggestions[1a,11] that hexaco-ordinate species may be involved in these reactions also.

It is possible that the hydrolysis of the adduct (252) proceeds by the dissociative mechanism shown in scheme 21. (254) is formed after BPR and loss of the diol from (261).



SCHEME 21

The hydrolysis of the adduct (247) cannot be occurring by this mechanism since the dissociative route would lead to formation of the trans amide. It also seems unlikely that the dissociative mechanism is operating in the case of (252) in view of the large increase in ring strain which would accompany ionisation to (260). It would seem reasonable to suppose that the dissociative route would be more favourable in the case of (247) then (252) because the dimethylamino group is better able to stabilise a positive charge than the isopropyl group and since (247) is

known not to hydrolyse by this route it also seems an unlikely hydrolysis pathway for (252).

EXPERIMENTAL

Instrumentation

Infrared spectra were recorded on Perkin-Elmer 237 or 257 spectrometers as Nujol mulls, except where otherwise stated. Mass spectra were determined with an A.E.I. MS9 instrument; in each case the molecular ion is given first (except where otherwise stated), followed by peaks of structural significance. Except where otherwise stated, routine ^{1}H n.m.r. spectra were recorded on a Varian T-60 spectrometer with tetramethylsilane as internal standard and deuteriochloroform as solvent, variable-temperature ^{1}H n.m.r. spectra were recorded on a Varian A-60 or a Jeol JNM-PS-100 spectrometer, ^{19}F n.m.r. spectra were recorded on a Varian D.A.-60 or a Jeol JNM-PS-100 spectrometer with benzotrifluoride as internal standard, and ^{31}P n.m.r. spectra were recorded on a Varian D.A.-60 spectrometer or by decoupling ^{1}H spectra using an HD-60 heteronuclear decoupler (N.M.R. Specialities) and are relative to external 85% phosphoric acid, with deuteriochloroform as solvent.

Melting points were recorded on a Kofler heating stage, except where otherwise stated, and are uncorrected.

General Details

All reactions involving air-sensitive reactants or products were carried out under an atmosphere of dry, oxygen-free nitrogen. Evaporation was performed with a rotary evaporator and solutions in organic solvents were dried over magnesium sulphate.

Light petroleum had b.p. 40 - 60°.

Solvents were dried as follows:

Diethyl ether and hydrocarbon solvents were dried over sodium wire; tetrahydrofuran was refluxed over, and distilled from, lithium aluminium hydride; dichloromethane was refluxed over, and distilled from, calcium hydride; chloroform was washed with concentrated sulphuric acid and distilled from anhydrous calcium chloride; methanol and ethanol were refluxed over their magnesium alkoxides and distilled.

Pyridine was refluxed over, and distilled from, potassium hydroxide and triethylamine was refluxed over, and distilled from, calcium hydride.

Preparation of Phenyl Phosphorodichloridite and Diphenyl Phosphorochloridite

These were prepared by the method of Forsman and Lipkin.[127] Distillation gave phenyl phosphorodichloridite (30%), b.p.78-84°/1mm (lit.[128] 90°/10mm) and diphenyl phosphorochloridite (33%), b.p. 130-132°/0.4mm (lit. 146.5-148°/4mm).

In a similar way, p-fluorophenol gave bis-(p-fluorophenyl) phosphorochloridite (37%), b.p. 120-140°/0.1mm .

General Procedure for the Preparation of N-Substituted Diaryl Phosphoramidites.

A solution of the amine (0.1 mol) in ether or hexane (30ml) was added dropwise to a stirred solution of diphenyl, or bis-(p-fluorophenyl), phosphorochloridite (0.05 mol) in ether or hexane (50ml), at 0°. After addition was complete (0.5h), the mixture was stirred at room temperature for 2-5h , and then filtered. Solvent was then removed and the residue distilled. In this way the following compounds were prepared: diphenyl NN-dimethylphosphoramidite (43%), b.p. 132-136°/0.5mm (lit.[129] 94-95°/0.02mm), ν_{max} (film) 1595, 1490, 1295, 1205, 975, 845, 765, and 690 cm^{-1}, τ 2.48-3.15 (10H, m), and 7.27 (6H, d, J 9 Hz); bis-(p-fluorophenyl) NN-dimethylphosphoramidite (72%), b.p. 128-134°/0.1mm, ν_{max} (film) 1495, 1185, 1086, 978, 880, 860, 834, 788, and 685 cm^{-1}, τ 2.93 (4H, s), 3.05 (4H, s), and 7.23 (6H, d, J 10 Hz); diphenyl pyrrolidin-1-yl phosphonite (73%), b.p. 161-165°/0.4mm, ν_{max} (film) 1598, 1492, 1221, 1199, 1163, 1069, 1023, 878, 860, 753, and 691 cm^{-1}, τ 2.43-3.13 (10H, m), 6.43-6.97 (4H, m), and 8.00-8.50 (4H, m); bis-(p-fluorophenyl) pyrrolidin-1-yl phosphonite (79%), b.p. 155-160°/0.4mm, ν_{max} (film) 1500, 1188, 1090, 1013, 875, 837,

800, and 665 cm^{-1}, τ 2.63-3.27 (8H, m), 6.38-6.90 (4H, m), and 7.83--8.35 (4H, m); diphenyl NN-di-isopropylphosphoramidite (86%), b.p. 138-142°/0.1mm (lit.[130] 122-123°/0.03mm), ν_{max} (film) 1590, 1485, 1205, 980, 870, 845, 760, and 690 cm^{-1}, τ 2.62-3.42 (10H, m), 6.23 (2H,sept, J 10 and 6 Hz), and 8.83 (12H, d, J 6 Hz); diphenyl N-phenylphosphoramidite (72%), b.p. 155-159°/0.1mm, m.p. 45-48° (sealed tube, from dichloromethane-hexane) (lit.[131] 48-50°), ν_{max} 3380, 1600, 1590, 1585, 1480, 1210, 1185, 865, 750, and 695 cm^{-1}, τ 2.58-3.33 (15H, m) and 4.83 (0.5H, d, J 6 Hz); diphenyl N-methyl-N-phenylphosphoramidite (78%), b.p. 170-174°/0.1mm, ν_{max} (film) 1590, 1485, 1270, 1200, 1060, 850, 755, and 685 cm^{-1}, τ 2.50-3.27 (15H, m), and 6.82 (3H, d, J 3 Hz); and bis-(p-fluorophenyl) N-methyl-N-phenylphosphoramidite (75%), b.p. 158-168°/0.1mm, ν_{max} (film) 1599, 1500, 1188, 1089, 1065, 869, 838, 800, 755, and 691 cm^{-1}, τ 2.57-3.05 (15H, m), and 6.82 (3H, d, J 4 Hz).

Preparation of Diphenyl NN-Diphenylphosphoramidite.

A solution of diphenyl phosphorochloridite (7.6g, 0.03 mol) in tetrahydrofuran (30ml) was added dropwise, over 0.5h, to a stirred solution of lithium diphenylamide (5.25g, 0.03 mol) in tetrahydrofuran (50ml). The mixture was then refluxed for 24h. Solvent was then removed and ether (50ml) was added. Filtration and removal of solvent followed by recrystallisation of the residue gave diphenyl NN-diphenylphosphoramidite (36%), m.p. 91-94° (sealed tube, from hexane) (lit.[129] 89-91°).

Preparation of p-Bromophenyl Phenyl NN-Dimethylphosphoramidite

Phenyl NNN'N'-tetramethylphosphorodiamidite (8.9g, 0.04 mol) and

p-bromophenol (7.3g, 0.04 mol) were heated together at 140° for 3h. Distillation then gave p-bromophenyl phenyl NN-dimethylphosphoramidite (62%), b.p. 168-176°/0.1mm, ν_{max} (film) 1594, 1482, 1234, 1205, 1163, 1069, 979, 875, 852, 824, 772, and 691 cm^{-1}, τ 2.38-3.12 (9H, m) and 7.23 (6H, d, J 10 Hz).

Preparation of Bis-(p-bromophenyl) NN-Dimethylphosphoramidite.

Hexamethylphosphorous triamide (4g, 0.025 mol) and p-bromophenol (8.5g, 0.05 mol) were heated together at 150° for 3h. Distillation then gave bis-(p-bromophenyl) NN-dimethylphosphoramidite (62%), b.p. 194-200°/0.1mm, ν_{max} (film) 1588, 1485, 1208, 1068, 1005, 978, 873, 850, 823, 713, and 691 cm^{-1}, τ 2.57 (4H, d, J 9 Hz), 3.10 (4H, d, J 9 Hz), and 7.25 (6H, d, J 9 Hz).

Preparation of Diphenyl Phenylphosphonite

This was prepared by the method of Arbusov et al[132] in 99% yield, b.p. 168-186/0.6mm (lit.[132] 222-223°/12mm).

Preparation of o-Phenylene Phosphorochloridite

This was prepared by the method of Arbuzov and Valitova[133] in 21% yield, b.p. 78-83°/6mm (lit. 80°/10mm).

Preparation of o-Phenylene NN-Dimethylphosphoramidite

This was prepared by treatment of o-phenylene phosphorochloridite

with dimethylamine, in the normal way. Distillation gave o-phenylene NN-dimethylphosphoramidite (94%), b.p. 71-72°/1mm (lit.[49b] 60-61°/0.5mm).

Preparation of Phenyl o-Phenylene Phosphite.

o-Phenylene phosphorochloridite (1.75g, 0.01 mol) and phenol (0.94g, 0.01 mol) were heated together at 120° for 12h. Distillation then gave phenyl o-phenylene phosphite (56%), b.p. 142-145°/0.1mm (lit.[134] 150°/12mm).

Preparation of S-Phenyl o-Phenylene Phosphorothioite.

A solution of o-phenylene phosphorochloridite (8.7g, 0.05 mol) in ether (30ml) was added dropwise, over 0.5h, to a stirred solution of thiophenol (5.5g, 0.05mol) and pyridine (3.95g, 0.05 mol) in ether (50ml) at 0°. The mixture was then stirred at room temperature for 3h. Filtration and removal of solvent, followed by distillation, gave S-phenyl o-phenylene phosphorothioite (79%), b.p. 168-172°/0.2mm (lit.[135] 182-186°/3mm), m.p. 43-46° (sealed tube, from dichloromethane-hexane).

Addition of Sulphur to S-Phenyl o-Phenylene Phosphorothioite.

S-Phenyl o-phenylene phosphorothioite (2.48g, 0.01 mol), sulphur (0.32g, 0.01 mol), and a small crystal of aluminium chloride were refluxed in toluene for 72h. Removal of solvent and recrystallisation gave S-phenyl o-phenylene phosphorodithioate (21%), m.p. 70-79° (from carbon tetrachloride-hexane), ν_{max} 1231, 882, 792, 738, 712, and 692 cm^{-1}, τ 2.52-2.83 (2H, m), 2.88-3.15 (3H, m), and 3.35 (4H, s), m/e 280, 264,

248, 171, 139, 110, and 109 (Found: C, 50.8; H, 3.2; P, 11.2. $C_{12}H_9O_2PS_2$ requires C, 51.4; H, 3.2; P, 11.1%).

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

A solution of pinacol (5.9g, 0.05 mol) in ether (50ml) was added dropwise, over 1h, to a stirred solution of phenyl phosphorodichloridite (9.75g, 0.05 mol) and triethylamine (10.1g, 0.1 mol) in light petroleum (200ml). The mixture was then refluxed for 5h. Filtration and removal of solvent followed by distillation gave 2-phenoxy--4,4,5,5-tetramethyl-1,3,2-dioxaphospholan (65%), b.p. 84-88°/0.2mm (lit.[136] 88-90°/2mm).

Preparation of 2-(p-Bromophenoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaphospholan.

This was prepared by treatment of 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholan with p-bromophenol in the presence of triethylamine, in the usual way. Distillation gave 2-(p-bromophenoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaphospholan (86%), b.p. 120-124°/0.3mm, ν_{max} (film) 1587, 1486, 1228, 1138, 959, 916, 854, 827, 759, 725, and 696 cm^{-1}, τ 2.50 (2H, d, J 9 Hz), 3.00 (2H, d, J 9 Hz), 8.53 (6H, s), and 8.68 (6H, s).

Preparation of 2-Phenylthio-1,3,2-dithiaphospholan

Hexamethylphosphorous triamide (8.15g, 0.05 mol) and thiophenol (5.5g, 0.05 mol) were heated together at 120° for 2h. The solution was then allowed to cool, ethane-1,2-dithiol (4.7g, 0.05 mol) was added, and heating was continued for a further 2h. Distillation then gave

2-phenylthio-1,3,2-dithiaphospholan (47%), b.p. 184-189°/0.1mm, ν_{max} (film) 1580, 1471, 1439, 1277, 1021, 933, 825, 741, and 688 cm^{-1}, τ 2.45-2.85 (5H, m) and 6.35-6.98 (4H, m).

Addition of Sulphur to 2-Phenylthio-1,3,2-dithiaphospholan.

2-Phenylthio-1,3,2-dithiaphospholan (2.32g, 0.01 mol), sulphur (0.32g, 0.01 mol), and a small crystal of aluminium chloride were refluxed in toluene for 72h. Removal of solvent and recrystallisation gave 2-phenylthio-2-thiono-1,3,2-dithiaphospholan (32%), m.p. 103-106° (from carbon tetrachloride), ν_{max} 1413, 1282, 1017, 933, 743, 683, and 670 cm^{-1}, τ 2.25-2.82 (5H, m), and 5.97-7.23 (4H, m), m/e 264, 232, 218, 186, 155, 123, and 109 (Found: C, 36.35; H, 3.35; S, 48.4. $C_8H_9PS_4$ requires C, 36.35; H, 3.4; S, 48.5%).

Preparation of 2-Chloro-3-methyl-1,3,2-oxazaphospholan.

This was prepared by the method of Martynov et al[137] in 31% yield, b.p. 60-64°/8mm (lit.[137] 57-58°/2mm).

Preparation of 2-Dimethylamino-3-methyl-1,3,2-oxazaphospholan.

This was prepared by the method of Sanchez et al[49b] in 50% yield, b.p. 60-64°/14mm (lit.[49b] 66-68°/16mm).

Preparation of 3-Methyl-2-phenoxy-1,3,2-oxazaphospholan.

This was prepared by addition of 2-methylaminoethanol to phenyl

phosphorodichloridite in the presence of triethylamine, in the usual way. Distillation gave 3-methyl-2-phenoxy-1,3,2-oxazaphospholan (38%), b.p. 85-87°/0.2mm, ν_{max} (film) 1594, 1491, 1213, 1165, 1068, 1018, 928, 847, 765, and 685 cm^{-1}, τ 2.40-3.13 (5H, m), 5.33-5.93 (2H, m), 6.63-7.30 (2H, m), and 7.13 (3H, d, J 12 Hz).

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

This was prepared by addition of thiophenol to 2-chloro-3-methyl--1,3,2-oxazaphospholan in the presence of triethylamine, in the usual way. Distillation gave 3-methyl-2-phenylthio-1,3,2-oxazaphospholan (62%), b.p. 115-116°/0.4mm, τ 2.33-2.92 (5H, m), 5.28-6.05 (2H, m), 6.70-7.08 (2H, m), and 7.27 (3H, d, J 14 Hz).

Preparation of Phenyl NNN'N'-Tetramethylphosphorodiamidite

This was prepared by the method of Bentrude et al[138] in 80% yield, b.p. 76-82°/0.2mm (lit. [138] 52-53°/0.1mm).

Preparation of Phenyl Phosphorodichloridothioite

Thiophenol (11g, 0.1 mol) and phosphorus trichloride (13.75g, 0.1 mol) were heated together for 8h at 130°. Distillation then gave phenyl phosphorodichloridothioite (30%), b.p. 120-124°/0.5mm (lit.[139] 125°/10mm).

Preparation of 2-Dimethylamino-1,3-dimethyl-1,3,2-diazaphospholan

A solution of NN'-dimethylethylenediamine (8.8g, 0.1 mol) in ether

(20ml) was added dropwise, over 1h, to a stirred solution of phosphorus trichloride (6.9g, 0.05 mol) in ether (40ml) at 0°. The mixture was stirred for 2h, and a solution of dimethylamine (4.5g, 0.1 mol) in ether (15ml) was then added over 1h. Stirring was continued for a further 2h. Filtration and removal of solvent, followed by distillation then gave 2-dimethylamino-1,3-dimethyl-1,3,2-diazaphospholan (81%), b.p. 65-68°/0.5mm (lit.[35] 36°/0.5mm).

Preparation of 1,3-Dimethyl-2-phenoxy-1,3,2-diazaphospholan.

This was prepared by addition of NN'-dimethylethylenediamine to phenyl phosphorodichloridite in the presence of triethylamine, in the usual way, Distillation gave 1,3-dimethyl-2-phenoxy-1,3,2-diazaphospholan (91%), b.p. 112-114°/0.3mm, ν_{max} (film) 1596, 1493, 1222, 1162, 1032, 939, 844, 767, 694, and 658 cm^{-1}, τ 2.47-3.17 (5H, m), 6.63-7.10 (4H, m), and 7.17 (6H, d, J 13 Hz).

In a similar way, phenyl phosphorodichloridothioite gave 1,3-dimethyl-2-phenylthio-1,3,2-diazaphospholan (62%), b.p. 140-142°/0.1mm, τ 2.23-2.87 (5H, m), 6.82 (2H, m), 6.93 (2H, s), and 7.30 (6H, d, J 15 Hz).

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

This was prepared by the method of Lucas et al[140] in 51% yield, b.p. 95-100°/15mm (lit.[140] 66.5-67.5°/15mm).

Preparation of 2-Dimethylamino-1,3,2-dioxaphosphorinane.

Hexamethylphosphorous triamide (8.15g, 0.05 mol) and propane-1,3-

-diol (3.8g, 0.05 mol) were heated together at 130° for 3h. Distillation then gave 2-dimethylamino-1,3,2-dioxaphosphorinane (24%), b.p. 58-59°/10mm.

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

This was prepared by addition of phenol to 2-chloro-1,3,2-dioxaphosphorinane in the presence of pyridine, in the usual way. Distillation gave 2-phenoxy-1,3,2-dioxaphosphorinane (71%), b.p. 120-124°/1.5mm, m.p. 43-45° (sealed tube, from dichloromethane-hexane) (lit.[141] 45-48°).

Preparation of 3-Methyl-2-phenoxy-1,3,2-oxazaphosphorinane

This was prepared by addition of 3-methylaminopropanol to phenyl phosphorodichloridite in the presence of triethylamine, in the usual way. Distillation gave 3-methyl-2-phenoxy-1,3,2-oxazaphosphorinane (26%), b.p. 100-106°/1mm, ν_{max} (film) 1599, 1495, 1222, 1201, 1045, 950, 924, 849, 764, 733, 690, and 664 cm^{-1}, τ 2.62-3.22 (5H, m), 5.45-6.87 (3H, m), 7.02-8.63 (3H, m), and 7.42 (3H, d, J 16 Hz).

Preparation of 1,3-Dimethyl-2-phenoxy-1,3,2-diazaphosphorinane

This was prepared by addition of 1,3-bis(methylamino)propane to phenyl phosphorodichloridite in the presence of triethylamine, in the usual way. Distillation gave 1,3-dimethyl-2-phenoxy-1,3,2-diazaphosphorinane (20%), b.p. 106-110°/0.4mm, ν_{max} (film) 1596, 1493, 1221, 1163, 1124, 1051, 953, 843, 763, 693, and 648 cm^{-1}, τ (dichloromethane) 2.72-3.18 (5H, m), 6.53-7.62 (4H, m), 7.40 (6H, d, J 16 Hz), and 7.82-8.50 (2H, m).

Preparation of Phenyl Diphenylphosphinite

This was prepared by addition of phenol to diphenylphosphinous chloride in the presence of triethylamine, in the usual way. Distillation gave phenyl diphenylphosphinite (81%), b.p. 176-182°/0.2mm (lit.[132] 172-173°/2mm).

In a similar way, thiophenol gave phenyl diphenylphosphinothioite (80%), b.p. 184-188°/0.1mm, m.p. 50-51° (sealed tube, from hexane) (lit.[142] 52°).

Preparation of Tetraethylphosphinous Amide

This was prepared by the method of Issleib and Seidel[143] with the slight modification that addition of the Grignard solution was carried out at -78°, and the reaction mixture was stirred at this temperature for 2h before work-up. Distillation gave tetraethylphosphinous amide (73%), b.p. 92-94°/15mm (lit.[143] 181°).

In a similar way, methyl magnesium bromide gave NN-diethyldimethylphosphinous amide (68%), b.p. 136-139°, ν_{max} (film) 1372, 1290,1184, 1020, 924, 871, 839, 783, and 672 cm^{-1}, τ 7.12 (4H, dq, J 10 and 7 Hz), 8.94 (6H, d, J 5 Hz), and 9.01 (6H, t, J 7 Hz).

Addition of Sulphur to NN-Diethyldimethylphosphinous Amide

The phosphinous amide (1.33g, 0.01 mol) and sulphur (0.32g, 0.01 mol) were stirred together in benzene for 0.5h. Removal of solvent and recrystallisation then gave (the hygroscopic) NN-diethyldimethylphosphinothioic amide (57%), m.p. 26.5-27° (sealed tube, from hexane), ν_{max} 1295, 1199, 1169, 1016, 937, 894, 844, 782, 733, and 665 cm^{-1}, τ 6.88 (4H, dq,

J 12 and 7 Hz), 8.24 (6H, d, J 13 Hz), and 8.90 (6H, t, J 7 Hz), m/e 165, 150, 132, 118, 93, and 72 (Found: C, 43.4; H, 9.85; P, 19.2. $C_6H_{16}NPS$ requires C, 43.6; H, 9.7; P, 18.8%).

Preparation of Phenyl Dimethylphosphinite

NN-Diethyldimethylphosphinous amide (10g, 0.075 mol) and phenol (7.1g, 0.075 mol) were heated together at 130° for 2h. Distillation then gave phenyl dimethylphosphinite (94%), b.p. 197-200°, ν_{max} (film) 1597, 1490, 1287, 1220, 1162, 1068, 1019, 942, 858, 753, 707, and 686 cm^{-1}, τ 2.53-3.17 (5H, m), and 8.58 (6H, d, J 6H).

Addition of Sulphur to Phenyl Dimethylphosphinite

Phenyl dimethylphosphinite (1.54g, 0.01 mol) and sulphur (0.32g, 0.01 mol) were stirred together in benzene (20ml) for 0.5h. Removal of solvent and recrystallisation gave phenyl dimethylphosphinothionate (75%), m.p. 38.5-39.5° (from carbon tetrachloride-hexane) (lit.[144] 36-38°), ν_{max} 1592, 1493, 1212, 952, 922, 892, 764, 740, 714, and 687 cm^{-1}, τ (carbon tetrachloride) 2.63-3.13 (5H, m) and 8.13 (6H, d, J 14 Hz), m/e 186, 171, 154, 139, 93, and 77 (Found: C, 51.7; H, 6.1; P, 17.0. Calc. for $C_8H_{11}OPS$: C, 51.6; H, 5.9; P, 16.7%).

Preparation of Phenyl Diethylphosphinite

Tetraethylphosphinous amide (8.05g, 0.05 mol) and phenol (4.7g, 0.05 mol) were heated together at 130° for 2h. Distillation then gave phenyl diethylphosphinite (84%), b.p. 94-96°/10mm, ν_{max} 1598, 1491, 1219,

1160, 1069, 1020, 867, 753, and 688 cm^{-1}, τ 2.50-3.22 (5H, m), 8.05-8.68 (4H, m) and 8.91 (6H, dt, J 14.5 and 7 Hz).

Addition of Sulphur to Phenyl Diethylphosphinite.

Phenyl diethylphosphinite (1.82g, 0.01 mol) and sulphur (0.32g, 0.01 mol) were stirred together in benzene (20ml) for 0.5h. Removal of solvent and distillation (Kügel-Rohr) gave a clear oil (2.1g). Chromatography of 1g of the distillate on basic alumina (50g), and elution with ether-light petroleum (1:5), followed by distillation (Kügel-Rohr) gave phenyl diethylphosphinothionate (90%), b.p. 160° (oven)/0.5mm, ν_{max} (film) 1595, 1493, 1205, 1162, 1070, 1022, 910, 890, 780, and 690 cm^{-1}, τ (carbon tetrachloride) 2.63-3.15 (5H, m), 7.98 (4H, dq, J 12 and 8 Hz), and 8.80 (6H, dt, J 20 and 8 Hz), m/e 214, 186, 153, 121, 105, and 94 (Found: C, 56.0; H, 6.9; P, 14.3. $C_{10}H_{15}OPS$ requires C, 56.1; H, 7.0; P, 14.5%).

Preparation of Di-isopropylphosphinous Chloride.

This was prepared by the method of Voskuil and Arens[145] in 81% yield, b.p. 48-52°/10 mm (lit. 46-47°/10 mm).

Preparation of Phenyl Di-isopropylphosphinite.

A solution of sodium phenoxide (5.8g, 0.05 mol) in tetrahydrofuran (50 ml) was added dropwise, over 0.25h, to a stirred solution of di-isopropylphosphinous chloride (7.6g, 0.05 mol) in tetrahydrofuran (80ml). The mixture was then refluxed for 6h, and after cooling, light petroleum (150 ml) was added. Filtration and removal of solvent, followed by

distillation, then gave phenyl di-isopropylphosphinite (77%), b.p. 76-80°/0.3mm, ν_{max} (film) 1596, 1492, 1220, 1162, 864, 753, 714, and 687 cm^{-1}, τ 2.32-3.08 (5H, m), 7.70-8.24 (2H, m), and 8.40-9.00 (12H, m).

Addition of Sulphur to Phenyl Di-isopropylphosphinite

Phenyl di-isopropylphosphinite (2.1g, 0.01 mol) and sulphur (0.32g, 0.01 mol) were refluxed in benzene (20ml) for 0.5h. Removal of solvent, chromatography of 1g of the residue on basic alumina (50g), and elution with ether-light petroleum (1:10) gave, after distillation (Kugel-Rohr), phenyl di-isopropylphosphinothionate (85%), b.p. 170° (oven)/0.3mm, ν_{max} 1597, 1492, 1208, 1164, 1071, 1023, 908, 882, 766, 737, 714, and 690 cm^{-1}, τ (carbon tetrachloride) 2.62-3.17 (5H, m), 7.38-8.13 (2H, m), 8.73 (dd, J 17 and 7 Hz), and 8.77 (dd, J 17 and 7 Hz) - total integration 12H, m/e 242, 217, 210, 200, 167, 157, and 94 (Found: C, 59.7; H, 7.7; P, 12.8. $C_{12}H_{19}OPS$ requires C, 59.5; H, 7.85; P, 12.8%).

Preparation of Di-t-butylphosphinous Chloride

This was prepared by the method of Voskuil and Arens [145] in 50% yield, b.p. 69-70°/10mm (lit. 69-70°/10mm).

Preparation of Phenyl Di-t-butylphosphinite

A solution of sodium phenoxide (5.8g, 0.05 mol) in tetrahydrofuran (50ml) was added to a stirred solution of di-t-butylphosphinous chloride (9g, 0.05 mol) in tetrahydrofuran (100 ml). The mixture was refluxed for 3 days, cooled, and light petroleum (50ml) was then added. Filtration

and removal of solvent, followed by distillation, gave phenyl di-t-butylphosphinite (86%), b.p. 80-82°/0.1mm (lit.[146] 92-95°/0.2mm).

Preparation of NN-Diethyl-t-butylphosphonamidous Chloride

This was prepared by the method of Scherer and Gick[147] in 41% yield, b.p. 55-60°/2mm (lit.[147] 86°/12mm).

In a similar way, reaction of phenylphosphonous dichloride with diethylamine gave NN-diethylphenylphosphonamidous chloride (78%), b.p. 94-96°/0.4mm (lit.[148] 146-148°/2mm).

Preparation of NN-Diethylmethyl-t-butylphosphinous amide

A solution of methyl magnesium bromide (48.8g, 0.41 mol) in ether (250ml) was added dropwise, over 1h, to a stirred solution of NN-diethyl--t-butylphosphonamidous chloride (80g, 0.41mol) in ether (800ml) at -78°. Stirring was continued for 1h at -78° and a further 0.5h at -20°. The mixture was then warmed to room temperature, filtered, and the solvent was removed. Distillation then gave NN-diethylmethyl-t-butylphosphinous amide (81%), b.p. 60-62°/12mm (lit.[147] 66-68°/9mm), ν_{max} (film) 1462, 1378, 1360, 1198, 1184, 1025, 924, 860, 805, 790, and 691 cm^{-1}, τ 7.06 (4H, dq, J 9 and 7 Hz), 8.89 (3H, d, J 6 Hz), 8.99 (6H, t, J 7 Hz), and 9.06 (9H, d, J 12 Hz).

In a similar way, reaction of NN-diethylphenylphosphonamidous chloride with methyl magnesium bromide gave NN-diethylmethylphenylphosphinous amide (72%), b.p. 79-81°/0.4mm (lit.[149] 102-110°/0.2mm), ν_{max} 1432, 1374, 1184, 1021, 921, 856, 784, 737, and 694 cm^{-1}, τ 2.57-3.28 (5H, m), 7.05 (4H, dq, J 10 and 7 Hz), 8.55 (3H, d, J 6 Hz), and 8.98 (6H, t, J 7 Hz).

Addition of Sulphur to NN-Diethylmethyl-t-butylphosphinous Amide.

The amide (1.75g, 0.01 mol) and sulphur (0.32g, 0.01 mol) were stirred in benzene (30ml) for 0.5h. Removal of solvent, chromatography of the residue on silica (100g), and elution with ether-light petroleum (1:3) gave NN-diethylmethyl-t-butylphosphinothioic amide (95%), ν_{max} (film) 1461, 1378, 1293, 1196, 1169, 1023, 934, 878, 752, 674, and 634 cm^{-1}, τ (benzene) 6.98 (4H, dq, J 10 and 7 Hz), 8.53 (3H, d, J 11 Hz), 8.97 (9H, d, J 16 Hz), and 9.12 (6H, t, J 7 Hz), m/e 207, 174, 150, 136, 118, 72, and 57 (Found: C, 52.1; H, 10.5; P, 15.1. $C_9H_{22}NPS$ requires C, 52.2; H, 10.6; P, 15.0%).

In a similar way, reaction of NN-diethylmethylphenylphosphinous amide with sulphur gave NN-diethylmethylphenylphosphinothioic amide (92%), b.p. 160° (oven)/0.1mm, ν_{max} (film) 1436, 1380, 1293, 1197, 1165, 1105, 1017, 935, 885, 744, 706, and 693 cm^{-1}, τ 2.03-2.47 (2H, m), 2.53-2.83 (3H, m), 7.03 (4H, dq, J 12 and 7 Hz), 8.11 (3H, d, J 13 Hz), and 8.97 (6H, t, J 7 Hz), m/e 227, 194, 180, 155, 141, 123, and 72 (Found: C, 58.4; H, 7.8; P, 13.75. $C_{11}H_{18}NPS$ requires C, 58.1; H, 7.9; P, 13.65%).

Preparation of Phenyl Methyl-t-butylphosphinite.

NN-diethylmethyl-t-butylphosphinous amide (17.5g, 0.1 mol) and phenol (9.4g, 0.1 mol) were heated together at 160° for 4h. Distillation then gave phenyl methyl-t-butylphosphinite (85%), b.p. 72-75°/ 0.5mm ν_{max} 1600, 1496, 1363, 1226, 1165, 1072, 1024, 870, 854, 754, 714, and 690 cm^{-1}, τ 2.67-3.17 (5H, m), 8.73 (3H, d, J 6 Hz), and 8.95 (9H, d, J 13 Hz).

In a similar way, NN-diethylmethylphenylphosphinous amide gave phenyl methylphenylphosphinite (82%), b.p. 116-122°/0.4mm, ν_{max} (film) 1599,

1493, 1434, 1220, 860, 755, 740, and 689 cm^{-1}, τ 2.30-3.35 (10H, m), and 8.41 (3H, d, J 7 Hz).

Addition of Sulphur to Phenyl Methyl-t-butylphosphinite.

The phosphinite (1.96g, 0.01 mol) and sulphur (0.32g, 0.01 mol) were refluxed in benzene (20ml) for 0.5h. Removal of solvent, chromatography of 1g of the residue on basic alumina (50g), and elution with ether-light petroleum (1:10), followed by distillation (Kügel-Rohr), gave phenyl methyl-t-butylphosphinothionate (90%), b.p. 170° (oven)/0.3mm, m.p. 29.5-31° (from light petroleum), ν_{max} 1595, 1494, 1292, 1212, 1195, 911, 893, 764, 728, 690, and 663 cm^{-1}, τ (carbon tetrachloride) 2.67-3.17 (5H, m), 8.25 (3H, d, J 12 Hz), and 8.72 (9H, d, J 17 Hz), m/e 228, 213, 196, 172, 157, 139, 94, and 57 (Found: C, 58.0; H, 7.6; P, 13.55. $C_{11}H_{17}OPS$ requires C, 57.9; H, 7.5; P, 13.6%).

Addition of Sulphur to Phenyl Methylphenylphosphinite.

The phosphinite (2.16g, 0.01 mol) and sulphur (0.32g, 0.01 mol) were refluxed in benzene (20ml) for 2h. Removal of solvent, chromatography of the residue on silica (125g), and elution with ether-light petroleum (1:4), followed by distillation (Kügel-Rohr), gave phenyl methylphenylphosphinothionate (97%), b.p. 170° (oven)/0.2mm, ν_{max} 1588, 1490, 1430, 1198, 1112, 908, 888, 783, 745, 725, 711, and 690 cm^{-1}, τ 1.88-2.30 (2H, m), 2.33-2.70 (3H, m), 2.75-3.25 (5H, m), and 7.87 (3H, d, J 13 Hz), m/e 248, 233, 215, 201, 171, 155, 139, and 77 (Found: C, 63.2; H, 5.3; P, 12.7. $C_{13}H_{13}OPS$ requires C, 62.9; H, 5.2; P, 12.5%)

Preparation of 2,2,3,4,4-Pentamethylphosphetan.

A solution of r-1-chloro-2,2-trans-3,4,4-pentamethylphosphetan 1-oxide (6.5g, 0.033 mol) in ether (20ml) was added dropwise, with care, to a stirred suspension of lithium aluminium hydride (1.9g, 0.05 mol) in ether (25ml). After addition was complete (0.5h), the mixture was refluxed for 1h. Water (5ml) was then carefully added, followed by anhydrous magnesium sulphate (5g) and, after 2h, the mixture was filtered. Removal of solvent and distillation then gave 2,2,3,4,4-pentamethylphosphetan (73%), b.p. 85-88°/100mm (lit.[150] 80°/80mm).

Preparation of 1-Acetyl-2,2,3,4,4-pentamethylphosphetan.

A solution of acetyl chloride (1.2g, 0.015 mol) in light petroleum (15ml) was added dropwise, over 0.25h, to a stirred solution of 2,2,3,4,4-pentamethylphosphetan (2.2g, 0.015 mol) and triethylamine (1.55g, 0.015 mol) in ether-light petroleum (1:1, 30ml). The mixture was then refluxed for 4h. Filtration and removal of solvent, followed by distillation, gave 1-acetyl-2,2,3,4,4-pentamethylphosphetan (76%), b.p. 63-65°/0.8mm, ν_{max} (film) 1655, 1458, 1375, 1348, 1130, and 936 cm^{-1}, τ (major isomer) 7.47 (1H, m), 7.75 (3H, d, J 5 Hz), 8.62 (6H, d, J 11 Hz), 8.68 (6H, d, J 14 Hz), and 9.10 (3H, dd, J 7 and 1 Hz); the minor isomer had peaks at τ 7.67 (3H, d, J 6 Hz), and 9.18 (3H, dd, J 7 and 1 Hz), the other peaks were obscured by those from the major isomer. Ratio of isomers 1.8:1. ^{31}P δ (chloroform) -64 (major) and -73 (minor) p.p.m.

Preparation of Benzoyldimethylphosphine.

Phenyl dimethylphosphinite (12g, 0.078 mol) in toluene (10ml) was

added dropwise to a stirred suspension of lithium aluminium hydride (5g, 0.13mol) in toluene (50ml). The resulting dimethylphosphine was passed into a stirred solution of benzoyl chloride (10.95g, 0.078 mol) and triethylamine (7.9g, 0.078mol) in light petroleum (50ml). After 6h the mixture was filtered, and solvent was removed, to leave a yellow liquid. Distillation then gave <u>benzoyldimethylphosphine</u> (46%), b.p. 68-72°/1mm, ν_{max} (film) 1643, 1597, 1579, 1448, 1427, 1208, 1173, 920, 763, 693, and 646cm^{-1}, τ 2.05-2.27 (2H, m), 2.50-2.70 (3H, m), and 8.75 (6H, d, <u>J</u> 2 Hz).

Quaternisation of the phosphine with methyl iodide gave initially a light yellow solid. Attempted purification, by recrystallisation from dry, ethanol-free chloroform lead to formation of benzoic acid and trimethylphosphonium iodide.

General Procedure for Reaction of Hexafluoroacetone with Tervalent Phosphorus Compounds.

Hexafluoroacetone (0.022 mol) was passed into a stirred solution of the tervalent phosphorus compound (0.01 mol) in ether or hexane (30ml) at -78°. In some cases a white solid precipitated but quickly redissolved. The solution was kept at -78° for 2h, and solvent was then removed at reduced pressure, below room temperature. Purification was achieved by recrystallisation and/or sublimation.

Reaction of hexafluoroacetone with the following tervalent phosphorus compounds gave the stated 4,4,5,5-tetrakis(trifluoromethyl)--1,3,2-dioxaphosph(V)olans in nearly quantitative yields: diphenyl NN--dimethylphosphoramidite gave the 2:1 adduct (112), m.p. 110-110.5° (from ethanol), ν_{max} 1595, 1235, 1215, 1115, 1010, 965, 940, 895, 770, 715, and 690 cm^{-1}, τ (carbon tetrachloride) 2.60-3.33 (10H, m) and 6.97 (6H, d, J 11 Hz), ^{19}F δ (toluene) + 5.2 (s) p.p.m., ^{31}P δ + 54.5 p.p.m., m/e 574 (M-19), 549, 524, 500, 417, and 262 (Found: C, 40.7; H, 2.7; F, 38.0; N, 2.5. $C_{20}H_{16}F_{12}NO_4P$ requires C, 40.5; H, 2.7; F, 38.4; N, 2.4%); bis-(p-fluorophenyl) NN-dimethylphosphoramidite gave the 2:1 adduct (122), m.p. 101.5-102.5° (sublimation), ν_{max} 1499, 1238, 1212, 1118, 1009, 964, 940, 840, 812, 750, 740, 711, 700, and 675 cm^{-1}, τ (carbon tetrachloride) 2.80-3.43 (8H, m), and 7.00 (6H, d, J 11 Hz), ^{19}F δ (light petroleum) +4.5 (12F, s) and +55.5 (2F, m) p.p.m., ^{31}P δ (carbon tetrachloride) +53.5 p.p.m., m/e 629, 610, 585, 560, and 518 (Found: C, 38.2; H, 2.2; F, 42.0; N, 2.4. $C_{20}H_{14}F_{14}NO_4P$ requires C, 38.2; H, 2.2; F, 42.3; N, 2.2%); p-bromophenyl phenyl NN-dimethylphosphoramidite gave the 2:1 adduct (113), m.p. 57-71° (from ethanol), ν_{max} 1595, 1484, 1242,

1214, 1154, 1119, 1009, 964, 942, 896, 832, 765, and 714cm^{-1}, τ 2.43-3.37 (9H, m), and 7.00 (6H, d, J 11 Hz), ^{19}F δ (ether-light petroleum) + 4.9 (s) p.p.m., ^{31}P δ +54.5 p.p.m., m/e (for ^{79}Br) 652 (M-19), 627, 602, 578, and 500 (Found: C, 35.9; H, 2.1; Br, 11.6; F, 34.0. $C_{20}H_{15}BrF_{12}NO_4P$ requires C, 35.7; H, 2.2; Br, 11.9; F, 33.9%); bis-(p-bromophenyl) NN-dimethylphosphoramidite gave the 2:1 adduct (114), m.p. 87.5-88° (from ethanol), ν_{max} 1588, 1488, 1244, 1215, 1122, 1011, 957, 930, 900, 833, 770, 720, and 694cm^{-1}, τ (carbon tetrachloride) 2.82 (4H, d, J 9 Hz), 3.42 (4H, d, J 9 Hz), and 7.08 (6H, d, J 12 Hz), ^{19}F δ (ether-light petroleum) + 4.49 (s) p.p.m., ^{31}P δ (carbon tetrachloride) + 54p.p.m., m/e (for ^{79}Br) 730 (M-19), 705, 680, 578, 534, 499, and 417 (Found: C, 31.8; H, 1.9; F, 30.2. $C_{20}H_{14}Br_2F_{12}NO_4P$ requires C, 32.0; H, 1.9; F, 30.4%); diphenyl pyrrolidin-1-yl phosphonite gave the 2:1 adduct (115), m.p. 108-108.5° (from ethanol), ν_{max} 1595, 1240, 1215, 960, 930, 890, 765, and 690 cm^{-1}, τ 2.33-3.23 (10H, m), 6.25-6.60 (4H, m), and 7.92-8.28 (4H, m), ^{19}F δ (toluene) +5.13 (s) p.p.m., ^{31}P δ (toluene) +56 p.p.m., m/e 619, 600, 549, 526, 484, 376, and 327 (Found: C, 42.7; H, 2.8; N, 2.5. $C_{22}H_{18}F_{12}NO_4P$ requires C, 42.7; H, 2.9; N, 2.3%); bis-(p-fluorophenyl) pyrrolidin-1-yl phosphonite gave the 2:1 adduct (123), m.p. 98.5- 100.5° (sublimation), ν_{max} 1502, 1247, 1218, 1100, 965, 832, 813, 745, 708, and 685cm^{-1}, τ (carbon tetrachloride) 2.73-3.47 (8H, m), 6.17-6.80 (4H, m), and 7.75-8.40 (4H, m), ^{19}F δ (light petroleum) +4.55 (12F, s) and +56.6 (2F, m) p.p.m., ^{31}P δ (ether) +60 p.p.m., m/e 655, 636, 582, 581, and 540 (Found: C, 40.4; H, 2.5; F, 40.5. $C_{22}H_{16}F_{14}NO_4P$ requires C, 40.3; H, 2.5; F, 40.6%); diphenyl NN-di-isopropylphosphoramidite gave the 2:1 adduct (116), m.p. 83.5-84° (from ethanol), ν_{max} 1600, 1495, 1245, 1220, 970, 895, 765, and 750cm^{-1}, τ 2.75-3.40 (10H, m), 6.07 (2H, d sept, J 24 and 7 Hz), and 8.70 (12H, d, J 7 Hz), ^{19}F δ (toluene) + 4.2 (s) p.p.m., ^{31}P δ +51 p.p.m.,

m/e 630 (M-19), 580, 556, 549, 526, 514, 472, 317, and 224 (Found: C, 44.5; H, 3.8; F, 34.9. $C_{24}H_{24}F_{12}NO_4P$ requires C, 44.4; H, 3.7; F, 35.1%); diphenyl N-methyl-N-phenylphosphoramidite gave the 2:1 adduct (117), m.p. 95-95.5° (from ethanol), ν_{max} 1595, 1245, 1215, 1120, 1070, 965, 910, 780, 760, 715, and 695cm^{-1}, τ 2.40-3.33 (15H, m), and 6.60 (3H, d, J 10 Hz), ^{19}F δ (toluene) +4.9 (s) p.p.m., ^{31}P δ +57 p.p.m., m/e 636 (M-19), 586, 562, 549, 525, 323, and 230 (Found: C, 46.0; H, 2.7; F, 34.75; P, 4.7. $C_{25}H_{18}F_{12}NO_4P$ requires C, 45.8; H, 2.7; F, 34.8; P, 4.7%); bis-(p-fluorophenyl) N-methyl-N-phenylphosphoramidite gave the 2:1 adduct (124), m.p. 68.5-69.5° (from ethanol), ν_{max} 1498, 1240, 1212, 1154, 1111, 1082, 964, 835, 810, 742, and 699cm^{-1}, τ (carbon tetrachloride) 2.40-3.67 (13H, m), and 6.65 (3H, d, J 11 Hz), ^{19}F δ (ether) + 4.65 (12F, s), and +53.5 (2F, m) p.p.m., ^{31}P (ether) +58.5 p.p.m., m/e 691, 672, 622, 585, and 580 (Found: C, 43.2; H, 2.35; F, 38.7; P, 4.5. $C_{25}H_{16}F_{14}NO_4P$ requires C, 43.4; H, 2.35; F, 38.5; P, 4.5%); diphenyl NN-diphenyl phosphoramidite gave the 2:1 adduct (118), m.p. 118-120° (from ethanol), ν_{max} 1602, 1497, 1261, 1248, 1221, 1113, 1031, 1001, 970, 895, 774, and 691cm^{-1}, τ 2.68-3.42 (m), ^{19}F δ (ether-light petroleum) +4.22 (s), ^{31}P δ +60 p.p.m., m/e 717, 698, 624, 573, 549, and 399 (Found: C, 50.1; H, 2.8; F, 31.65. $C_{30}H_{20}F_{12}NO_4P$ requires C, 50.2; H, 2.8; F, 31.8%); diphenyl phenylphosphonite gave the (hygroscopic) 2:1 adduct (126), m.p. 73-74.5° (from ethanol), ν_{max} 1595, 1245, 1215, 1115, 965, 940, 895, 745, and 690cm^{-1}, τ 1.40-2.05 (2H, m), 2.15-2.48 (3H, m), and 2.50-3.23 (10H, m), ^{19}F δ (toluene) +4.8 (s) p.p.m., ^{31}P δ (toluene) +40 p.p.m. (lit.[31] + 40.1 p.p.m.), m/e 626, 607, 557, 549, 533, 395, and 217 (Found: C, 45.9; H, 2.4; F, 36.4. Calc. for $C_{24}H_{15}F_{12}O_4P$: C, 46.0; H, 2.4; F, 36.4%); 2-phenoxy-4,4,5,5-tetramethyl-1,3,2-dioxaphospholan gave the 2:1 adduct (164), m.p. 105-106° (from ethanol) (lit.[151] 100-101.5°), ν_{max} 1599

1491, 1251, 1239, 1210, 1112, 991, 952, 932, 901, 800, 771, 748, and 708cm^{-1}, τ (carbon tetrachloride) 2.40-3.07 (5H, m), 8.73 (6H, s), and 8.93 (6H, s), ^{19}F δ (light petroleum) +4.47 (s) p.p.m., ^{31}P δ +39 p.p.m. (lit. [151] +44 p.p.m.), m/e 572, 557, 553, 516, 503, 499, 479, 473, 472, and 456 (Found: C, 37.85; H, 3.0; F, 39.7; P, 5.7. Calc. for $C_{18}H_{17}F_{12}O_5P$: C, 37.75; H, 3.0; F, 39.85; P, 5.4%); 2-(p-bromophenoxy)--4,4,5,5-tetramethyl-1,3,2-dioxaphospholan gave the 2:1 adduct (165), m.p. 82-90° (from ethanol), ν_{max} 1589, 1487, 1273, 1248, 1217, 1158, 1113, 980, 964, 930, 838, and 800cm^{-1}, τ (carbon tetrachloride) 2.47 (2H, d, J 9 Hz), 2.93 (2H, d, J 9 Hz), 8.70 (6H, s), and 8.88 (6H, s), ^{19}F δ (ether-light petroleum) +4.77 (s) p.p.m., ^{31}P δ +39.5 p.p.m., m/e (for ^{79}Br) 635 (M-15), 631, 593, 583, 552, 549, 534, and 479 (Found: C, 33.6; H, 2.55; Br, 12.2; F, 35.2. $C_{18}H_{16}BrF_{12}O_5P$ requires C, 33.2; H, 2.5; Br, 12.3; F, 35.0%); 2-dimethylamino-3-methyl-1,3,2-oxazaphospholan gave the 2:1 adduct (158), m.p. 37-39° (from ethanol), ν_{max} 1246, 1217, 1156, 1129, 1077, 997, 967, 957, 878, 812, 752, 742, 716, and 689cm^{-1}, τ 5.88-6.47 (2H, m), 6.58-7.35 (2H, m), 7.16 (3H, d, J 9 Hz), and 7.39 (6H, d, J 11 Hz), ^{19}F δ (ether) +4.62 (9F, m), and +5.22 (3F, m) p.p.m., ^{31}P δ +33 p.p.m., m/e 480, 461, 436, 424, 411, 248, 155, 139, and 104 (Found: C, 27.6; H, 2.7; F, 47.6; P, 6.6. $C_{11}H_{13}F_{12}N_2O_3P$ requires C, 27.4; H, 2.7; F, 47.5; P, 6.5%); 3-methyl-2-phenylthio-1,3,2-oxazaphospholan gave the 2:1 adduct (159), m.p. 128-129° (from hexane), ν_{max} 1256, 1238, 1216, 1116, 1056, 957, 884, 798, 756, 746,and 687cm^{-1}, τ 2.20-2.70 (5H, m), 5.90-7.17 (m), and 7.05 (d, J 10 Hz) - total integration 7H, ^{19}F δ (chloroform) +4.04 (9F, m), and +5.96 (3F, m) p.p.m., ^{31}P δ +17.5 p.p.m., m/e 545, 526, 476, 436, 394, 297, and 197 (Found: C, 33.3; H, 2.25; N, 2.8. $C_{15}H_{12}F_{12}NO_3PS$ requires C, 33.1; H, 2.2; N, 2.6%); phenyl NNN'N'-tetramethylphosphorodiamidite gave the 2:1 adduct (125), m.p.

about 15° (from light petroleum), ν_{max} (film) 1602, 1493, 1278, 1238, 1211, 1128, 998, 963, 883, 748, and 708cm^{-1}, τ 2.50-3.20 (5H, m) and 7.17 (12H, d, J 11 Hz), ^{19}F δ (light petroleum) +5.45 (s) p.p.m., ^{31}P δ +41 p.p.m., m/e 525 (M-19), 500, 475, 451, 311, and 212 (Found: C, 35.1; H, 3.0; F, 41.9; N, 5.35. $C_{16}H_{17}F_{12}N_2O_3P$ requires C, 35.3; H, 3.1; F, 41.9; N, 5.15%); 2-dimethylamino-1,3-dimethyl-1,3,2-diazaphospholan gave the 2:1 adduct (139), m.p. 78-82° (from hexane) (lit.[152] 86-87°), ν_{max} 1265, 1240, 1210, 990, 960, and 880cm^{-1}, τ 6.93 (2H, s), 7.13 (2H, s), 7.13 (6H, d, J 12 Hz), and 7.32 (6H, d, J 10 Hz), ^{19}F δ (ether) +4.56 (s) p.p.m., ^{31}P δ +29.5 p.p.m. (lit.[152] +28.3 p.p.m.), m/e 474,(M-19), 449, 424, 400, 380, and 349 (Found: C, 29.4; H, 3.2; F, 46.4; N, 8.7. Calc. for $C_{12}H_{16}F_{12}N_3O_2P$: C, 29.2; H, 3.3; F, 46.2; N, 8.6%); 1,3-dimethyl-2-phenoxy-1,3,2-diazaphospholan gave the 2:1 adduct (137), m.p. 69.5-71° (from hexane), ν_{max} 1590, 1260, 1240, 1210, 960, 915, 740, and 705 cm^{-1}, τ (carbon tetrachloride), 2.47-3.20 (5H, m), 6.97 (2H, s), 6.80-7.40 (2H, m), and 7.43 (6H, d, J 10 Hz), ^{19}F δ (1-bromonaphthalene) +4.35 (6F, m), and +7.16 (6F, m) p.p.m., ^{31}P δ +36.5 p.p.m., m/e 542, 523, 473, 448, 311, and 217 (Found: C, 35.5; H, 2.7; N, 5.4. $C_{16}H_{15}F_{12}N_2O_3P$ requires C, 35.4; H, 2.8; N, 5.2%); 1,3-dimethyl-2-phenylthio-1,3,2-diazaphospholan gave the 2:1 adduct (138), m.p. 66-72° (from hexane), ν_{max} 1265, 1240, 1210, 1110, 960, 880, 750, 705, and 690cm^{-1}, τ 2.33-2.83 (5H, m), 6.82-7.67 (4H, m), and 7.43 (6H, d, J 12 Hz), ^{19}F δ (1-bromonaphthalene) +4.7 (6F, m), and +5.5 (6F, m) p.p.m., ^{31}P δ +13.5 p.p.m., m/e 558, 539, 489, 449, 399, 311, and 281 (Found: C, 34.3; H, 2.6; F, 41.1; S, 6.1. $C_{16}H_{15}F_{12}N_2O_2PS$ requires C, 34.4; H, 2.7; F, 40.8; S, 5.7%); 2-dimethylamino-1,3,2-dioxaphosphorinane gave the 2:1 adduct (220), m.p. 56-58° (from hexane), ν_{max} 1273, 1230, 1216, 1086, 1051, 1021, 964, 881, 810, 751, and 720cm^{-1}, τ 5.77-6.06 (4H, m), 7.26 (6H, d, J 11 Hz), and 7.73-8.33 (2H, m), ^{19}F δ (ether-light petroleum) +5.15 (s)

p.p.m., ^{31}P δ +44 p.p.m., m/e 481, 462, 437, 424, 412, 397, and 354 (Found: C, 27.7; H, 2.4; P, 6.6. $C_{11}H_{12}F_{12}NO_4P$ requires C, 27.4; H, 2.5; P, 6.4%); 2-phenoxy-1,3,2-dioxaphosphorinane gave the (hygroscopic) 2:1 adduct (221), m.p. 93-97° (sealed tube, from hexane), ν_{max} 1593, 1491, 1273, 1245, 1216, 1161, 1117, 1077, 1052, 970, 883, 829, 781, and 705cm^{-1}, τ 2.53-3.35 (5H, m), 5.32-6.42 (4H, m), and 7.52-8.42 (2H, m), ^{19}F δ (ether-light petroleum) +4.78 (s) p.p.m., ^{31}P δ +68 p.p.m., m/e 530, 511, 473, 461, 437, 397, and 345 (Found: C, 33.35; H, 2.0; P, 5.9. $C_{15}H_{11}F_{12}O_5P$ requires C, 34.0; H, 2.1; P, 5.85%); 3-methyl--2-phenoxy-1,3,2-oxazaphosphorinane gave the 2:1 adduct (222), m.p. 98.5-99° (from ethanol), ν_{max} 1593, 1490, 1268, 1244, 1230, 1213, 1159, 1065, 964, 943, 879, 756, and 717 cm^{-1}, τ 2.65-3.25 (5H, m), 5.75-7.87 (4H, m), 7.10 (3H, d, J 10 Hz), and 7.93-8.55 (2H, m), ^{19}F δ (ether-light petroleum) +3.94 (6F, m), and 5.39 (6F, m), p.p.m., ^{31}P δ +58 p.p.m., m/e 543, 524, 474, 450, 422, 396 (metastable, 450-422), 350, 211, and 118 (Found: C, 35.5; H, 2.4; F, 41.8; P, 5.7. $C_{16}H_{14}F_{12}NO_4P$ requires C, 35.35; H, 2.6; F, 42.0; P, 5.7%); 1,3-dimethyl-2-phenoxy-1,3,2-diazaphosphorinane gave the 2:1 adduct (223), m.p. 50-52° (from hexane), ν_{max} 1598, 1493, 1264, 1240, 1213, 1155, 1110, 1050, 966, 882, 767, 743, 720, 691, and 642cm^{-1}, τ 2.56-3.14 (5H, m), 6.66-7.62 (4H, m), 7.40 (6H, d, J 12 Hz), and 8.04-8.32 (2H, m), ^{19}F δ (light petroleum) +4.88 (s) p.p.m., ^{31}P δ +37 p.p.m., m/e 556, 537, 487, 463, 240, 224, 166, and 147 (Found: C, 37.0; H, 3.0; F, 41.3; P, 5.7. $C_{17}H_{17}F_{12}N_2O_3P$ requires C, 36.7; H, 3.1; F, 41.0; P, 5.6%); Phenyl diphenylphosphinite gave the (hygroscopic) 2:1 adduct (127), m.p. 102-103° (sealed tube, from hexane), ν_{max} 1602, 1262, 1250, 1237, 1212, 1113, 960, 877, 801, 756, 730, 722, 705, and 693 cm^{-1}, τ 1.78-2.27 (4H, m), 2.27-2.38 (11 Hz, m), ^{19}F δ (ether-light petroleum) +4.19 (s) p.p.m., ^{31}P δ +25 p.p.m.,

m/e 610, 591, 541, 526, 517, 459, 379, and 278 (Found: C, 47.1; H, 2.6; F, 37.4; P, 5.4. $C_{24}H_{15}F_{12}O_3P$ requires C, 47.2; H, 2.5; F, 37.4; P, 5.1%).

On warming in ethanol, the adduct (127) was rapidly converted into the 2:1 adduct (128), m.p. 110-112° (from ethanol) (lit.[31] 111°).

Phenyl di-t-butylphosphinite gave the (hygroscopic) 2:1 adduct (234), m.p. 62-64° (sealed tube, from hexane), ν_{max} 1595, 1493, 1244, 1221, 1205, 1125, 1024, 925, 865, 814, 765, 744, 705, and 645cm^{-1}, τ 2.72-3.18 (5H, m), and 8.52 (18H, d, J 19 Hz), ^{19}F δ (ether) +2.05 (s) p.p.m., ^{31}P δ -18 p.p.m., m/e 567 (M-3), 555, 551, 513, 501, 477, 421, and 372 (metastable, 477-421) (Found: C, 41.9; H, 4.1; F, 40.0; P, 5.6. $C_{20}H_{23}F_{12}O_3P$ requires C, 42.1; H, 4.0; F, 40.0; P, 5.4%).

Reaction of hexafluoroacetone with 3-methyl-2-phenoxy-1,3,2-oxazaphospholan, in the same way gave 2-phenoxy-3,3,5,5-tetrakis(trifluoromethyl)--1,4,2-dioxaphospholan-2-spiro-2'-3'-methyl-1',3',2'-oxazaphospholan in nearly quantitative yield, m.p. 82-84° (from hexane), ν_{max} 1594, 1493, 1280, 1230, 1190, 1065, 967, 925, 786, 761, 750, 717, 707, and 689cm^{-1}, τ 2.37-3.13 (5H, m), 5.90-7.43 (4H, m), and 6.98 (3H, d, J 10 Hz), ^{19}F δ (1-bromonaphthalene) +4.29 (3F, m), +5.55 (3F, m), +16.45 (3F, dq J 10 and 10 Hz), and +18.03 (3F, dq, J 10 and 10 Hz), ^{31}P δ +33 p.p.m., m/e 529, 510, 472, 460, 436, 297, 197, 147, 120, and 104 (Found: C, 34.3; H, 2.3; F, 43.1; P, 5.85. $C_{15}H_{12}F_{12}NO_4P$ requires C, 34.4; H, 2.3; F, 43.1; P, 5.9%).

Reaction of Hexafluoroacetone with o-Phenylene NN-Dimethylphosphoramidite

Hexafluoroacetone failed to react with the phosphoramidite under normal reaction conditions. Extension of the reaction time to 1 month, at -40°, resulted in quantitative formation of the 2:1 adduct (134),

m.p. 76-78° (from hexane), ν_{max} 1623, 1493, 1470, 1280, 1248, 1220, 969, 885, 780, 750, and 720cm^{-1}, τ 2.88 (4H, s), and 7.10 (6H, d, J 11 Hz), ^{19}F δ (1-bromonaphthalene) +5.77 (6F, m), and +6.62 (6F, m), p.p.m., ^{31}P δ + 27 p.p.m., m/e 515, 496, 471, 446, 431 (metastable, 515-471), 421, and 376 (metastable, 471-421) (Found: C, 32.8; H, 2.15; F, 44.3; P, 6.0. $C_{14}H_{10}F_{12}NO_4P$ requires C, 32.6; H, 1.9; F, 44.3; P, 6.0%).

Reaction of Hexafluoroacetone with Phenyl Diphenylphosphinothioite

Treatment of the phosphinothioite with hexafluoroacetone in the usual way gave quantitative recovery of the phosphinothioite. Extension of the reaction time to 14 days, at -40°, gave, after recrystallisation, the starting phosphinothioite. The ^{19}F n.m.r. spectrum, infrared spectrum, and mass spectrum of the crude product, however, did indicate formation of a small amount of 2,2-diphenyl-2-thiophenyl-4,4,5,5-tetrakis(trifluoromethyl)-1,3,2-dioxaphospholan, ν_{max} 1262, 1240, and 1210, ^{19}F (δ) (ether-light petroleum) +3.88 (s) p.p.m., and m/e 626, 607, 557, 517, and 459; the ^{31}P n.m.r. spectrum showed only the signal due to the starting phosphinothioite.

Hexafluoroacetone failed to react with phenyl o-phenylene phosphite, or with 2-thiophenyl-1,3,2-dithiaphospholan, even after prolonged reaction times, and, in the case of the former, even after ampouling and setting aside at room temperature for 2 months.

Reaction of Hexafluoroacetone with Diphenyl N-Phenylphosphoramidite.

Reaction of hexafluoroacetone and the phosphoramidite, in the

usual way, gave 2-(2',2',2'-trifluoro-1'-trifluoromethylethoxy)-2,2--diphenoxy-3-phenyl-4,4-bistrifluoromethyl-1,3,2-oxazaphosphetan (196) in nearly quantitative yield, m.p. 72.5-73.5° (from ethanol), ν_{max} 1600, 1495, 1245, 1205, 1140, 920, 770, 720, and 690cm^{-1}, τ 2.47-3.27 (15H, m), and 4.92 (1H, d sept, J 15 and 6 Hz), ^{19}F δ (ether) +10.25 (6F, d, J 6 Hz), and +12.8 (6F, s) p.p.m., ^{31}P δ (ether) +64 p.p.m., m/e 622 (M-19), 548, 475, 400, 384, 241, and 166 (Found: C, 45.0; H, 2.7; F, 35.3; N, 2.4. $C_{24}H_{16}F_{12}NO_4P$ requires C, 45.0; H, 2.5; F, 35.5; N, 2.2%).

Thermolysis of the Oxazaphosphetan (196)

The oxazaphosphetan (2.49g, 3.88 mmol) was heated at 150° for 1h, and the volatile products were trapped out at -78°. The trap contained hexafluoroisopropylideneaniline (0.446g, 1.85 mmol), ν_{max} 1590, 1480, 1330, 1250, 1175, 985, 775, 750, 715, and 690cm^{-1}, ^{19}F δ (toluene) -1.16 (3F, m) and +6.97 (3F, m) p.p.m., m/e 241, 222, 172, 123 (metastable, 241-172), 103, and 77. After 1 week at -20°, the mass spectrum showed peaks at 463 and 394, indicating dimerisation of the imine. Chromatography of 1g of the residue (1.794g) on silica (50g), and elution with benzene, gave 2,2,2-trifluoro-1-trifluoromethylethyl diphenyl phosphate (0.3g), m.p. and mixed m.p. with an authentic sample, prepared from hexafluoropropan-2-ol and diphenyl phosphorochloridate, in the presence of triethylamine, 35.5-36.5° (from dichloromethane-light petroleum) (lit.[153] 35-36°), ν_{max} 1590, 1490, 1275, 1205, 1105, 970, 905, 770, and 690cm^{-1}, τ 2.33-2.93 (10H, m), and 4.55 (1H, d sept, J 12 and 6 Hz), ^{19}F δ (ether) +11.4 (d, J 6 Hz) p.p.m., ^{31}P δ +13p.p.m., m/e 400, 381, 307, 233, and 169 (Found: C, 45.0; H, 3.0. Calc.for $C_{15}H_{11}F_6O_4P$: C, 45.0; H, 2.8%). Elution with methanol gave diphenyl N-phenylphosphoramidate (0.5g), m.p. and mixed

m.p. with an authentic sample prepared by addition of aniline to diphenyl phosphorochloridate, 128.5-130° (from ethanol) (lit.[154] 129-130°).

Reaction of 1-Acetyl-2,2,3,4,4-pentamethylphosphetan with Hexafluoroacetone.

Treatment of the phosphetan with hexafluoroacetone in the normal way gave a clear oil. The ^{19}F and ^{1}H n.m.r. spectra of the oil showed a complex mixture of products, which could not be separated by distillation or chromatography.

Reaction of 2-Dimethylamino-4,4,5,5-tetrakis(trifluoromethyl)-1,3,2-dioxaphospholan-2-spiro-2'-1',3'-dimethyl-1',3',2'-diazaphospholan with 1,1,1,3,3,3-Hexafluoropropan-2-ol.

The adduct was treated with an excess of the alcohol and the solution was allowed to stand for 0.5h. Removal of solvent gave the 2:1 adduct (140) in quantitative yield, m.p. 63-64° (sublimation), $\nu_{max.}$ 1265, 1245, 1220, 1110, 965, 885, 750, 740, and 690 cm^{-1}, τ 4.67 (1H, d sept, J 15 and 6 Hz), 6.60-7.00 (2H, m), 7.07 (2H, s), and 7.35 (6H, d, J 11 Hz), ^{19}F δ (1-bromonaphthalene) +4.83 (6F, m), 7.55 (6F, m), and 11.83 (6F, d, J 6 Hz), ^{31}P δ +36 p.p.m., m/e 616, 597, 547, 474, 446, and 256 (Found: C, 25.3; H, 1.9; F, 55.85. $C_{13}H_{11}F_{18}N_2O_3P$ requires C, 25.3; H, 1.8; F, 55.6%).

Reaction of 2-Dimethylamino-4,4,5,5-tetrakis(trifluoromethyl)-1,3,2-dioxaphospholan-2-spiro-2'-3'-methyl-1',3',2'-oxazaphospholan with 1,1,1,3,3,3-Hexafluoropropan-2-ol.

The adduct (1g) was refluxed in the alcohol (3ml) for 24h. Removal of solvent and recrystallisation gave the 2:1 adduct (161) (61%), m.p. 74-74.5° (from hexane), ν_{max} 1248, 1235, 1218, 1192, 1113, 1065, 958, 899, 885, 788, 721, and 688 cm^{-1}, τ 4.40-5.22 (1H, m), 5.53-6.38 (2H, m), 6.38-7.57 (2H, m), and 7.18 (3H, d, J 10 Hz), ^{19}F δ (1--bromonaphthalene) +3.39 (3F, m), + 5.64 (6F, m), +8.09 (3F, m), +11.2 (3F, m), and +12.15 (3F, m) p.p.m., ^{31}P δ +41.5 p.p.m., m/e 602 (M-1), 583, 525, 436, and 271 (Found: C, 23.9; H, 1.2; F, 56.6; P, 5.1. $C_{12}H_8F_{18}NO_4P$ requires C, 23.9; H, 1.3; F, 56.7; P, 5.1%).

Reaction of 1-Acetyl-2,2,3,4,4-pentamethylphosphetan with Tetrachloro-o-benzoquinone.

A solution of the quinone (2.36g, 9.6mmol) in ether (25ml) was added dropwise, over 0.5h, to a stirred solution of the phosphetan (0.8g, 4.8mmol) in ether (20ml). The solution was then refluxed for 1h. Removal of solvent and recrystallisation gave the 2:1 adduct (174) (72%), m.p. 158-163° (from hexane), ν_{max} 1794, 1160, 1001, 832, 809, 785, 711, and 669cm^{-1}, τ (benzene) (major isomer) 8.02 (3H, s), 8.72 (6H, d, J 22 Hz), 8.95 (6H, d, J 22 Hz), and 9.32 (3H, dd, J 7 and 1.5 Hz). The ring 3-H signal could not be identified. The minor isomer had peaks at 8.08 (3H, s), 8.58 (6H, d, J 18 Hz), 8.91 (6H, d, J 21 Hz) - the other peaks were obscured by the major isomer. Ratio of the isomers 3:1, ^{31}P δ -15 p.p.m., m/e (for ^{35}Cl) 604 (M-70), 561, 387, 344, and 275. (Found: C, 39.2; H, 2.9; Cl, 41.6; P, 4.8. $C_{22}H_{19}Cl_8O_5P$ requires C, 38.9; H, 2.8; Cl, 41.9; P, 4.6%).

Preparation of 4,4,5,5-Tetramethyl-1,3,2-dioxaphospholan-2-spiro-2'--4',4',5',5'-tetramethyl-1',3',2'-dioxaphospholan.

This was prepared by the method of Sanchez et al[49b] in 80% yield, m.p. 87-89° (sealed tube, from light petroleum) (lit. 90°).

Preparation of 2-Benzoyl-4,4,5,5-tetramethyl-1,3,2-dioxaphospholan-2--spiro-2'-4',4',5',5'-tetramethyl-1',3',2'-dioxaphospholan.

A solution of 4,4,5,5-tetramethyl-1,3,2-dioxaphospholan-2-spiro--2'-4',4',5',5'-tetramethyl-1',3',2'-dioxaphospholan (1.32g, 5mmol) in tetrahydrofuran (10ml) was added to a stirred solution of lithium cyclohexylisopropylamide (0.735g, 5mmol) in tetrahydrofuran (20ml) at -78°. The mixture was stirred for 0.5h, and a solution of benzoyl chloride (0.703g, 5mmol) in tetrahydrofuran (10ml) was added. The mixture was then allowed to warm to room temperature and subsequently refluxed for 0.5h. Solvent was then removed, and the residue was taken up in ether-light petroleum (1:1, 30ml). Refluxing for a further 0.5h, followed by filtration, removal of solvent,and recrystallisation gave the title compound (86%), m.p. 158-160° (sublimation), ν_{max} 1659, 1161, 1148, 970, 922, 878, 838, 793, 778, 758, and 691cm^{-1}, τ 1.50-1.77 (2H, m), 2.20-2.63 (3H, m), 8.65 (12H, s), and 8.92 (12H, s), ^{31}P δ (dichloromethane) +39.5 p.p.m., m/e 353 (M-15), 310, 263, 181, 147, and 105 (Found: C, 61.2; H, 7.8; P, 8.3. $C_{19}H_{29}O_5P$ requires C, 61.0; H, 7.9; P, 8.4%).

Preparation of Hexafluorobiacetyl.

This was prepared by the method of Ramirez and Kugler[155] in 26% yield, ^{19}F δ (ether) +10.9 (s) p.p.m.

General Procedure for the Reaction of Hexafluorobiacetyl with Tervalent Phosphorus Compounds.

Hexafluorobiacetyl (0.01mol) was passed into a stirred solution of the tervalent phosphorus compound (0.01mol) in ether (15ml) at -78°. The solution was stirred at -78° until the yellow colour of the hexafluorobiacetyl was discharged. The solution was then stored at -20°, and aliquots were taken, when required, for spectral analysis.

Reaction of Hexafluorobiacetyl with Phenyl Dialkyl- and Alkylaryl-phosphinites.

In all cases, the ^{19}F n.m.r. spectrum of a solution of the freshly prepared crude product showed the presence of one fluorine-containing species, which is formulated as the 4,5-bistrifluoromethyl-1,3,2-dioxaphosph(V)olen on the basis of mass spectral, ^{19}F n.m.r., and ^{31}P n.m.r. data. The ^{1}H n.m.r. spectra showed other compounds to be present, and the yields given are estimated from the ^{1}H n.m.r. spectra. All the adducts were hydrolytically unstable, and this precluded isolation and complete characterisation.

Phenyl dimethylphosphinite gave the 1:1 adduct (227) (58%), τ 8.02 (d, J 15 Hz) - the aromatic resonance was not discernable from that due also to other products, ^{19}F δ (ether) +65.4 (s) relative to

internal $CFCl_3$, ^{31}P δ -8 p.p.m., m/e 348, 333, 329, 272, and 255; phenyl diethylphosphinite gave the 1:1 adduct (228) (the yield could not be estimated accurately), τ 7.75 (4H, dq, J 10 and 7 Hz), and 8.80 (6H, dt, J 24 and 7 Hz), ^{19}F δ (ether) +65.5 (s) p.p.m., relative to internal $CFCl_3$, ^{31}P δ -13 p.p.m., m/e 376, 357, 347, 310, 283, and 271; phenyl di-isopropylphosphinite gave the 1:1 adduct (229) (the yield could not be estimated accurately), τ 7.12-8.33 (2H, m), and 8.82 (12H, dt, J 22 and 7 Hz), ^{19}F δ (ether) +65.4 (s, broad) p.p.m. relative to internal $CFCl_3$, ^{31}P δ -13 p.p.m., m/e 404, 385, 375, 361, 328, 311, 285, 239, and 226; phenyl di-t-butylphosphinite gave the 1:1 adduct (230) (40%), τ 8.65 (d, J 17 Hz), ^{19}F δ (ether) +63.9 (3F, m), and +66.5 (3F, m) p.p.m. relative to internal $CFCl_3$, ^{31}P δ -8 p.p.m., m/e 432, 417, 413, 393, 376, 357, 339, and 290; phenyl methyl-t-butylphosphinite gave the 1:1 adduct (231) (70%), τ (dichloromethane) 8.15 (3H, d, J 12 Hz) and 8.63 (9H, d, J 20 Hz), ^{19}F δ (ether) +65.1 (s) p.p.m. relative to internal $CFCl_3$, ^{31}P δ (dichloromethane) -11p.p.m., m/e 390, 375, 371, 333, 297, 248, and 212; phenyl methylphenylphosphinite gave the 1:1 adduct (232) (80%), τ 7.82 (d, J 14 Hz), ^{19}F δ (ether) +64.2 (s) p.p.m. relative to internal $CFCl_3$, ^{31}P δ ($CDCl_3$) +5 p.p.m., m/e 410, 395, 391, 334, 317, and 232.

Reaction of 2-Phenoxy-1,3,2-dioxaphosphorinane with Hexafluorobiacetyl.

Hexafluorobiacetyl (0.445g, 2.29mmol) was passed into a stirred solution of the phosphite (0.454g, 2.29mmol) in ether (15ml) at -78°. The solution was stirred for 0.5h and then warmed to room temperature. Removal of solvent under reduced pressure gave the (hygroscopic) 2-phenoxy--1,3,2-dioxaphosphorinane-2-spiro-2'-4',5'-bistrifluoromethyl-1',3',2'-

-dioxaphospholen (88%), m.p. 70-75° (sealed tube, from hexane), τ 2.50-3.23 (5H, m), 5.82 (4H, dt, J 17 and 7 Hz),and 8.00 (2H, quin, J 7 Hz), ^{19}F δ (ether) +71 p.p.m. relative to internal $CFCl_3$, ^{31}P δ +51 p.p.m., m/e 392, 373, 334, 299, 259, and 254. A satisfactory analysis was not obtained for this compound, owing to its hydrolytic instability.

Reaction of Phenyl Dimethylphosphinite with Xenon Difluoride.

Xenon difluoride (< 1mol equivalent) was sublimed onto the inner wall of a 'Kel-F' polytrifluorochloroethylene n.m.r. tube above a solution of the phosphinite (1mol equivalent) in trichlorofluoromethane, cooled to -197°. The solution was allowed to warm until mobile and brought into contact with the xenon difluoride. An immediate and extremely vigorous reaction ensued, as evidenced by gas liberation and a small amount of charring. After the reaction was complete, the solution was warmed to room temperature, the xenon was pumped off, and the tube was sealed. Examination of the ^{19}F n.m.r. spectrum showed the presence of one major compound (> 90%) which is formulated as difluorodimethylphenoxyphosphorane on the basis of ^{19}F n.m.r. and ^{31}P n.m.r. data: ^{19}F δ ($CFCl_3$) +3.3 (d sept, J_{P-F} 745, J_{H-F} 13 Hz) p.p.m. relative to $CFCl_3$ [lit.[111] ^{19}F δ (neat) + 4.2 (J_{P-F} 736 Hz)], τ ($CFCl_3$) 8.22 (dt, J_{P-H} 18, J_{F-H} 13 Hz).

In the same way, reaction of xenon difluoride with benzoyldimethylphosphine gave one major product (85%), in the ^{19}F n.m.r. spectrum, which is formulated as benzoyldifluorodimethylphosphorane from ^{19}F n.m.r., ^{31}P n.m.r., and ^{1}H n.m.r. data: ^{19}F δ ($CFCl_3$) +29.3 (d sept, J_{P-F} 627, J_{H-F} 13 Hz) p.p.m. relative to $CFCl_3$, τ ($CFCl_3$) 8.0 (dt, J_{P-H} 18, J_{F-H} 13 Hz), ^{31}P δ ($CFCl_3$) +25 p.p.m.

Reaction of r-1-Chloro-2,2,trans-3,4,4-pentamethylphosphetan 1-Oxide with 1,1,1,4,4,4-Hexafluoro-2,3-bis(trifluoromethyl)-2,3-butanediol.

A solution of butyl-lithium (0.02mol) in hexane (10ml) was added slowly to a stirred solution of the diol (6.7g, 0.02mol) in tetrahydrofuran

(40ml). A solution of the acid chloride (3.9g, 0.02mol) in tetrahydrofuran (20ml) was then added and the mixture was refluxed for 24h. Removal of solvent and recrystallisation gave 1-(2'-hydroxy-1',1',2',2'--tetrakis(trifluoromethyl)ethoxy)-2,2,3,4,4-pentamethylphosphetan 1-oxide (60%), as a mixture of isomers, ratio 1:2.2, m.p. 140-161° (from dichloromethane-hexane), ν_{max} 3510, 1646, 1240, 1235, 1115, 957, 933, 875, 739, and 715cm^{-1}, τ 3.08 (1H, s broad, which collapsed on addition of 1 drop of D_2O), 7.98-8.52 (1H, m), 8.73 (6H, d, J 21 Hz), 8.74 (6H, d, J 19.5 Hz), and 9.06 (3H, d, J 7 Hz); peaks due to the minor isomer were obscured by those due to the major isomer; ^{19}F δ (ether) +6.73 (s) p.p.m., ^{31}P δ -83 (major) and -63.5 (minor)p.p.m., m/e 334 (M-158), 319, 295, 265, 264, 223, and 159. A satisfactory analysis for this compound could not be obtained.

Preparation of r-2-Dimethylamino-4,4,5,5-tetrakis(trifluoromethyl)-1,3,2-dioxaphospholan-2-spiro-1'-2',2',trans-3',4',4'-pentamethylphosphetan.

This was prepared by the method of Oram and Trippett[63] in 77% yield, m.p. 77-84° (sealed tube, from hexane) (lit 65-75°).

Hydrolysis of r-2-Dimethylamino-4,4,5,5-tetrakis(trifluoromethyl)-1,3,2--dioxaphospholan-2-spiro-1'-2',2',trans-3',4',4'-pentamethylphosphetan.

(a) The adduct (1.004g) and 2 drops of hydrochloric acid (2N) were refluxed in benzene (10ml) for 48h. Solvent was then removed, the residue was taken up in dichloromethane (5ml), and the solution was washed with sodium hydroxide solution (2N; 2 x 5ml). The solution

was then dried, and solvent was removed to give (the hygroscopic) r-1-dimethylamino-2,2,cis-3,4,4-pentamethylphosphetan 1-oxide (83%), m.p. 51-53° (sealed tube, from hexane), ν_{max} 1278, 1206, 1153, 1137, 1088, 960, 757, 718, and 667cm^{-1}, τ 7.77 (6H, d, J 10 Hz), 8.25 (1H, dq, J 4 and 7 Hz), 8.83 (6H, d, J 17 Hz), 9.08 (6H, d, J 16 Hz), and 9.44 (3H, dd, J 7 and 2 Hz), ^{31}P δ -57.5 p.p.m., m/e 203, 188, 160, 147, 133, 112, 97, and 92 (Found: H, 11.0; P, 15.1. $C_{10}H_{21}NOP$ requires H, 10.85; P, 15.3%. A satisfactory carbon analysis was not obtained.).

(b) The adduct (1.044g), sodium hydroxide solution (0.1N, 1ml), and water (10ml) were refluxed for 48h. Extraction with dichloromethane (4 x 5ml), washing of the combined extracts with sodium hydroxide solution (2N; 2 x 5ml), followed by drying, removal of solvent, and recrystallisation gave a product identical to that formed in the acid hydrolysis of the adduct (61%), m.p. and mixed m.p. 51-53°.

Preparation of r-1-Dimethylamino-2,2,trans-3,4,4-pentamethylphosphetan 1-Oxide.

A solution of r-1-chloro-2,2,trans-3,4,4-pentamethylphosphetan 1-oxide (7.8g, 0.04mol) in tetrahydrofuran (30ml) was added dropwise over 0.5h, to a stirred solution of lithium dimethylamide (2.04g, 0.04 mol) in tetrahydrofuran (50ml). The solution was then stirred at room temperature for 24h. Solvent was then removed and ether (30ml) was added. Filtration and removal of solvent, followed by distillation (Kügel-Rohr) gave r-1-dimethylamino-2,2,trans-3,4,4-pentamethylphosphetan 1-oxide (48%), m.p. 88-91° (sealed tube, from hexane) (lit.[156] 94-95°).

Hydrolysis of r-2-Isopropyl-4,4,5,5-tetrakis(trifluoromethyl)-1,3,2--dioxaphospholan-2-spiro-1'-2',2',trans-3',4',4'-pentamethylphosphetan.

The adduct (1.022g), water (1ml), benzene (10ml), and 2 drops of hydrochloric acid (0.1N) were refluxed for 48h. Removal of solvent gave back the starting adduct. There was also no reaction when the adduct was refluxed for 48h in ethanol (5ml) and sodium hydroxide (2N; 5ml). The adduct was then refluxed in potassium hydroxide solution (5N; 10ml) for 48h, and the solution was extracted with dichloromethane. The combined extracts were washed with water, dried and evaporated, to give r-1-isopropyl-2,2,trans-3,4,4-pentamethylphosphetan 1-oxide (98%), m.p. and mixed m.p. with an authentic sample, prepared by the method of Oram and Trippett[63] 136-138° (from hexane).

PART TWO

9. FIRE-RESISTANT HYDRAULIC FLUIDS.

9.1 Desirable Properties of Compounds for Use as Fire-Resistant Hydraulic Fluids.

The work to be described in the second part of this thesis is concerned with an investigation into the properties of several phosphorus compounds with an aim to assessing their suitability for use as fire-resistant hydraulic fluids. This work was undertaken in collaboration with CIBA-GEIGY (U.K.) Limited.

The fire-resistant hydraulic fluids which are currently in service are based on the aryl phosphate molecule. Other types of fire-resistant fluids are available, e.g. silicones and halogenated hydrocarbons but these generally suffer from several drawbacks, such as poor lubricating properties, high price or high specific gravity.

A compound must have a combination of several properties if it is to be suitable for use as a hydraulic fluid, e.g. fire resistance, hydrolytic stability, good lubricating properties, low compressibility and low manufacturing cost. In addition it must be a liquid at ambient temperature and have a viscosity suitable for the application. The three chief properties relate to hydrolytic stability, fire resistance and melting point.

Hydrolytic Stability.

This is an important property since one of the main requirements of a hydraulic fluid is that it should undergo no physical or chemical change during its use. If a compound is fairly readily hydrolysed, not only will its lubricating efficiency gradually decline but also the hydrolysis products may promote corrosion of the system.

The hydrolytic stability of a compound was measured as outlined below: this is a standard test devised by CIBA-GEIGY (U.K.) Limited.

The phosphorus compound (5g) and water (5g) were heated together at 130° for three days, using a flask with a long air condenser. When cool, a mixture of ethanol:toluene (3:2) (20ml) was added and the acidity developed in both layers was determined by titration against potassium hydroxide solution (0.1N) to pH 11. The hydrolysis tests were performed in duplicate.

Although this test probably gives a reliable indication of the hydrolytic stability of a compound in actual working conditions, it is not sufficiently refined to enable accurate rate data to be determined. The major factors which are likely to introduce errors into the results are the following.

(a) Solubility

All the compounds studied were essentially immiscible with water and so the rates of hydrolysis would be expected to be influenced by the extent that the organic and aqueous layers are mutually soluble.

(b) Superheating.

No stirring was applied to the hydrolysis mixture and no granules were added to ensure efficient refluxing of the water. There is thus the possibility that superheating may occur in some hydrolyses and this will also affect the relative rates of hydrolysis.

(c) Molecular Weight Variations.

The molecular weights of the compounds studied cover a wide range but there is no compensation for this variation in the amount of material used for the test. This is certain to lead to inaccurate hydrolysis data in cases where the molecular weight difference is large.

(d) Autocatalysis.

Probably the most significant source of error stems from the fact that the hydrolysis tests are performed in water. This means that if the hydrolysis products are acid, as they are for aryl phosphates, the hydrolysis medium itself will soon become acid. If a hydrolysis is acid catalysed, the acid medium will promote hydrolysis, thus forming more acid, and so on. This autocatalysis will become more effective as more of the compound is hydrolysed and conversely, a compound which is more resistant to hydrolysis will be affected to a lesser extent.

The results from this test, then, are useful in that they enable trends in hydrolytic stability to be obtained for different compounds but the actual rate ratios would be expected to differ from data obtained under more controlled conditions.

Fire Resistance.

This was assessed from the autogenous ignition temperature (A.I.T.) The standard test used by CIBA-GEIGY (U.K.) Limited for measurement of A.I.T.'s is as follows.

The compound is dropped into a 'Pyrex' conical flask, which is surrounded by an electrically heated furnace or is immersed in a bath of molten metal, as the temperature of the flask is slowly increased. The test is completed when ignition occurs. The A.I.T. is recorded as 5° below the lowest temperature at which the compound ignites.

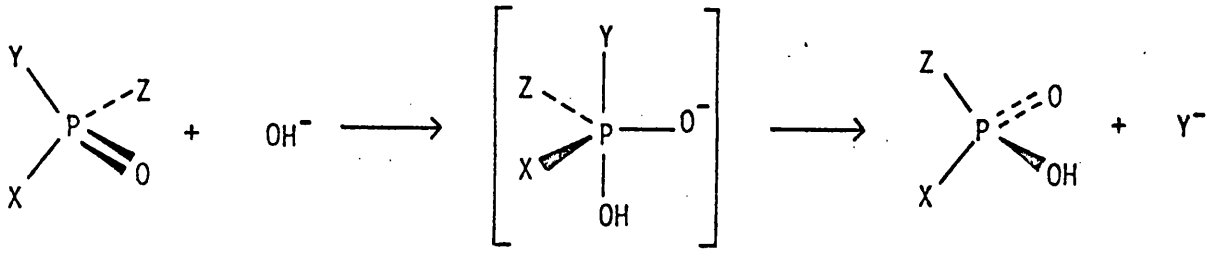
Melting Point.

As stated earlier, a hydraulic fluid must be a liquid at ambient temperature and so it is desirable that the individual compounds being tested as potential hydraulic fluids are also liquids. Low-melting solids

may also be of use, however, since it may be possible to produce a liquid sample from a blend of several such compounds.

9.2 Hydrolysis of Phosphate Esters.

The hydrolysis of a phosphate ester or related compound is merely a special case of a nucleophilic substitution reaction at tetraco-ordinated phosphorus as discussed in sections 1.1 and 3.3. With reference to scheme 22, the rate of hydrolysis of a phosphoryl compound may be



SCHEME 22

retarded by controlling any of the following three aspects of the reaction pathway.

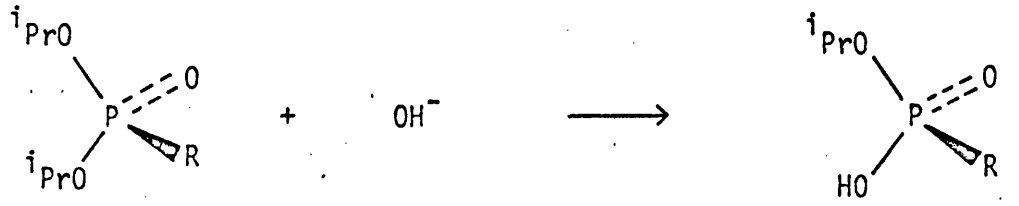
(1) The rate of initial nucleophilic attack.

The rate of nucleophilic attack may be controlled in two main ways.

(a) By increasing the size of the groups bonded to phosphorus.

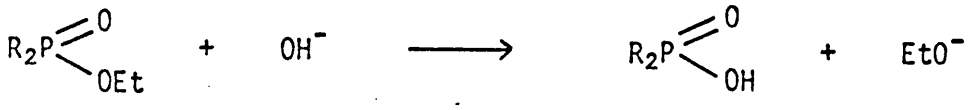
Hudson and Keay,[157] and Hawes and Trippett[119] have shown that the rates of alkaline hydrolysis of phosphonate esters are subject to steric retardation but the effect is fairly small when there is only one bulky group bonded to phosphorus, e.g. the ratio of the rate constants for

hydrolysis of (262, R = Me) and (262, R = t-butyl) is only 500:1.



(262)

The presence of two bulky substituents, however, does decrease the rate of hydrolysis substantially, as is shown by the work of Hawes and Trippett[119] on the rates of alkaline hydrolysis of phosphinate esters (see table 12)



(263)

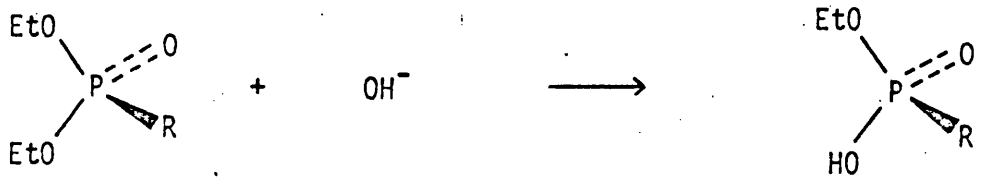
(263)	Rate Constant ($l.mole^{-1}\ sec^{-1} \times 10^6$)
R = ethyl	260/70°
R = t-butyl	0.08/120°

TABLE 12

(b) By reducing the electrophilicity of the phosphorus.

Inductively electron-donating or -withdrawing substituents do not affect the rate of hydrolysis very much because, although an electron--donating substituent tends to make the phosphorus more negative, electron

release also tends to decrease any p-d π-bonding between the leaving group and the phosphorus. These two effects oppose each other, giving rise to a fairly small overall variation, as is illustrated in table 13.[158]



(264)

(264), R =	Me	Et	$ClCH_2$	Cl_2CH
Relative rate constants for hydrolysis	1	0.13	15.6	108

TABLE 13

Substituents that can interact mesomerically with the phosphorus also affect the rate of hydrolysis, e.g. in table 14, the esters are hydrolysed by hydroxide ion at the relative rates per methoxy group shown.[159]

$Et_2P(O)OMe$	$EtP(O)(OMe)_2$	$(MeO)_3PO$
5.9	4.2	1

TABLE 14

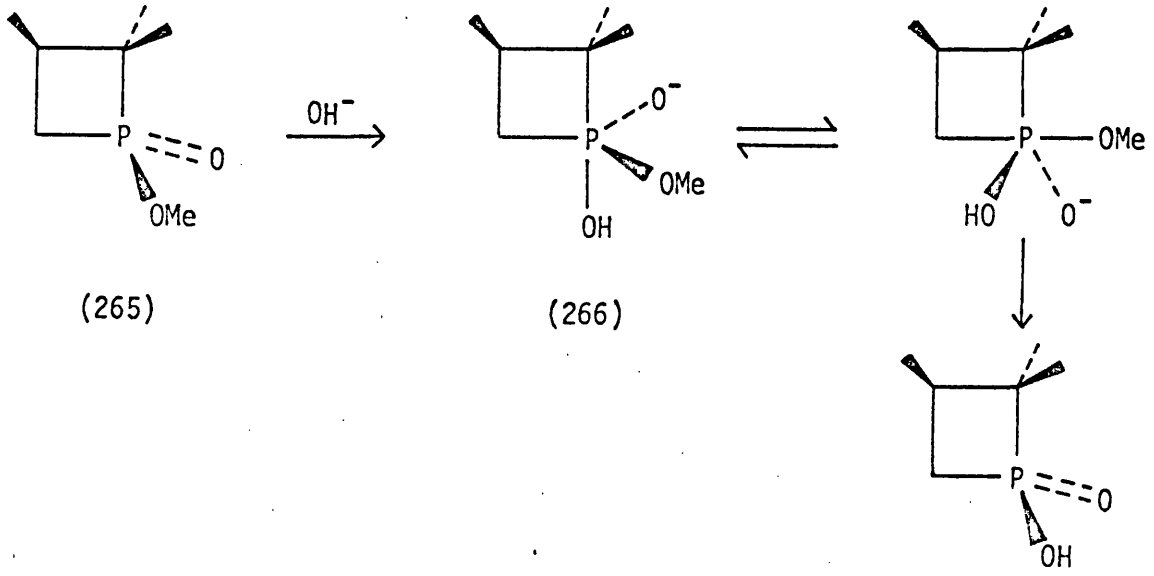
Successive substitution of methoxy groups for ethyl groups leads to a decrease in the hydrolysis rate because, although alkoxy groups withdraw electrons inductively, this is outweighed by their π-donor

ability and so the electron density at phosphorus is increased. Again, this does not seem to be a particularly large effect presumably because, like inductive electron donation, π-donation, although reducing the electrophilicity of the phosphorus, also decreases the π interaction between the leaving group and the phosphorus.

(2) The rate of formation of the quinquecovalent intermediate.

In a substitution reaction involving an acyclic tetraco-ordinated phosphorus compound attack of the nucleophile generally leads to formation of the most stable of the four possible TBP intermediates, i.e. the most apicophilic group, which is usually the leaving group, occupies an apical position. If the leaving group were to be constrained to an equatorial position and a group of much lower apicophilicity forced to occupy an apical position, then the energy of the phosphorane intermediate, relative to the starting phosphoryl compound, would be raised and so the rate of hydrolysis would be decreased.

This constraint is difficult to apply in acyclic systems but is commonplace in cyclic systems, where ring strain considerations often force

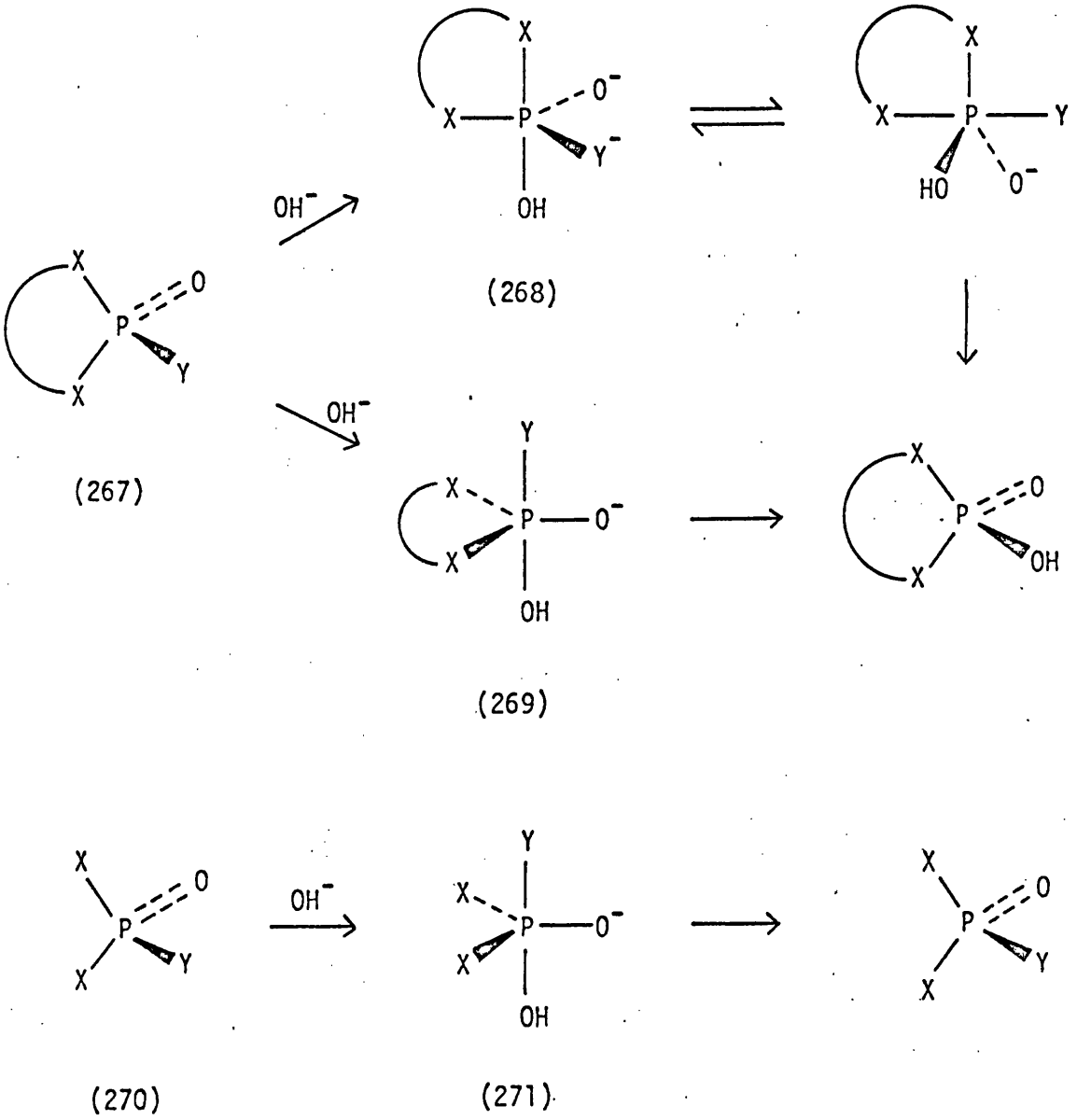


(265) (266)

SCHEME 23

the nucleophile to attack opposite one of the ring termini, e.g., the phosphinate (265) is believed[119] to undergo hydrolysis by the route shown in scheme 23. In this case, however, the rate of hydrolysis of (265) is much greater than that of the analogous acyclic compound because the unfavourable stereoelectronic arrangement of ligands is more than compensated by the relief of ring strain accompanying formation of the TBP (266).

With reference to scheme 24, where Y is the leaving group, if the



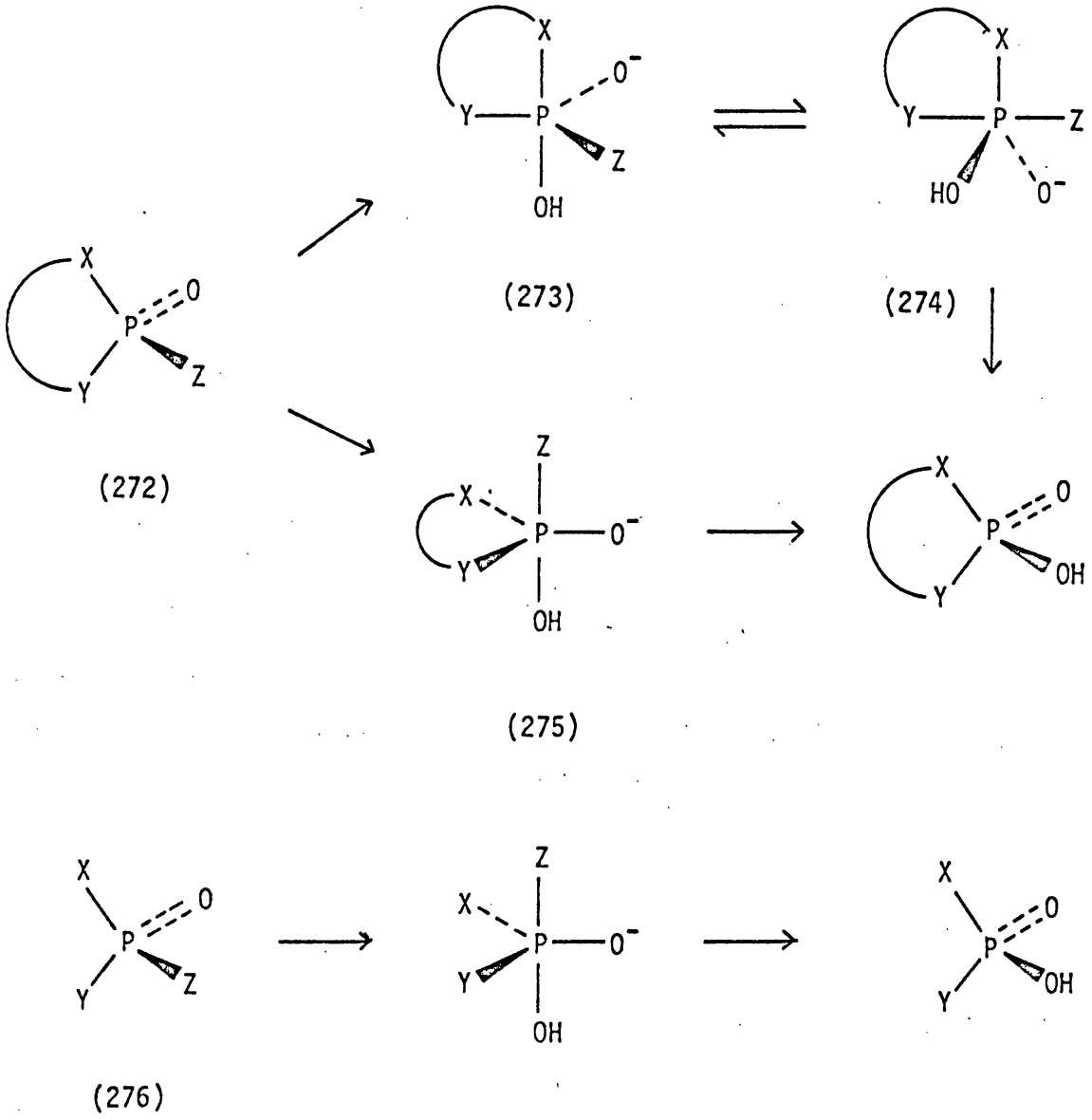
SCHEME 24

cyclic compound (267) is to undergo hydrolysis at a slower rate than its acyclic analogue (270) the relief of ring strain on forming (268) must be smaller than the difference in apicophilicity between X and Y. If the strain factor is sufficiently low, hydrolysis of (267) will proceed *via* (269) but this is still destabilised, relative to (271), by any strain energy present in the *ee* ring.

(3) The rate of decomposition of the quinquecovalent intermediate.

As has already been mentioned, substitutions in acyclic phosphoryl compounds generally proceed by attack of the nucleophile directly opposite the leaving group and so there is usually little to prevent the phosphorane from decomposing immediately to products. The main factor, therefore, that will affect the rate of this decomposition is the leaving group ability of the apical ligand. For cyclic systems, however, it may be possible to prevent the leaving group from moving into an apical position. Thus, for the compound (272), where Z is the leaving group and the apicophilicities of the groups decrease in the order Z,X,Y, attack of the nucleophile may give (273) or (275). In order to lose Z^- from an apical position BPR to (274) must occur. If Y is a very poorly apicophilic group (274) may be of high energy and the conversion of (273) to (274) correspondingly slow. Thus, provided that the apicophilicity difference between the nucleophile and Y is greater than the relief of ring strain accompanying the formation of (273), (272) will hydrolyse at a slower rate than its acyclic analogue (276).

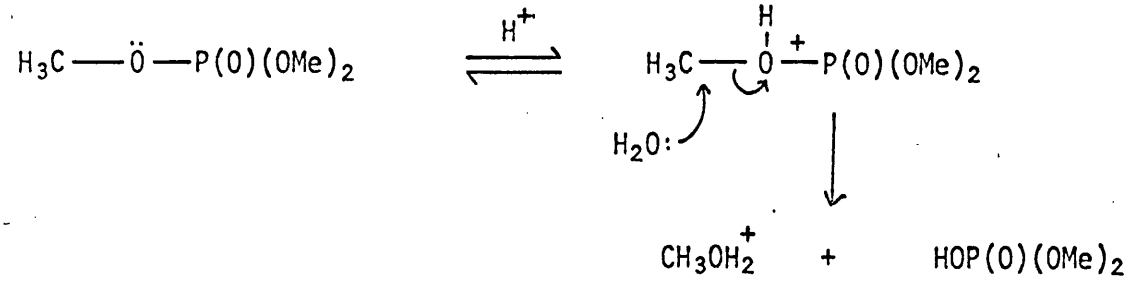
If hydrolysis proceeds *via* (275) any strain present in the *ee* ring will cause the hydrolysis rate to be smaller than that for the acyclic analogue (276).



9.3 Alternative Hydrolysis Routes.

(1) SN2 reaction at carbon.

The hydrolysis of trimethyl phosphate in acidic $H_2{}^{18}O$ has been shown[160] to lead to dimethyl phosphate containing no ^{18}O. This was interpreted in terms of a mechanism involving attack at carbon, as in scheme 25.

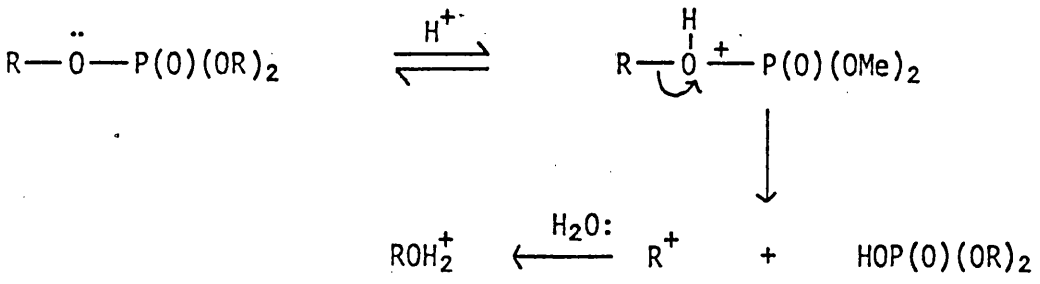


SCHEME 25

For a methyl ester where the other two groups on the phosphorus are bulky, attack at carbon may represent a much lower energy pathway for hydrolysis than attack at phosphorus.

(2) SN1 reaction at carbon.

A number of phosphorus esters containing secondary or tertiary alkyl groups are believed to undergo hydrolysis in acid solution by the SN1 mechanism shown in scheme 26.[157]

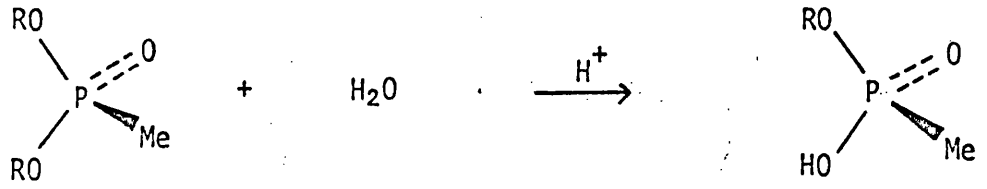


SCHEME 26

Support for this mechanism comes from the fact that the acid hydrolysis of phosphonates of optically active alcohols leads to completely racemic products,[161] implying formation of a free carbonium ion. Also, the acid hydrolysis of dineopentyl methylphosphonate leads to formation of 2-methyl--2-butene (neopentyl alcohol is stable under the reaction conditions).[157]

The operation of this SN1 mechanism often leads to much higher rates of hydrolysis than would be expected for attack at phosphorus. This is

evident from the rate sequence shown in table 15 for the acid hydrolysis of a series of dialkyl methylphosphonates[157] and also from the hydrolytic instability of tri-t-butyl phosphate which decomposes spontaneously in



(277)

(277), R =	Me	Et	i-Pr	Neopen
Relative rate constants for hydrolysis	1.2	1	25	1

TABLE 15

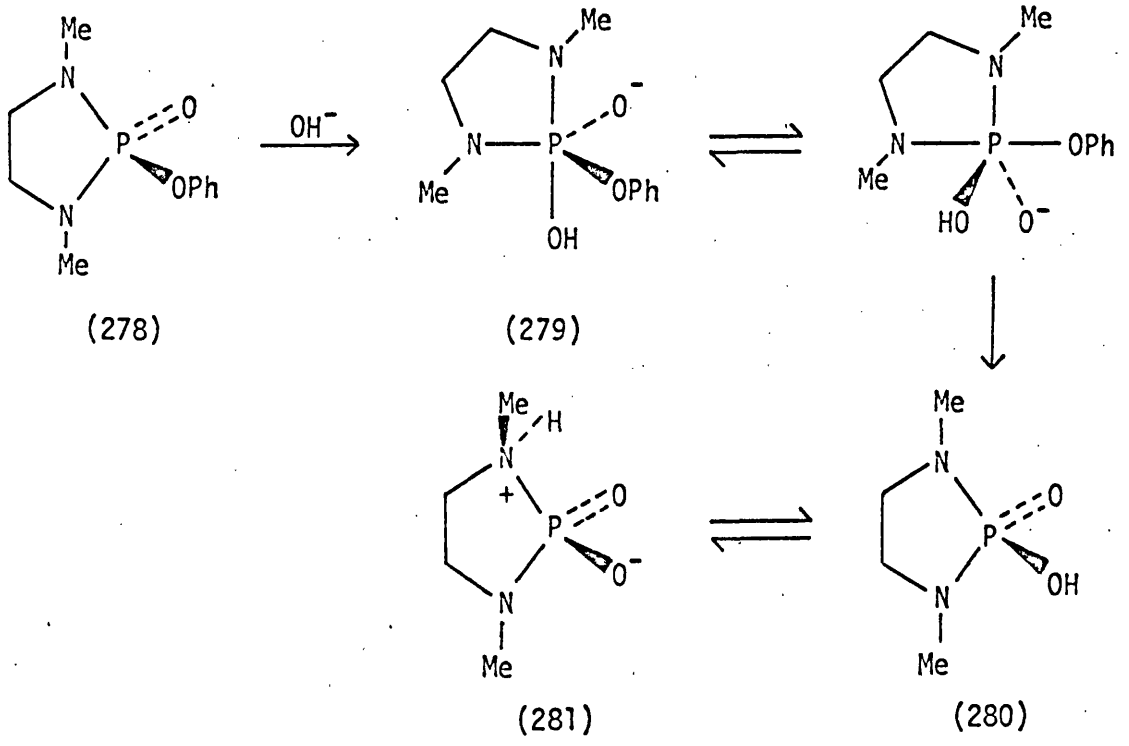
water at room temperature.[162]

In order to avoid these two alternative hydrolysis pathways the compounds that were prepared had aryloxy, and not alkoxy, groups bonded to phosphorus.

10. SYNTHESIS AND TESTING OF SOME PHOSPHORYL COMPOUNDS FOR USE AS FIRE-RESISTANT HYDRAULIC FLUIDS.

10.1 The Hydrolytic Stability of 1,3-Dimethyl-2-oxo-2-phenoxy-1,3,2--diazaphospholan.

It was expected that the hydrolysis pathway for (278) would be as is indicated in scheme 27. Since oxygen is more apicophilic than nitrogen



(278) (279) (281) (280)

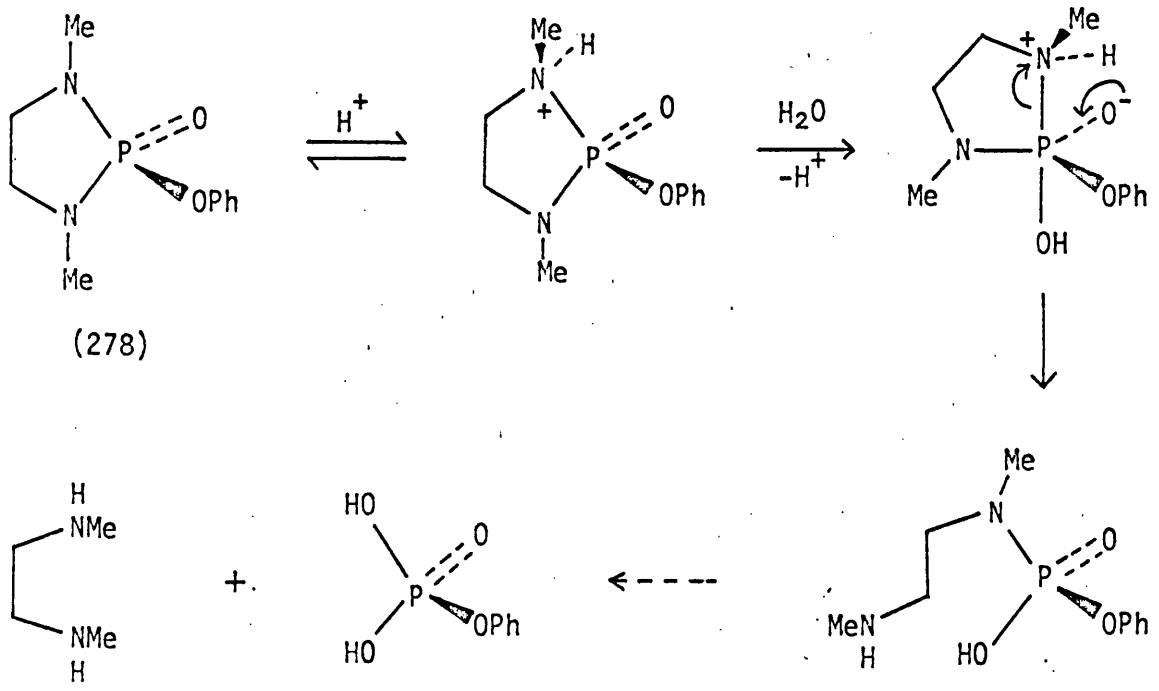
SCHEME 27

by about 9 kcal mol^{-1} (see section 4.2 and ref. 63), if the relief of ring strain on forming (279) is smaller than this then (278) will hydrolyse more slowly than its acyclic analogue.

The product may exist as the zwitterion (281) and not as the acid (280) and this may also be effective in reducing the hydrolysis rate since

any rate enhancement due to acid catalysis will be less.

In fact, (278) showed extremely poor hydrolytic stability: the acid value for hydrolysis in the standard way was 590 mg KOH/g which corresponds to the formation of about 2.5 mole equivalents of acid. This high acid value indicates that hydrolysis proceeds further than the stage reached in scheme 27. It may be that (280) undergoes further hydrolysis or, more likely in view of the results of Koizumi et al,[163] that protonation of a nitrogen atom of (278) occurs with subsequent decomposition as illustrated in scheme 28. Formation of the TBP is now a favourable step



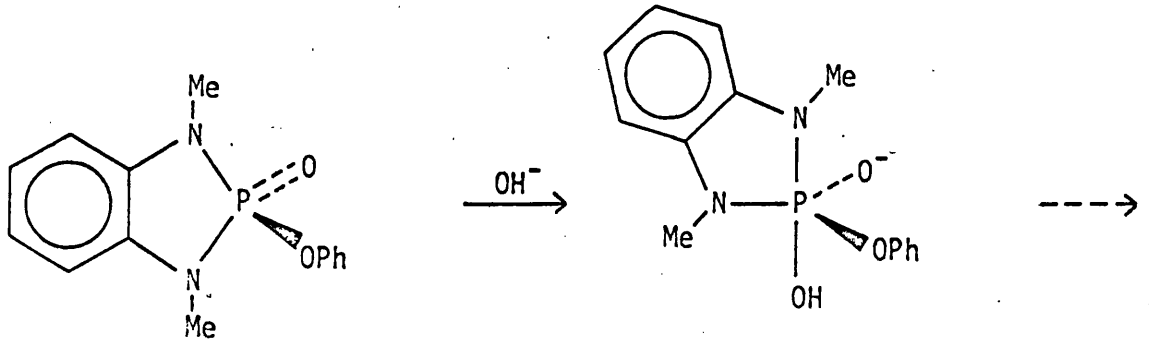
(278)

SCHEME 28

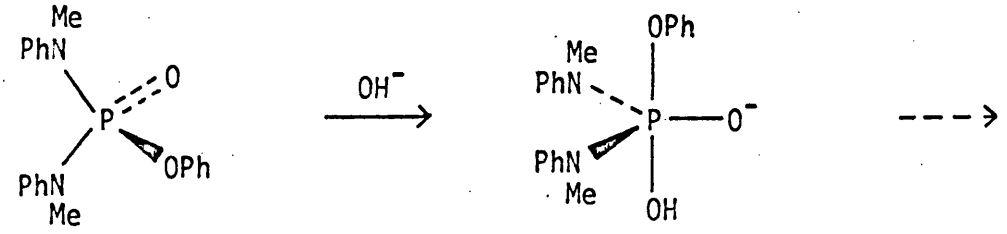
since the protonated amino group is likely to be highly apicophilic and so hydrolysis by this route would be expected to be fast.

Westheimer[4] has reported that the cyclic phosphorodiamidate (282) undergoes alkaline hydrolysis one million times faster than its acyclic

analogue (284). The main reason for this rate ratio was thought to be the relief of ring strain accompanying formation of the quinquecovalent



(282) (283)

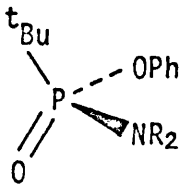
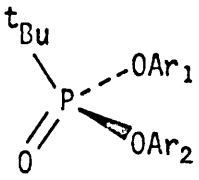
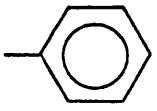
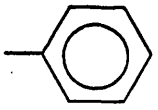
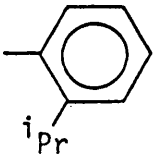
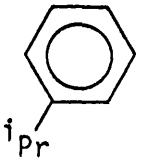
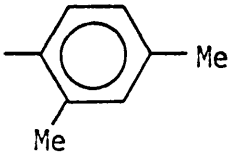
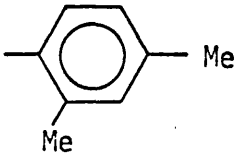
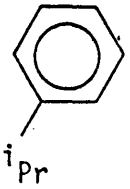


(284)

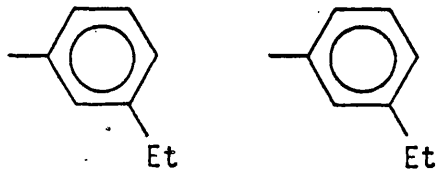
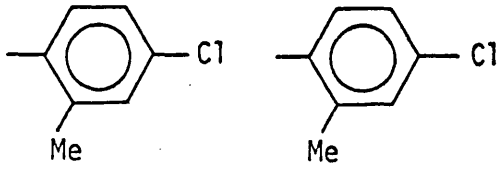
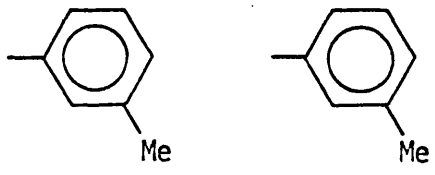
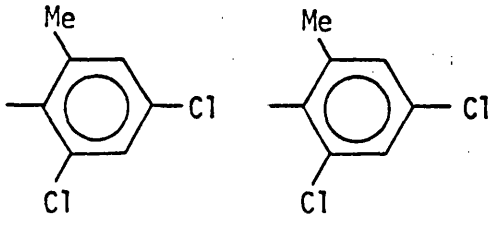
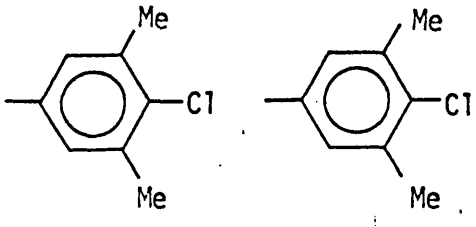
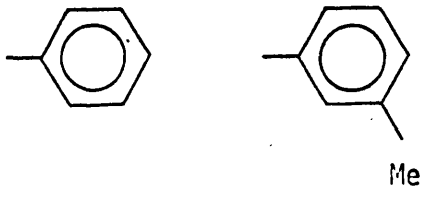
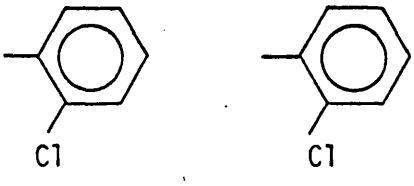
intermediate (283). If this ring strain is also present in (278) then it is, perhaps, not surprising that it should show such poor hydrolytic stability.

10.2 The Fire Resistance and Hydrolytic Stability of Some Aryl t-Butylphosphonamidates and Diaryl t-Butylphosphonates.

Since the cyclic phosphorodiamidate (278) showed such poor hydrolytic stability it was decided to investigate the possibility of controlling the hydrolysis rate by increasing the size of the groups bonded to phosphorus. Accordingly, the compounds (285) to (287) were prepared.

Compound	m.p.	Acid value (mg KOH/g)	A.I.T.
			
(285) R = Et	liquid	-	495°
(286) R = Me	47-51°	-	510
			
Ar_1 Ar_2			
(287)  	107-107.5	0.11	625
(288)  	liquid	0.19	520
(289)  	liquid	0.38	565
(290)  	liquid	0.16	565

[cont.]

	Compound.	m.p.	Acid value (mg KOH/g)	A.I.T.
(291)		liquid	0.40	575°
(292)		63-64°	0.51	590
(293)		37-40	0.00	620
(294)		146-148	0.39	630
(295)		98-100	0.00	630
(296)		58-60	9.64	630
(297)		71-72	0.23	635

[cont.]

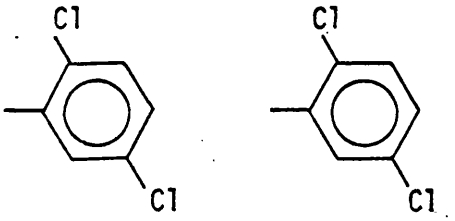
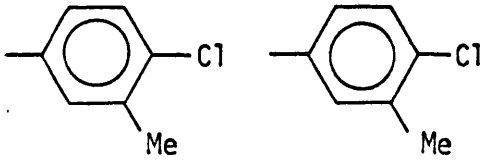
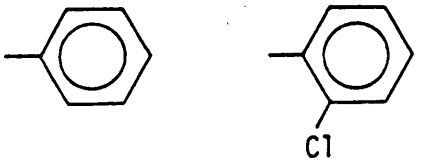
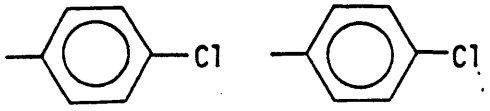
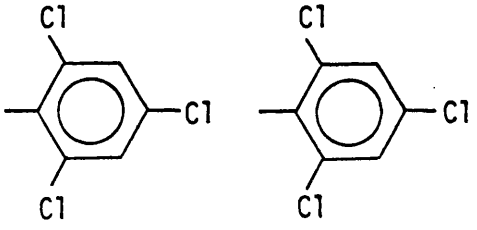
	Compound	m.p.	Acid value (mg KOH/g)	A.I.T.
(298)		73-74°	0.20	640°
(299)		84-86	5.6	640
(300)		49-50	0.00	650
(301)		87-89	0.29	650
(302)		154-157	-	655
	$(PhO)_3PO$		171.3 [164]	

TABLE 16

The A.I.T.'s of triaryl phosphates range from about 550-590°[164] and the very low values for the compounds (285) and (286) (see table 16) would preclude their use as hydraulic fluids. It would appear, however, from the A.I.T. of (287) that replacement of an aryloxy group by a t-butyl group increases the A.I.T. by 35-75°. The increase is probably due to the higher percentage of phosphorus in (287); this is known[164] to lead to higher A.I.T. values.

The phosphonate (287) also showed remarkable resistance to hydrolysis compared with triphenyl phosphate (see table 16). If the effect of the t-butyl group is purely steric in nature the reduction in rate is larger than would have been anticipated from the work of Hudson[157] and Trippett.[119] It may be that replacement of a phenoxy by a t-butyl group results in an increased electron donation onto phosphorus, i.e. in this case, the inductive effect of the t-butyl group is greater than the mesomeric interaction of the phenoxy group. A more likely explanation, however, is that since the hydrolysis of triphenyl phosphate is acid catalysed[165] the acid value for triphenyl phosphate will be increased by autocatalysis (see section 9.1). For (287), which is more resistant to hydrolysis, this acid catalysis will occur to a very much smaller extent and an equivalent rate enhancement will not be observed.

The compounds (288)-(302) were prepared, by reaction of t-butylphosphonic dichloride with the sodium salt of the appropriate phenol(s), in order (a) to obtain a liquid sample of a phosphonate analogous to (287) and (b) to investigate the effect of alkyl or chlorine substitution in the aromatic ring on the A.I.T. and hydrolytic stability of diaryl t-butylphosphonates.

Fire Resistance.

It appears that alkyl substitution lowers the A.I.T., as is shown by the values for (288)-(291). This would be expected since it is known[164] that an increase in the carbon content usually leads to a lower A.I.T.

Chlorine substitution in general seems to increase the A.I.T. but the effect is small, as can be seen from the values for (297)-(302).

An interesting point is that ortho substitution leads to a much lower A.I.T. than does meta or para substitution, whether the substituent is a methyl group [compare (292) with (299)] or a chlorine atom [compare (297) with (301)]. The reason for this difference is unknown.

Hydrolytic Stability.

From the data presented in table 16 it is evident that substitution in the aromatic ring has virtually no effect on the hydrolytic stability of the phosphonates. This would seem to indicate that the stability towards hydrolysis of (287) compared with triphenyl phosphate is due mainly to a steric effect and not to the greater electron donating power of the t-butyl group since, if the latter were the main reason for the hydrolytic stability, the rates of hydrolysis would be expected to correlate with the acidity of the phenols. While it may be that if the hydrolysis conditions were made more severe, so that appreciable amounts of the phosphonates would be hydrolysed, this correlation might become detectable, nevertheless the large difference in hydrolytic stability between triphenyl phosphate and the phosphonates (287)-(301) does imply that a steric effect is the major reason for this difference.

Melting Point.

Substitution of alkyl groups into the aromatic ring leads to a lowering of melting point but in some cases, e.g. (288)-(291), the accompanying

drop in A.I.T. would probably preclude the use of these compounds as hydraulic fluids.

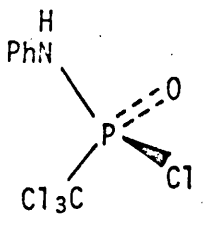
Chlorine substitution initially leads to a lowering of melting point but excessive substitution, as in (294) or (302), leads to prohibitively high values and it is unlikely that these compounds could be used as constituents of a hydraulic fluid.

However, a small degree of alkyl and/or chlorine substitution, as in compounds (292), (293) and (296)-(301), has the effect of lowering the melting point without adversely affecting the A.I.T. and it may be possible to use such compounds as mixtures to obtain a liquid sample.

10.3 The Fire Resistance and Hydrolytic Stability of Diphenyl Trichloromethylphosphonate.

Diphenyl trichloromethylphosphonate was prepared, in 63% yield, by addition of two equivalents of phenol to trichloromethylphosphonic dichloride in the presence of two equivalents of triethylamine. Reaction of the phosphonic dichloride with two equivalents of sodium phenoxide gave triphenyl phosphate as the major product, indicating ready displacement of the trichloromethyl group by the more nucleophilic reagent.

It was thought that replacement of the t-butyl group by the trichloromethyl group would increase the A.I.T. but would not appreciably affect the hydrolytic stability of the phosphonate since the compound (303)



(303)

is reported[166] to be recovered unchanged after dissolution in basic solution. Unfortunately, diphenyl trichloromethylphosphonate was found to have very poor hydrolytic stability and a low A.I.T. (see table 17).

	Acid Value (mg KOH/g)	A.I.T.
$Cl_3C-P(OPh)_2$ (304)	324	580°

TABLE 17

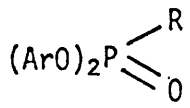
Presumably the greatly increased electrophilicity of the phosphorus outweighs any steric hindrance to attack presented by the bulky trichloromethyl group. Electron donation from the aniline group, which probably exists as the anilide anion in basic solution, presumably accounts for the stability of (303) since this would counteract the electron-withdrawing effect of the trichloromethyl group and allow the steric effect to assume greater importance.

The low A.I.T. for (304) is rather surprising since increase in chlorine content and decrease in carbon content usually leads to a higher value (see section 10.2 and ref. 164). Presumably the stability of the radicals formed by hydrolysis of a C - Cl bond provides a favourable decomposition route for (304).

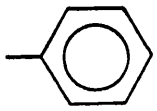
10.4 The Fire Resistance and Hydrolytic Stability of Some Diaryl Secondary-alkylphosphonates.

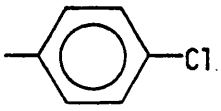
Because of the anomalously high hydrolytic stability of the diaryl t-butylphosphonates it was decided to prepare a range of secondary-alkylphosphonates to see whether these also possessed the same degree of stability.

Compound	m.p.	Acid Value (mg KOH/g)	A.I.T.

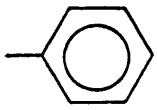


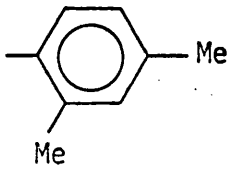
R = Cyclohexyl

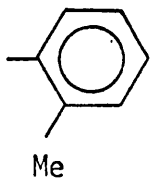
(305)  58-60° 0.90 640°

(306)  76-78 34.7 645

R = Isopropyl

(307)  42-43 0.11 650

(308)  liquid 0.17 625

(309)  liquid 0.22 625

[cont.]

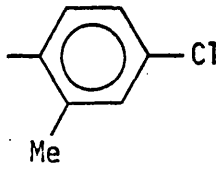
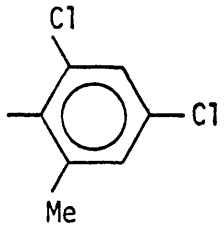
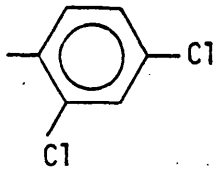
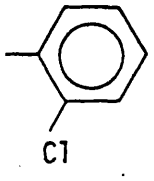
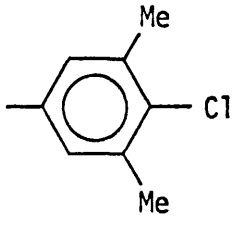
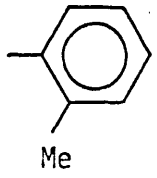
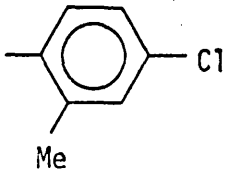
	Compound	m.p.	Acid Value (mg KOH/g)	A.I.T.
(310)		liquid	0.34	650°
(311)		133-136°	0.11	650
(312)		59-60	2.30	670
(313)		liquid	12.8	680
(314)		53-54	0.11	> 680
(315)		liquid	0.22	> 680
(316)		liquid	0.34	> 680

TABLE 18

The compounds listed in table 18 were all prepared by reaction of one equivalent of cyclohexyl- or isopropylphosphonic dichloride with two equivalents of the sodium salt of the appropriate phenol.

Fire Resistance.

In general, the A.I.T.'s for the secondary-alkylphosphonates are higher than those for the corresponding t-butylphosphonates (see table 18). The trends in the A.I.T.'s that were observed for the t-butylphosphonates are also apparent in the values for the isopropylphosphonates, namely alkyl substitution lowers the A.I.T. while chlorine substitution tends to increase slightly the A.I.T. Substitution at the ortho position of the aromatic ring again results in a lower A.I.T. than substitution at a meta position: this effect is illustrated particularly well by the A.I.T.'s for (310) and (316).

Hydrolytic Stability.

With reference to table 18, it appears that compounds (305) and (307), and those where alkyl groups are incorporated into the aromatic ring, possess the same resistance to hydrolysis as their t-butyl analogues (within the limitations of the hydrolysis test itself). However, chlorine substitution in the aromatic ring does reduce the hydrolytic stability, e.g. in compounds (306), (313) and especially (312). This indicates that as the size of the alkyl group bonded to phosphorus decreases other factors, namely the electron-donating power and leaving group ability of the substituents, become more important in controlling the reaction pathway, as would be expected. In order to obtain a more informative comparison of hydrolysis rates it would be necessary to subject the compounds to a more severe test so that appreciable amounts of hydrolysis occur even for the

more stable compounds.

Again, it is highly likely that the acid values for the phosphonates that show reduced hydrolytic stability are increased by acid catalysis.

Melting Point.

The isopropylphosphonates are generally lower melting than the corresponding t-butylphosphonates and, probably of most significance, the compounds that have the highest A.I.T. values, and are hydrolytically stable, are all liquids.

10.5 Conclusion.

It appears, from the results presented in tables 16 and 18, that the basic requirements of low melting point and high fire resistance and hydrolytic stability have been met by some of the compounds studied. The t-butylphosphonates show a greater hydrolytic stability than the isopropylphosphonates although the latter show higher thermal stability and lower melting points. Presumably the specific application of the hydraulic fluid will decide which of these properties is of most importance.

The major drawback with the alkylphosphonates is their mode of preparation. The preparative route that was used is not suitable for use on an industrial scale and another method of preparation would have to be found.

Phosphonates are commonly prepared by the 'Michaelis-Arbuzov' reaction[167] but this route is of only very limited use in this application because the reaction of a triaryl phosphite with a secondary or tertiary alkyl halide requires high temperatures and long reaction periods.[168]

Another widely used preparative route involves reaction of phosphorus

trichloride with an alkane[169-171], alkene[172-174] or alkyl halide[170,172] in the presence of oxygen (scheme 29).

$$PCl_3 + O_2 + \left\{\begin{array}{l}\text{alkane,}\\ \text{alkene, or}\\ \text{alkyl halide.}\end{array}\right\} \rightarrow RPOCl_2$$

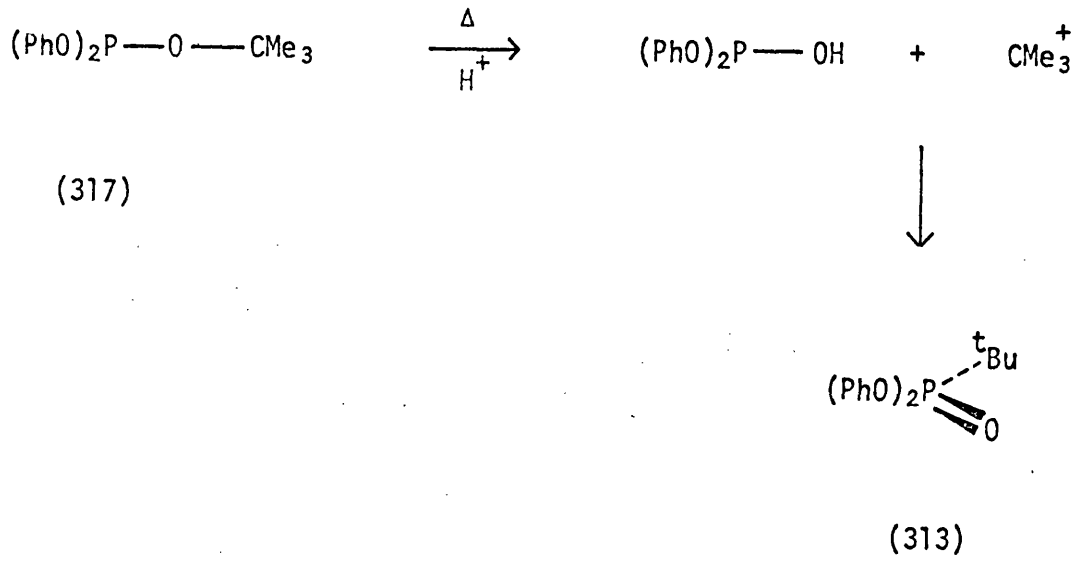
Scheme 29

The main disadvantage with this type of reaction is the low yield and the difficulty in separating the products.

It is known[175] that if triphenylphosphine and t-butyl chloride are refluxed together in benzene, triphenylphosphine hydrochloride and isobutene are formed, whereas if the reaction is performed in a sealed vessel triphenyl-t-butylphosphonium chloride is obtained.[176] There was, however, essentially no reaction when triphenyl phosphite, t-butyl chloride and a trace of toluene-p-sulphonic acid were heated in a sealed tube at 100° for 24 hours, although in retrospect, this was probably not a long enough reaction period.

Reaction of diphenyl phosphorochloridite with t-butyl alcohol in the presence of triethylamine gave a crude product which contained 70% (by integration of the ^1H n.m.r. spectrum) of diphenyl t-butyl phosphite (317). The remainder of the product was presumably diphenyl phosphite, formed by dealkylation of (317) in a similar way to that observed for tri-t-butyl phosphite.[177] (317) decomposed on attempted distillation with gas evolution and formation of diphenyl phosphite.

In order to determine whether (317) would undergo an acid-catalysed thermal rearrangement to (287), the phosphite and a trace of aluminium chloride were heated in a sealed tube at 130° for 7 days. The ^1H n.m.r.



(317)

(313)

spectrum of the crude reaction product, however, showed no absorption due to a t-butyl group.

EXPERIMENTAL

The instrumental and general experimental details are as described in the first part of this thesis.

Preparation of Phenyl Phosphorodichloridate.

This was prepared by reaction of phosphoryl chloride with phenol in the presence of pyridine in the usual way. Distillation gave phenyl phosphorodichloridate (71%), b.p. 80-84%/0.4mm (lit.[178] 91°/10mm).

Preparation of 1,3-Dimethyl-2-oxo-2-phenoxy-1,3,2-diazaphospholan.

This was prepared by reaction of phenyl phosphorodichloridate with NN'-dimethylethylenediamine in the usual way. Recrystallisation of the crude reaction product gave 1,3-dimethyl-2-oxo-2-phenoxy-1,3,2-dioxaphospholan (80%), m.p. 56-58° (from carbon tetrachloride) (lit.[179] 56-58°).

Preparation of t-Butylphosphonous Dichloride.

This was prepared by the method of Voskuil and Arens[145] in 73% yield, b.p. 145-150° (lit. 145-150°).

NN-Diethyl-t-butylphosphonamidous chloride was prepared as in the first part of this thesis. In a similar way, dimethylamine gave NN-dimethyl-t-butylphosphonamidous chloride (60%), b.p. 55-60°/2mm, τ 7.22 (6H, d, J 11 Hz) and 8.80 (9H, d, J 15 Hz).

Preparation of Phenyl NN-Diethyl-t-butylphosphonamidite.

A solution of sodium phenoxide (4.75g, 0.041 mol) in ether-tetra-

hydrofuran (1:1, 60 ml) was added dropwise, over 0.25 h, to a stirred solution of NN-diethyl-t-butylphosphonamidous chloride (8 g, 0.041 mol) in ether-light petroleum (1:1, 100 ml). The mixture was then stirred for 8 h. Filtration and removal of solvent, followed by distillation, gave phenyl NN-diethyl-t-butylphosphonamidite (70%), b.p. 110-112°/0.2mm, τ 2.42-3.03 (5H, m), 6.82 (4H, dq, J 10 and 7 Hz), 8.87 (9H, d, J 14 Hz), and 9.00 (6H, t, J 7 Hz).

In a similar way, NN-dimethyl-t-butylphosphonamidous chloride gave phenyl NN-dimethyl-t-butylphosphonamidite (79%), b.p. 96-102°/0.4mm, τ 2.37-3.03 (5H, m), 7.22 (6H, d, J 8 Hz), and 8.88 (9H, d, J 14 Hz).

Preparation of Phenyl NN-Diethyl-t-butylphosphonamidate.

Hydrogen peroxide solution (100 vol; 1.02 g, 0.03 mol) was added dropwise to a stirred solution of phenyl NN-diethyl-t-butylphosphonamidite (7 g, 0.03 mol) in benzene (30 ml), and the mixture was stirred for 12 h. The organic layer was then separated and the aqueous layer was extracted with ether. The combined extracts and organic layer were then dried, filtered, and evaporated. Chromatography of the residue on silica (250 g) and elution with ether-light petroleum (1:3), followed by distillation, gave Phenyl NN-diethyl-t-butylphosphonamidate (72%), b.p. 118-120°/0.1 mm, $\nu_{max.}$ 1592, 1489, 1241, 1212, 1028, 944, 905, 821, 760, and 698 cm^{-1}, τ 2.38-3.02 (5H, m), 6.80 (4H, dq, J 9 and 8 Hz), 8.72 (9H, d, J 17 Hz), and 9.02 (6H, t, J 8 Hz), m/e 269, 253, 240, 212, 198, 140, and 120 (Found: C, 62.4; H, 9.0; N, 5.2. $C_{14}H_{24}NO_2P$ requires C, 62.4; H, 9.0; N, 5.2%).

In a similar way, phenyl NN-dimethyl-t-butylphosphonamidite reacted with hydrogen peroxide solution to give a viscous liquid, which, after

distillation, slowly solidified. Recrystallisation of the distillate gave phenyl NN-dimethyl-t-butylphosphonamidate (88%), b.p. 115-120°/0.1 mm, m.p. 47-51° (from dichloromethane-light petroleum), $\nu_{max.}$ 1598, 1497, 1311, 1210, 1000, 919, 902, 830, 771, 720, and 690 cm^{-1}, τ (carbon tetrachloride) 2.65-3.03 (5H, m), 7.30 (6H, d, J 8 Hz), and 8.77 (9H, d, J 16 Hz), m/e 241, 226, 184, 149, 140, and 120 (Found: C, 59.9; H, 8.5; N, 5.8. $C_{12}H_{20}NO_2P$ requires C, 59.7; H, 8.4; N, 5.8%).

Preparation of Diphenyl t-Butylphosphonate.

A solution of sodium phenoxide (11.6 g, 0.1 mol) in tetrahydrofuran (40 ml) was added dropwise, over 0.5 h, to a stirred solution of t-butylphosphonous dichloride (8 g, 0.05 mol) in ether (100 ml), and the mixture was then refluxed for 8 h. Filtration and removal of solvent gave diphenyl t-butylphosphonite, τ 2.43-3.17 (10H, m) and 8.82 (9H, d, J 13 Hz). The phosphonite was then taken up in benzene (40ml), excess hydrogen peroxide solution (100 vol) was carefully added, and stirring was then continued for 12 h. The organic layer was then separated, and the aqueous layer was extracted with dichloromethane. The combined extracts and organic layer were dried, evaporated, and the residue was recrystallised to give diphenyl t-butylphosphonate (73%), m.p. 107-107.5° (from dichloromethane-hexane), $\nu_{max.}$ 1593, 1489, 1268, 1213, 1165, 921, 825, 763, 731, 692, and 651 cm^{-1}, τ 2.33-3.00 (10H, m), and 8.58 (9H, d, J 18 Hz), m/e 290, 274, 233, 170, and 140 (Found: C, 66.4; H, 6.7; P, 10.8. $C_{16}H_{19}O_3P$ requires C, 66.2; H, 6.6; P, 10.7%).

The following phosphonic dichlorides were prepared by the method of Kinnear and Perren:[180] t-butyl- (80-90%), m.p. 115-118° (sealed tube,

sublimed sample) (lit. 110°), m.p. of dianilide 253-256° (lit. 256-257°); trichloromethyl- (85%), m.p. 153-155° (sealed tube, sublimed sample), (lit. 156°); Cyclohexyl- (88%), b.p. 104-110°/2 mm (lit. 90°/1 mm), m.p. of dianilide 227.5-230° (lit. 229-230°); and isopropyl- (68%), b.p. 74-75°/12 mm (lit. 35°/1.5 mm), m.p. of dianilide 198-200° (lit. 199-200°).

Preparation of Phenyl t-Butylphosphonochloridate.

A solution of phenol (47 g, 0.5 mol) in toluene (150 ml) was added to a stirred solution of t-butylphosphonic dichloride (87.5 g, 0.5 mol) and triethylamine (50.5 g, 0.5 mol) in toluene (200 ml), and the mixture was refluxed for 6 days. Filtration and removal of solvent, followed by distillation of the residue gave a colourless liquid which solidified on standing. Recrystallisation gave phenyl t-butylphosphonochloridate (52%), b.p. 165-170°/0.2 mm, m.p. 67-69° (from hexane), $\nu_{max.}$ 1591, 1267, 1190, 1167, 934, 822, 774, 743, 692, and 651 cm^{-1}, τ 2.53-2.88 (5H, m) and 8.60 (9H, d, J 22 Hz), m/e (for ^{35}Cl) 232, 197, 176, 140, 94, and 57 (Found: C, 51.65; H, 6.0; Cl, 15.4. $C_{10}H_{14}ClO_2P$ requires C, 51.6; H, 6.0; Cl, 15.3%).

Preparation of Phenyl m-Tolyl t-Butylphosphonate.

A solution of sodium m-methylphenoxide (10 g, 0.077 mol) in tetrahydrofuran (40 ml) was added dropwise, over 0.5 h, to a stirred solution of phenyl t-butylphosphonochloridate (18 g, 0.077 mol) in tetrahydrofuran (50 ml). The mixture was refluxed for 24 h, allowed to cool, and light petroleum (100 ml) was then added. Filtration and removal of solvent gave

a viscous liquid which solidified on standing. Recrystallisation gave phenyl m-tolyl t-butylphosphonate (79%), m.p. 58.5-60.5° (from ethanol), $\nu_{max.}$ 1608, 1586, 1493, 1273, 1144, 954, 929, 846, 795, 763, 693, and 657 cm^{-1}, τ 2.57-3.25 (9H, m), 7.72 (3H, s), and 8.67 (9H, d, J 18 Hz), m/e 304, 288, 247, 184, and 108 (Found: C, 67.5; H, 6.9; P, 10.2. $C_{17}H_{21}O_3P$ requires C, 67.3; H, 6.9; P, 10.1%).

In a similar way, sodium o-chlorophenoxide gave o-chlorophenyl phenyl t-butylphosphonate (80%), m.p. 49-50° (from ethanol), $\nu_{max.}$ 1596, 1494, 1277, 1261, 1235, 1206, 1192, 1165, 1062, 926, 828, 761, and 681 cm^{-1}, τ 2.30-2.90 (9H, m) and 8.58 (9H, d, J 18 Hz), m/e (for ^{35}Cl) 324, 309, 289, 258 (metastable, 324-289), 233, 187 (metastable, 289-233), 128, and 94 (Found: C, 59.2; H, 5.5; P, 9.55. $C_{16}H_{18}ClO_3P$ requires C, 59.5; H, 5.7; P, 9.5%), and sodium o-isopropylphenoxide gave o-isopropylphenyl phenyl t-butylphosphonate (89%), b.p. 145-150°/0.4 mm, $\nu_{max.}$ (film) 1595, 1494, 1271, 1226, 1207, 1177, 1085, 925, 828, 757, 687, and 657 cm^{-1}, τ 2.33-3.10 (9H, m), 6.60 (1H, sept, J 7 Hz), 8.55 (9H, d, J 18 Hz), 8.77 (3H, d, J 7 Hz), and 8.82 (3H, d, J 7 Hz), m/e 332, 317, 289, 275, 259, 215, and 181 (Found: C, 68.6; H, 7.5; P, 9.2. $C_{19}H_{25}O_3P$ requires C, 68.6; H, 7.5; P, 9.3%).

General Procedure for the Preparation of Diaryl t-Butylphosphonates.

A solution of the sodium salt of the phenol (0.2 mol) in tetrahydrofuran (40 ml) was added dropwise, over 0.5 h, to a stirred solution of t-butylphosphonic dichloride (0.1 mol) in tetrahydrofuran (40 ml). The mixture was refluxed for 12 h, cooled, and light petroleum (100 ml) was added. Filtration and evaporation followed by distillation and/or recrystallisation gave the following diaryl t-butylphosphonates:

bis-(m-tolyl)- (87%), b.p. 147-151°/0.05 mm, m.p. 37-40° (from light petroleum), $\nu_{max.}$ (film) 1613, 1590, 1488, 1249, 1152, 1140, 1010, 955, 845, 780, 689, and 660 cm^{-1}, τ 2.55-3.17 (8H, m), 7.68 (6H, s), and 8.58 (9H, d, J 17 Hz), m/e 318, 303, 261, 243, 211, 198, 164, and 108 (Found: C, 67.9; H, 7.3; P, 9.5. $C_{18}H_{23}O_3P$ requires C, 67.9; H, 7.2; P, 9.75%); bis-(m-ethylphenyl)- (83%), b.p. 160-165°/0.4 mm, $\nu_{max.}$ (film) 1610, 1588, 1483, 1446, 1274, 1237, 1139, 988, 940, 837, 788, and 688 cm^{-1}, τ (carbon tetrachloride) 2.70-3.25 (8H, m), 7.42 (4H, q, J 8 Hz), 8.67 (9H, d, J 18 Hz), and 8.83 (6H, t, J 8 Hz), m/e 346, 330, 317, 289, 271, 243, 226, 200, and 122 (Found: C, 69.4; H, 7.7; P, 8.9. $C_{20}H_{27}O_3P$ requires C, 69.4; H, 7.8; P, 9.0%); bis-(2,4-xylyl)- (87%), b.p. 159-160°/0.4 mm, $\nu_{max.}$ (film) 1505, 1272, 1251, 1208, 1190, 1125, 1115, 946, 909, 811, 690, and 659 cm^{-1}, τ (carbon tetrachloride) 2.80 (2H, d, J 8 Hz), 3.08 (2H, s), 3.15 (2H, d, J 8 Hz), 7.77 (6H, s), 7.80 (6H, s), and 8.63 (9H, d, J 17 Hz), m/e 346, 330, 289, 241, 226, 208, and 193 (Found: C, 69.4; H, 7.8; P, 9.0. $C_{20}H_{27}O_3P$ requires C, 69.4; H, 7.8; P, 9.0%); bis-(o-isopropylphenyl)-(81%), b.p. 161-163°/0.6 mm, $\nu_{max.}$ (film) 1601, 1587, 1495, 1288, 1269, 1226, 1176, 1086, 1037, 930, and 753 cm^{-1}, τ (carbon tetrachloride) 2.40-2.68 (2H, m), 2.70-3.02 (6H, m), 6.68 (2H, sept, J 7 Hz), 8.53 (9H, d, J 18 Hz), 8.78 (6H, d, J 7 Hz), and 8.88 (6H, d, J 7 Hz), m/e 374, 358, 331, 317, 301, 287, 257, and 215 (Found: C, 70.3; H, 8.4; P, 8.2. $C_{22}H_{31}O_3P$ requires C, 70.6; H, 8.3; P, 8.3%); bis-(o-chlorophenyl)- (83%), m.p. 71-72.5° (from dichloromethane-hexane), $\nu_{max.}$ 1587, 1581, 1485, 1242, 1225, 1065, 947, 923, 827, 758, 675, and 653 cm^{-1}, τ 2.37-2.98 (8H, m), and 8.53 (9H, d, J 19 Hz), m/e (for ^{35}Cl) 358, 343, 323, 289, 267, 175, 139, and 128 (Found: C, 53.6; H, 4.8; P, 8.65. $C_{16}H_{17}Cl_2O_3P$ requires C, 53.5; H, 4.7; P, 8.6%); bis-(p-chlorophenyl)- (70%), m.p. 87-89° (from

dichloromethane-hexane), $\nu_{max.}$ 1590, 1488, 1261, 1219, 1160, 1085, 1008, 920, 840, 758, 700, and 650 cm^{-1}, τ 2.85 (4H, d, J 8 Hz), 3.01 (4H, d, J 8 Hz), and 8.62 (9H, d, J 17 Hz), m/e (for ^{35}Cl) 358, 343, 324, 301, 238, 174, and 128 (Found: C, 53.7; H, 4.9; Cl, 19.8. $C_{16}H_{17}Cl_2O_3P$ requires C, 53.5; H, 4.7; Cl, 19.8%); bis-(4-Chloro-2-methylphenyl - (86%), b.p. 175-182°/0.1 mm, m.p. 63-64° (from hexane), $\nu_{max.}$ 1480, 1270, 1238, 1220, 1179, 1162, 1115, 935, 921, and 861 cm^{-1}, τ 2.68 (2H, d, J 9 Hz), 2.84 (2H, s), 2.92 (2H, d, J 9 Hz), 7.78 (6H, s) and 8.57 (9H, d, J 18 Hz), m/e (for ^{35}Cl) 386, 371, 351, 329, 266, 261, 213, 203, 188, and 142 (Found: C, 55.8; H, 5.4; Cl, 18.3. $C_{18}H_{21}Cl_2O_3P$ requires C, 55.8; H, 5.4; Cl, 18.35%); bis-(4-chloro-3-methylphenyl)- (89%), m.p. 84-86.5° (from hexane), $\nu_{max.}$ 1598, 1567, 1475, 1258, 1225, 1159, 1143, 1000, 957, 868, 860, and 848 cm^{-1}, τ 2.72 (2H, d, J 8 Hz), 2.94 (2H, s), 3.10 (2H, d, J 8 Hz), 7.72 (6H, s), and 8.60 (9H, d, J 16 Hz),m/e (for ^{35}Cl) 386, 371, 351, 329, 266, 188, 180, 153, and 142 (Found: C, 56.1; H, 5.5; Cl, 18.3%); bis-(2,4-dichlorophenyl)- (75%), m.p. 73-74° (from ethanol-water), $\nu_{max.}$ 1578, 1482, 1218, 1095, 939, 828, 805, 791, 787, and 751 cm^{-1}, τ 2.37 (2H, d, J 2 Hz), 2.57 (2H, d, J 9 Hz), 2.87 (2H, dd, J 9 and 2 Hz), and 8.50 (9H, d, J 19 Hz), m/e (for ^{35}Cl) 426, 410, 391, 334, 208, 173, and 162 (Found: C, 44.6; H, 3.3; Cl, 33.4. $C_{16}H_{15}Cl_4O_3P$ requires C, 44.9; H, 3.5; Cl, 33.2%); bis-(4-chloro-3,5-dimethylphenyl) t-butyl-phosphonate was prepared in the normal way, but with the modification that refluxing was continued for 72 h. Light petroleum (100 ml) and water (50 ml) were then added, and the organic layer was separated. The aqueous layer was extracted with dichloromethane (3 x 30 ml) and the combined extracts and organic layer were dried, evaporated, and recrystallised to give the product (80%), m.p. 98-100° (from hexane), $\nu_{max.}$ 1588, 1302, 1290, 1262, 1220, 1158, 1142, 1025, 970, 880, 862, and 840 cm^{-1}, τ 3.22 (4H, s), 7.73 (12H, s), and 8.65 (9H, d, J 18 Hz), m/e (for ^{35}Cl)

414, 399, 380, 357, 294, 202, 194, 167, and 156 (Found: C, 58.0; H, 6.0; Cl 16.8. $C_{20}H_{25}Cl_2O_3P$ requires C, 57.8; H, 6.0; Cl, 17.1%); bis-(2,4--dichloro-6-methylphenyl)- (15%), m.p. 146.5-148° (from hexane), $\nu_{max.}$ 1585, 1562, 1462, 1265, 1208, 1170, 1159, 920, 890, 825, and 722 cm^{-1}, τ 2.80 (2H, d, J 2 Hz), 3.02 (2H, d, J 2 Hz), 7.82 (6H, s), and 8.43 (9H, d, J 19 Hz), m/e (for ^{35}Cl) 454, 439, 419, 363, 334, 281, 222, and 176 (Found: C, 47.2; H, 4.15; Cl, 31.1. $C_{18}H_{19}Cl_4O_3P$ requires C, 47.4; H, 4.2; Cl, 31.1%); and bis-(2,4,6-trichlorophenyl)-t-butylphosphonate. This was prepared in the normal way, but the crude product was taken up in chloroform (50 ml), washed with sodium hydroxide solution (2N; 4 x 20 ml),and water (20 ml), dried, evaporated, and recrystallised to give the product (14%), m.p. 154-157° (from chloroform-hexane), $\nu_{max.}$ 1560, 1278, 1264, 1242, 1138, 929, 905, 857, 834, 721, and 671 cm^{-1}, τ 2.75 (4H, s), and 8.46 (9H, d, J 19 Hz), m/e (for ^{35}Cl) 494, 459, 280, 242, 207, and 196 (Found: C, 38.8; H, 2.6; Cl, 42.6; P, 6.3. $C_{16}H_{13}Cl_6O_3P$ requires C, 38.6; H, 2.6; Cl, 42.9; P, 6.2%).

Preparation of Diphenyl Trichloromethylphosphonate.

This was prepared by the method of Berlin and Roy.[181] Chromatography of the crude reaction product (14 g) on silica (600 g), and elution with ether-light petroleum (1:4), followed by recrystallisation, gave the title compound (63%), m.p. 65-66° (from hexane) (lit. 66°).

Reaction of Trichloromethylphosphonic Dichloride with Sodium Phenoxide.

A solution of sodium phenoxide (9.3 g, 0.08 mol) in tetrahydrofuran was added dropwise to a stirred solution of trichloromethylphosphonic

dichloride (9.45 g, 0.04 mol) in tetrahydrofuran (50 ml). The solution immediately turned deep red, but the colour discharged after about 10 seconds, leaving an orange solution. After addition was complete (0.25 h), the mixture was refluxed for 12 h and light petroleum (100 ml) was then added. Filtration and evaporation gave a deep red oil (13.9 g). Chromatography on silica (600 g) and elution with ether-light petroleum (1:4) gave diphenyl trichloromethylphosphonate (1.38 g), m.p. 65-66° (from hexane), phenol (0.17 g), and triphenyl phosphate (4.82 g), m.p. and mixed m.p. 47.5-48.5°.

Preparation of Diaryl Cyclohexyl-, and Isopropylphosphonates.

These were prepared as for the diaryl t-butylphosphonates, on a 0.1 molar (of the alkylphosphonic dichloride) scale, but with the following modification: after refluxing the reaction mixture for 4 - 8 h, light petroleum (100 ml) and water (50 ml) were added. The organic layer was separated and the aqueous layer was extracted with dichloromethane (3 x 30 ml). The combined extracts and organic layer were washed with sodium hydroxide solution (2N), and with water, dried, and evaporated. Purification of the residue was carried out as detailed for the individual compounds.

Cyclohexylphosphonates: diphenyl- (86%), purified by recrystallisation, m.p. 58-60° (from hexane) (lit.[171] 62°); and bis-(p-chlorophenyl)- (84%), purified by distillation and recrystallisation, b.p. 195-199°/0.4 mm, m.p. 76-78° (from hexane) (lit.[171] 79°).

Isopropylphosphonates: diphenyl- (57%), purified by recrystallisation,

m.p. 42-43° (from hexane), $\nu_{max.}$ 1596, 1490, 1292, 1217, 1186, 1165, 1071, 1045, 1026, 928, 764, 740, and 688 cm^{-1}, τ 2.70-3.06 (10H, m), 7.72 (1H, d sept, J 18 and 7 Hz), and 8.64 (6H, dd, J 20 and 7 Hz), m/e 276, 275, 261, 233, 170, 141, 94, and 77 (Found: C, 65.4; H, 6.4; P, 11.15. Calc. for $C_{15}H_{17}O_3P$: C, 65.2; H, 6.2; P, 11.2%); bis-(m-tolyl)- (90%), purified by distillation, b.p. 150-155°/0.05 mm, $\nu_{max.}$ (film) 1613, 1589, 1489, 1247, 1144, 1011, 957, 856, 782, and 690 cm^{-1}, τ 2.62-3.02 (8H, m), 7.40-7.90 (m), 7.67 (s) - total integration 7H, and 8.60 (6H, dd, J 20 and 8 Hz), m/e 304, 289, 261, 243, 198, 155, and 108 (Found: C, 67.25; H, 7.0; P, 10.1. $C_{17}H_{21}O_3P$ requires C, 67.1; H, 7.0; P, 10.2%); bis-(o-tolyl)- (91%), purified by distillation, b.p. 149-151°/0.2 mm, $\nu_{max.}$ (film) 1586, 1490, 1228, 1170, 1108, 1040, 928, 801, 756, and 706 cm^{-1}, τ 2.56-2.88 (8H, m), 7.67 (1H, d sept, J 20 and 7 Hz), and 8.56 (6H, dd, J 21 and 7 Hz), m/e 304, 289, 261, 243, 213, 197, 180, 165, 155, and 108 (Found: C, 67.3; H, 7.0; P, 10.1%); bis-(2,4-xylyl)- (78%), purified by distillation, b.p. 158-162°/0.1 mm, $\nu_{max.}$ (film) 1502, 1250, 1209, 1196, 1116, 947, 908, and 813 cm^{-1}, τ 2.60 (2H, d, J 9 Hz), 2.76 (2H, s), 2.85 (2H, d, J 9 Hz), 7.30-7.92 (m), 7.64 (s), 7.68 (s) - total integration 13 H, and 8.52 (6H, dd, J 20 and 7 Hz), m/e 332, 317, 227, 208, 193, 169, and 122 (Found: C, 68.8; H, 7.6; P, 9.15. $C_{19}H_{25}O_3P$ requires C, 68.65; H, 7.5; P, 9.3%); bis-(o-chlorophenyl)- (86%), purified by chromatography on silica (600 g), and elution with ether-light petroleum (1:3), followed by distillation, b.p. 158-162°/0.05 mm, $\nu_{max.}$ (film) 1586, 1480, 1235, 1217, 1062, 926, 766, 680, and 670 cm^{-1}, τ 2.48-2.96 (8H, m), 7.52 (1H, d sept, J 19 and 7 Hz), 8.52 (dd, J 21 and 7 Hz), and 8.57 (dd, J 21 and 7 Hz) - total integration 6H , m/e (for ^{35}Cl) 344, 309, 275, 267, 249, 233, 175, 139, and 128. A satisfactory analysis for this compound could not be obtained;

bis-(4-chloro-2-methylphenyl)- (80%), purified by chromatography on silica (600 g), and elution with ether-light petroleum (1:3), followed by distillation (Kügel Rohr), b.p. 200° (oven)/0.1 mm, $\nu_{max.}$ 1484, 1238, 1185, 1170, 1118, 935, 865, 815, and 735 cm^{-1}, τ 2.78-3.06 (6H, m), 7.64 (m), 7.82 (s) - total integration 7H, and 8.60 (6H, dd, J 20 and 7 Hz), m/e (for ^{35}Cl) 372, 357, 337, 315, 213, 167, and 142 (Found: C, 54.8; H, 5.2; P, 8.45. $C_{17}H_{19}Cl_2O_3P$ requires C, 54.7; H, 5.1; P, 8.3%); bis-(4-chloro-3-methylphenyl)- (92%), purified by distillation, b.p. 177-180°/0.15 mm, $\nu_{max.}$ 1602, 1579, 1478, 1228, 1149, 1007, 962, 877, 807, and 749 cm^{-1}, τ 2.46 (2H, d, J 9 Hz), 2.70 (2H, m), 2.78 (2H, d, J 9 Hz), 7.62 (s), 7.63 (d sept, J 19 and 7 Hz),- total integration 7H, and 8.58 (6H, dd, J 20 and 7 Hz), m/e (for ^{35}Cl) 372, 338, 266, 232, 189, 167, and 142 (Found: C, 54.8; H, 5.0; P, 8.3%); bis-(2,4-dichlorophenyl)- (69%), purified by chromatography on silica (650 g), and elution with ether--light petroleum (1:3), followed by distillation (Kügel Rohr), and recrystallisation, b.p. 220° (oven)/0.1 mm, m.p. 59-60° (from hexane), $\nu_{max.}$ 1299, 1255, 1228, 1100, 1062, 960, 945, 923, 866, 834, 819, and 720 cm^{-1}, τ 2.30 (2H, m), 2.39 (2H, dd, J 9 and 1.5 Hz), 2.57 (2H, dd, J 9 and 2.5 Hz), 7.42 (1H, d sept, J 17.5 and 6.5 Hz), and 8.50 (6H, dd, J 20 and 6.5 Hz), m/e (for ^{35}Cl) 412, 377, 343, 309, 251, 209, 173, and 162 (Found: C, 43.6; H, 3.3; P, 7.6; $C_{15}H_{13}Cl_4O_3P$ requires C, 43.5; H, 3.1; P, 7.5%); bis-(4-chloro-3,5-dimethylphenyl)- (67%), purified by recrystallisation, m.p. 53-54° (from ethanol-water), $\nu_{max.}$ 1590, 1467, 1315, 1297, 1246, 1158, 1144, 1024, 974, and 876 cm^{-1}, τ 3.00 (4H, s), 7.66 (s), 7.42-7.90 (m) - total integration 13H, and 8.60 (6H, dd, J 20 and 7 Hz), m/e (for ^{35}Cl) 400, 385, 365, 294, 203, 181, and 156 (Found: C, 57.05; H, 5.75; Cl, 17.4. $C_{19}H_{23}Cl_2O_3P$ requires C, 56.9; H, 5.7; Cl, 17.7%); and bis-(2,4--dichloro-6-methylphenyl)- (75%), purified by recrystallisation, m.p.

133-136° (from dichloromethane-hexane), $\nu_{max.}$ 1585, 1564, 1465, 1294, 1243, 1172, 1162, 926, 898, 824, 726, and 704 cm^{-1}, τ 2.66 (2H, d, J 3 Hz), 2.86 (2H, d, J 3 Hz), 7.34 (1H, d sept, J 18.5 and 7 Hz), 7.82 (6H, s), and 8.46 (6H, dd, J 20 and 7 Hz), m/e (for ^{35}Cl) 440, 405, 369, 334, 281, 223, and 176 (Found: C, 46.3; H, 3.8; Cl, 32.0. $C_{17}H_{17}Cl_4O_3P$ requires C, 46.15; H, 3.85; Cl, 32.1%).

Reaction of Triphenyl Phosphite with t-Butyl Chloride.

Triphenyl phosphite (7.75 g, 0.025 mol), t-butyl chloride (2.31 g, 0.025 mol) and a trace of toluene-p-sulphonic acid were heated in a sealed tube at 100° for 24 h. Removal of solvent then gave a clear liquid which showed only aromatic absorption in its ^1H n.m.r. spectrum.

Preparation of Diphenyl t-Butyl Phosphite.

This was prepared by reaction of diphenyl phosphorochloridite with t-butyl alcohol in the presence of triethylamine in the usual way. After removal of solvent, the ^1H n.m.r. spectrum of the crude reaction product showed diphenyl t-butyl phosphite (70% by integration) to be present. On attempted distillation (140°) decomposition occurred with gas evolution and formation of diphenyl phosphite. (characterised by ^1H n.m.r. and ^{31}P n.m.r.).

Attempted Thermal Rearrangement of Diphenyl t-Butyl Phosphite.

The crude product (2 g) from the preceding reaction and a trace of aluminium chloride were heated to 150° in a sealed tube and kept at this

temperature for 7 days. The ^{1}H n.m.r. of the crude reaction product showed no absorption due to a t-butyl group.

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SUMMARY

PART 1.

A number of cyclic oxyphosphoranes have been prepared and their dynamic n.m.r. spectra investigated. The changes in the spectra with temperature are interpreted in terms of the slowing of certain pseudo-rotations available to the molecule and the energetic data derived from the spectral changes are suggested to be a measure of the relative apicophilicities of the groups bonded to phosphorus. The scale of apicophilicity values so obtained is explained in terms of the following properties of the ligand: electronegativity, π-donor ability, π-acceptor ability, polarisability and size.

From a study of the energy required to place the five-membered ring of various cyclic oxyphosphoranes in the diequatorial position it is concluded that this energy increases considerably with the presence of endocyclic heteroatoms bonded to phosphorus. The increase in ring strain is attributed to the changes in orientation of the donor orbitals of the heteroatoms when the ring is moved from an apical-equatorial to a diequatorial position.

The same donor orbital orientation effect has been shown to be present in six-membered cyclic oxyphosphoranes, although in this case it is suggested that the conformation of the six-membered ring may decrease the heteroatom rotation terms compared with the values for five-membered rings.

D.n.m.r. data for a series of oxyphosphoranes, where the size of the alkyl groups bonded to phosphorus is varied, have been interpreted in

terms of the following two tenets:

(a) the apical position of a trigonal bipyramid is the more hindered position;

and (b) steric effects in phosphoranes are not appreciable unless there are at least two bulky groups bonded to phosphorus.

Evidence has been presented that nucleophilic substitution at the phosphorus of oxyphosphoranes need not necessarily proceed by attack of the nucleophile directly opposite the leaving group.

PART 2.

A range of phosphoryl compounds has been synthesised and their suitability for use as fire-resistant hydraulic fluids has been assessed by determining their hydrolytic stability, fire resistance and melting point.