

Oxidative addition reactions of cyclic aryloxy-, amino- and chloro-phosphites and arsenites

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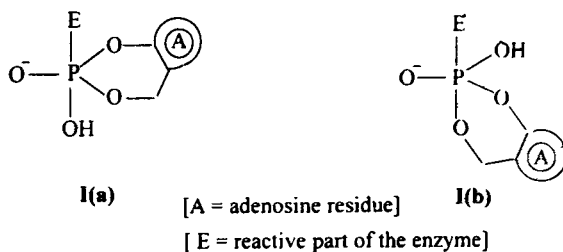
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Abstract. Reaction of cyclic phosphites with 1,2-diketones and with diol/*N*-chlorodiisopropylamine has been studied. A large number of penta- and hexacoordinated phosphorus derivatives with varying ring sizes have been synthesized and structurally characterized. The reactivity of phosphites is compared with that of arsenites and pentacoordinated phosphoranes. Several phosphonates that are important as synthetic reagents have been prepared by reacting cyclic phosphites with aldehydes.

Keywords. Cyclic phosphites; phosphoranes, arsoranes, penta- and hexacoordination, phosphonates.

1. Introduction

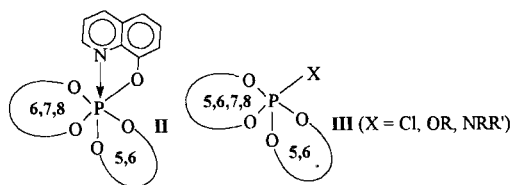
The pentacoordinated state has a unique place in the chemistry of phosphorus for several reasons; for instance, (i) its involvement in the transition state in numerous reactions at a tetrahedral P(V) centre, (ii) the diversity of structural types exhibited by phosphorus and the distortion in geometry from a square pyramid (SP) to a trigonal bipyramid (TBP) and (iii) the possibility of apical-equatorial *vs* diequatorial (*e-e*) disposition for those compounds with phosphorus as a part of the ring in a TBP structure^{1,2}. An example is that of the metabolic reactions involving cyclic adenosine monophosphate, *c*-AMP, featuring a saturated 1,3,2-dioxaphosphorinane ring. In the enzymatic action, it is not clearly known whether the six-membered ring assumes a diequatorial position (**Ia**) in the proposed phosphorane intermediate or an apical-equatorial position (**Ib**) or if the conformation is enzyme dependent³.



Since synthesis and characterization of species like **I** in the laboratory is difficult, an alternative approach is to look at the structures and reactivity of the more easily accessible

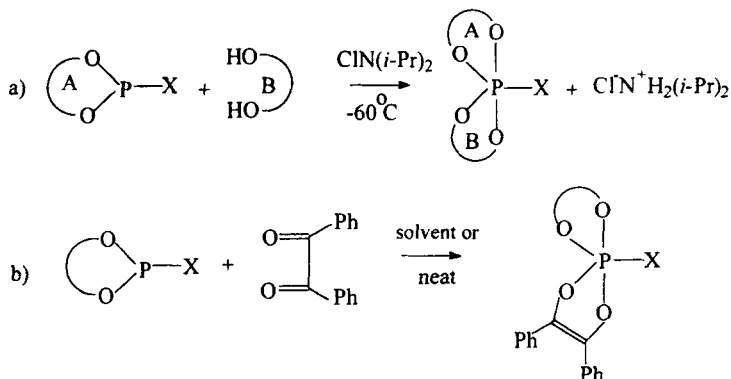
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neutral phosphoranes as model systems. Reactions of pentacoordinated phosphorus may sometimes involve hexacoordination^{4,5}. Therefore a knowledge of the nature of these hexacoordinated species would also be useful in understanding the structure and reactivity of phosphoranes. Thus we have been interested in the synthesis, reactivity and structures of phosphoranes of the types **II** and **III** as well as their arsenic analogues. One of the routes employed for the synthesis of these compounds is the oxidative addition of a 1,2-diketone to a cyclic phosphite and hence as an extension of our studies we have investigated the reactions of cyclic phosphites with aldehydes (in place of a diketone) that lead to phosphonates or phosphoranes. Some of our results are described below.



2. Phosphites vs arsenites

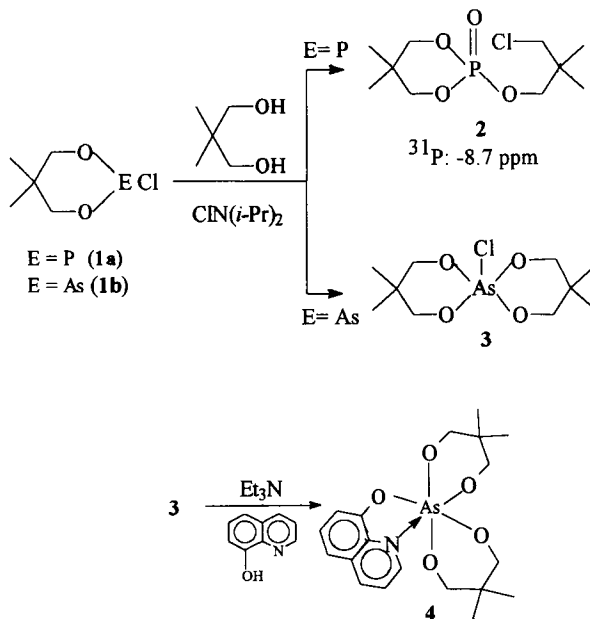
Two methods have been used for the oxidative addition reactions of cyclic phosphites in the present work (scheme 1). When X is oxinate ($-\text{OC}_9\text{H}_6\text{N}$), the resulting product is either hexa- or pentacoordinated depending on the presence or absence of the $\text{N} \rightarrow \text{P}$ donor-acceptor bond.



Scheme 1

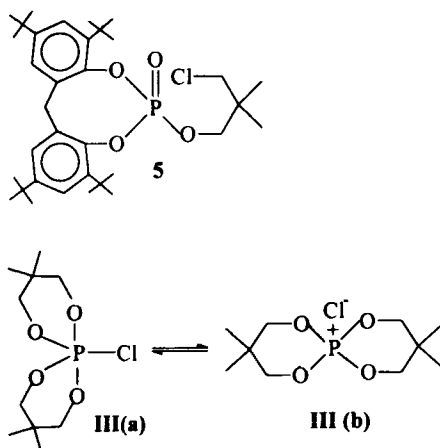
Method (a) is applicable to the synthesis of phosphoranes and arsenoranes with varying ring sizes. An interesting and complicating feature observed in the current study, however, is that ring exchange could take place leading to a product other than the anticipated one (*vide infra*). The second method (b) is suitable for introducing the 1,3,2-dioxaphospholene (five-membered) ring. It has the limitation that we cannot introduce a six- or a higher membered ring on to the phosphite unless they are already present on the phosphite precursor.

To begin with, we reacted the chlorophosphites/arsenites **1(a-b)** with 2,2-dimethylpropane-1,3-diol/*N*-chlorodiisopropylamine (scheme 2). Whereas the phosphite **1(a)** leads to the ring-cleaved (modified Arbuzov) product **2**, the arsenite **1(b)** affords the



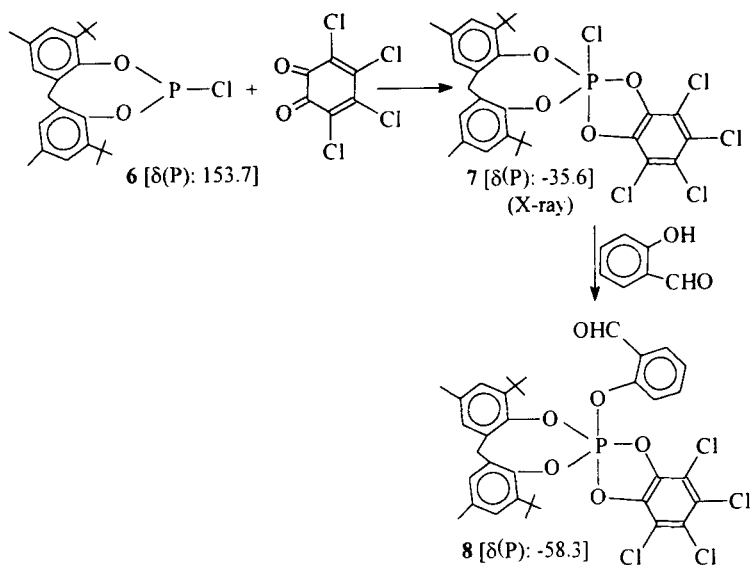
Scheme 2

pentacoordinated arsorane **3**. Compound **2** has been characterized by NMR (1H , ^{13}C , ^{31}P) and elemental analysis. An analogous derivative **5** is also obtained in the reaction of **1(a)** with 2,2'-methylene bis(4,6-di-(tert)-butylphenol); this compound has been characterized by an X-ray structure⁶. The reaction of **1(a)** with the 1,2-diketones benzil and 9,10-phenanthrene quinone again leads to products in which the six-membered phosphorinane ring is cleaved. These results suggest that the initially formed phosphorane (e.g. **IIIa**) has



some phosphonium ion (**IIIb**) character; the attack of the chloride on the α -carbon of the phosphorinane ring results in the observed products (e.g. **2**). If the α -carbon is a part of an aromatic ring (as in **6**) we can obtain the chlorophosphoranes (e.g. **7**) which can be suitably derivatized (scheme 3) (Sudha Kumaraswamy, *unpublished results*).

The arsorane **3** is an air-sensitive, low melting solid; it shows a single resonance each for the OCH₂ and CH₃ protons showing that it is undergoing a pseudorotational process at room temperature. Treatment of this compound with 8-hydroxy quinoline/triethylamine afforded the hexacoordinated derivative **4** (scheme 2). Unlike our analogous



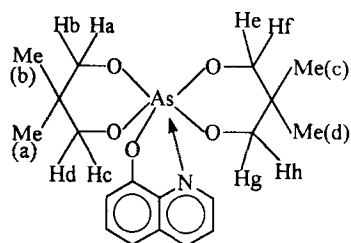
Scheme 3

hexacoordinated phosphoranes (see below) or the chloroarsorane **3**, compound **4** is *air-stable* and shows a *rigid structure* in solution⁷. Each of the OCH₂ protons shows a distinct signal in the ¹H NMR; likewise, there are four methyl signals (figure 1). The methyl carbons appear as separate signals in the ¹³C NMR also. For the synthesis of the phosphorane (OC₉H₆N)P(OCH₂CMe₂CH₂O)₂ the route adopted for the analogous arsorane **4** is not feasible because the intermediate ClP(OCH₂CMe₂CH₂O)₂ is not insoluble.

A second distinction between the arsenic and the phosphorus systems is that it is much more difficult to achieve oxidative addition of a 1,2-diketone to an arsenite than to a phosphite. For example, whereas *o*-chloranil adds on to the phosphite (2,6-Me₂C₆H₃O)P(OCH₂CMe₂CH₂O) (**9**) exothermically to lead to the phosphorane (2,6-Me₂C₆H₃O)P(OCH₂CMe₂CH₂O)(1,2-O₂C₆Cl₄) (**10**) [$\delta(P)$: -50.4], the corresponding arsenite (2,6-Me₂C₆H₃O)As(OCH₂CMe₂CH₂O) (**11**) is unreactive under these conditions⁸. These results are attributable to the so-called '*d*-orbital contraction' which makes arsenic reluctant to undergo oxidation from As(III) to As(V)^{9,10}.

3. Phosphites vs phosphoranes

We have been interested in introducing H-bonding into the cyclic phosphoranes *via* an acyclic amino group such as -NHR in an effort to see its effect on the stereochemistry in cyclic P(III) and P(V) compounds. A second point of interest to us is the relative ease of amino substitution in aminophosphites and aminophosphoranes with phosphorus as a part



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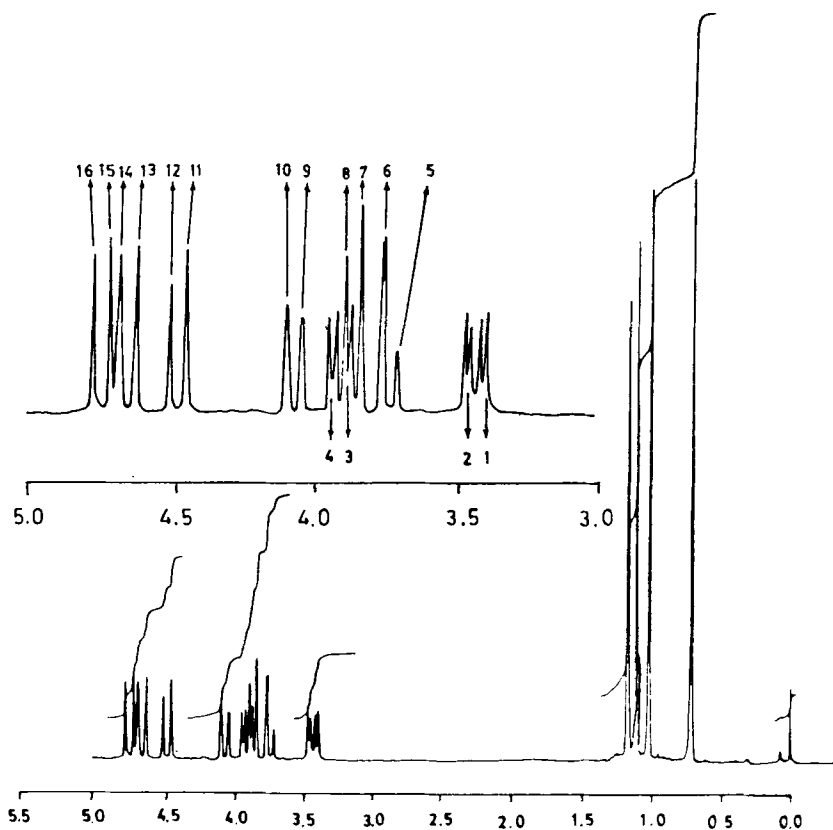


Figure 1. ^1H NMR spectrum of **4**; the structure of **4** is also shown at the top.

of a ring; this information could be useful for preparing phosphoranes with the desired substituents.

Structural aspects: In the above context we have obtained the X-ray structures of the pairs (**12**, **13**) and (**14**, **15**· $\frac{1}{2}$ Et $_2$ O) (Chart 1); the *cycl*-C $_6$ H $_{11}$ NH group was chosen to introduce H-bonding. Whereas **12** exhibits intermolecular H-bonding leading to chains, in the pentacoordinated compound **13**, by contrast, hydrogen bonds are absent. Again, although

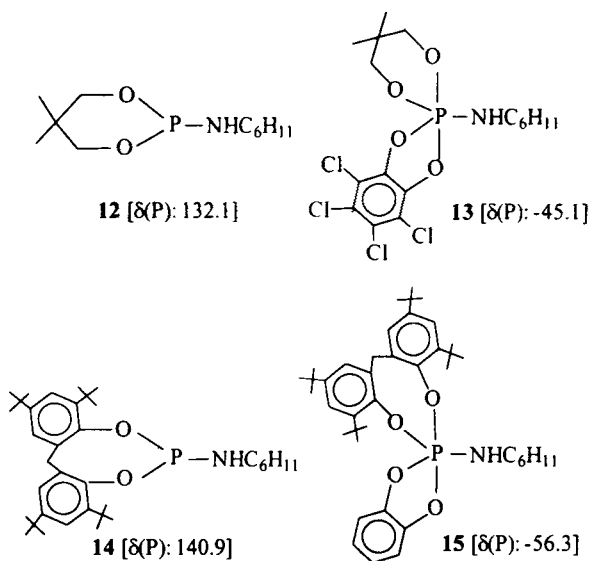


Chart 1

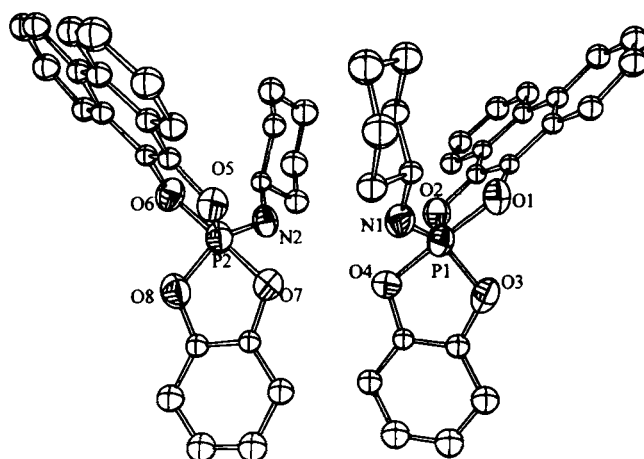


Figure 2. Molecular structure of $(1,2\text{-C}_6\text{H}_4\text{O}_2)\text{P}(\text{NHC}_6\text{H}_{11})(9,10\text{-O}_2\text{C}_{14}\text{H}_8)$ (**16**); two symmetry related molecules, exhibiting hydrogen bonding between them, are shown. Some interatomic distances and angles: P(1)-N(1) 1.620(4); P(1)-O(3) 1.634(3), P(1)-O(2) 1.637(3); P(1)-O(1) 1.688(3); P(1)-O(4) 1.718(3), N(1)-O(7) and N(2)-O(4) 3.312 Å. N(1)-P(1)-O(3) 119.7(2); N(1)-P(1)-O(2) 124.3(2); O(3)-P(1)-O(2) 115.9(2); O(1)-P(1)-O(4) 177.5(2)°.

the phosphite **14** forms dimers by weak H-bonds, there are no hydrogen bonds in the corresponding pentacoordinated structure of $15 \cdot \frac{1}{2}\text{Et}_2\text{O}$ ¹¹. The only case of a phosphorane in which there is some interaction, *albeit* very weak, is in the compound $(1,2\text{-C}_6\text{H}_4\text{O}_2)\text{P}(\text{NHC}_6\text{H}_{11})(9,10\text{-O}_2\text{C}_{14}\text{H}_8)$ (**16**) (figure 2) in which NH of one molecule

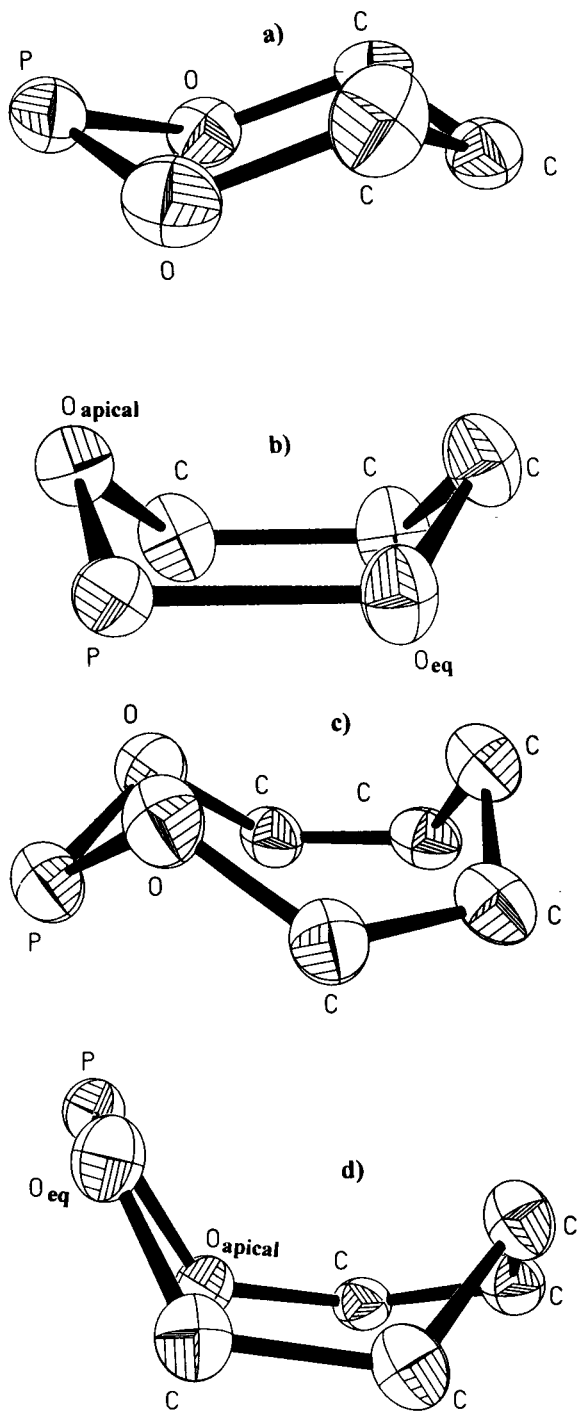


Figure 3. a) Conformation of the 1,3,2-dioxaphosphorinane ring in **12**; b) same as in (a) for **13**; c) Conformation of the 1,3,2-dioxaphosphocin ring in **14**; d) Same as in (c) for **15**.

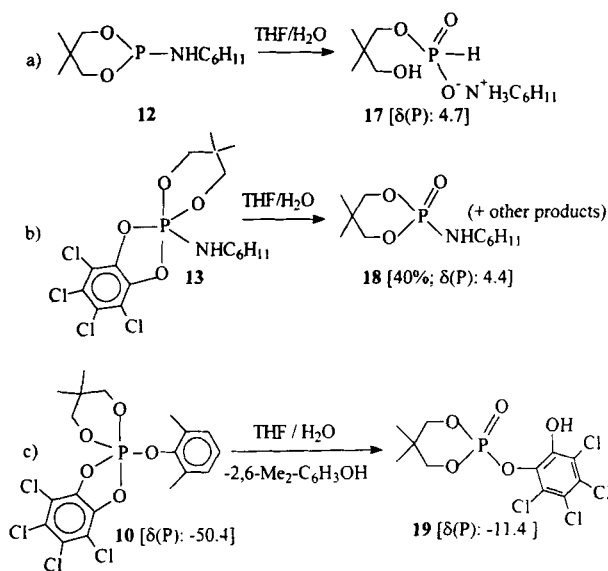
interacts very weakly with the catecholic oxygen of a second molecule and vice versa (K C Kumara Swamy and C Muthiah, unpublished results).

The 1,3,2-dioxaphosphorinane ring in **12** adopts a *chair* conformation [figure 3(a)] which is quite typical for tricoordinated cyclic phosphites¹²⁻¹⁴. In the corresponding pentacoordinated phosphorane **13** [figure 3(b)] the same phosphorinane ring adopts a *boat* conformation. Such a feature allows the lone pair of the *equatorial* oxygen to approach the equatorial plane in a trigonal bipyramidal (TBP) structure and is energetically favourable¹⁵.

The eight-membered ring adopts a *boat-chair* conformation in **14** [figure 3(c)]. This ring exhibits a distorted *tub* conformation in **15** where it is located *apical-equatorially* in a TBP structure [figure 3(d)].

Thus the present study firmly establishes the change in conformation for a 1,3,2-dioxaphosphorinane ring from *chair* in cyclic phosphites to *boat* when this ring is located apical-equatorially in a TBP arrangement by our choice of the same substituents on both the P(III) and P(V) compounds. A similar change in conformation from *boat-chair* in phosphites to *tub* in phosphoranes is demonstrated for the 1,3,2-dioxaphosphocin ring.

Reactivity: Hydrolytically compound **12** is much less stable than **13**. The ring opened product **17** is obtained upon treating **12** with THF/water; even exposing a THF solution of **12** to air for 24 h leads to **17** quantitatively [scheme 4(a)]. The pentacoordinated



Scheme 4

compound **13** hydrolyzed to give **18** as one of the major products (scheme 4(b)); the identity of **18** is confirmed by an independent synthesis. This reaction is interesting because when the 2,6-dimethylphenoxy phosphorane **10** is hydrolyzed, the crystalline product (**19**) obtained has the five-membered ring residue connected to phosphorus [scheme 4(c)]; this latter product is *not detected* in the hydrolysis of **13** (³¹P NMR). The

rationale for the difference in the hydrolysis of **13** and **10** may lie in the relative apicophilicities of the $\text{NHC}_6\text{H}_{11}$ and OPh groups in a TBP environment.

3. Penta- and hexacoordinated phosphoranes with an oxinate substituent

Although oxinate is a common ligand in transition metal coordination chemistry, use of this ligand to obtain compounds containing hexacoordinated phosphorus was limited to those with, primarily, five-membered rings, prior to our work¹⁶. We have synthesized a large number of these derivatives with varying ring sizes by methods described above; some representative examples are shown in chart 2; only one isomeric product was

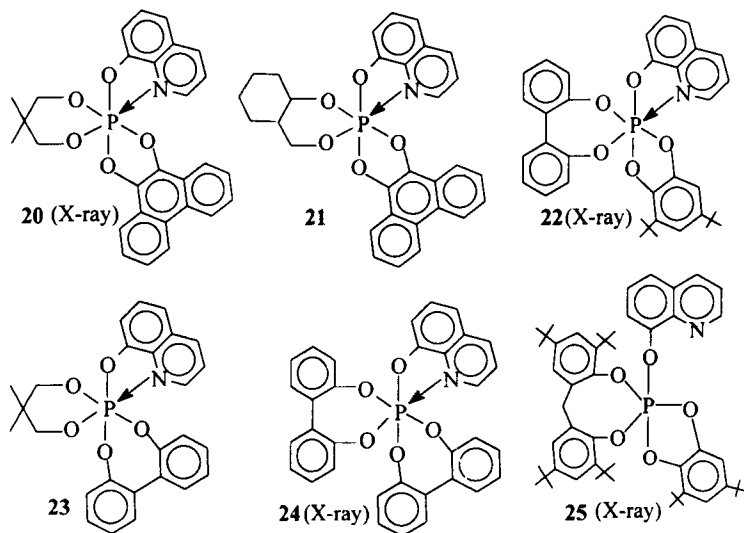
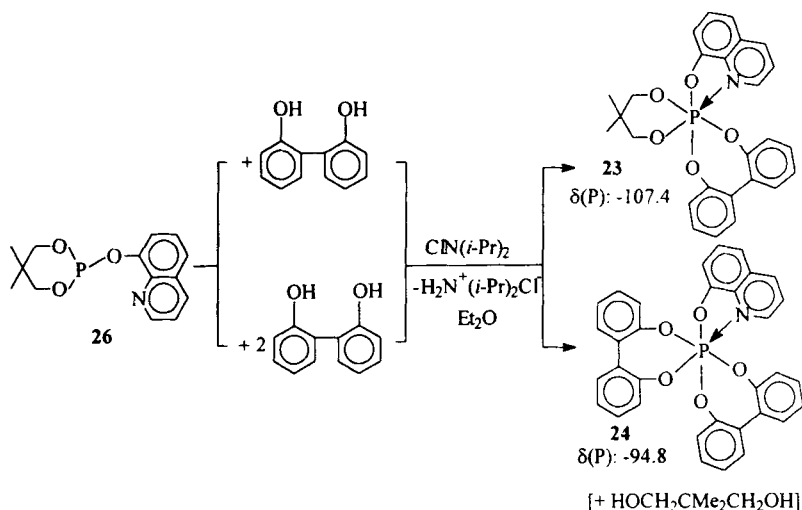


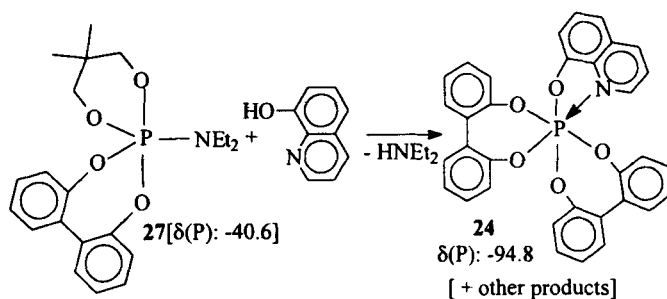
Chart 2

observed where isomerism is possible. Compound **24** is obtained, *rather surprisingly*, during the synthesis of **23** [by reacting $(\text{OCH}_2\text{CMe}_2\text{CH}_2\text{O})\text{P}(\text{OC}_9\text{H}_6\text{N})$ (**26**) with 2,2'-biphenol/*N*-chlorodiisopropylamine] from the exchange of the six-membered *phosphorinane* ring by the seven-membered *phosphhepin* ring; the yield of **24** could be substantially increased by using 1:2 molar ratio of the cyclic phosphite to 2,2'-biphenol¹⁷ (scheme 5). This ring exchange reaction leading to **24** is unique because when a 2,6-dimethylphenoxy¹⁸ or 2,4,6-trimethylphenoxy or diethylamino group is used in place of oxinate, no such phenomenon is observed. What is perhaps more puzzling is the reaction of the aminophosphorane **27** with 8-hydroxy quinoline to yield **24** (scheme 6). It can be noted that *even though no 2,2'-biphenol has been added, the reorganization still takes place*.

Two factors which may be responsible for the ring exchange observed here are (i) the aromatic residues on the seven-membered 1,3,2-dioxaphosphhepin rings increase the acidity of phosphorus and hence its ability to form a stronger $\text{N} \rightarrow \text{P}$ bond in **24** than in either **20** or **22** as seen by the shortest $\text{N} \rightarrow \text{P}$ bond (1.938 Å in **24** when compared to 1.956 Å in **20**) and (ii) the presence of two identical seven-membered rings imparts a certain stability to the molecule as it tends to resist any deformation of its bonds and hence the compound does not react further.



Scheme 5

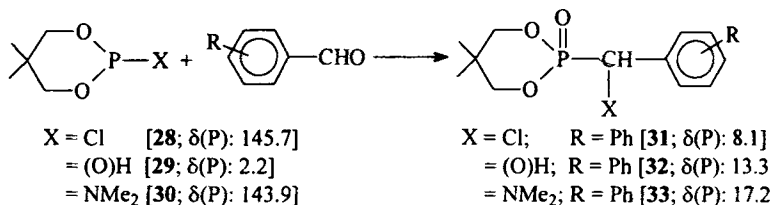


Scheme 6

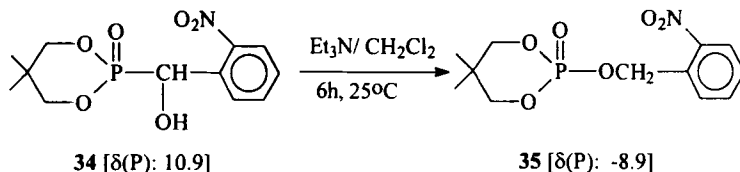
In contrast to compounds **20–24** where the oxinate nitrogen coordinates to phosphorus, there is no such $\text{N} \rightarrow \text{P}$ bond in **25**. This is probably a result of steric interaction involving the *t*-butyl groups. That this behaviour is observed in solution also is shown by the ^{31}P NMR shift values which are in the range -88 to -107 ppm for the hexacoordinated derivatives **20–24** when compared to the value of -56.9 ppm for **25**.

4. Reaction of cyclic phosphites with aldehydes

Instead of using the 1,2-diketones in the oxidative addition reactions described above, if an aldehyde is used the product obtained most often is a phosphonate which contains a P-C bond. These are the familiar Abramov and Pudovik reactions¹⁹. If the aromatic aldehyde bears an electron withdrawing group a pentacoordinated derivative may be formed. We have investigated this topic using the cyclic phosphites $(\text{OCH}_2\text{CMe}_2\text{CH}_2\text{O})\text{PX}$ [$\text{X} = \text{Cl}$ (**28**), $(\text{O})\text{H}$ (**29**), NMe_2 (**30**)] and obtained the phosphonates **31–33**²⁰ (scheme 7; Sudha Kumaraswamy and C Muthiah, unpublished data). Interestingly, in the reaction of 2-nitrobenzaldehyde with **29** we have observed the rearrangement of the phosphonate **34** to the phosphate ester **35** when traces of triethylamine are present in the reaction medium (scheme 8). Although there are a few



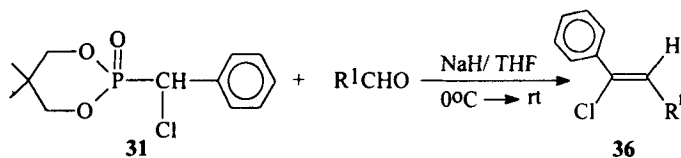
Scheme 7



Scheme 8

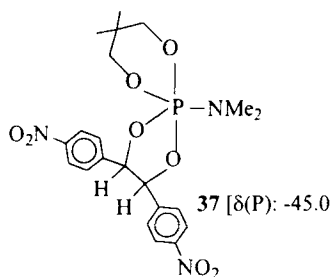
reports of such rearrangements, more drastic conditions have been utilized (high temperature, strong base).

It can be noted that in compound **31** there is an acidic proton on the α -carbon atom and hence compounds of this type should be useful in Wadsworth–Emmons reactions to yield chlorostilbenes; indeed we have recently shown that products of the type **31** are excellent substrates for such a reaction^{21,22} (scheme 9).



Scheme 9

In contrast to the above, in the reaction of $(\text{OCH}_2\text{CMe}_2\text{CH}_2\text{O})\text{P}(\text{NMe}_2)$ with *p*-nitrobenzaldehyde, the phosphorane $(\text{OCH}_2\text{CMe}_2\text{CH}_2\text{O})\text{P}(\text{NMe}_2)(\text{OCH}(\text{Ar})\text{-CH}(\text{Ar})\text{O})$, {Ar = 4- $\text{NO}_2\text{C}_6\text{H}_4$ } [**37**; $\delta(\text{P})$: -45.0] was identified.



5. Summary

Utilizing the reaction of cyclic phosphites with a 1,2-diketone or diol/N-chlorodiisopropylamine, a variety of penta- and hexacoordinated phosphorus compounds with ring sizes varying from five to eight have been synthesized; the structure and reactivity of many of these have been studied in detail. The study has been extended to the reaction with aldehydes to give synthetically useful phosphonates.

Acknowledgements

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