RINGS AND CAGES CONTAINING PHOSPHORUS, ARSENIC AND ANTIMONY

A THESIS

SUBMITTED FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

BY

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JUNE 1996

Dedicated to my:

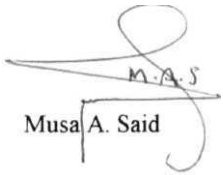
Parents, Brothers,
Sisters and wife

CONTENTS

STATEMENT

I hereby declare that the matter embodied in this thesis is the result of investigations carried out by me in the School of Chemistry, University of Hyderabad, Hyderabad, under the supervision of Dr. K.C. Kumara Swamy.

In keeping with the general practice of reporting scientific observations, due acknowledgements have been made wherever the work described is based on the findings of other investigators.



Musa A. Said

Hyderabad
June 1996

CERTIFICATE

Certified that the work contained in this thesis entitled **"Rings and** Cages **Containing Phosphorus, Arsenic and Antimony"** has been carried out by Mr Musa A. Said, under my supervision and same has not been submitted elsewhere for a degree.

Kumara Swamy

K.C. Kumara Swamy
(Thesis supervisor)

Hyderabad
June 1996

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School of Chemistry
University of Hyderabad

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LIST OF PUBLICATIONS

1. Oxidative Addition Reactions of Cyclic Chlorophosphites and Arsenites with Diols and 1,2-Quinones: X-ray Structure of the Phosphocin $(ClCH_2CMe_2CH_2O)P(O)\{(O\text{-}2,4\text{-}(t\text{-}bu)_2C_6H_2)_2CH_2\}$.

   Musa A. Said, K. C. Kumara Swamy, K. Chandra Mohan and N. Venkata Lakshmi, *Tetrahedron*, 1994, 50, 6989.

2. Diphenylantimony(V) Oxo/Chloro Carboxylates and Phosphinates: Crystal Structures of $\{SbPh_2Cl[O_2P(C_6H_{11})_2]\}_2O$ and $[SbPh_2(O_2CPh)_2]_2O$.

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3. Reactivity of Cyclic Arsenites and Phosphites: X-ray Structures of bis(5,5-dimethyl-l,3,2-dioxarsenane-2-yl)ether and bis(2,4,8,10-tetra-tert-butyl-12H-dibezo[d,g][l,3,2]dioxarsenocin-6-yl)ether.

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4. Dinuclear and Tetranuclear Cages of Oxodiphenylantimony Phosphinates: Synthesis and Structures.

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6. Bi- and Tri-Cyclic Penta- and Hexa-Coordinated Phosphoranes with Varying Ring Sizes: Synthesis, Structures and Reactivity.

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7. First Examples of Internally Co-ordinated Cyclic Arsenites with Seven- and Eight Membered Rings.

   Musa A. Said, K. C. Kumara Swamy, M. Veith and V. Huch, [Manuscript in preparation].

8. Hydrolysis of Spirophosphoranes with a Saturated 1,3,2-Dioxaphosphorinane ring: X-ray Structure of Intermolecularly H-bonded Phosphate Ester

   Musa A. Said, Melanie Piilm, R. Herbst-Irmer and K. C. Kumara Swamy, [Manuscript in preparation].

9. Cyclic Amino-Phosphites and Phosphoranes Possessing Six- and Higher-Membered Rings: A Comparative Study of Structure and Reactivity

   Musa A. Said, Melanie Piilm, R. Herbst-Irmer and K. C. Kumara Swamy, [Manuscript in preparation].

10. Mono- and Multi-nuclear Benzyltin (IV) Carboxylates and Phosphinates: Synthesis and Structures.

    Musa A. Said, S. Nag.brahmanandachari, K. C. Kumara Swamy, Damodara M. Poojary, A. Clearfield [Manuscript in preparation].

11. Hexa-coordinated Phosphoranes with an Oxinate Substituent: X-ray structure of $[OCH_2CMe_2CH_2O]P[OC_9H_6N][O_2C_2Ph_2]$.

    Musa A. Said, Melanie Piilm, R. Herbst-Irmer and K. C. Kumara Swamy, [Manuscript in preparation]

12. Structure of Monomeric Hepta-coordinated (Diphenyl)chloroantimony bis(o-toluate)

    Musa A. Said, K. C. Kumara Swamy and M. Nethaji (to be submitted)

PAPERS PRESENTED IN SYMPOSIA (POSTERS)

1. Synthesis and Reactivity of Hydrolysis Products of Cyclic Phosphites With Amino Substituents.

   Musa A. Said and K.C. Kumara Swamy, *XI11 International Conference on Phosphorus Chemistry. 1CPC Jerusalem-Israel, July 16-21, 1995.*

2. Rings and Cages Containing Phosphorus, Arsenic and Antimony- New Chemistry.

   Musa A. Said, M. Vijjulatha and K.C. Kumara Swamy, *Modern Trends in Inorganic Chemistry, MTIC, August 17-19, 1995, University of Hyderabad, INDIA.*

3. Synthesis and Structures of New Mono- and Multi-nuclear Organotin Phosphinates.

   Musa A. Said, C. Hemavathi, S. Nagabrahmanandachari, K. C. Kumara Swamy, Damodara M. Poojary and A. Clearfield, *Modern Trends in Inorganic Chemistry, MTIC, August 17-19, 1995, University of Hyderabad, INDIA.*

SYNOPSIS

This thesis is divided into two parts. Part-A embodies the results of investigations on the synthesis, reactivity and structures of tri-, tetra-, penta- and hexa-coordinated phosphorus and arsenic derivatives that possess ring sizes varying from five- to eight-membered. The purpose here is to study mainly (i) conformational preferences (X-ray) of different sized rings with change in coordination number at the central P/As atom and (ii) reactivity comparison between P and As as well as between tri-coordinated P(III) and penta-coordinated P(V) compounds.

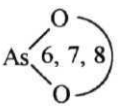
Part-B involves synthetic and structural investigations on oxo-carboxylate and phosphinate cages of antimony. The aim here is (i) to uncover new cages/clusters and (ii) to study structural interconversions.

In the Appendix details of structure solution and refinement for the compounds studied by X-ray are summarized as reference material.

PART-A

Chapter I reviews the literature on tri- to hexa-coordinated phosphorus and arsenic compounds possessing ring systems (A) or (B). The survey entails (i) description of the importance, (ii) conformational preferences of the different sized rings as revealed by solution (NMR)/ solid (X-ray) state studies, (iii) synthetic

(A)



(B)

routes and (iv) substituent effects on ^{31}P NMR for penta-coordinated systems. The existing lacunae have been pointed out at appropriate places.

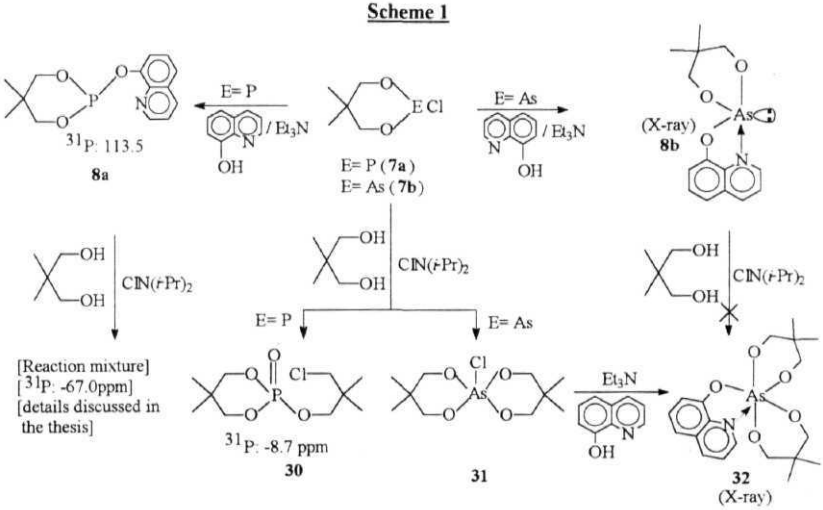
Selected results from Chapter II (Results and Discussion) are described below:

(i) Difference in chemical behaviour of P^{III} and As^{III}

(a) Towards oxidative addition reaction:

As shown in Scheme 1, the hexa-coordinated arsorane 32 can be readily obtained by oxidative addition on 7b using diol/ $ClN(i\text{-}Pr)_2$ followed by reaction

Scheme 1



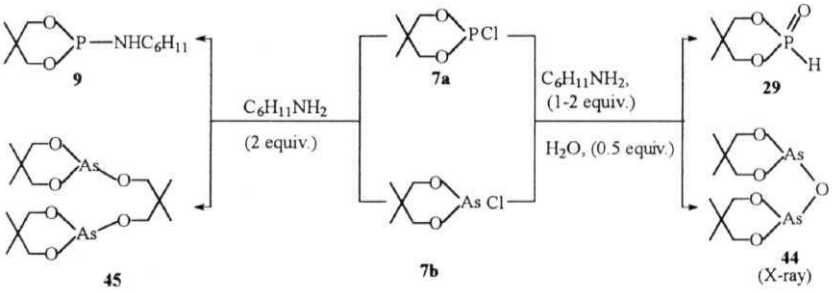
of the chloro product 31 with 8-hydroxy quinoline/ Et_3N. Such a route is not possible for phosphorus because of the formation of 30. Although phosphite 8a reacts readily with diol/ $ClN(i\text{-}Pr)_2$, the corresponding arsenite 8b fails to react;

from the former reaction the hexa-coordinated compound $(OC_9H_6N)_3P(OCH_2CMe_2CH_2O)$ **[42, δ_p:-127.0 ppm]** with an N→P bond is isolated (by reorganization of ligands) in an attempt to crystallize the product with δ_p: -67.0 ppm.

(b) Hydrolytic behaviour of cyclic arsenites and phosphites:

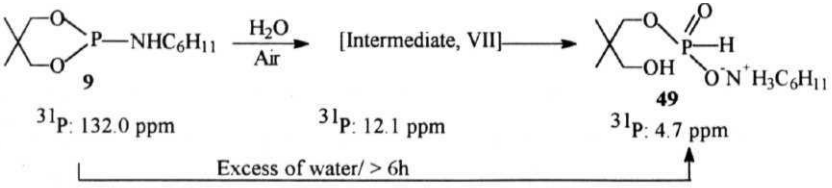
In our attempts to prepare cyclic phosphites and arsenites with cyclohexylamino substituents, the following differences, attributed mainly to the extreme lability of As-N bonds and the reluctance of As to achieve the As(V) state (compared to phosphorus), are observed [Scheme 2].

Scheme 2

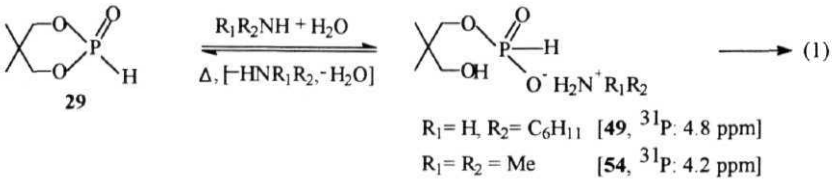


Hydrolysis of the aminophosphite 9 takes place stepwise (Scheme 3) to lead to 49.

Scheme 3

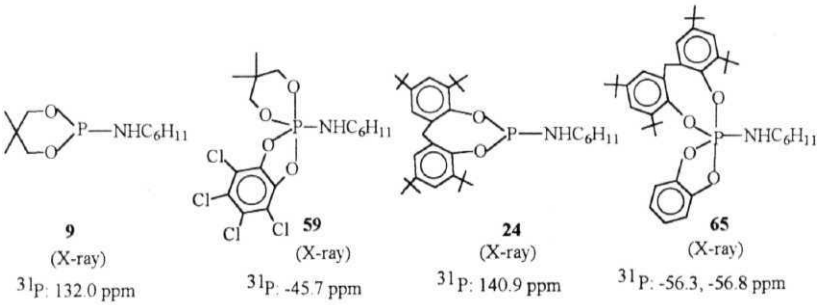


What is perhaps unique is the following reversible reaction (eq. 1).



(ii) Cyclic phosphites and phosphoranes with the cyclohexylamino substituent:

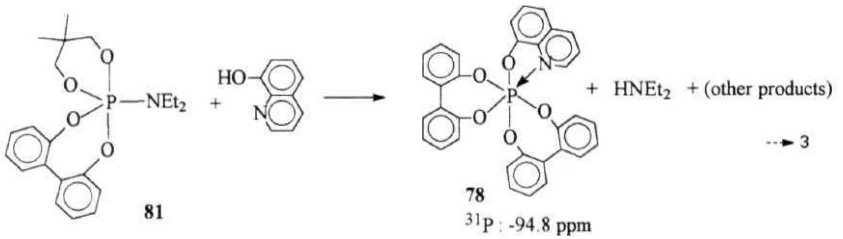
The X-ray structures of the amino phosphites (9 and 24) and amino phosphoranes (59 and 65) give a concrete evidence of the conformational preferences for the rings in compounds possessing the same substituents on phosphorus. Replacement (hydrolysis,reaction with 8-hydroxy quinoline) of the

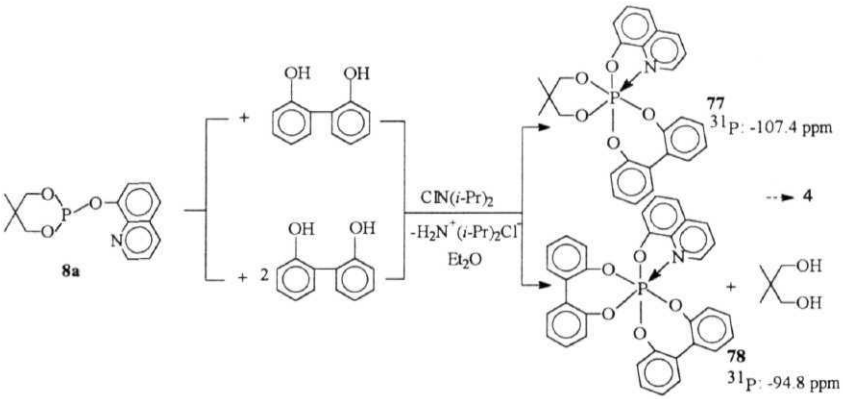


NHC_6H_{11} group from the penta-coordinated phosphorane 59 is more difficult than from the tri-coordinated derivative 9.

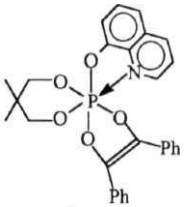
(iii) Bi- and tri-cyclic penta- and hexa-coordinated phosphoranes with an oxinate substituent

An interesting reaction chemistry is found in these systems (eqs. 2 and 3).

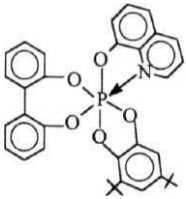




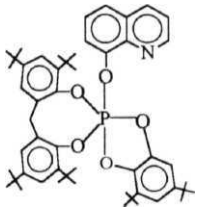
These reactions suggest a preferential stability for **the** 7+7+5 ring compound 78. Other derivatives with varying ring sizes have also been synthesized and characterized (e.g.: 75, 76 and 79). Compound 79 is penta-coordinated both in the solid and solution state, perhaps due to steric factors



75
(^{31}P: -56 9 ppm, X-ray)



76.CH_2Cl_2
(^{31}P: -89 3 ppm, X-ray)



79.1/2 H_2O
(^{31}P: -56.9 ppm. X-ray)

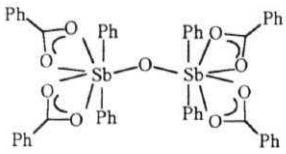
Another notable feature is that the eight-membered ring spans a diequatorial position [with a boat-chair conformation] in 79 but an axial-equatorial position [with a tub conformation] in 65 in a TBP structure.

Chapter III gives details of the experimental procedures.

Part B

The first chapter in Part B [Chapter IV] contains a brief survey of literature on antimony(V) cages with a carboxylate/ phosphinate/ chloro group; comparison to cages formed by other metals [Sn, Mn] is also made.

In Chapter V [Results and Discussion] synthetic routes, structural aspects and interconversion (wherever feasible) among diphenylantimony(V) carboxylates/ phosphinates are discussed. The following compounds have been synthesized by primarily reacting diphenylantimony trichloride with the silver salts of carboxylic/ phosphinic acids:



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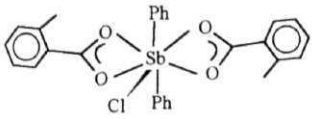

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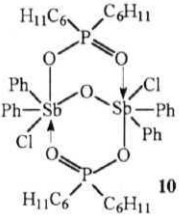

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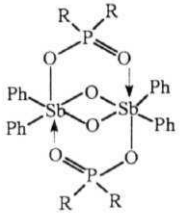
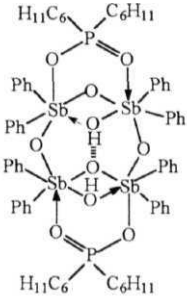


R= cycl-C_6H_{11} (**12**)
= cycl-C_8H_{15} (**13**)



.MeCOOH

15

Important features include the following:

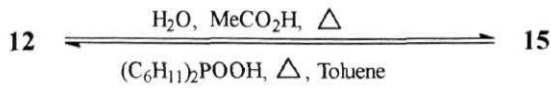
(i) Whereas the reaction of Ph_2SbCl_3 (1) with the silver salt of the acid [1:2 molar ratio] led to the six-coordinated dinuclear compound 10, a similar reaction with $AgO_2C\text{-}2\text{-}MeC_6H_4$ led to the mononuclear hepta-coordinated derivative 8. The 1:3 stoichiometric reaction of Ph_2SbCl_3 (1) with AgO_2PR_2 [R= cycl-C_6H_{11}, cycl-C_8H_{15}] led to the novel dimeric compounds 12 and 13; a similar reaction of Ph_2SbCl_3 with AgO_2CPh led to 3 in which antimony is hepta-coordinated.

(ii) Compound 12 and **13** are also prepared by an exchange route as given below (eq. 4):

$$SbPh_2Cl_3 + 3AgO_2CMe \xrightarrow[+(H_2O)]{+R_2PO_2H} [Ph_2Sb(O_2PR_2)O]_2 \quad \text{(4)}$$

R= cycl-C_6H_{11} (**12**)
= cycl-C_8H_{15} (**13**)

(iii) Structural interconversion is possible between 12 and 15 (^{1}H and ^{31}P NMR):



(iv) Structural analogies between oxo-carboxylates/ phosphinates of n-butyltin(IV) and diphenylantimony(V) compounds have been discussed.

In the last chapter [Chapter VI] experimental details for the synthesis of antimony compounds have been described.

X-ray structures, of necessity, have been obtained mainly from the following sources: 1. Uni. Saarlandes (Germany); 2. Uni. Gottingen (Germany); 3. Texas A & M Univ. (U.S.A.); 4. I.I.Sc., Bangalore (India). Analysis of the structures has been done using the hpplot program.

Part A

Cyclic Phosphites/ Arsenites and Phosphoranes/ Arsoranes

CHAPTER I

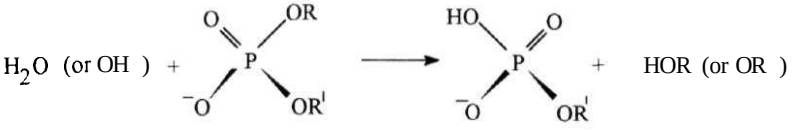
INTRODUCTION

Cyclic Phosphites/ Arsenites and Phosphoranes/ Arsoranes

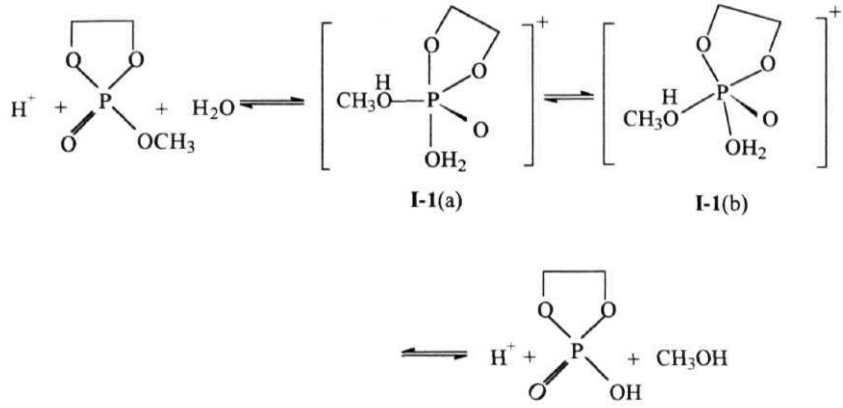
I.1 *General **Introduction:***

Phosphorus has an extensive and varied chemistry which transcends the traditional boundaries of inorganic chemistry not only because of its propensity to form innumerable covalent "organophosphorus" compounds, but also because of the numerous and crucial roles it plays in the biochemistry of all living beings.[1] An important reaction in biochemical processes is the hydrolysis of phosphate esters for which three basic mechanistic pathways can be envisioned.

(a) One step nucleophilic displacement (S_N2) with inversion (similar to carbon chemistry):

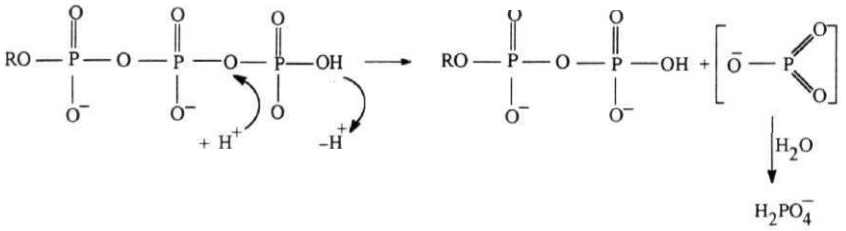


(b) Nucleophilic attack in which a five-coordinated intermediate is formed, which then undergoes pseudorotation:[2]

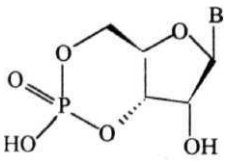


I-1(a) I-1(b)

(c) Release of a short-lived "metaphosphate" anion, which is rapidly converted by H_2O to $H_2PO_4^-$.[2a,3]



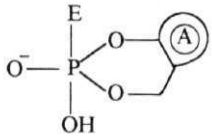
Penta-coordinated species analogous to **I-1** have also been implicated in both enzymatic and nonenzymatic reactions involving phosphate esters and phosphonium salts.[4] An example is that of the metabolic reactions involving cyclic adenosine monophosphate, c-AMP **(I-2),** featuring a saturated 1,3,2-dioxaphosphorinane ring. In the enzymatic action, it is not clearly known whether the six-membered ring assumes a diequatorial position (I-3a) in the proposed phosphorane

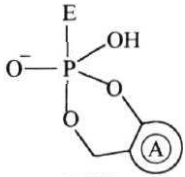


B= adenin-1-yl

I-2

intermediate or an apical-equatorial position (I-3b) or if the conformation is enzyme dependent.[4]





I-3(b)

[A = adenosine residue]

[E = reactive part of the enzyme]

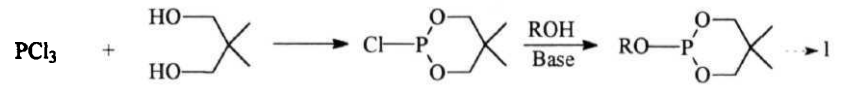
Since synthesis and characterization of species like **I-1** or **I-3** in the laboratory is difficult, an alternative approach is to look at the structures and reactivity of the more readily accessible neutral phosphoranes as model systems. Reactions of penta-coordinated phosphorus may sometimes involve hexa-coordination.[5] Therefore a knowledge of the nature of these hexa-coordinated species would also be useful in understanding the structure and reactivity of phosphoranes. Hence there has been a prodigious growth in the chemistry of $P^{V}(5)$ and $P^{V}(6)$* compounds, during the past two decades.[4,6,7] Corresponding literature on analogous arsoranes is scanty.

This review is mainly restricted to penta- and hexa-coordinated phosphoranes with O-P, N-P and S-P bonds in which phosphorus is a part of a six or higher-membered ring. An effort is made to compare related phosphorus and arsenic systems based on the available literature. Since cyclic phosphites/ arsenites are, by and large, used as precursors, relevant aspects of their structures and reactivities are also included here.

* Superscript Roman numeral denotes oxidation state and the number in parenthesis gives the coordination number.

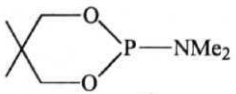
I.2 *Cyclic Phosphites and Arsenites*

These compounds are, in general, synthesized by (a) reacting the respective trichloride with a diol in the presence/ absence a base and when required, the residual chlorine replaced by an alkoxy/ aryloxy group (eq. 1)[8] or (b) by replacing an amino functionality by a diol (eq. 2).[9,10] The second route is more useful when the compounds are thermally sensitive.[10]

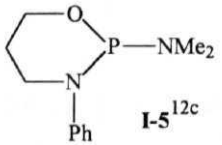


(T = Thymidine residue)

On the basis of several studies (mostly based on ^1H NMR), it has been established that alkoxy/ aryloxy and chloro subsituents on trivalent phosphorus prefer an *axial* disposition in the *chair* conformation for 1,3,2-dioxaphosphorinanes.[11,12] By contrast, the -NMe_2 substituent in **I-4** is disposed towards *equatorial* position.[13] Interestingly however, Bentrude and coworkers in a later study have shown that the -NMe_2 group in the 1,3,2-oxazaphosphorinane I-5 is *axial* both in the solid and solution state.[12(c)]



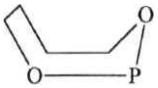
I-4[13]



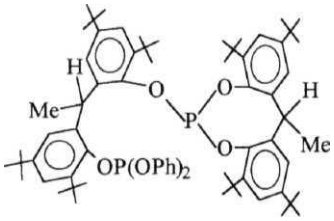
I-5[12c]

Aksnes and coworkers have investigated the corresponding 1,3,2-dioxarsenanes in depth by solution state ^{1}H and ^{13}CNMR spectroscopy and have established an *axial* orientation of the alkoxy/ aryloxy and chloro substituents on arsenic with a *chair* conformation for the six-membered ring.[14] By contrast an X-ray structure available for $ClAs(OCMe_2CH_2CMe_2O)$ shows a *twist-boat* conformation for the arsenane ring in this compound.[15]

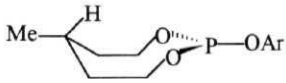
Much less literature is available on seven- and higher- membered ring systems. A few X-ray structures for 1,3,2-dioxaphosphepin ring systems involving 2,2-biphenoxy and related rings have been determined.[16-19] From these studies it appears that the preferred conformation for the seven-membered ring is that of a *row-boat* **I-6**. To our knowledge similar arsenic systems have not been investigated by X-ray.



Studies on 1,3,2-dioxaphosphocin systems are to a large extent limited to those by Pastor and coworkers.[20] The X-ray structure of **I-7** reveals a *boat-chair* conformation **I-8** for the eight-membered ring with the bulky aryloxy substituent on phosphorus being *equatorial.*



I-7 [20]

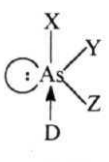


I-8

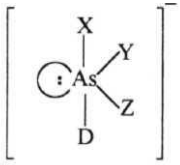
Again as far as we are aware, no structural information is available on analogous arsenites.

s

It is well-known that a large number of phosphites (P^{III} systems) tend to achieve the P^{V} state by forming a P=O bond *via* reaction such as Michaelis-Arbuzov rearrangement or hydrolysis.[1(b),2(c)] Analogous chemistry for arsenites is not common; in fact it is difficult to oxidize As^{III} to As^{V} in most cases.[21] Additionally, although both P-N and As-N bonds can be readily replaced by P-0 (eq. 2) or As-O bonds in phosphites and arsenites respectively, it appears from the literature that As-N bonds are (notoriously) more labile than P-N bonds.[22] However a comparative assessment, under similar conditions, of the reactivity of phosphites vv arsenites is scanty (or lacking) in the literature.

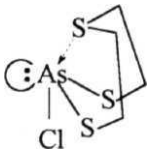


I-9(a)

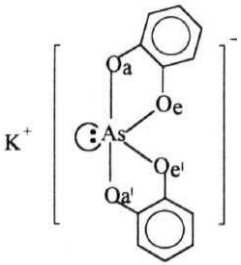


I-9(b)

It is known that As^{III} compounds can act as Lewis acids.[23] Compounds such as **I-9** in which an electron pair is donated to arsenic, are isoelectronic with penta-coordinated arsenic/ phosphorus [10-e system]. Compounds $S(CH_2CH_2S)_2AsCl$ **(I-10)**[24a] and $K^+[As(O_2C_6H_4)_2]^-$ **(I-11)**[24b] are examples of such systems. Studies on six- and higher-membered rings of As could be of interest in learning the effect of the lone



MO [24a]

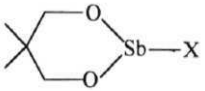


I-11[24b]

As-Oa (mean): 1.995 Å
As-Oe(mean): 1.807 A
Oa-As-Oa' 166.2°

pair on conformational preferences.

Arbuzov *et al* have reported some cyclic antimony systems, for example I-12,[25] but no structural information is available about this system.

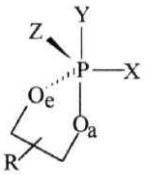


I-12 X= OMe, OEt, Cl

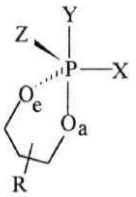
I.3 *Cyclic* ***Phosphoranes/Arsoranes***

I.3.1 Penta-coordinated systems

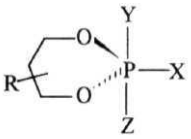
It has been well established that five-membered rings invariably span *apical-equatorial* sites in a trigonal bipyramidal (TBP) geometry for phosphorus (**I-13**).[1(b),6(a-b),7(d)] However, the *apical-equatorial* (**I-14**) *vs* ***diequatorial*** (**I-15**) preference for six-membered ring compounds remained less certain till recently.



I-13

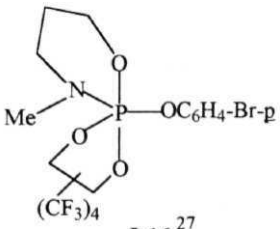


I-14

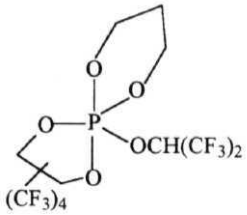


I-15

Trippett had earlier proposed that the 1,3,2-dioxa- or 1,3,2-oxaza-phosphorane ring bonded *apical-equatorially* in a TBP should be in a non-chair *(boat* or *twist-boat)* form[26] and later provided an example (I-16)[27]. However several other workers suggested a *diequatorial* placement for saturated six-membered rings

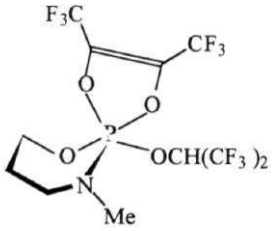


I-16 [27]

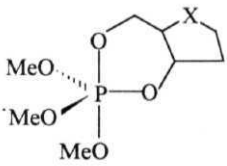


I-17 [32]

(**I-15**).[28-31] The first structural study of a penta-oxyphosphorane **I-17** reported by Schomburg *et al*[2] is in conformity with Trippett's predictions. In the same year Yu and Bentrude[33] provided unequivocal ^{1}H NMR evidence for the non-chair *(twist-boat)* conformation in solution with an *apical-equatorial* 1,3,2-oxazaphosphorinane ring in **I-18**. Further investigation on penta-oxyphosphoranes of the type **I-19** - **I-20** by ^{1}H and ^{13}CNMR have shown that the phosphonnane ring spans an axial-equatorial position with a *twist-boat* or *boat* conformation[34,36] in solution.



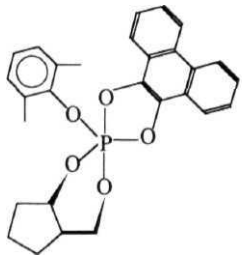
I-18 [33]



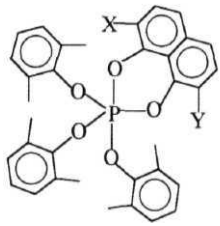
I-19: X= O
I-20: X= CH_2

Recent reports of structural work on cyclic oxyphosphoranes have been mainly by the research teams of Holmes[4,7(a),7(c),16,20(b),37,40,41] and Bentrude.[33,34,35(b),36,38] These studies have firmly established the preference for 1,3,2-dioxa-phosphorinane rings to be in the *apical-equatorial* position with a *boat*

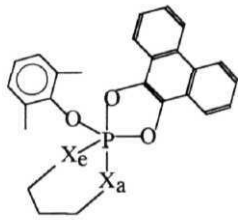
or twist-boat conformation (for non H-bonded systems).[4] Even for 1,3,2-dithia- and 1,3,2-diaza-phosphorinane rings such a preference is observed.[37(f),37(i)] Selected examples [(I-21) - (I-23)] are shown below. It is interesting that despite



I-21[37(0



I-22(a), X = Y = H,[37(g)]
I-22(b), X = Y= Cl,
I-22(c), X = H, Y = Cl
[Six-membered ring planar except P which is a flap atom]

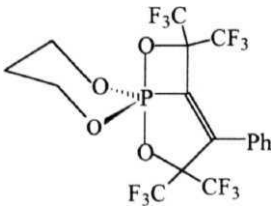


I-23(a), X= NMe[37(0]

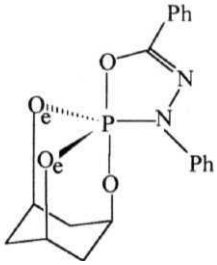
I-23(b), X- S[37(]

being supported by an unsaturated C-C-C skeleton *[ZC* ~ 120°] compound I-22 shows an *apical-equatorial* preference for the phosphorinane ring. The *apical* disposition of a ring sulfur/ nitrogen relative to the more electronegative xylyloxy oxygen in I-23(a) (both triclinic and monoclinic forms) and I-23(b) is also noteworthy.[4a,37(f),37(i)]

In contrast to the above, Bentrude has shown that if proper fused ring systems are present on phosphorus, a *chair* conformation with a diequatorial disposition for the 1,3,2-dioxaphosphorinane ring is observed.[38] Compound 1-24 is one such example. Another example (I-25) has a fused six-membered ring system.[39]

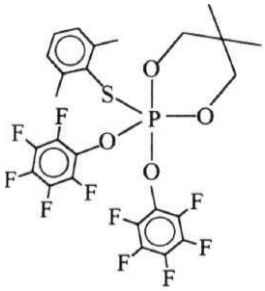


I-24[38]



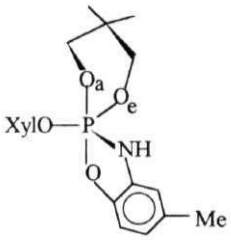
I-25[39]

For non H-bonded systems the only example of a *chair* conformation with an *apical-equatorial* disposition in a TBP arrangememt appears to be that of I-26 [7(e)] An explanation based on the combination of an electronegativity effect and a steric effect from the C_6F_5O- ligand has been offered for this observation.



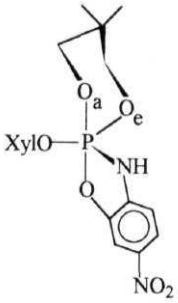
I-26

H-bonded systems should be perhaps more relevant to our understanding of c-AMP action because such a feature is present in biological systems. A few structures involving substituted o-aminophenoxy groups studied so far show *chair* as well as *boat* conformations.[7(c),40] These data suggest that the difference in energy between the *chair* and *boat* conformations is not high [see structures **[(I-27) - (I-28)]**.



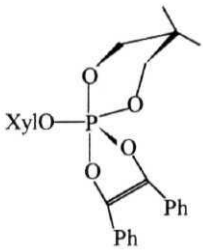
[Twist boat]

I-27(a)[40]



[Chair]

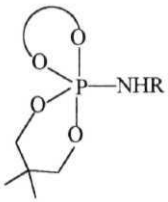
I-27(b)[7(c)]



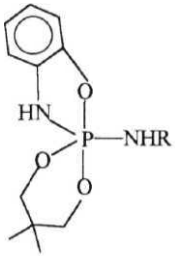
[Boat] (no H-bonding)

I-28[37(h)]

Studies on H-bonded systems involving an acyclic NH- group have not been carried out so far (e.g. **I-29** and I-30).



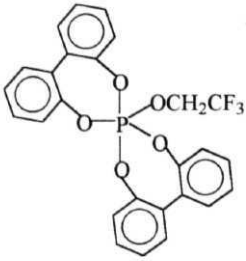
1-29



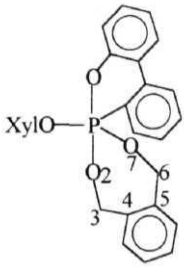
I-30

Structural investigations on phosphoranes with seven- and eight-membered rings are largely from Holmes' group.[4,7(a),7(c),16,20(b),37,41] Some significant features are summarized below:

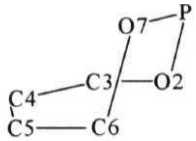
a) Phosphoranes containing a 2,2'-biphenoxy system invariably show an *a-e* disposition and a *row-boat* conformation for the seven-membered rings .[16,37(g)] Compound **I-31** is an example. However, when a 1,2-benzene dimethanoxy substituent is involved, a *boat* conformation [structure **I-32**] with the *apical* oxygen 02 and the opposing carbon C6 at the tips of the *boat* is observed.[7a]



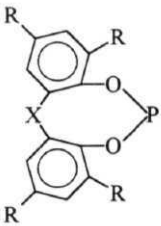
I-31[37(c)]



I-32[7(a)]

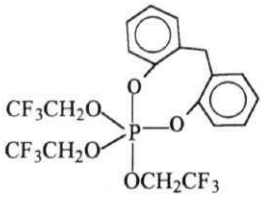


I-32(a)

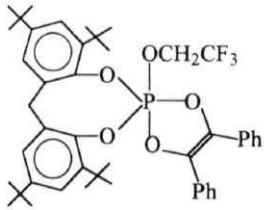


I-33, X=CH_2 , S

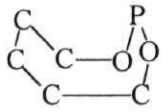
b) For phosphoranes containing the eight membered ring **I-33**, both *apical-equatorial* and *diequatorial* dispositions in a TBP structure are observed. The conformation of the eight-membered ring is described as a *twisted boat* or *tub* for I-**34**[37(b)] and a *symmetrical chair* for **I-35**.[37(a)] These are shown in structures **I-36**.



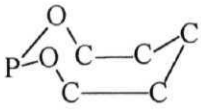
I-34[37(b)]



I-35[37(a)]

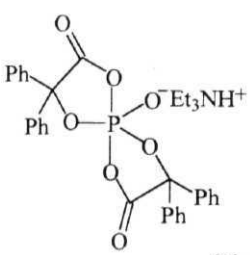


"Tub"
I-36(a)

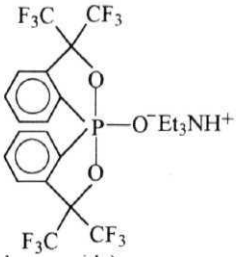


"Sym chair"
I-36(b)

In addition to the neutral phosphoranes discussed above, ionic compounds of types **I-37** - 1-39 are useful in studying the nature of the penta-coordinated

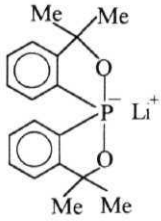


I-37 [42(a)]



(Phosphoranoxide)

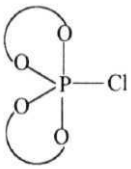
I-38 [42(c)]



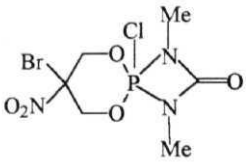
(Phosphoranide)

I-39 [42(c)]

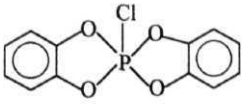
phosphorus.[42,44] However analogous species with six- or higher-membered rings are unknown as yet. Possible precursors towards synthesizing phosphoranoxides or phosphoranide [see **I-37** - **I-39**] anions are chlorophosphoranes of the type **I-40** [either by treating with H_2O/ Et_3N or by treating with Li/ Na / K]. A few chlorophosphoranes are known [**I-41** - **I-44**].[45-48] Compounds of this type could also be of interest for synthesizing other P-substituted derivatives such as iodo, azido or triphenylphosphazenyl phosphoranes.[47]



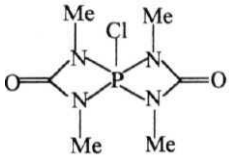
I-40



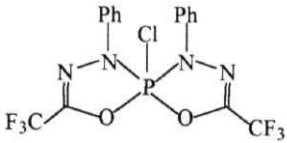
I-41[45]



I-42[46]

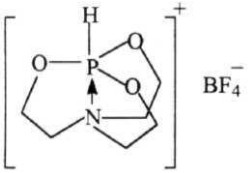


I-43[47]



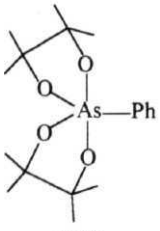
I-44[48]

At this point, it may be worth mentioning that there are penta-coordinated P^{III} compounds also; an example of this kind is provided by Verkade's phosphorane. **I-45**.[49] Since the present work does not involve such species this subject is not elaborated on further.



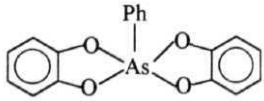
I-45

Aspects of penta-coordinated arsenic(V) have been reviewed earlier by Bohra and Roesky[50] and by Holmes [7(d),51] Structural studies have been limited to five-membered ring systems, the geometry around arsenic in these compounds is seen to vary from a TBP (e.g. I-46)[52] to a square pyramid (e.g. **I-47)**.[53]



TBP

I-46[52]



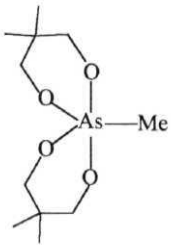
SP

I-47[53]

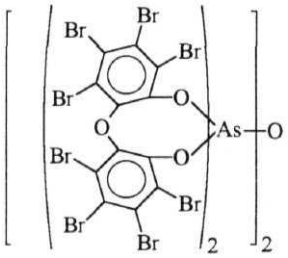
Fluxional behaviour of penta-coordinated phosphorus is also of considerable interest. Studies on six- and higher-membered ring systems are mainly due to Denney[54] and Holmes.[4,37] However since

this aspect has not been investigated in the present work, it will not be elaborated on any further.

Compounds **I-48**[55] and **I-49**[56] which represent examples of arsoranes with six- and eight-membered rings, respectively, have been reported, but no X-ray structural information is available.



I-48[55]



I-49[56]

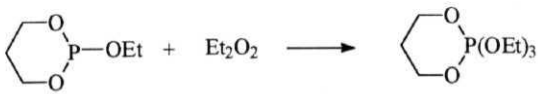
I.3.2 Methods of preparation of cyclic penta-coordinated phosphoranes:

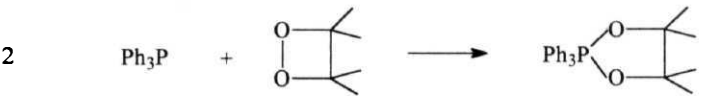
The major synthetic routes for phosphoranes are described below:

(i) *From trivalent phosphorus compounds*

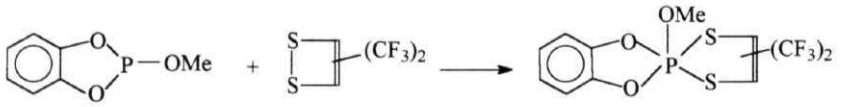
a) By reaction with diols in the presence of N-chlorodiisopropylamine:[4,37]

b) By reaction with peroxides:[2(c)]

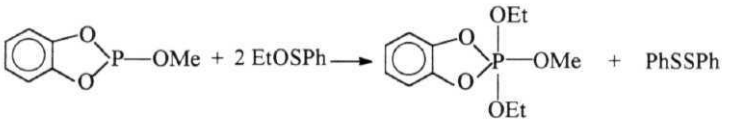


2 

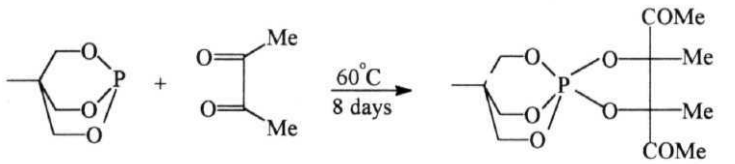
c) By reaction with dithietens:[2(c)]

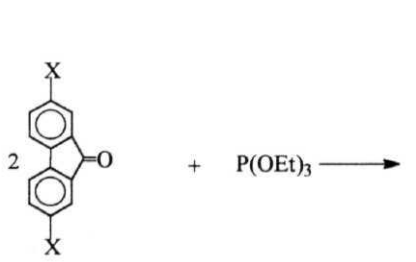


d) By reaction with sulphenate esters:[2(c)]

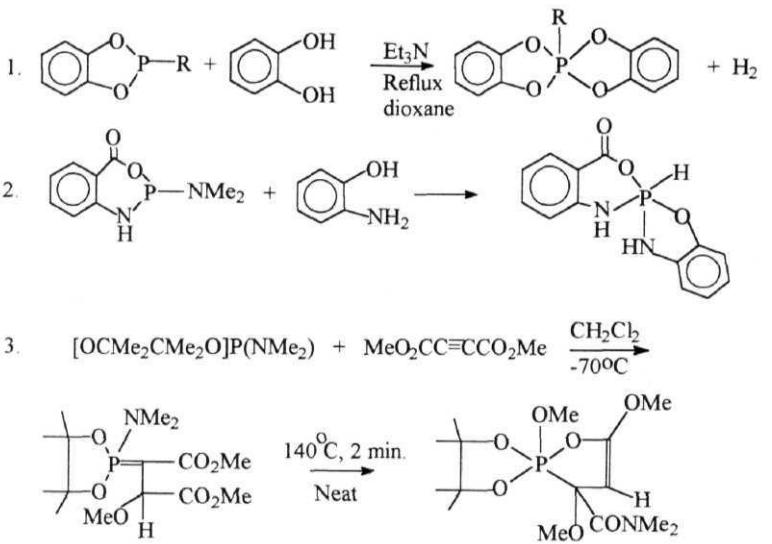


e) By reaction with a-diketones or carbonyl compounds:[2(c), 37]

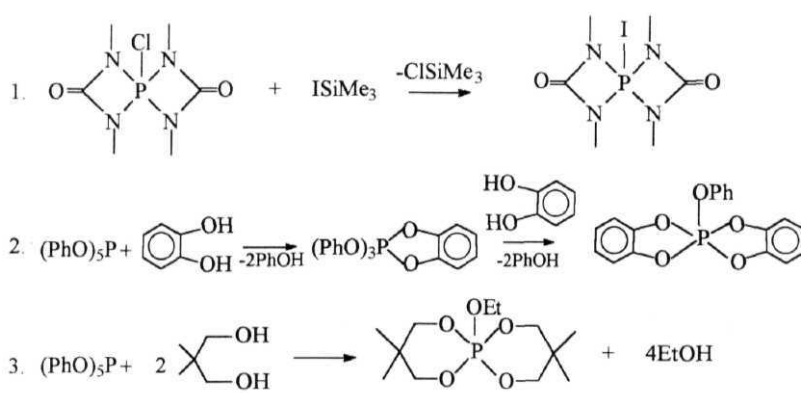
1 

2 

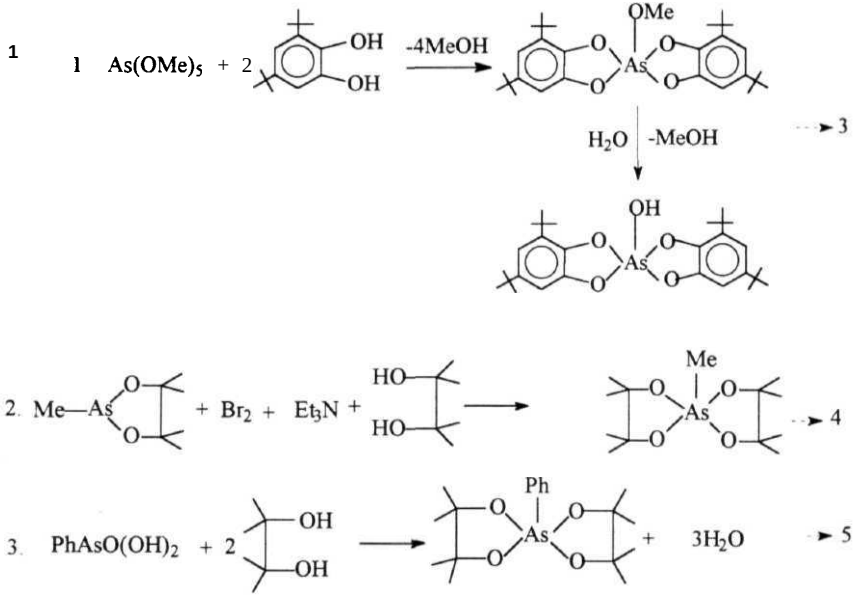
f) Miscellaneous preparations from P^{III} compounds.[2(c),57,58]



(ii) By exchange reaction[2(c),47]

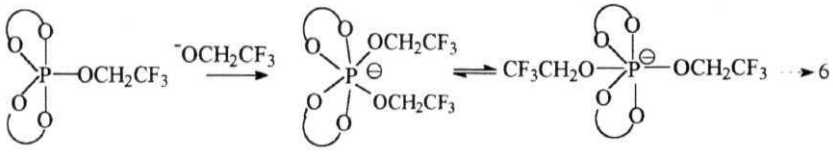


For the synthesis of arsoranes, methods (i)(e) and (ii) have been previously employed [see eq. 3 for an example using method **(ii)**][51]. Two other synthetic routes for arsoranes also shown in eqs. 4 and 5.[51]



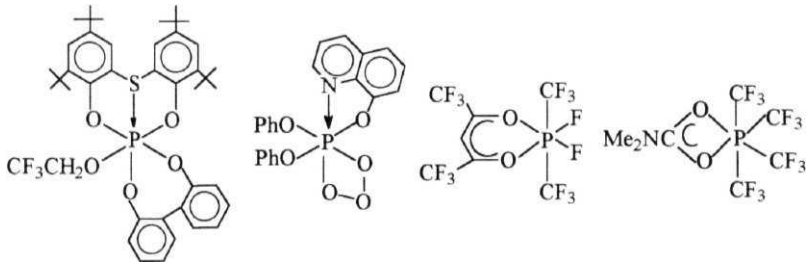
I.3.3 **Hexa-coordinated** systems

When penta-coordinated phosphorus itself is a substrate for **nucleophilic** attack, an associative mechanism would entail anionic hexa-coordinated species (eq.6)[5,1(b),59] and hence studies on these systems will also be beneficial in understanding the nature of the penta-coordinated state. The existence of such species in reactions of penta-coordinated phosphorus has been established by **Westheimer**[5(a)] and later by **Trippett**[59] Several anionic species similar to **I-51** are **known**.[60,61]



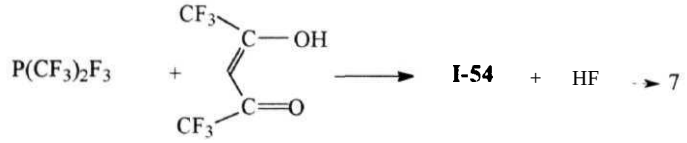
I-50 **I-51(a)** **I-51(b)**

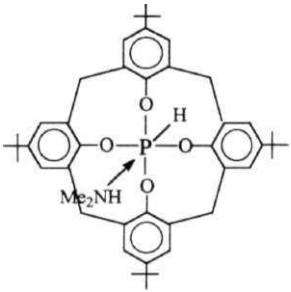
A neutral donor atom (instead of an anion) at the sixth coordination site in species of the type **I-51** will lead to neutral hexa-coordinated phosphoranes/ arsoranes. Example of such systems include **I-52** - **I-55**. Compounds **I-52** and I-**53** have been prepared by the oxidative addition reaction of biphenol (method i(a) in section **I.3.2**) or ozone on the corresponding phosphite. Synthesis of **I-54** and



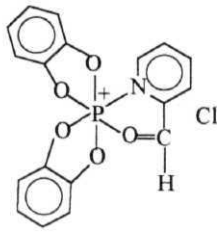
I-52[62] **I-53**[63] **I-54**[64] **I-55**[65]

I-55 have been accomplished by the reactions shown in eqs.7 and 8. It can be noted that a variety of hexa-coordinated systems, including isomers can in principle be generated utilizing the oxinate (e.g. **I-53**) or acetyl acetonate (e.g. I-54) ligands; thus the field is open for further investigations.



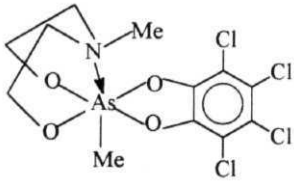


I-56[66]



I-57[67]

Other examples of hexa-coordinated systems include calixarene based derivatives (e.g. **I-56**) developed mainly by Lattman[66] and cationic species such as **I-57** studied by Schmidpeter.[67]



I-58[68]

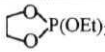
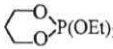
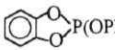
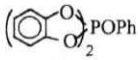
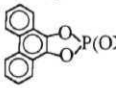
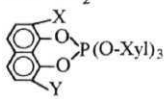
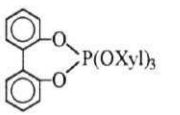
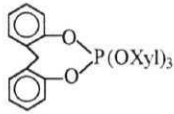
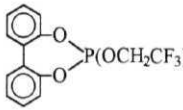
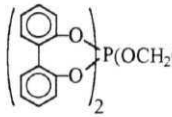
For arsenic systems, compound **I-58** represents the sole example of a neutral cyclic hexa-coordinated compound that we are aware of; this was prepared by adding o-chloranil to the cyclic arsenite.[68]

I.4 *^{31}P NMR Spectroscopy of Penta- and Hexa-coordinated Phosphorus*

Identification of penta-coordinated phosphoranes in solution is readily done by ^{31}P NMR spectroscopy. Several reviews are available on the utility of ^{31}P NMR in stereochemical analysis.[12,20(b),60,69] In this section the effects of (a) the ring size, (b) number of rings, (c) heteroatom, (d) electronegativity and (e) coordination number on the ^{31}P NMR chemical shifts are discussed.

(a) *Ring size and number of rings:*

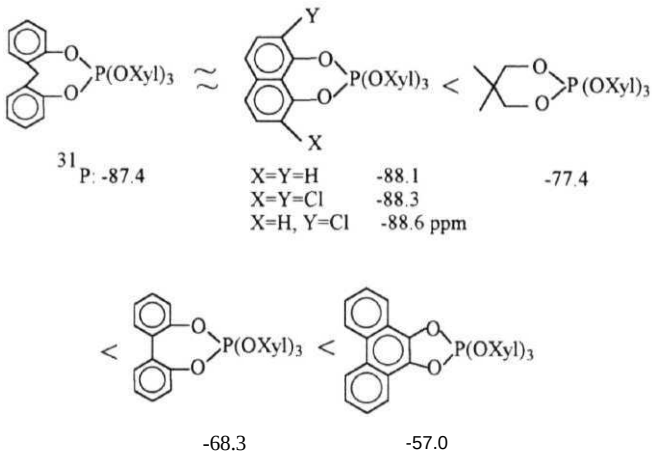
In general for oxyphosphoranes, five- and seven-membered rings appear to deshield the phosphorus; more the number of rings, more is the deshielding. Substitution of an acyclic group by a closely analogous six- or eight-memebered ring does not appear to change the $\delta(^{31}p)$ shift significantly. The following data corroborate these statements.[2(c),4(b),20(b),60,69]

Compound	^{31}P	Compound	^{31}P	Compound	^{31}P
$P(OEt)_5$	-71		-51	–	–
$P(OEt)_5$	-71		-72	–	–
$P(OPh)_5$	-88.7		-60.8		-30
$P(OPh)_5$	-88.7		-57.0		X=Y=H -88.2 X=Y=Cl -88.3 X=H, Y=Cl -88.6
$[P(OXyl)_5$ is not known]			-68.34		-87.44
$P(OCH_2CF_3)_5$	-76.6		-63.1		-47.3

(b) *Ring size in monocyclic phosphoranes*

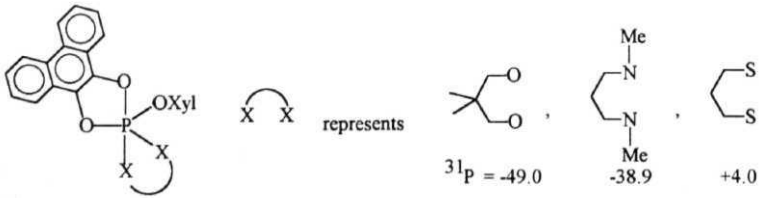
The flexibility decreases along the series of monocyclic derivatives in the order: eight-> six-> seven-> five-membered ring. This order parallels an increase in deshielding which is manifested in the ^{31}P chemical shift [see examples below]. Such a trend seems to be valid to a reasonable extent only. For example, although the phosphoranes with the 1,8-naphthaIene-dioxy group is less flexible than the

eight, six (saturated) and seven-membered rings, it has a ^{31}P chemical shift upfield to them.[20(b),37(g)]



(c) *Type of ring heteroatom*

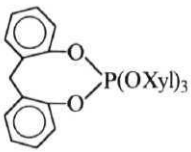
Deshielding increases along the series of ring heteroatoms in the order O> NMe> S. This is evident from the examples shown below:



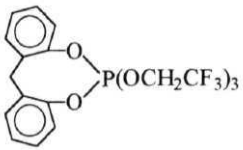
Holmes has ascribed the deshieling to a decrease in (p-d) *n* bonding where the effectiveness of such bonding lies in the order O> N> S.[20(b)]

(d) *Electronegativity of substituents*

It has been observed in several cases that the more electronegative $-OCH_2CF_3$ group causes deshielding when compared to an aryloxy group [-OPh or O-2,6-$Me_2C_6H_3$].[20(b)] Two sets of examples are given below:

(i) 

^{31}P: -87.4 ppm
[Xyl = 2,6-$Me_2C_6H_2$]



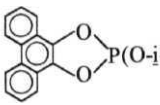
^{31}P: -78.3 ppm

(ii) $P(OPh)_5$
^{31}P: -88.7 ppm

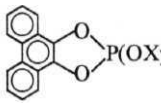
$P(OCH_2CF_3)_5$
^{31}P: -76.6ppm

However it should be noted that an alkoxy (-OEt, O-i-Pr etc) group deshields the phosphorus relative to an aryloxy or the $-OCH_2CF_3$ group although it is less electronegative than these groups[-OAr, OCH2CF3]. Three examples are given below:[2(c),60]

(i) $P(OEt)_5$ ^{31}P: -71.0; $P(OPh)_5$ ^{31}P: -88.7; $P(OCH_2CF_3)_5$ ^{31}P: -766 ppm

(ii) 

^{31}P: -48.0



^{31}P: -57.0 ppm

(iii) $Ph_3P(OR)_2$

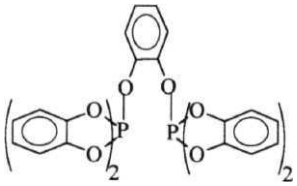
R = i-Pr ^{31}P: -48.0
= Ph ^{31}P: -65.5
= CH_2CF_3 ^{31}P: -58.5 ppm

Thus although electronegativity is important, the interpretation of ^{31}P chemical shifts would require the consideration of other effects [such as π-character for the bonds].

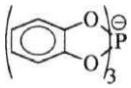
(e) *Coordination number*

In general it is acceptable that hexa-coordinated cyclic phosphorus compounds containing PO_6, PO5S, and PO5N arrangements show an upfield shift compared to analogous penta-coordinated species.[20(b),60] Two sets of examples are given below:

1

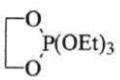


^{31}P: -27.6 ppm

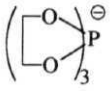


^{31}P: -82.0 ppm

2

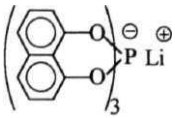


^{31}P: -52.0 ppm



^{31}P: -89.0 ppm

The observed $\delta(^{31}P)$ range for PO_6, PO5N, and PO5S is -79 to -168 ppm;[70] the highest $\delta(^{31}P)$ value for a PO_6 system has been recorded for the following compound:

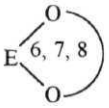


^{31}P: -168.0 ppm

OBJECTIVES OF THE PRESENT WORK

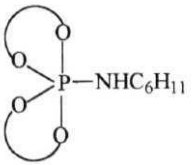
The principal objectives of the present work are:

(A) A comparative study of the reactivities of cyclic phosphites and arsenites of the type (a) with respect to (i) hydrolysis, (ii) oxidative addition reactions and (iii) reaction with sodium.

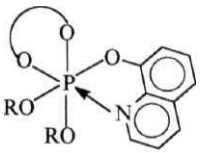


E = P, As

(B) Synthesis, reactivity and structural studies on penta- and hexa-coordinated phosphoranes of the types (b) and (c).



(b)



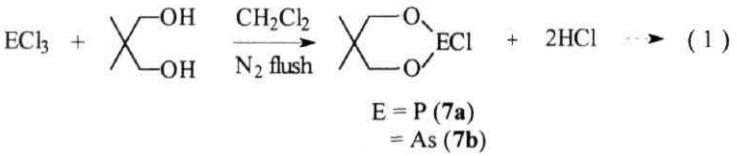
(c)

CHAPTER II

RESULTS AND DISCUSSION

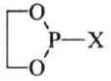
II. 1 *Synthesis- General Remarks*

The cyclic phosphites and arsenites used in the present study are shown in Chart 1 along with literature references where appropriate. Synthesis of the chloro compounds **1, 4(a-b), 7(a-b), 16(a-b), 21(a-b)** and **22** was accomplished by treating phosphorus/ arsenic trichloride with the respective diol in the presence/ absence of a base. An example is shown in eq. 1 for the synthesis of 7(a-b). For both 7a and 7b this route affords a much higher yield than by performing the reaction in the presence of a base.

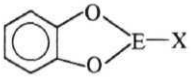


The cyclic amino/ alkoxy/ aryloxy derivatives shown in Chart 1 have been prepared by the standard routes of treating the corresponding chloro precursor with either two mole equivalents of the amine or one mole equivalent each of the

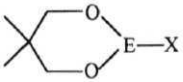
CHART 1



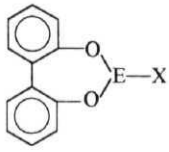
1 X = Cl[71]
2 X = NHC_6H_{11}
3 X = OC_9H_6N[63(b)]



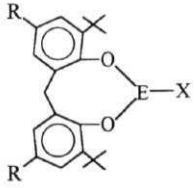
4a E = P; X = Cl[71]
4b E = As; X = Cl[72]
5a E = P; X = OC_9H_6N[63(b)]
5b E = As; X = OC_9H_6N
6 E = P; X = NHC_6H_{11}



7a E = P; X = Cl[8(a)]
7b E = As; X = Cl[14]
8a E = P; X = OC_9H_6N
8b E = As; X = OC_9H_6N
9 E = P; X = NHC_6H_{11}
10 E = P; X = NEt_2[73]
11a E = P; X = O-i-Pr
11b E = As; X = O-i-Pr
12a E = P; X = OCH_2CF_3
12b E = As; X = OCH_2CF_3
13a E = P; X = OPh[8(b)]
13b E = As; X = OPh
14a E = P; X = O-2,6-$Me_2C_6H_3$[37(h)]
14b E = As; X = O-2,6-$Me_2C_6H_3$
15 E = P; X = O-2,4,6-$Me_3C_6H_2$

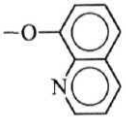


16a E = P; X = Cl[74]
16b E = As; X = Cl[75]
17a E = P; X = OC_9H_6N
17b E = As; X = OC_9H_6N
18 E = P; X = NHC_6H_{11}
19 E = P; X = NEt_2
20 E = P; X = O-2,6-$Me_2C_6H_3$



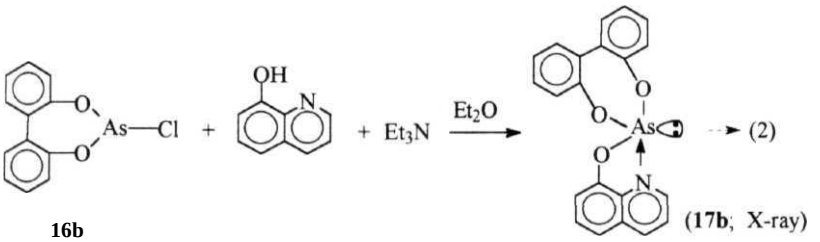
21a E = P; X = Cl; R = t-bu[76]
21b E = As; X = Cl; R = t-bu
22a E = P; X = OC_9H_6N; R = t-bu
22b E = As; X = OC_9H_6N; R = t-bu
23 E = P; X = Cl; R = Me[77]
24 E = P; X = NHC_6H_{11}; R = t-bu
25 E = P; X = NHC_6H_{11}; R = Me

OC_9H_6N =



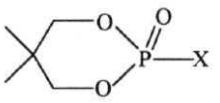
HNC_6H_{11} =

alcohol/ phenol and triethylamine. The synthesis leading to the arsepin 17b is illustrated in eq. 2. An analogous preparative method has been adapted for the



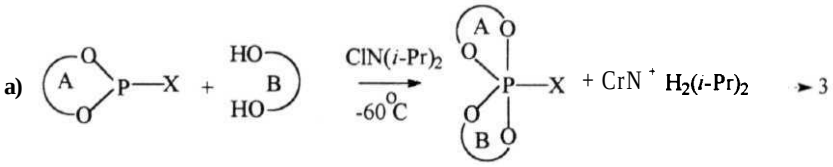
16b

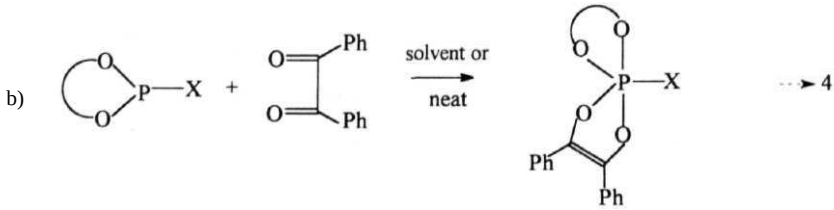
synthesis of 27-28 by starting with the chloro precursor 26;[78] compound 29 is obtained by the hydrolysis of **7a**.[8(a),79]



X = Cl (**26**)[69]
= NHC_6H_{11} (**27**)
= O-2,6-Me_2-C_6H_3 (**28**)[7f]
= H (**29**)[70]

In the present study, the penta and hexa-coordinated phosphoranes have been prepared by the oxidative addition reaction of cyclic phosphites with a diol in the presence of N-chlorodiisopropylamine (NCDA) (eq. 3)[37,80] or by the reaction of cyclic phosphites with a 1,2-diketone (eq. 4).[37,81]



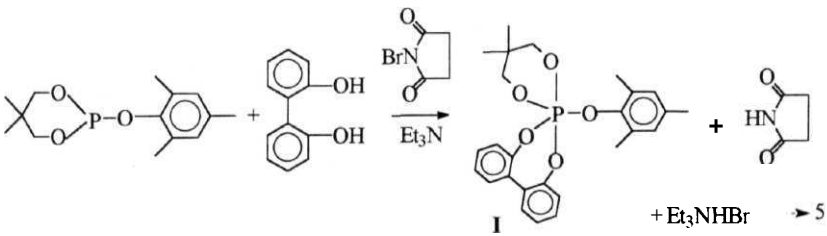


When X (in eqs. 3 or 4) is oxinate ($-OC_9H_6N$), the resulting product is either hexa- or penta-coordinated depending on the presence or absence of the $N \rightarrow P$ donor-acceptor bond.

Method (a) is applicable for the synthesis of phosphoranes and arsoranes 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.

Method (b) is suitable for introducing the 1,3,2-dioxa-phospholene (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.

We have also explored the possibility of using the commercially available N-bromosuccinimide (+ triethylamine) in place of NCDA for preparing the phosphorane I. Although product I is observed by ^{31}P NMR, the yield was too low (*ca* 5%) for the method to be practical; by contrast method (a) affords I in very good yields.



Details of the synthesis, reactivity and structures of the products, including phosphoranes and arsoranes, obtained by either hydrolysis or oxidative addition

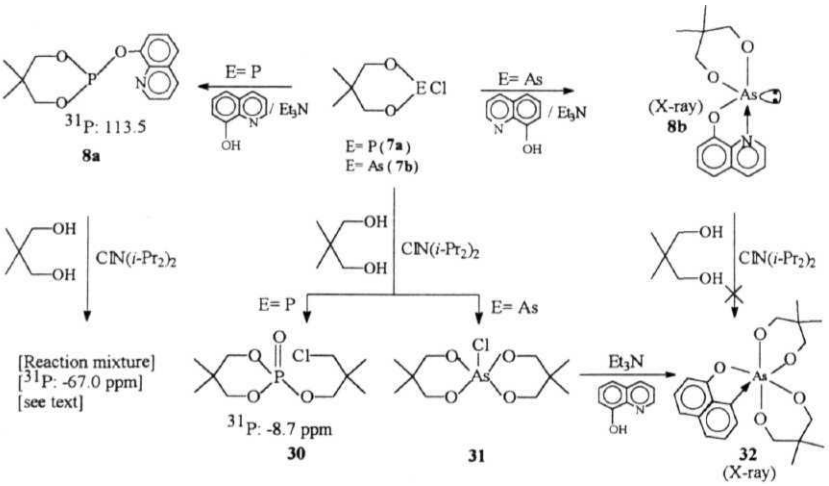
reactions of the cyclic phosphites and arsenites are discussed in the following sections. The reaction of cyclic chlorophosphites and arsenites with sodium are also compared.

II.2 *Phosphorus vs Arsenic Chemical Behaviour*

II.2.1 Oxidative addition reactions:

A set of reactions comparing the behaviour of arsenites and phosphites is depicted in Scheme 1. We shall first look into the oxidative addition reaction on chlorophosphites and arsenites which were intended for synthesizing penta-coordinated chlorophosphoranes and arsoranes.

Scheme-1

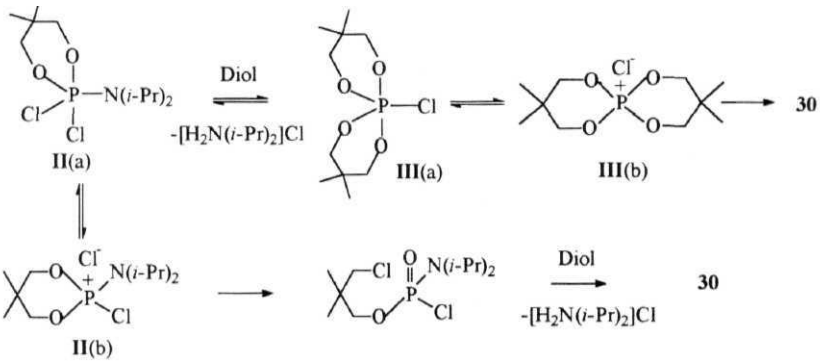


The reaction of 7a with 2,2-dimethyl-l,3-propanediol in the presence of NCDA affords the ring cleavage (modified Arbuzov) product 30 in good yield [Scheme 1]. Compound 30 is readily characterized by its ^{1}H NMR spectrum

which shows a multiplet pattern for the $OC\underline{H}_A\underline{H}_B$ protons (3.88-4.20 ppm) and two singlets for the CH3 protons (0.91, 1.25 ppm) of the phosphorinane ring; the cleaved part shows a doublet for $OC\underline{H}_2$ (3.91 ppm), a singlet for $C\underline{H}_2Cl$ (3.46 ppm) and another singlet for CH3 protons. ^{13}C NMR as well as elemental analysis confirm the identity of this product.

Since Denney and coworkers[82] have already demonstrated the intermediacy of the penta-coordinated species $(1,2\text{-}C_6H_4O_2)P(OEt)Cl(NEt_2)$ in the reaction of $(1,2\text{-}C_6H_4O_2)P(OEt)$ with N-chlorodiethylamine, an analogous species is likely to be involved in our reactions also [Scheme 2; structure Ha].

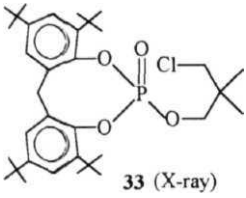
Scheme 2



Ring cleavage, in principle, could occur from both II and III. When the cyclic phosphite $(OCH_2CMe_2CH_2O)P(O\text{-}2,6\text{-}Me_2C_6H_3)$ is treated with vanous diols in the presence of NCDA, intermediate $(OCH_2CMe_2CH_2O)P(O\text{-}2,6\text{-}Me_2C_6H_3)(N(i\text{-}Pr)_2)(Cl)$ similar to II is involved; in these reactions only penta-oxyphosphoranes, and not cleavage products with $ClCH_2CMe_2CH_2O$- group, are observed.[37(h),40] Hence we conclude that in our reactions ring opening occurs from III and not from II. It can be readily seen that the formation of 30 from IIIb

is analogous to the elimination of ethyl chloride from [(1,2-$C_6H_4O_2$)P(OEt)(NEt_2)]$^+Cl^-$ to afford (1,2-$C_6H_4O_2$)P(O)(NEt_2) by Arbuzov reaction.[82]

It is known that ring cleavage takes place upon treatment of cyclic chloro phosphites with organosulfenyl chloride[83] or ROC(O)N(R')Cl[84] or chlorine,[83] but what is unique in our system is that we are still left with a ring on phosphorus in the final compound. Thus we have been able to obtain the phosphocin 33 by our route in high yields.



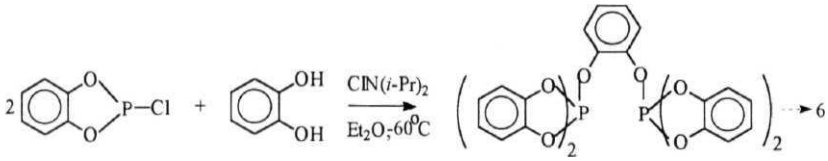
33 (X-ray)

The methylene protons of the eight membered ring show a broad signal [4.00-4.20 ppm] in the ^1H NMR spectrum. This feature could have arisen from different conformational possibilities (section **II.8**).

However, not all the reactions gave clean products. When 7a is reacted with 2,2'-biphenol/ NCDA, although the product (ClCH_2CMe_2CH_2O)P ($O_2C_{12}H_8$) (34) is readily identified, other products are certainly formed (^1H, ^{31}P NMR). In the reaction of the chlorosalicylate ClP($O_2CC_6H_4O$) (35) with salicylic acid/ NCDA, two products were observed [6 (^{31}P): -8.70, -20.83 ppm]: only the product with downfield chemical shift [δ(^{31}P): -8.70] could be isolated. This has been identified as (HO)(O)P($O_2CC_6H_4O$) (36) by elemental analysis. Obviously some hydrolysis must have occurred during the course of the reaction to lead to 36.

Diphosphorane ($C_6H_4O_2$)$_2$P(OC_6H_4O)P($O_2C_6H_4$)$_2$ (37) and not the chlorophosphorane ClP($O_2C_6H_4$)$_2$ is the product isolated when o-phenylene phosphorochloridite 4a is reacted with catechol/ NCDA (eq. 6). No trace of chlorophosphorane was observed even with 1:1:1 stoichiometry of the reactants; the reaction mixture shows only 4a and 37 (^{31}P NMR) when this stoichiometry is used. Compound 37 can be readily isolated from the mixture.

We also conducted the reaction by first adding NCDA to 4a followed by catechol but again observed the same result. At this point, it is pertinent to note that in the reaction of catechol with phosphorus pentachloride (1.5:1 stoichiometry), Wolf and coworkers also found 37 in significant quantities.[85] Our approach offers an alternative route to 37.



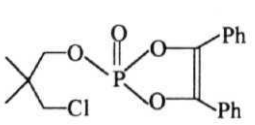
4a 37

A crystalline (moisture sensitive) product with m.p. 37°C is obtained readily by reacting $ClAs(OCH_2CMe_2CH_2O)$ (7b) with 2,2-dimethyl-l,3-propanediol/ NCDA. The chloroarsorane structure 31 is assigned to this compound from the following considerations: (a) Required amount of diisopropylamine hydrochloride was obtained. (b) ^1H NMR spectrum (25°C) is similar to that of the fast exchanging [Berry pseudorotation] phosphorane $PhP(OCH_2CMe_2CH_2O)_2$.[37(h)] Only one signal each with no apparent coupling was observed in 31 for $O\underline{CH_2}$ and CH3 protons. In the starting material 7a as well as its alkoxy/ aryloxy derivatives two doublets for $O\underline{CH_A}\underline{H_X}$ protons are observed. (c) Reaction of 31 with 2,4,6-trimethylphenol/ triethylamine afforded the required amount of amine hydrochloride. However, the product was too air sensitive to characterize further. (d) Elemental analysis is close to the hydroxy arsorane $(HO)As(OCH_2CMe_2CH_2O)_2$ which presumably is formed during handling. (e) Treatment of the product (or the reaction mixture 7b + 2,2-dimethyl-1,3-propanediol/ NCDA) with 8-hydroxy quinoline triethylamine led to the hexa-

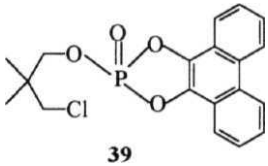
coordinated arsorane 32 [Scheme 1] and the required amount of amine hydrochloride (see below for more details).

Reaction of 7b with aromatic diols like 2,2'-biphenol, catechol and tetrachlorocatechol is beset with more difficulties due to competitive reaction of NCDA with these diols. In addition to the possible chlorination of the diol,[37(g)] oxidation occurs with catechols. Indeed, a blank reaction of catechol or tetrachlorocatechol with NCDA (in ether or benzene at 25°C) leads to a red coloured solution (possibly C-OH to C=O conversion) and in the latter case a red solid different from o-chloranil could be isolated. These reactions may be of some synthetic utility; however, since they do not form the theme of the present work, we have not analyzed them further.

As a second route to chlorophosphoranes we have examined the reaction of 7a with the o-diketones benzil and 9,10-phenanthrene quinone; the products 38 (8 (^{31}P): 9.43 ppm) and 39 ($\delta(^{31}P)$: 13.73 ppm) are formed readily *via* an intermediate similar to III [Scheme 2].



38



39

Both these compounds can be easily isolated. By contrast, the reaction of 7a with the more reactive 3,5-di-t-butyl-o-benzoquinone or o-chloranil gives several other products in addition to ring opened derivatives of the type 39; a notable feature however is that in the former case a peak at -28.0 ppm [^{31}P NMR] attributable to a chlorophosphorane can be observed in an NMR tube experiment.

Better results are achieved in the reaction of phenylenephosphorochloridite 4a with 3,5-di-(t-butyl)-o-benzoquinone and o-chloranil. The chlorophosphoranes $ClP(O_2C_6H_4)(O_2\text{-}3,5(t\text{-}bu)_2C_6H_2)$ (40) ($\delta(^{31}P)$: -8.9 ppm) and $ClP(O_2C_6H_4)(O_2C_6Cl_4)$ (41) ($\delta(^{31}P)$: -10.8 ppm) are formed in yields of >70%, the only other observed product is a penta-oxyphosphorane (<15%) with low intensity [$\delta(^{31}P)$: -31.0 ppm]. No unreacted quinone was present in the reaction mixture.

Compound 32 (*cf* Scheme 1) to our knowledge is the first hexa-coordinated arsorane with 1,3,2-dioxarsenane rings and with an internal N→As donor-acceptor bond [X-ray, Section **II.8.4].** In contrast to its precursor $ClAs(OCH_2CMe_2CH_2O)_2$ (31) or the product from the reaction of 31 with 2,4,6-trimethyl phenol/ triethylamine which were not sufficiently stable to be fully characterized, 32 is air stable. This stability may be associated with the strong internal coordination.

Assuming that hexa-coordination persists in solution, we can easily recognize that the two six-membered arsenane rings in 32 should be chemically and magnetically nonequivalent; the ^1H NMR spectrum [Fig. 1] shows four methyl signals [0.72, 1.02, 1.11 and 1.17 ppm] of equal intensity and a large number of lines (3.30-4.80 ppm] for the $OC\underline{H}_2$ protons showing the non-equivalence of these protons and thus the rigidity of the hexa-coordinated strucure. Assuming nonequivalence of all the $OC\underline{H}_A\underline{H}_B$ protons, 16 lines are expected for 32 with $J(H_A\text{-}H_B) \approx$ 12.0 Hz. This is actually observed with the peaks numbered (l)-(4) in Fig. 1 showing further fine structure due to $^4J(H\text{-}H)$ of *ca* 3 Hz [Such a $^4J(\underline{H}\text{-}\underline{H})$ coupling has been reported for cyclic phosphites before[86]]. The ^{13}C NMR spectrum of 32also exhibits four distinct signals for the methyl and $O\underline{C}H_2$ carbons.

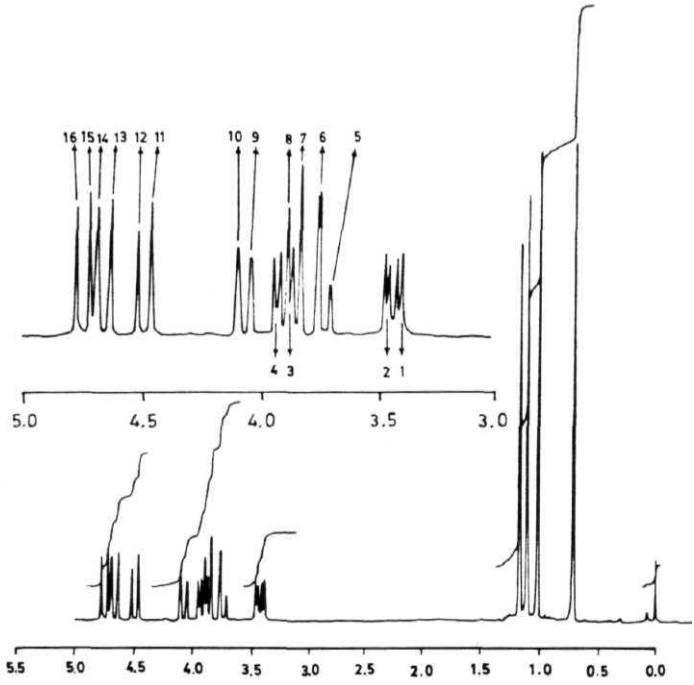
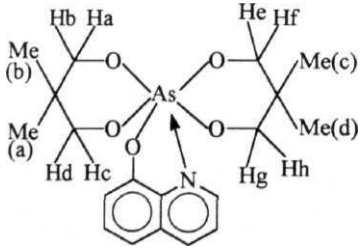


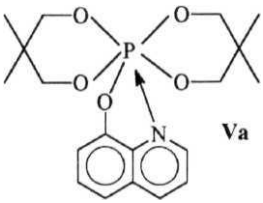
Fig. 1. ^1H NMR spectrum [0.0-5.0 ppm] of 32



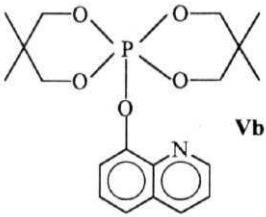
32

It should be noted here that both 31 and $PhP(OCH_2CMe_2CH_2O)_2$[37(h)] which contain two six-membered rings each show only one signal for either $OC\underline{H}_2$ or CH3 protons because of Berry pseudorotation (or an equivalent exchange) process.

For the synthesis of the phosphorane V the route adopted for the analogous arsorane 32 is not feasible because the intermediate $ClP(OCH_2CMe_2CH_2O)_2$ [III,



Va

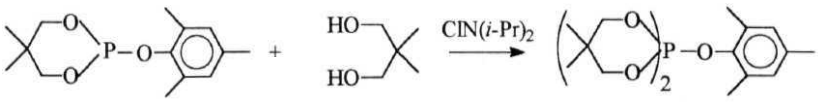


Vb

Scheme 2] is unstable and leads to the terra-coordinated derivative 30 (Schemes 1 and 2). As an alternative route, the phosphite $(NC_9H_6O)P(OCH_2CMe_2CH_2O)$ (8a) was reacted with 2,2-dimethyl-1,3-propanediol/ NCDA [Scheme 1]. The reaction occurs readily and the required amount of $[H_2N(i\text{-}Pr)_2]Cl$ is obtained. ^{31}P NMR spectrum of the reaction mixture exhibits a peak at -67.0 ppm. We attribute this signal to Vb* [see also ^{31}P NMR section for comparative data] which does not have $N\rightarrow P$ coordination.

On attempted crystallization from several batches, we obtained an air sensitive crystalline product 42 *(ca* 10% yield) with a $\delta(^{3}1p)$ of -127.0 ppm (br). In the ^{1}H NMR, this product showed a singlet for the CH3 protons and a doublet for the $O\underline{C}H_2$ protons [$^{3}\underline{J}(\underline{P}\text{-}\underline{H})$ * 20 Hz]; the signals were broad. The

* This assignment is based on the comparison of the ^{31}P NMR shift of V with that of the product mixture obtained from the following reaction:



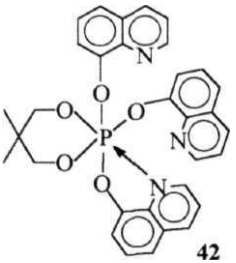
15

A

^{31}P: -68.9, -66.8 ppm

[possibly isomeric products differing in the dispositions of substituents or due to different conformations of the phosphorinane ring are formed; pure product could not be isolated].

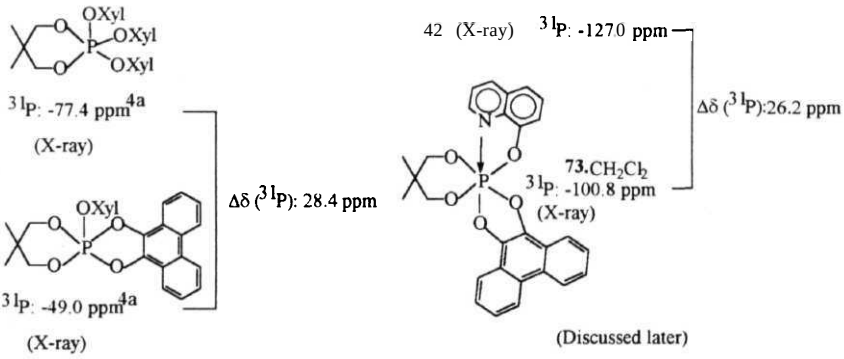
integrated intensities (^1H NMR) and the elemental analysis showed that the oxinate to glycolate ratio was *ca* 1:3; this clearly showed that 42 is not the expected product. A partial X-ray structure [sample was too unstable and good set of data could not be collected*] done on this sample shows that it has the structure shown. [see Appendix 1 for a plot of the molecule]. This assignment is consistent with ^{31}P NMR data also:**



42

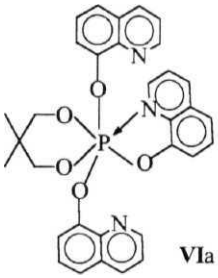
*R. H. Irmer, *personal communication.*

**

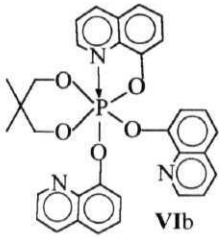


[Note that the right set has an oxinate in place of -OXyl found in the left set].

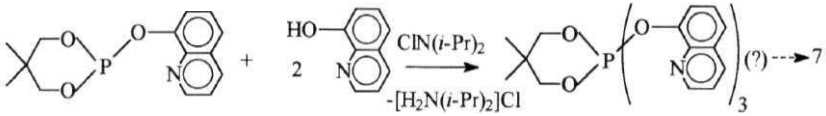
It can be readily recognized that two more isomers [**VIa** and **VIb**] are possible for this formula of (42) and hence we checked the direct route [eq. 7]



VIa



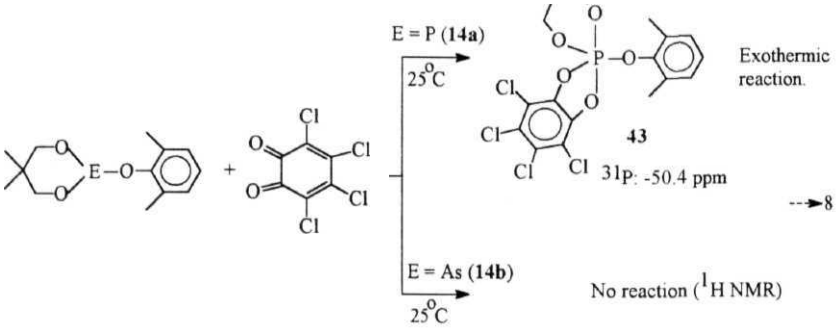
VIb



Surprisingly the reaction mixture showed a major signal (>95%) in the ^{31}P NMR at -111.6 ppm (hexa-coordinated region); unfortunately this product could not be isolated free of amine hydrochloride and the hydrolyzed product [δ_p: -14.1 ppm; attributed to $(OCH_2CMe_2CH_2O)P(O)(OC_9H_6N)$ by comparing the δ_p with that of $(OCH_2CMe_2CH_2O)P(O)(O\text{-}2,6\text{-}Me_2C_6H_3)$ (28) (δ_p: -14.1 ppm)] and hence this reaction was not analyzed further.

More reactions wherein ring exchange occurs are discussed in section **II.5**.

It can be noted that the arsenic derivative $(OCH_2CMeCH_2O)As(OC_9H_6N)$ (8b) (Scheme 1) did not react with 2,2-dimethyl-1,3-propanediol/ NCDA. Such a reluctance to undergo oxidative addition is observed for the arsenite 14b also (eq. 8); the corresponding reaction of the phosphite 14a with o-chloranil is highly exothermic and needs cooling (or dilution with a solvent).



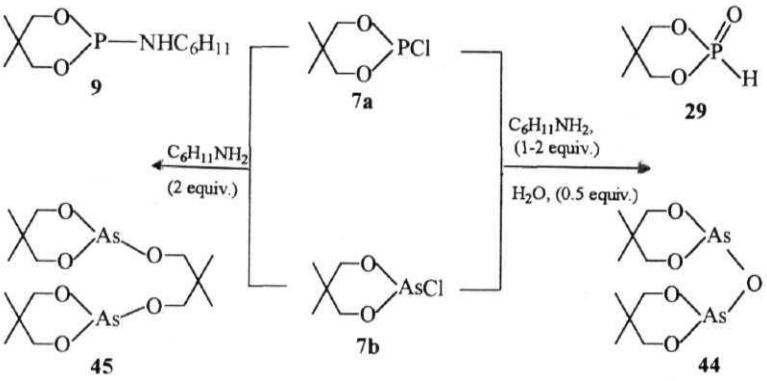
The difficulty in obtaining penta-coordinated arsoranes (e.g. $AsCl_5$) as compared to phosphoranes has been attributed to "d-block contraction" for arsenic [87] Our results in the present study are in line with this.

II.3 *Hydrolysis, Reaction with Sodium and Donor-acceptor Characteristics of Cyclic Phosphites/ Arsenites*

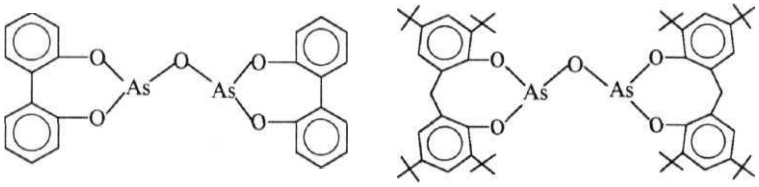
II.3.1 Reactions **with** amines in the presence/ absence of water (Hydrolysis)

The reaction of compounds 7a and 7b with cyclohexylamine in the presence and in the absence of water proceeds in entirely different ways (Scheme 3). Compound 29 is formed almost exclusively from 7a when 1 mole equiv. of water is used in the presence of triethylamine[8,79] or cyclohexylamine; even when 0.5 mol equiv. of water is used 29 is the only significant product observed. Under similar conditions, compound **16a** and **21a** also afforded products with =P(O)H linkages (^1H, ^{3} lp NMR). By contrast, when the arsenic precursors 7b, **16b** and

Scheme 3



21b are used the oxy-bridged derivatives 44, 46[88] and 47 are obtained as crystalline compounds.



46 [88] 47 (X-ray)

The formation of compounds 29 and 44 can be easily rationalized by invoking the reluctance of arsenic to achieve the +5 oxidation state as against the tendency of phosphorus to form P=O bonds.

Under anhydrous conditions, in contrast to the ready formation of the amino phosphites 2, 6, 9, **10**[73] and 18 from the chlorophosphites, the arsenite 7b afforded the bridged compound 45; the reaction mixture as well as the distillate showed cyclohexyl peaks (^{1}H NMR) in variable amounts indicating the presence

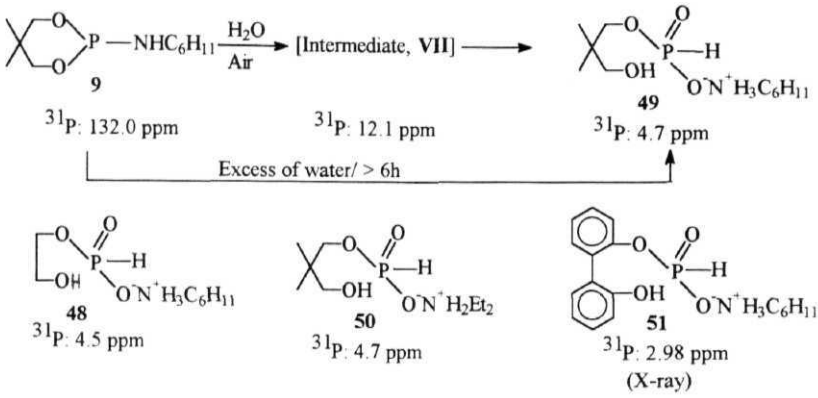
of other products, presumably of the type $ClAs(NHC_6H_4)_2$ or $[ClAsNC_6H_4]_n$. By treating 7b with sodium, pure compound 45 has been independently synthesized and characterized (see below for more details).

Although the formation of 45 is puzzling, it has been observed that arsenanes have a tendency to oligomerize leading to bridging groups as, for example, in the case of $MeAs(OCH_2CH_2CH_2O)$;[89] it is possible that the intermediate amine product undergoes reorganization to lead to 45 and other As-N derivatives.

Since the arsenic analogue of 9 could be a possible intermediate in the formation of 45 (or 44), we have explored the hydrolytic behaviour of 9 and similar phosphorus compounds 2, 6, 10, 18, and 24 in more detail. The only compound that we could characterize satisfactorily in these reactions were double hydrolysis products as their amine salts (Scheme 4). Thus compounds 48, 49, 50 and 51 were obtained from 2, 9, 10 and 18 respectively. Compound 24 did not react; in the case of 6 although the elemental analysis for the product is close to the expected values, the P-H proton was not clearly visible in the ^1H NMR spectrum. The identity of 51 is proved by X-ray structural analysis.

The hydrolysis of compound 9 occurs in a stepwise fashion. The phosphorinane ring is cleaved in the first step to afford the intermediate VII [compare the hydrolysis of compound 13a (Scheme 5)]. In Fig. 2, the ^1H and ^{13}C NMR spectra of the intermediate VII along with those of 9, 49, and 29 (^1H only) are shown. The appearance of two triplets in the ^1H NMR and an AB pattern for the cyclohexyl N-CH-C carbons with $^3J(P\text{-}C)$ 4.5 Hz in the ^{13}C NMR spectrum indicates a strongly H-bonded system involving $CH_2O\underline{H}$ and $N\underline{H}C_6H_{11}$ protons. Since no reaction occurs between cyclohexylamine and compound 29 upon

Scheme 4



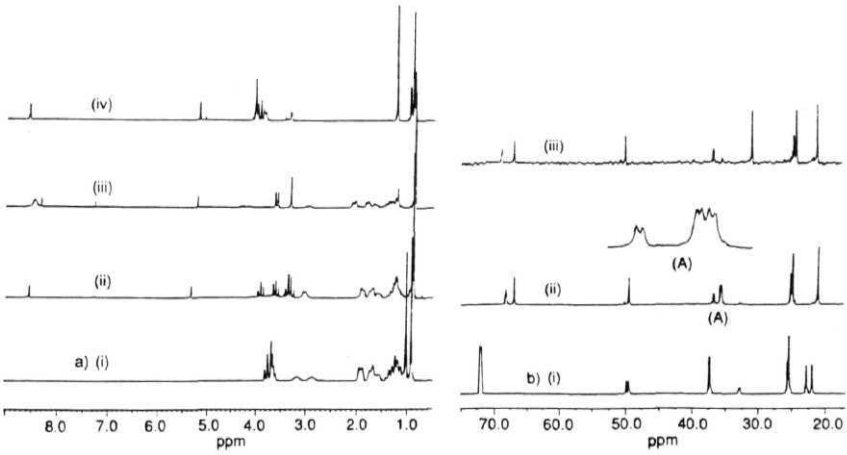
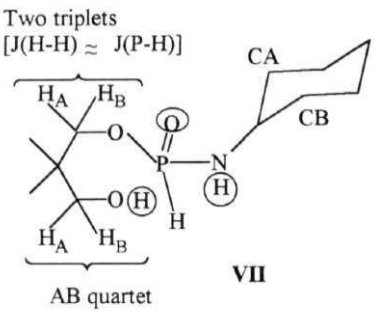


Fig. 2 (a) ^{1}H NMR spectra of (i) 9 (ii) intermediate **VII,** (iii) **the** amine salt 49, **and** (iv) phosphonate 29. (b) ^{13}CNMR spectra of (i) 9 (ii) **VII and** (iii) 29.

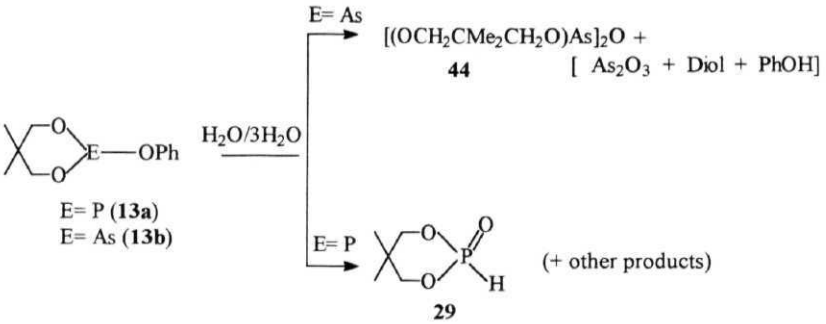
mixing, the ring-cleaved product $(HOCH_2CMe_2CH_2O)P(O)(H)(HNC_6H_{11})$ (note that this formula corresponds to an equimolar mixture of 29 and cyclohexylamine) is a likely structure for **VII.** The non-equivalence of the protons and carbons due to H-bonding as observed for **VII** is, to our knowledge, quite rare. H-bonding involving the circled atoms (and water molecules) as shown above may be operative.



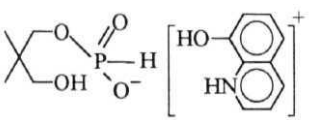
VII

The synthesis of alkoxy/ aryloxy phosphites (Chart 1) as well as arsenites is very straightforward; however their β hydrolysis leads to different types of products. For example, compound **13a** gives the cyclic phosphite 29 whereas the corresponding arsenite **13b** affords **44** as the major product along with As_2O_3, 2,2-dimethyl-l,3-propanediol and phenol [Scheme 5]. Hydrolysis of the arsenites **11b**, **12b** and **14b** also gave the same product 44 along with diol, As_2O_3 and the alcohol/ phenol. The same factors as explained for the behaviour of amine derivatives are responsible for this difference. In this connection, it is also interesting to note that we have been able to make use of the lability of As-0 bonds to obtain 44 by treating As_2O_3 with 2,2-dimethyl-l,3-propanediol (and *vice versa).*

Preservation of the phosphorinane ring in the hydrolysis of **13a** [Scheme 5] and its cleavage in the case of 9 [Scheme 4] is an interesting contrast between aryloxy and aminophosphites and may be attributed to the difference in H-bonding and the presence/ absence of a basic nitrogen centre in the mechanistic pathways of the two reactions.



Interestingly, hydrolysis of the oxinate compounds 8a and 17 afforded only the double hydrolysis products 52 and 53 respectively *[cf.* hydrolysis of 13a; Scheme 5]. It is likely that the oxinate nitrogen (basic site) plays a role in this hydrolysis.



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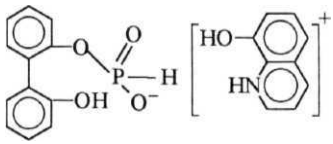
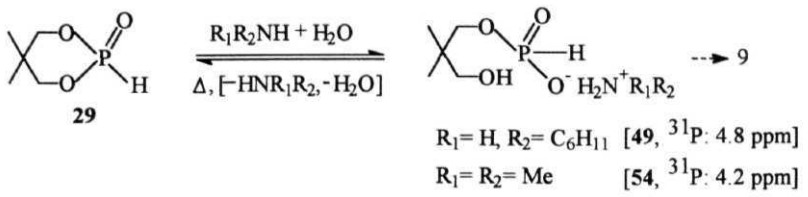
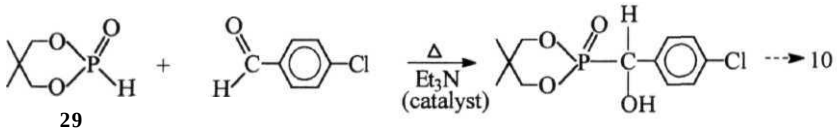


53

Although intermediate VII [Scheme 4] is detected in the hydrolysis of 9 leading to 49, it should also be noted that the cyclic phosphite 29 upon treatment with amine/H_2O leads to ring cleavage readily (eq. 9). This suggests that the formation of products such as 49 can occur either by cleavage of the phosphorinane ring or the P-NR_1R_2 bond as the first step.



The reaction shown in eq. 9 is REVERSIBLE. In the backward reaction we have confirmed the formation of 29 by distilling the compound as well as by derivatization using the Pudovik reaction (eq. 10).[90]

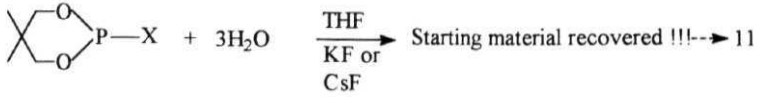


M.p. 173°C

^{31}P: 12.9 ppm[90]

Although there are a few reports of cyclization of analogous nature,[91] we believe that we have provided a concrete example of such a reaction.

It has been shown by Corriu and coworkers that KF and CsF activate alcoholysis of $(OCH_2CH_2CH_2O)P(O)F$;[92(a)] similarly the hydrolysis of phosphate esters (ArO)P(O)(OMe)2 is catalysed by KF.[92(b)]. In effort to study activation, if any, in the hydrolysis of cyclic phosphites we treated 9, **11a** and **13a** with KF (or CsF)/ water in THF (eq. 11). Surprisingly, however, the $CDCl_3$ extract of the residue obtained after the removal of the solvent (THF + water) contained >90 % of the P^{III} precursor [^{31}P and ^{1}H NMR; note that the hydrolyzed products 29 and 49 are very soluble in chloroform]. Thus it appears that KF (or CsF) inhibits the hydrolysis of phosphites.



X = NHC_6H_{11} **9**

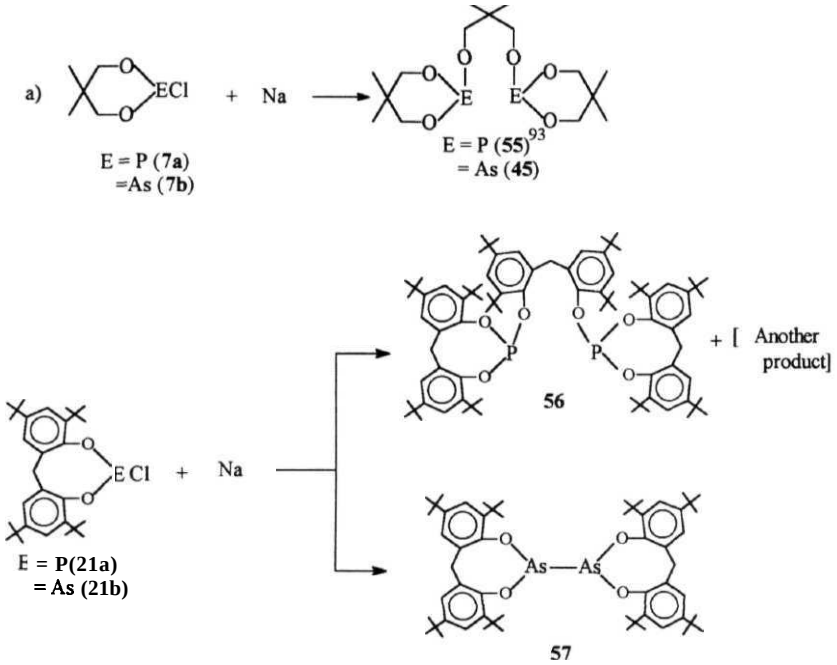
= OPr^i **11a**

= OPh **13a**

The opposing effect of KF in the hydrolysis of phosphate esters *vis* a *vis* phosphites may be due to different mechanistic pathways; it would require a more detailed study under comparable conditions.

II.3.2 Reaction with sodium:

As another line of activity towards a comparative assessment, we have conducted reactions of chlorophosphites and arsenites with sodium [Scheme 6]. The ^1H and ^{13}C NMR spectra [Fig. 3] as well as mass spectrum conclusively establish the identity of 55.[93] Three signals of equal intensity [two axial methyls, two equatorial methyls and two methyls of bridging glycolate] are observed in the ^1H NMR: a triplet (or a dd, J(H-H) = J(P-H) * 8 Hz, equatorial protons),[86] a doublet [J(P-H)= 8 Hz, OCH_2 or bridging glycolate] and a doublet (J(H-H)= 12 Hz, $^3J(\underline{P}\text{-}\underline{H}) < 1$ Hz, axial protons)[86] are also observable. The ^{13}CNMR shows a characteristic triplet at 36.8 ppm [$^3J(\underline{P}\text{-}\underline{C})$ = 6.6 Hz] for the $\underline{C}Me_2$ of the bridging glycolate as expected.



The arsenic precursor 7b also behaved similarly; the ^{1}H and ^{13}C NMR spectra of pure 45 are analogous to that of **55**. In contrast to earlier reports on similar reactions with 2-chloro-l,3,2-dioxaphosphorinanes[94] $ClP(1,2\text{-}S_2C_6H_4)$,[95] or $(OC_6H_4C_6H_4O)AsCl$ (16b),[96] we did not observe any E-E bonded species in the reactions of 7a and 7b.

In the case of the eight-membered ring systems, using **21a** we obtained the bridged compound 56 [^{31}P: 136.4 ppm; Scheme 6] whereas the arsenic analogue **21b** afforded the As-As bonded compound 57 [^{1}H NMR CH analysis]. Both 56 and 57 are crystalline products.

In the reaction of **21a** with sodium an additional peak at 185.3 ppm was observed in the ^{31}P NMR but the product could not be isolated; it is tentatively assigned to a P-P bonded compound similar to 57.

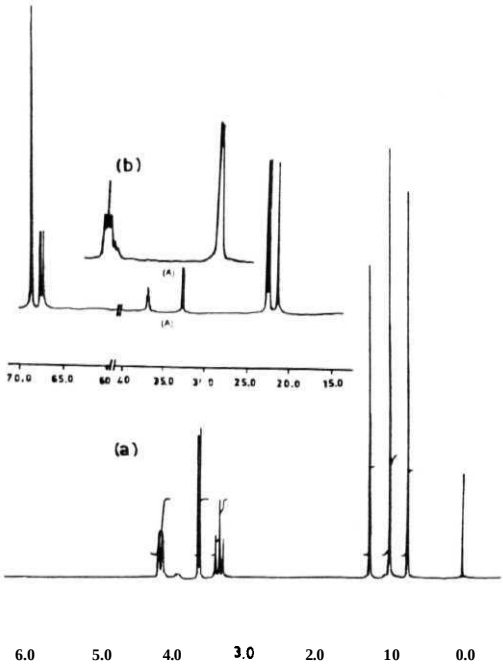


Fig. 3. ^{1}H and ^{13}C NMR spectra of 55

From the two pairs of examples studied here and from the literature data it appears that reactions of chlorophosphites/ arsenites with sodium give either E-E bonded species [e.g. 57] or bridged compounds (e.g: 45, 55, 56) depending on the substituents; the phosphorus and arsenic systems probably do not show significant differences.

The mechanism of formation of a bridged species like 55 would involve ring opening and formation of NaP_X (or $NaAs_X$); indeed the insoluble material obtained during these reactions is black [$\therefore$ not entirely NaCl] suggesting the formation of a phosphide/ arsenide also.

II.3.3 Donor-Acceptor properties:

Although the phosphite $(OCH_2CMe_2CH_2O)P(OPh)$ (13a) reacted readily with $Mo(CO)_4(NBD)$ upon heating [^{31}P NMR]: the corresponding arsenite 13b was unreactive. The oxo-bridged derivative 44 also was unreactive towards $Mo(CO)_4(NBD)$, bipyridyl (a base) or 2,2-dimethyl-l,3-propanediamine showing that it has weak or no donor-acceptor character.

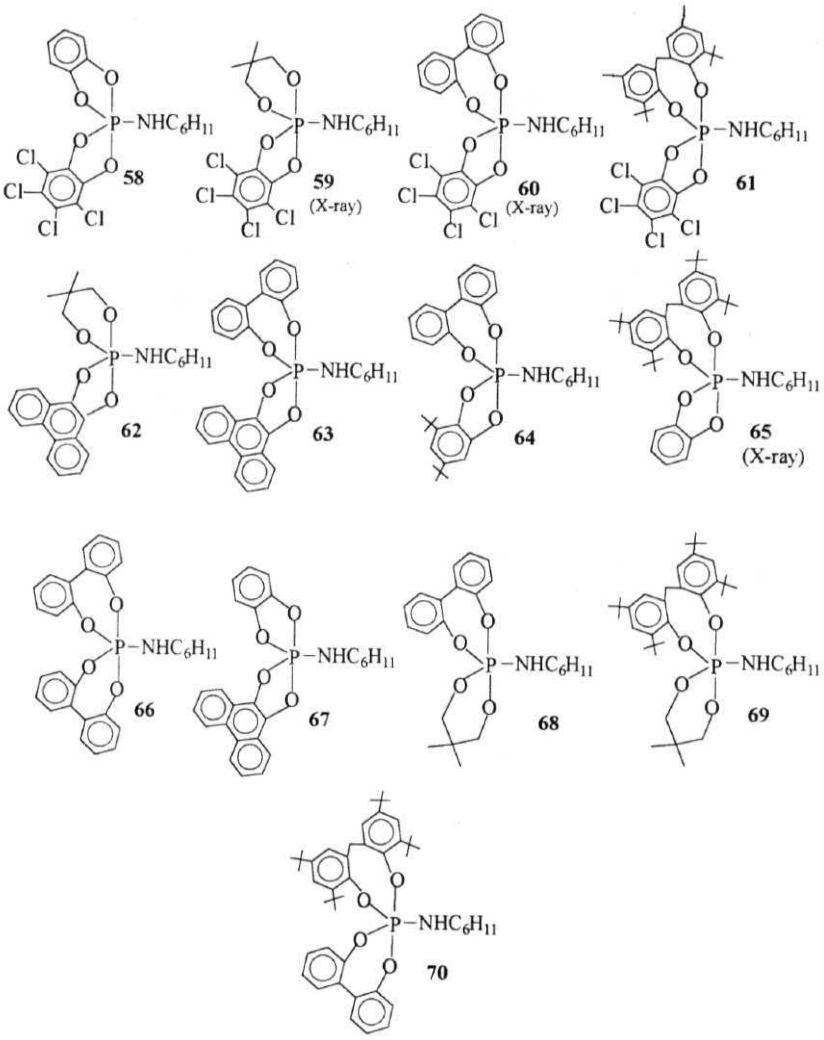
However, the arsenic in compound 44 appears to be weakly acidic; in the solid state, weak interactions are observed between arsenic and one of the oxygen atoms of the 1,3,2-dioxarsenane ring. The acidity at the arsenic centre is also reflected in compounds 8b, 17b and 22b which show internal N→As coordination (see section II.8.1 for more details).

II.4 *Spirocyclic Phosphoranes with a Cyclohexylamino Substituent: Synthesis, Structure and Reactivity*

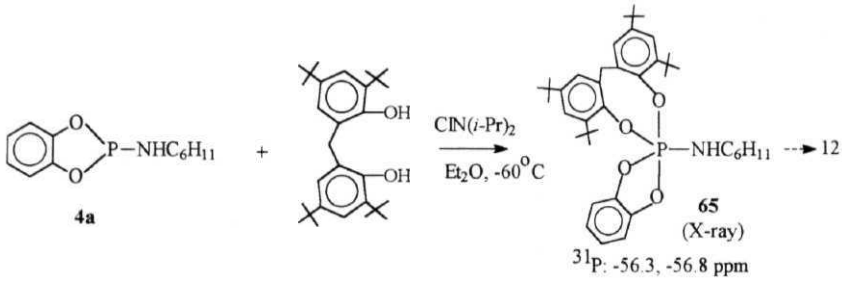
Several phosphoranes with cyclohexylamino substituent have been synthesized in the present study in an effort to (i) study the effect of H-bonding (if any) on the conformational features of different sized rings [see Introduction, section I.3.1], (ii) study the effect of ring size on ^{31}P NMP chemical shifts and (iii) compare their structure and reactivity with the respective tri-coordinate species. Points (i) and (iii) will be discussed in later sections II.7 and II.8 respectively.

The structural formulae for the isolated compounds 58-66 are shown in Chart 2 along with those identified by NMR spectra [67-70]. Synthesis of all these compounds is accomplished by the general routes given in section III.3. The

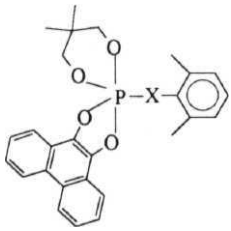
CHART 2



reaction using diol/ NCDA is illustrated for the preparation of 65 (eq. 12).



The ^{31}P NMR spectra of **58-70** are in the expected penta-coordinated region [-29 to -71 ppm][6(a),60,69]. The ^{1}H NMR spectra in the region 3.0-4.58 for compounds 59, 60, 43 (penta-oxyphosphorane), phosphite 9 and phosphoramidate 7 are shown in Fig. 4. The spectra of 9 and 7 in the $OC\underline{H}_2$ region are of AA'BB'X



X = S **(VIII)** [37(f)]

= O **(IX)** [37(f)]

[X = ^{31}P] **and** AA'MM'X [X = ^{31}P] respectively as expected for a chair conformation of the phosphorinane ring.[12] The spectrum of 62 is similar to that for the phosphorane **VIII**[37(f)] where as the oxyphosphorane 43 shows a spectrum similar to that of **IX**[37(f)] **[all** recorded at 24°C]. The $OC\underline{H}_2$ region in 59 (24°C) is a doublet ($^{3}J(\underline{P}\text{-}\underline{H})$ = 20 Hz) and is analogous to the spectrum of **VIII** at > 41°C.

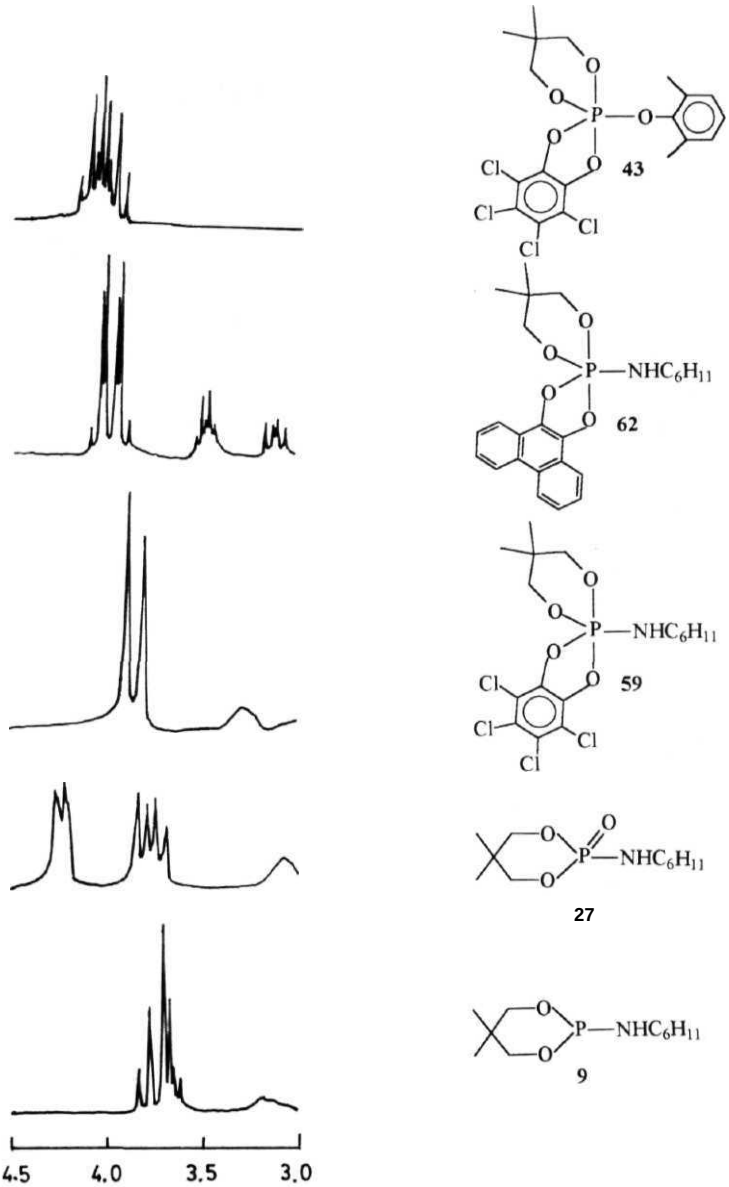
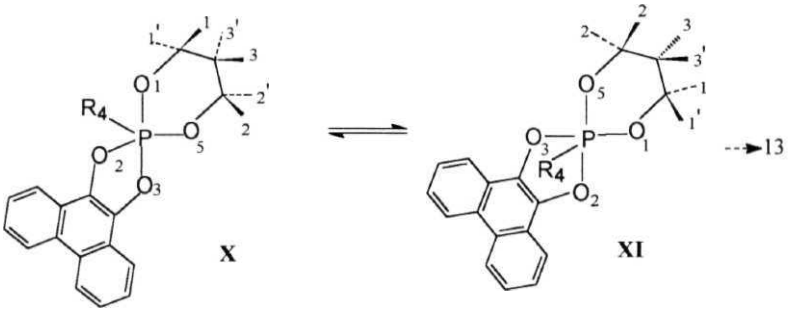


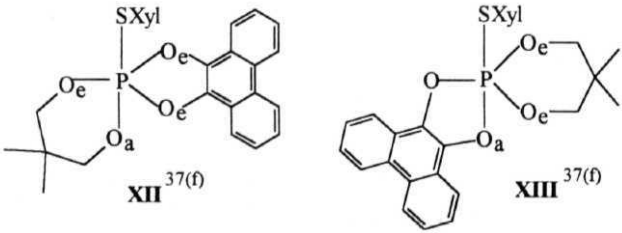
Fig. 4 The ^{1}HNMR spectra of compounds 9, 27, 59, 62 and 43 in the OCH_2 region

The room temperature (24°C) spectra of **VIII** and **IX** have earlier been interpreted as due to the Berry process depicted below:

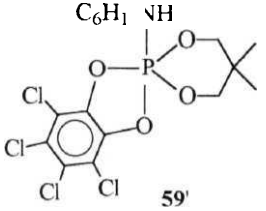


This process leads to two types of methylene ring protons [with $^{3}J(P\text{-}H)$] for the phosphorinane ring. By analogy we believe that such a process is taking place for compounds 43 and 62 at 24°C [VT NMR facility was not accessible for the current study].

The OCH_2 doublet observed for **VIII** at > 41°C has been interpreted by Holmes as due to an intermediate of the type **XII** and not due to **XIII**;[37(f)] it has been said that the structure **XIII** will not make all the OCH_2 protons equivalent. We think that a Berry process involving **XIII** *can* make the OCH_2 protons equivalent because a *diequatorial* placement of the phosphorinane ring as in **XIII**

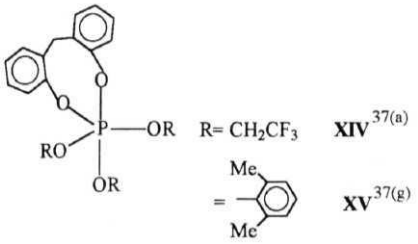


could change the ring conformation [from *boat* to *chair*].[26] It can be noted that placing the flexible six-membered ring *diequatorial* as in XIII would require less energy than placing the more rigid five membered ring *diequatorial* as in XII. Thus intramolecular processes involving (i) a-e ↔ e-a exchange as in eq.13 and (ii) a-e ↔ e-e exchange involving 59' are proposed for the observed equivalence of the $OC\underline{H}_2$ protons in 59.



59'

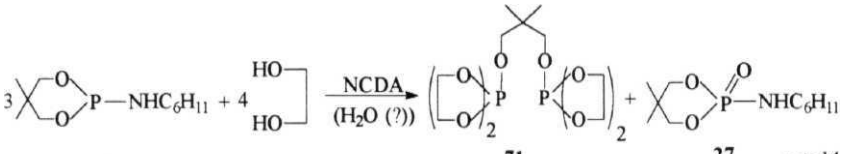
Compound 65 exhibits two closely spaced signals (probably isomers) in the ^{31}P NMR [-56.3, -56.8 ppm]; the ^{1}H NMR spectrum shows broadened signals and isomers were not distinguishable. The $C\underline{H}_2$ region in 61 and 65 shows a non-coalesced AX pattern with $^{2}J(H_A\text{-}H_X)$ of 14 Hz. This feature contrasts with that observed for **XIV**[37(a)] and **XV**[37(g)] for the $C\underline{H}_2$ protons; in the case of XV the $C\underline{H}_2$ protons were resolved into an AX pattern at -44°C. Thus it appears that the exchange process [a-e↔e-a or a-e↔e-e] occurring in XIV or XV is hindered in our compounds 61 and 65; its exact nature is difficult to ascertain due to the nonavailability of VT ^{1}H NMR data.



Since the compounds 58-66 are sufficiently stable to be readily isolated, we expected that it should be possible to isolate compound 69 (Chart 2). However, no matter whether we used 9 or 24 as the P^{III} precursor, the product 69 (^{31}P:-70.3)

was always contaminated with the hydrolyzed product (^{31}P: -13.7 ppm)*; when 9 was used a small quantity *(ca 5%)* of 27 (^{31}P NMR: 4.2 ppm) was also often observed.

In contrast to the above reactions, when $(OCH_2CMe_2CH_2O)P(NHC_6H_{11})$ (9) is treated with ethylene glycol/ NCDA the expected phosphorane $(OCH_2CMe_2CH_2O)(OCH_2CH_2O)P(NHC_6H_{11})$ is *not isolated;* instead the phosphoramidate 27 and a diphosphorane formulated as 71 (eq. 14) are isolated as crystalline solids.



9 71 27 ⟶ 14

^{31}P: -28.1 ppm

Compound 71 (^{1}H, ^{31}P, CHN) is very moisture sensitive and becomes a liquid as soon as it is exposed to air. It can be noted that the δ_p value for 71 is close to that for the monophosphorane $(OCH_2CH_2O)_2P(OEt)$[97] [^{31}P: -27.0]. Although this is a surprising result, we have noted the cleavage of six-membered rings while preparing the hexa-coordinated phosphoranes also [section **II.5**].

In an effort to compare the relative ease of replacing the amino groups, we reacted 9, 27 and 62 with 8-hydroxy quinoline (Scheme 7). Only in refluxing p-xylene (10h) 62 reacted with 8-hydroxy quinoline, but instead of the expected product $(OCH_2CMe_2CH_2O)(O_2C_{14}H_8)P(OC_9H_6N)$ [^{31}P: -100.8; section II.7], a

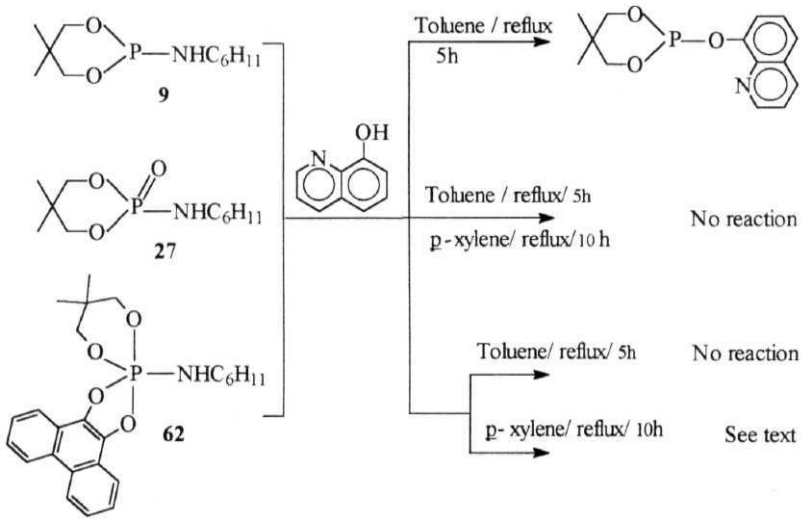
* Assigned to $(OCH_2CMe_2CH_2O)P(O)(O\text{-}(t\text{-}bu)_2C_6H_2\text{-}CH_2(t\text{-}bu)_2C_6H_2\text{-}OH)$ [^{1}H NMR for the reaction mixture shows that the phosphorinane ring is retained; ^{31}P NMR chemical shift is close to that for 28 (6 - -14.1)].

peak at $\delta(^{31}P)$: -78 ppm (corresponding to a hexa-coordinated system with only five membered rings) was observed.

The important point to note here is that the tri-coordinated derivative 9 is more reactive than either the tetra-coordinated (27) or the penta-coordinated (62). derivative. Both 27 and 62 are more resistant to hydrolysis and can be handled in air for a few hours *[cf.* Compound 9, Scheme 4].

The results are similar in the reaction of 8-hydroxy quinoline with 18 (tri-coordinated) and 64 (penta-coordinated).

Scheme 7



The above observations can not be simply due to steric factors because for 9 and 27 at least there does not appear to be much hindrance for a nucleophilic attack; P-N bond lability as well as bond strength may contribute significantly. In

fact it can be noted that the P-N bond is longer in the phosphites 9 and **21**, *albeit marginally*, than in the phosphoranes 59 and 65 respectively [section II.8].

II.5 *Penta- and **Hexa-coordinated** Phosphoranes with an **Oxinate/ Carboxylate Substituent***

When oxinate is used as one of the substituents in oxyphosphoranes its nitrogen can provide the sixth coordination site by means of a donor-acceptor N→P bond to form a chelate five-membered ring unless there are adverse steric and electronic factors involved. Even a carboxylate group can, in principle, provide the sixth coordination site *via* the carbonyl oxygen. This section covers the results obtained in the oxinate/ carboxylate systems. The isolated oxinate compounds 72-79 are shown in Chart 3.

Synthesis of these compounds involves the same general methods as described in section III.3; however formation of 77 involves a novel ring exchange and hence its synthesis is illustrated in eq. 14 (along with that of 77):

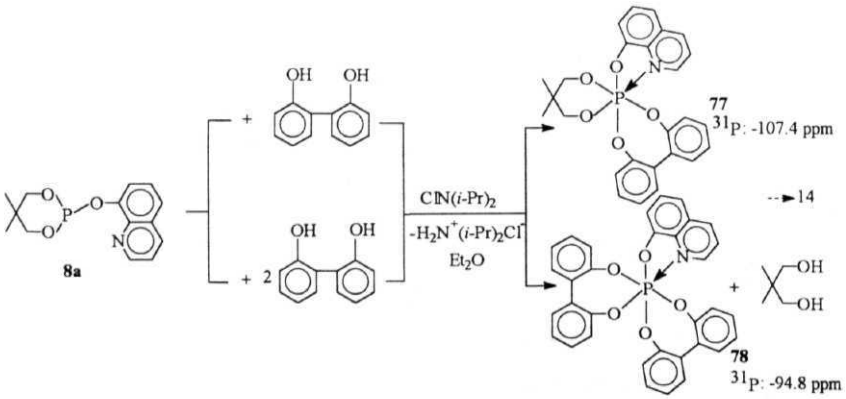
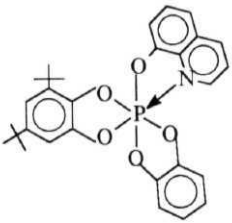
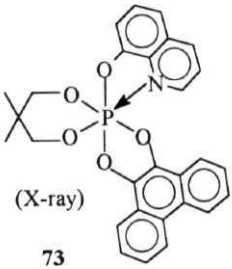


CHART-3

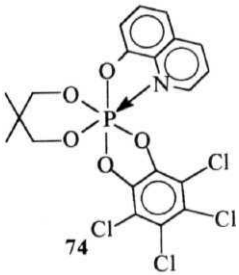


72

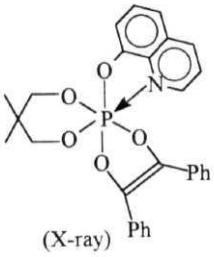


(X-ray)

73

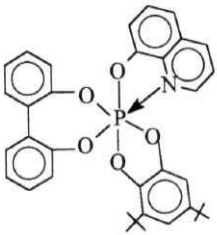


74



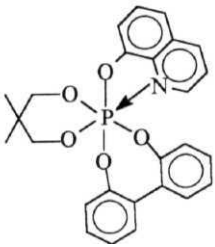
(X-ray)

75

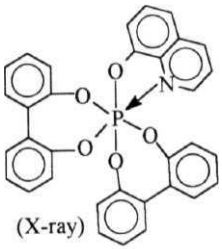


(X-ray)

76

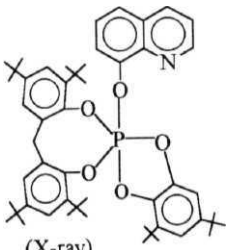


77



(X-ray)

78



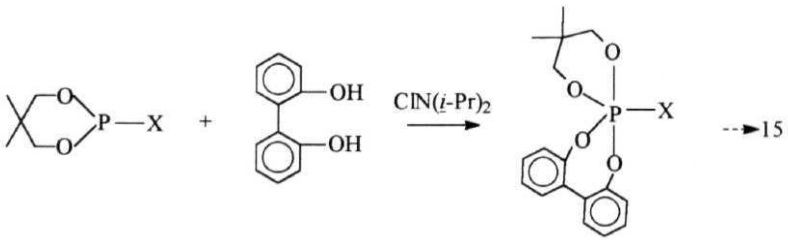
(X-ray)

79

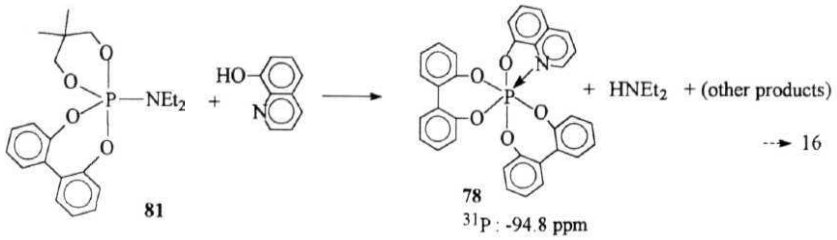
By careful fractional crystallization of the precipitate (1:1 reaction) from dichloromethane-heptane mixture compound 77 was isolated in yields of *ca* 50%. However the crystalline solid 78 which came out from the ether filtrate as the etherate in 6-7% yield *was a surprise.* This compound containing two 2,2'-biphenoxy units must arise from the exchange of the six-membered phosphorinane ring by the seven-membered phosphepin ring; the yield of 78 could be significantly enhanced (to 30%) by using a 1:2 molar ratio of cyclic phosphite to 2,2'-biphenol.

The above exchange reaction leading to 78 is unique because when a 2,6-dimethyl phenoxy or 2,4,6-trimethyl phenoxy or diethylamino group is used in place of oxinate, no such phenomenon is observed (eq. 15).

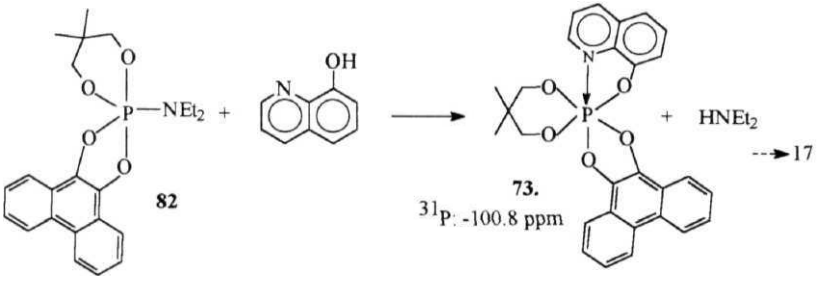
What is perhaps more puzzling is the reaction of 81 with 8-hydroxy quinoline to yield 78 (eq. 16). It can be noted that *even though no 2,2'-biphenol has been added, the reorganization still lakes place.*



X= 2,6-$Me_2C_6H_3O$ [37(h)]
= 2,4,6-$Me_3C_6H_2O$ I
= NEt_2 81

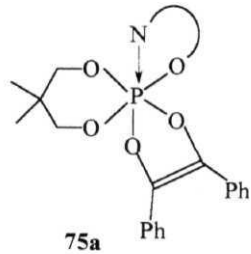


By contrast, the aminophosphorane 82 upon treatment with 8-hydroxy quinoline afforded the ring preserved compound 73 which could be readily isolated (eq. 17) [the normal route of adding quinone to phosphite 8a also gives a better yield of 73].

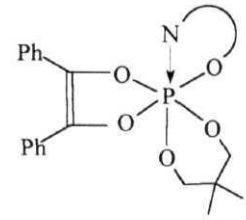


It is difficult to ascertain the reason for the exchange of the six-membered phosphorinane ring by the seven-membered phosphepin ring thereby leading to the preferential formation of the (7+7+5) ring compound 78. Two factors which may be responsible for this are (i) the aromatic residues on the seven membered 1,3,2-dioxa-phosphepin rings increase the acidity on phosphorus and hence its ability to form a stronger N→P bond in 78 than in either 73 (and 75) or 76 as seen by the shortest N→P bond (1.938A^0; section **II.8**) 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.

The solution state ^{31}P NMR chemical shifts of 72-78 [-80 to -110 ppm] are upfield to those of the analogous penta-coordinated derivatives [section II.7]; the δ_p value of -56.9 ppm for 79 shows that this compound is penta-coordinated in solution. All these data suggest that the coordination numbers (6 or 5) observed in the solid state [X-ray structures obtained for 73, 75, 76, 78 and 79] are retained in solution for these compounds. Only one isomer is observed (e.g. 75a) in each case, although isomeric products [*cf.* 75a, 75b] are possible.



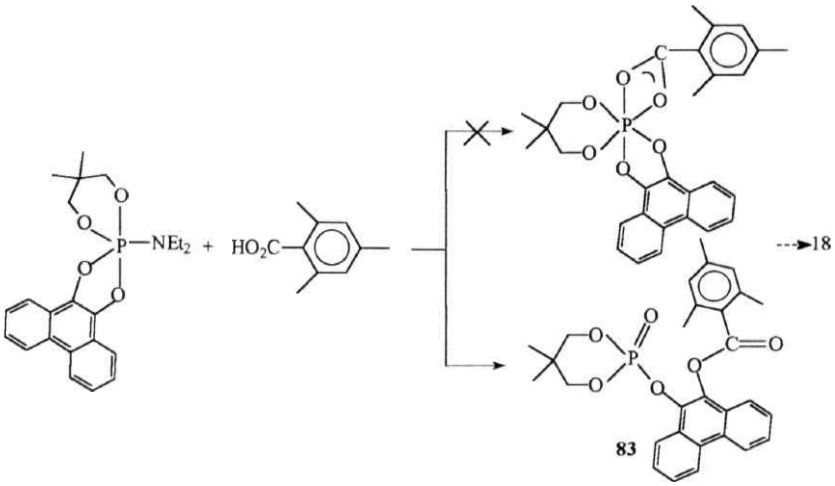
75a



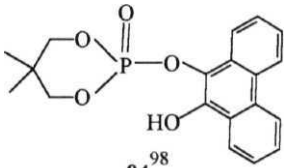
75b

Assuming a rigid hexa-coordinated structure with the N→P bond *trans* to a P-0 bond of the phosphorinane ring [section II.8], we can expect a maximum of 16 lines for the $OC\underline{H}_2$ protons and two lines for the CH3 proton" of 73-75 in the ^1H NMR. Actually 73 shows a broad doublet at 4.15 ppm [^3J(P-H) = 18 Hz] whereas 74 and 75 exhibit a multiplet pattern for $OC\underline{H}_2$ protons; the axial and equatorial CH3 protons show distinct signals in all the three compounds. We ascribe the observation of the doublet in 73 to accidental coincidence of the $OC\underline{H}_2$ protons since isomerism is not observed.

As far as the carboxylates are concerned we first tried the reaction shown in eq. 18.



The crystalline compound 83 (M.p. 160°C) obtained from the above reaction showed a peak at -14.4 ppm in ^{31}P NMR, consistent with a tetra-coordinated phosphate ester; the IR spectrum showed an ester band at 1742 cm^{-1} with no v (O-H) bands. Finally, the ^{1}H NMR spectrum as well as elemental analysis confirm that the structure of the compound is as shown. When benzoic acid is used in place of 2,4,6-trimethyl benzoic acid, the only phosphorus compound we could isolate was the known product **84**.[98]

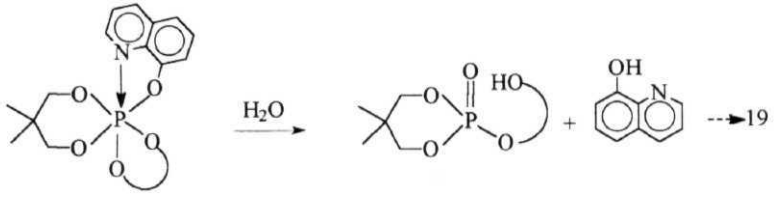


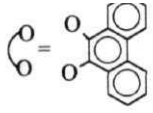
84[98]

Although the formation of 84 is similar of 83, the transfer of an entire acid residue as observed in the latter, is unprecedented. [However, transfer of an $-NEt_2$ group is known.[6]]

II.6 *Hydrolysis of **Hexa-coordinated** Phosphoranes*

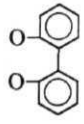
In our attempts to obtain crystalline hexa-coordinated derivatives, we often encountered hydrolysis leading to phosphate esters as a major problem. Since phosphorus bears more than one ring in our penta- and hexa-coordinated phosphoranes, different products result depending on which ring is cleaved. This aspect relates to the stability of phosphoranes containing different ring systems. Selected results are described below. Eq. 19 represents the general reaction.



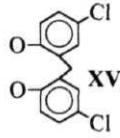


73 (^{31}P: -100 ppm) **84** (^{31}P: -10.2 ppm)[98]

XVII (^{31}P: -102.4 ppm) **85** (31P:-12.7 ppm)



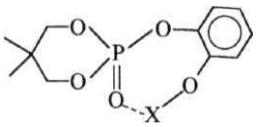
77 (^{31}P: -107.4 ppm) 86(31p-15.1ppm)



XVIII (^{31}P: -127.1 ppm) **87** (^{31}P: -14.4 ppm)

Compounds 84-87 are pure by ^{31}P NMR. However 84 obtained from this route is contaminated with 8-hydroxy quinoline; analytically pure 84 is obtained by either (i) reaction of 82 with benzoic acid or (ii) hydrolysis of Ramirez's

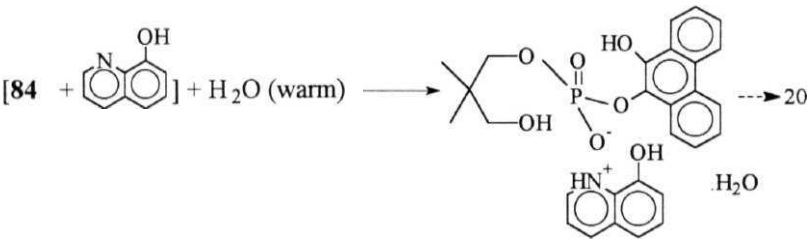
phosphorane $(OCH_2CMe_2CH_2O)P(OPh)(O_2C_{14}H_8)$ (88)." In fact Gallucci and Holmes obtained 84 in an attempt to obtain pure **88**.[98]



X = H (**85**) or ^{2}D

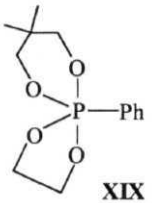
It is likely that 85 exhibits intramolecular H-bonding similar to that observed for **84**.[98] Compound 85 in the reaction mixture (along with $[H_2N(i\text{-}Pr)_2](Cl)$ exhibited a peak at -12.7 ppm in the ^{31}P NMR; after giving a water-wash it exhibited a 1:1:1 triplet centred at -11.5 ppm [$^2J(P\text{-}O\text{-}^2D)$ = 22.2 Hz]. Such a pattern could arise from the exchange of ^{2}D from $CDCl_3$ with the hydroxy group of ester 85 in the presence of traces of moisture. Observation of $^2J(P\text{-}O\text{-}^2D)$ is also consistent with strong intramolecular H-bonding. This is in contrast to 86 which shows intermolecular H-bonding [section **II.8.2**; compounds **84-87** were rather insoluble in nonpolar solvents to study these details by IR].

In the hydrolysis of 73, when the crystalline mixture containing 84 was washed with warm water in an effort to remove 8-hydroxy quinoline, further hydrolysis occurred (eq. 20). ^{1}H and ^{31}P NMR as well as elemental analysis are consistent with the structure 89 for the hydrolysis product.



89 (^{31}P: -0.6 ppm)

To summarize, the first stage of hydrolysis of spirophosphoranes containing a saturated 1,3,2-dioxaphosphorinane ring occurs by *retaining this six membered ring* . Even in the reaction of $(OCH_2CMe_2CH_2O)P(OC_9H_6N)$ (9a) with pinacol/ NCDA, the product mixture after exposure to air showed that the phosphorinane ring is preserved during hydrolysis [^1H NMR evidence]. It is likely that the oxinate nitrogen is involved in the hydrolysis *{via* H-bonding); however the cleavage of seven- and eight-membered rings in preference to the phosphorinane ring is hard to explain.



XIX

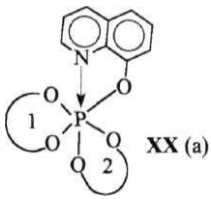
The other point to be noted is that our results are different from those obtained in the acid hydrolysis of the spirophosphorane XIX wherein a product with the phosphorinane ring intact was not observed. [100]

II.7 ^{31}p *NMR Spectroscopy of Penta- and Hexa-coordinated Compounds*

This section deals with the analysis of the ^{31}P NMR data obtained in the present study with respect to (i) coordination number and (ii) ring size effect. Data for our compounds along with a few others from the literature are shown in Table 1.

Table 1: ^{31}p NMR data for selected penta- and hexa-coordinated compounds with oxinate/ aryloxy/ alkoxy/ cyclohexylamino groups

(I) Hexa-coordinated compounds



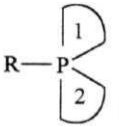
XX (a)

Sl No.	Ring 1[a]	Ring 2[a]	δ(^{31}P) (ppm)	Ring syst Assgnmnt (Compd No.)	Method of Prepn[b]	Ref
1	A	$(OPh)_2$	-123.0	0+4+5	i	63
2	A	B	-1020	5+4+5	i	63
3	B	B	-89 5[c]	5+5+5 (XXI)	ii	This work
4	B	C	-88.3	5+5+5 (72)	i	TO.™*
5	D	$(OC_9H_6N)_2$	-127.0[d]	6+0+5 (42)	i	This work
6	D	B	-102.3	6+5+5 **(XVII)**[e]	ii	This work
7	D	C	-101.0	6+5+5 (74)	i	This work
8	D	E	-100.8	6+5+5 (73)	i	This work
9	D	F	-101.8	6+5+5 (75)	i.	This work
10	H	C	-89.3	7+5+5 (76)	i	This work
11	H	D	-107.5	7+6+5 (77)	ii	This work
12	H	H	-94.5	7+7+5 (78)	ii	This work
13	I	B	-106.7	8+5+5 (XXII)	ii	This work
14	I	D	-127.1	8+6+5 (XVIII)	ii	This work

Contd...

Table 1.contd...

(II) Penta-coordinated compounds



XX (b)

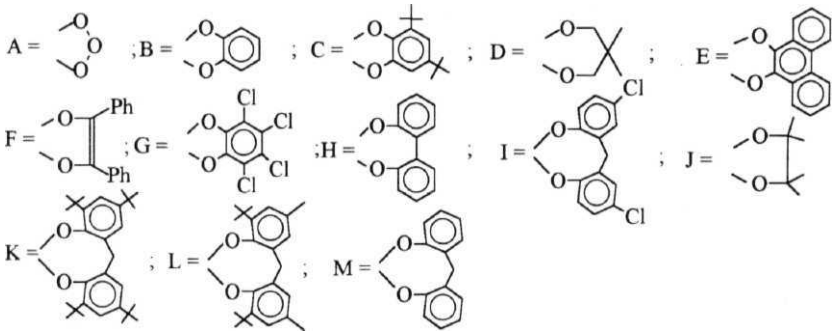
Sl. No	Ring 1[a]	Ring 21	R	δ(^{31}P) (ppm)	Ring syst Assgnmnt (Compd. No.)		Meth of Prepn[b]	Ref.
15	D	J	OC_9H_6N	-57.5	6+5	(XXIII)		This work
16	D	D	OC_9H_6N	-67.0	6+6	**(IVb)**	ii	This work
17	C	K	OC_9H_6N	-56.9	8+5	(79)	i	This work
18	E	K	OC_9H_6N	-56.1	8+5	(XXIV)	i	This work
19	B	B	OPh	-30.2	5+5		g	101
20	D	C	2,6-$Me_2C_6H_2O$	-51.3	6+5		i	37h
21	D	E	2,6-$Me_2C_6H_2O$	-49.0	6+5		i	4, 37f
22	D	F	2,6-$Me_2C_6H_2O$	-53.0	6+5		i	4,37h
23	D	G	2,6-$Me_2C_6H_2O$	-50.4	6+5		i	This work
24	D	D	2,4,6-$Me_2C_6H_2O$	-68.8, -66.9[h]	6+6		ii	This work
25	H	D	2,6-$Me_2C_6H_2O$	-60.0	7+6		ii	4, 37h
26	H	H	2,6-$Me_2C_6H_2O$	-47.3	7+7		ii	37c
27	C	K	OCH_2CF_3	-54.5	8+5		i	4,37a
28	D	M	2,6-$Me_2C_6H_2O$	-69.0	8+6		ii	4, 37a
29	B	E	NHC_6H_{11}	-28.2	5+5	(67)	i	This work
30	B	G	NHC_6H_{11}	-29.4	5+5	(58)	i	This work
31	D	C	NHC_6H_{11}	-48.8	6+5	(XXVI)	i	This work
32	D	E	NHC_6H_{11}	-46.2	6+5	(62)	i	This work
33	D	F	NHC_6H_{11}	-51.7	6+5	(90)	i	This work
34	D	G	NHC_6H_{11}	-45.7	6+5	(59)	i	This work
35	H	C	NHC_6H_{11}	-36.6	7+5	(64)	i	This work

contd....

Table 1. contd...

36	**H**	E	NHC_6H_{11}	-34.4	7+5 (63)	1	This work
37	H	F	NHC_6H_{11}	-39.4	7+5 (XXVII)	1	This work
38	**H**	G	NHC_6H_{11}	-34.7	7+5 (60)	1	This work
39	H	D	NHC_6H_{11}	-54.2	7+6 (68)	11	This work
40	**H**	H	NHC_6H_{11}	-39.6	7+7 (66)	ii	This work
41	K	B	NHC_6H_{11}	-563, -568	8+5 (65)	11	This work
42	L	G	NHC_6H_{11}	-54.6	8+5 (61)	i	This work
43	K	D	NHC_6H_{11}	-70.3	8+6 (69)	ii	This work
44	K	H	NHC_6H_{11}	-58.8	8+7 (70)	11	This work

[a]Ring types



b Method (i): Oxidative addition of ozone/quinone to the phosphite.
Method (ii): Oxidative addition of diol to the phosphite in the presence of N-chloro diisopropylamine (NCDA).

c Another peak observed at -84.8 ppm ascribed to $[P(O_2C_6H_4)_3]^-$ anion.[85]

d Obtained in the reaction of 8a with $HOCH_2CMe_2CH_2OH$/ NCDA (method ii as given in foot note b)

e The reaction was conducted in two ways either by starting with $(OCH_2CMe_2CH_2O)P(OC_9H_6N)$ (8a) or $(C_6H_4O_2)P(OC_9H_6N)$ (5a).

f OC_9H_6N= 

g Different route by starting with PCl_5.

h. Two peaks were observed; two different isomers or conformers.

(I) Effect of co-ordination number [*cf.* Table 1]

The hexa-coordinated oxinate derivatives in general show an upfield shift of 48-60 ppm when compared to their close penta-coordinated analogues.

E.g.: (i) Entry 7-9 *vs* entries 20-22. The oxinate in entries 7-9 is replaced by $2,6\text{-}Me_2C_6H_3O$ in 20-22.

(ii) entry 12 *vs* entry 26.

(iii) entry 11 *vs* entry 25.

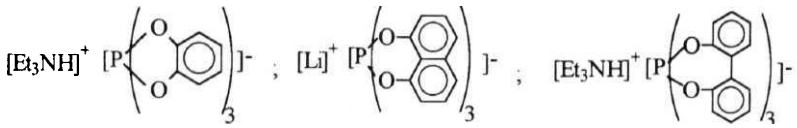
This is useful because if in the oxinate compounds there is no N→P coordination, δ_p should be in the penta-coordinated region. Thus the presence of N→P co-ordination in the eight membered ring compounds containing the 2,2'-methylene bis(4-chlorophenoxy) group (entries 13 and 14) and its absence in those containing the 2,2'-methylene-bis(4,6-di-(t-butyl)phenyl) group (entries 17 and 18) is noteworthy; steric factors may be partly responsible for the absence of N→P co-ordination in the latter case. The ^{31}P NMR chemical shift values for there compounds (entries 17 and 18) are comparable to those in which there is no possibility of internal co-ordination (entries 27 and 28).

When saturated 1,3,2-dioxa-phosphorinane [entry No. 16] or phospholane [entry No. 15] are present, the nitrogen of the oxinate refuses to form a co-ordinate bond, thus leaving the phosphorus penta-coodinated. It is likely that in these cases phosphorus does not become sufficiently acidic to accept the lone pair of electrons from the oxinate nitrogen. Thus chemical shifts in entries 15 and 16 are comparable to those in which N→P co-ordination in not possible [entries 22 and 24 respectively].

(II) **Effect of ring size**

Among the oxinate hexa-coordinated compounds investigated, the deshielding effect of ring size is in the order: five>seven>six ≈ four>eight. A comparable effect is discernible in anionic hexacoordinated phosphates **XXVIII-**

XXX also.[70, 85] A similar trend has been observed by Holmes and co-workers in pentaoxy phosphoranes.[20(b),69(b)] Even in the amino phosphoranes studied here, the deshielding is in the order five> seven> six> eight [entries 30, 34, 37, 42].



XXVIII
31P: -84.0 ppn

XXIX
31P: -168.0 ppn

XXX
31P: -93.2 ppn

These trends suggest that phosphorus experiences more deshielding in compounds with odd membered rings. It will be useful if a few more examples containing seven (those more flexible than the 2,2'-biphenoxy system) and nine membered rings could be studied in order to understand these effects more clearly.

The observed δ_p values of -12.7, -8.7, 0.4 and 13.7 for 33, 30, 34 and 39 respectively are also in the same order as observed for penta- and hexa-coordinated derivatives showing a similar ring size effect.

II.8 *Structural Aspects*

One of the objectives of the present work is to investigate the variation in conformations and geometrical parameters for tri-, terra- penta- and hexa-coordinated cyclic phosphorus compounds differing in ring size. In addition, assuming that solid state structures are retained in solution such studies are useful in understanding reaction chemistry and NMR behaviour. Important structural features are described below; selected crystal data and structure solution details are given in Appendix 2. Selected atomic coordinates are available in Appendix 3.

II.8.1 Trivalent cyclic phosphorus and arsenic derivatives

Compounds for which structures have been determined: 9, 24, **8b**, **17b**, **22b,** 44, and 47.

Compound 9 contains four molecules in the asymmetric unit [Fig. 5] connected by H-bonding; in all of these the 1,3,2-dioxaphosphorinane ring has a *chair* conformation as expected.[12,13] The dihedral angle between the planes 0(1)-P-0(2) and O(2)-C(19)-C(17)-O(1) is 39.7°. Between O(2)-C(19)-C(17)-O(1) and

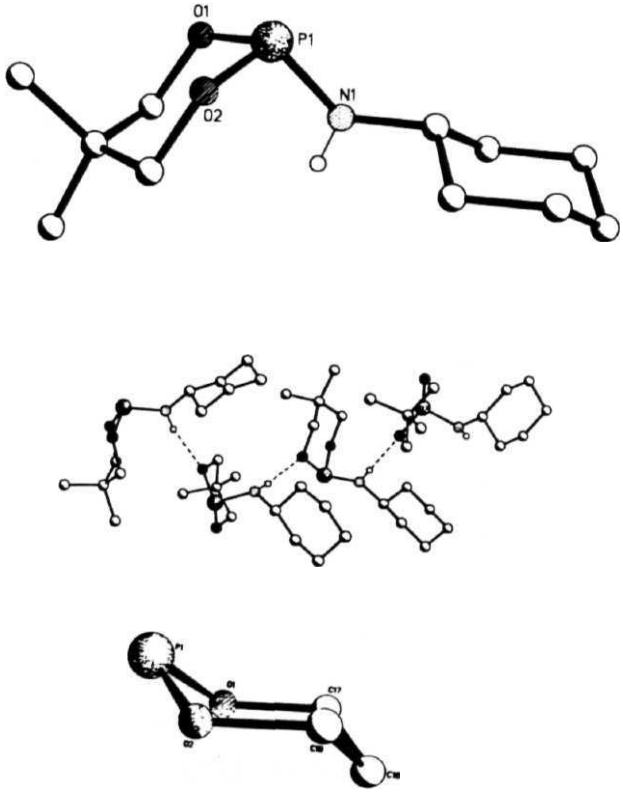
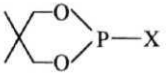


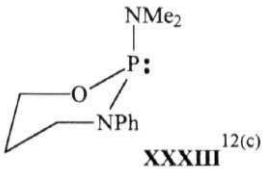
Fig. 5. a) Molecular structure of 9, b) structure of 9 showing H-bonding interactions and c) conformation of the phosphorinane ring

C(17)-C(18)-C(19) the dihedral angle is 50.2°. [The corresponding angle m cyclohexane is 49.2° [102]]. In contrast to Verkade's compounds XXXI and



X= $-NMe_2$ XXXI, X =  XXXII

XXXII[13] in which the amino group is *equatorial,* the cyclohexylamino (-NHC_6H_{11}) group in 9 is *axial.* The -NHC_6H_{11} group is probably (slightly) less sterically demanding than dimethylamino or piperidino groups; this along with the H-bonding effects possibly results in the *axial* disposition of the -HNC_6H_{11} group.



XXXIII[12(c)]

It can, however, be noted that the -NMe_2 group can prefer an *axial* position as in Bentrude's 1,3,2-oxaza-phosphorinane XXXIII.[12(c)]

An important difference between 9 and **XXXI-XXXIII** is the presence of H-bonding in 9 (Fig. 5); no conformational change, similar to that noted for oxyphosphoranes[40] is observed.

The bond lengths and bond angles [Table 2] are normal and comparable to those in XXXI and XXXII.[12,13]

Table 2. Selected bond lengths (A) and bond angles (°) for compound 9 with esd's in parentheses (for only one molecule in the asymmetric unit).

P(1)-O(2)	1.624(5)	O(2)-P(1)-O(1)	98 6(2)
P(1)-O(1)	1.642(4)	O(2)-P(1)-N(1)	107 7(3)
P(l)-N(l)	1.652(5)	O(1)-P(1)-N(1)	101.3(2)
O(1)-C(17)	1.439(7)	C(17)-O(1)-P(1)	120.3(4)
O(2)-C(19)	1435(9)	C(19)-O(2)-P(1)	120.2(4)
N(l)-C(ll)	1.462(8)	C(11)-N(1)-P(1)	119 9(4)

Table 2 contd

C(17)-C(18)	1.519(8)
C(18)-C(19)	1.522(9)

The cyclic phosphite 24 [Fig. 6] has a *boat-chair* conformation similar to Pastor's compound [section **I.2**, structures **I-7** and **I-8**].[20(a)] The most interesting feature, however, is the presence of H-bonding in 24 leading to a dimer instead of forming a chain as in 9. This is probably a result of steric factors operating in 24.

The P-N bond in 24 [1.63 5(3)Å; Table 3] is slightly shorter than that in 9 [1.652(5)A]. This is line with the sum of the bond angles around nitrogen [In 9, for four molecules it is 352.1-355.5°; in 24 the sum is 359°] which show greater planarity for nitrogen in 24 resulting from a stronger P-N interaction.

Table 3. Selected bond lengths (A) and bond angles (°) for compound 24 with esd's in parentheses.

P(1)-O(1)	1.670(2)	O(2)-P(1)-O(1)	101.56(11)
P(1)-O(2)	1.662(2)	O(2)-P(1)-N(1)	100.38(14)
P(l)-N(l)	1.635(3)	O(1)-P(1)-N(1)	94.89(13)
O(1)-C(11)	1.398(4)	C(11)-O(1)-P(1)	120(2)
N(l)-C(l)	1.470(4)	C(21)-O(2)-P(1)	121.6(2)
C(11)-C(16)	1.396(4)	C(l)-N(l)-P(l)	124.0(2)
C(16)-C(10)	1.512(4)	H(1N)-N(1)-P(1)	120(2)
N(1)-H(1N)	0.82(2)	C(11)-C(16)-C(10)	121.2(3)
C(10)-C(26)	1.516(4)	H(1N)-N(1)-C(1)	115(2)
O(2)-C(21)	1.402(4)	C(16)-C(11)-O(1)	117.3(3)
C(21)-C(26)	1.385(4)	C(26)-C(21)-O(2)	117.8(3)
		C(21)-C(26)-C(10)	120.7(3)

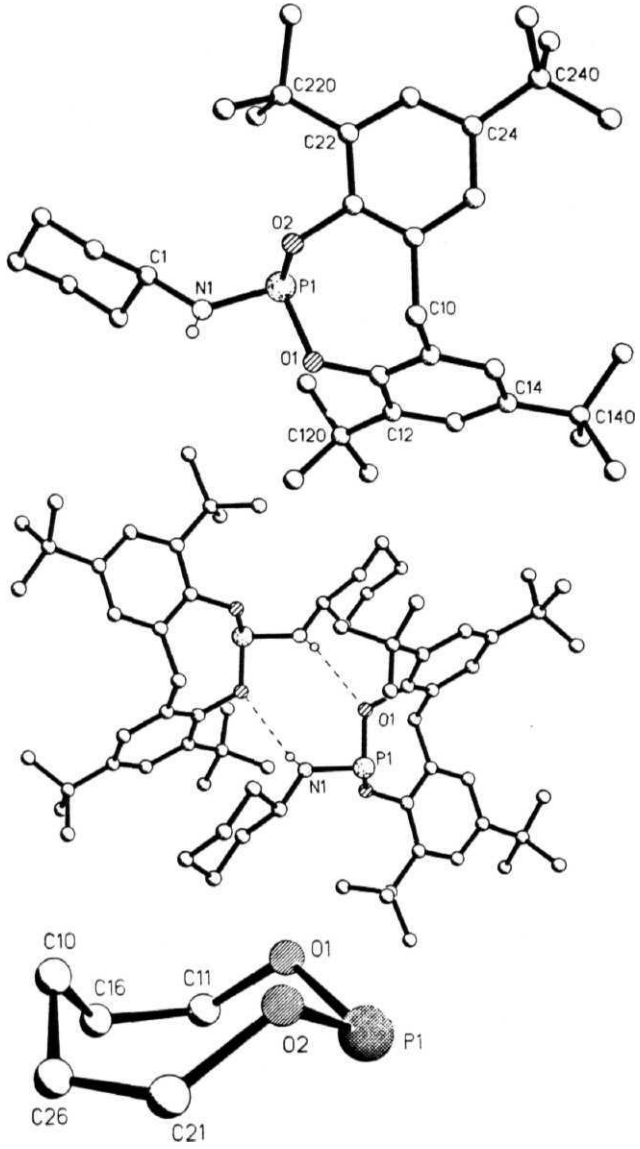


Fig. 6.a) Molecular structure of 24, b) structure of 24 showing H-bonding interactions and c) conformation of the phosphocin ring

Compound 8b, 17b and **22b** show intramolecular $N \rightarrow As$ coordination [Figs 7-9; Table 4]. The As-N bond lengths decrease in the order 8b [2.602 A (mean)] **>17b** (2.534 A) **>22b** (2.433 A). In the 2,2'-biphenoxy compound **17b** having no electron donating substituent on the aromatic rings the arsenic is the most acidic leading to the shortest $N \rightarrow As$ interaction. However, all these $N \rightarrow As$ bonds are weaker than those in $Me_3N \rightarrow AsCl_3$ (2.28Å)[103] or the hexa-coordinated compound $(NC_9H_6O)As(OCH_2CMe_2CH_2O)_2$ (32) (2.04 A). The geometry of 8b, **17b** and **22b** (including the lone pair) can be considered to be approximately trigonal bipyramidal (TBP) with the lone pair of electrons on arsenic in an *equatorial* position and the nitrogen of the oxinate in an *apical* position [as in **XXXIV**]

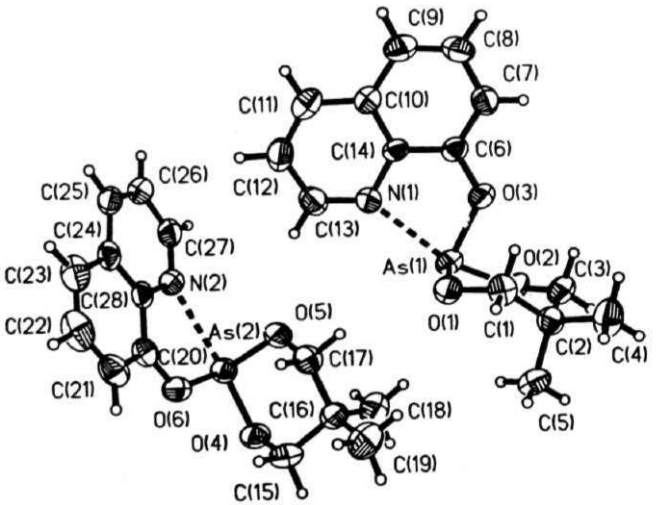


Fig.7 Molecular structure of 8b

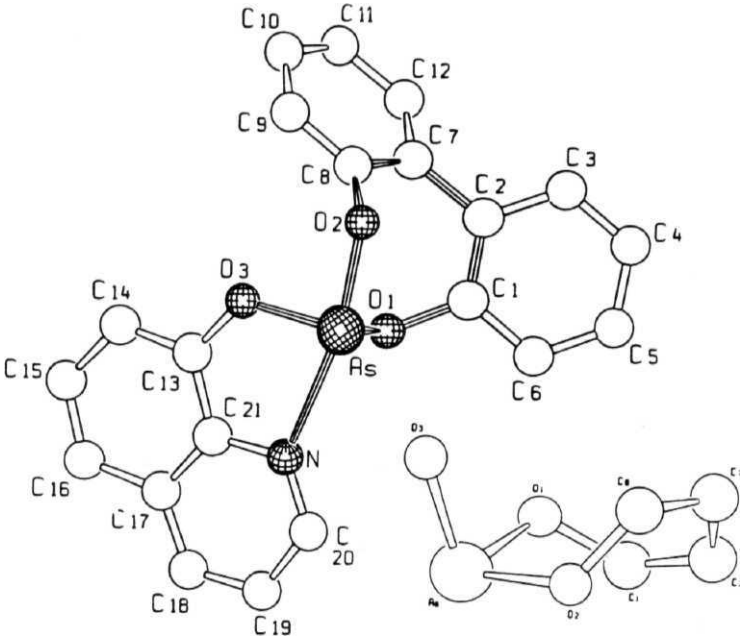


Fig.8. Molecular structure of **17b**

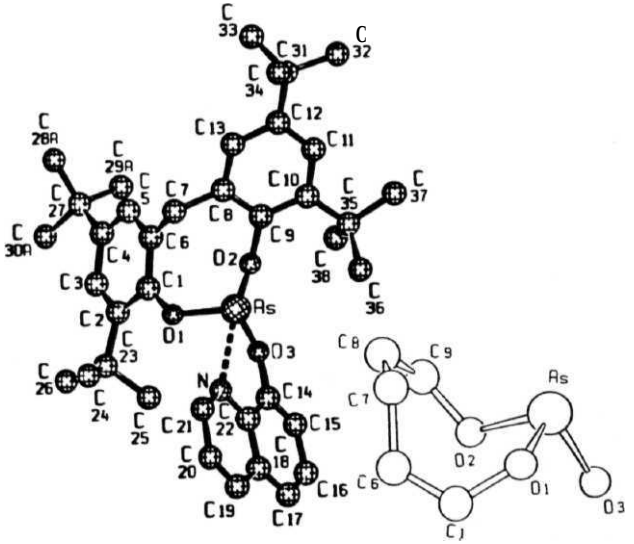


Fig. 9. Molecular structure of 22b

Table 4. Selected bond lengths (A) and bond angles (°) for 8b, 17b and **22b** with esd's in parentheses

Compound 8b

As(1)-O(1)	1.771(4)	As(2)-O(4)	1.790(4)
As(1)-O(2)	1.790(3)	As(2)-O(5)	1.767(3)
As(1)-O(3)	1.830(4)	As(2)-O(6)	1.838(4)
O(1)-C(1)	1.442(6)	O(4)-C(15)	1.433(6)
O(2)-C(3)	1.433(6)	O(5)-C(17)	1.420(6)
O(3)-C(6)	1.362(6)	O(6)-C(20)	1.356(6)
N(l)-C(14)	1.367(6)	N(2)-C(28)	.1.359(7)
C(l)-C(2)	1.523(7)	C(15)-C(16)	1.510(7)
C(2)-C(3)	1.510(8)	C(16)-C(17)	1.528(7)
C(6)-C(14)	1.426(6)	C(20)-C(28)	1.432(7)
As(l)-N(l)	2.599(4)	As(2)-N(2)	2.606(5)
O(1)-As(1)-O(2)	97.7(2)	O(5)-As(2)-O(4)	97.6(2)
O(1)-As(1)-O(3)	98.9(2)	O(5)-As(2)-O(6)	99.0(2)
O(2)-As(1)-O(3)	90.1(2)	O(4)-As(2)-O(6)	90.1(2)
C(1)-O(1)-As(1)	119.0(3)	C(15)-O(4)-As(2)	119.7(3)
C(3)-O(2)-As(1)	120.2(3)	C(17)-O(5)-As(2)	120.7(3)
C(6)-O(3)-As(l)	126.3(3)	C(20)-O(6)-As(2)	125.0(3)
O(1)-C(1)-C(2)	113.7(4)	O(4)-C(15)-C(16)	113.3(5)
C(3)-C(2)-C(l)	109.1(4)	C(15)-C(16)-C(17)	108.9(4)
O(2)-C(3)-C(2)	114.3(4)	O(5)-C(17)-C(16)	114.0(4)
O(3)-C(6)-C(14)	120.6(4)	O(6)-C(20)-C(28)	121.4(5)
N(l)-C(14)-C(6)	116.8(4)	N(2)-C(28)-C(20)	116.5(5)
N(l)As(l)-O(l)	84.3(2)	N(2)-As(2)-O(6)	74.08(15)
N(1)-As(1)-O(2)	164.1(2)	N(2)-As(2)-O(5)	80.0(2)
N(1)-As(1)-O(3)	74.02(14)	N(2)-As(2)-O(4)	163.3(2)
C(14)-N(l)-As(l)	102.2(3)	C(28)-N(2)-As(2)	101.9(3)

Compound **17b**

As-O(1)	1.802(2)	N-C(21)	1.357(5)
As-O(2)	1.836(3)	C(l)-C(2)	1.377(5)
As-O(3)	1.814(3)	C(2)-C(7)	1.476(5)
O(1)-C(1)	1.387(4)	C(7)-C(8)	1.416(5)
O(2)-C(8)	1.370(5)	C(13)-C(21)	1.409(6)
O(3)-C(13)	1.360(5)	As-N	2.433(6)
O(1)-As-O(3)	95.89(12)	C(8)-C(7)-C(2)	119.8(3)

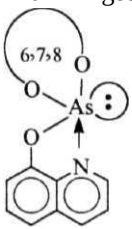
Table 4 contd...

O(1)-As-O(2)	94.27(11)	O(2)-C(8)-C(7)	118.8(3)
O(2)-As-O(3)	88.96(12)	O(3)-C(13)-C(21)	119.4(3)
C(1)-O(1)-As	116.7(2)	N-C(21)-C(13)	115.8(3)
C(8)-O(2)-As	120.6(2)	N-As-O(2)	163.7(2)
C(13)-O(3)-As	123.6(2)	N-As-O(l)	80.8(2)
C(2)-C(1)-O(1)	120.4(3)	N-As-O(3)	76.3(2)
C(l)-C(2)-C(7)	121.2(3)		

Compound **22b**

As-O(l)	1.801(2)	C(6)-C(7)	1.514(4)
As-O(2)	1.817(3)	C(7)-C(8)	1.514(4)
As-O(3)	1.811(2)	C(8)-C(9)	1.393(4)
O(1)-C(1)	1.386(4)	N-C(22)	1.350(4)
O(2)-C(9)	1.402(3)	C(14)-C(22)	1.409(5)
O(3)-C(14)	1.369(4)	As-N	2.534(3)
C(l)-C(6)	1.395(4)		
O(1)-As-O(2)	98.30(10)	C(22)-N-As	101.9(2)
O(1)-As-O(3)	99.60(11)	C(l)-C(6)-C(7)	120.7(3)
O(2)-As-O(3)	85.50(11)	C(6)-C(7)-C(8)	118.7(3)
O(1)-As-N	80.78(10)	C(7)-C(8)-C(9)	121.9(3)
O(2)-As-N	159.71(10)	O(2)-C(9)-C(8)	118.0(3)
O(3)-As-N	74.75(11)	O(3)-C(14)-C(22)	119.7(3)
C(1)-O(1)-As	124.7(2)	O(1)-C(1)-C(6)	119.2(3)
C(9)-O(2)-As	117.3(2)	N-C(22)-C(14)	117.0(3)
C(14)-O(3)-As	123.5(2)		

The apical As-0 bonds are longer than the equatorial As-0 bonds of the six- or seven- or eight-membered ring in 8b, **17b** and 22b respectively as expected in a TBP geometry.



XXXIV

The N-As-0 (apical) angle in 8b, **17b** and **22b** is 160-164° whereas in Me_3N-$AsCl_3$ the N-As-Cl (apical) angle is 178.1°,[15] thus suggesting a greater distortion from the TBP structure for 8b, **17b** and **22b.** By using the dihedral angle method[7(d),104] with the lone pair as pivotal, 8b, **17b,** and **22b**

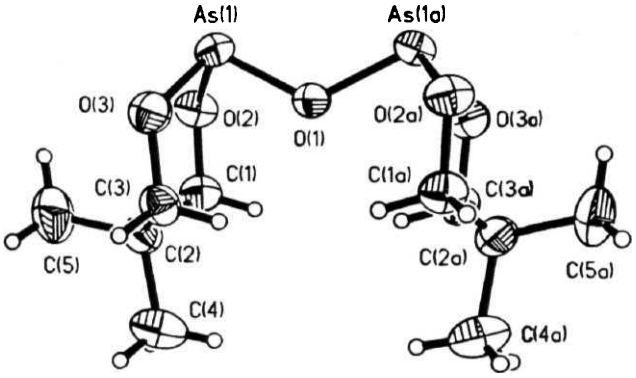
are found to be distorted from TBP (5 = 53.1°) square pyramid (5 = 0°) to an extent of 17.5%, 11.2% and 18.9% respectively [% distortion = {(53.1-5) x 100} + 53.1].

As in $O[As(OCH_2CMe_2CH_2O)]_2$ (44) (discussed later) a *chair* conformation is observed for the arsenane ring in 8b. Compound **17b,** is to our knowledge the first arsepin to be structurally characterized; here the seven-membered ring has a *row-boat* conformation that is commonly observed for several phosphorus systems with the same 2,2'-biphenoxy moiety.[16,17,20(b)] The atoms As, 0(2), C(2) and C(l) form the base and are coplanar to within 0.07A; the prow atoms 0(1) as well as C(7) and C(8) are displaced in the same direction from this plane.

The arsocin **22b** exhibits a *distorted tub* conformation with the atoms C(7), C(8), 0(1) and As displaced from the mean plane containing C(9), 0(2), C(l) by 0.96, 0.66, 0.53 and 1.28A respectively. This conformation, interestingly, differs from the *symmetrical anti (boat-chair)* conformation observed in 47 and may be responsible for the difference in the ^1H NMR for the CH_2 protons. The two protons of the CH_2 group in **22b** show up as an AB quartet in contrast to the tri-coordinated compound 47 which exhibited a well-defined AX pattern [5(A) = 3.50, 5(X) = 4.70, J(AX) = 13.0 Hz].

The As-0 bond distances in compounds 44 and 47 [see Figs. 10 and 11 and Table 5] fall in the normal range,[105] but are longer than those observed for $ClAs(OCMe_2CH_2CMe_2O)$ **(XXXV)** [mean: 1.74A];[15] even the As-0 (bridging) distances in 44 [1.78A] and 47[1.76A] are longer than the As-O(ring) distance in **XXXV.** The As-O-C bond angles in 44 (mean: 117.4°) are smaller than those in 47 (mean 124.5°) most likely as a result of steric strain in the latter. Also the widening of the As-O-As angle in 47 (139.2°) when compared to 44 (125.8°) is

probably a result of steric effect rather than the interaction of the orbitals of the bridgehead oxygen containing the lone pair electrons with the arsenic d-orbitals.[15]



Figs. 10. Molecular structure of 44

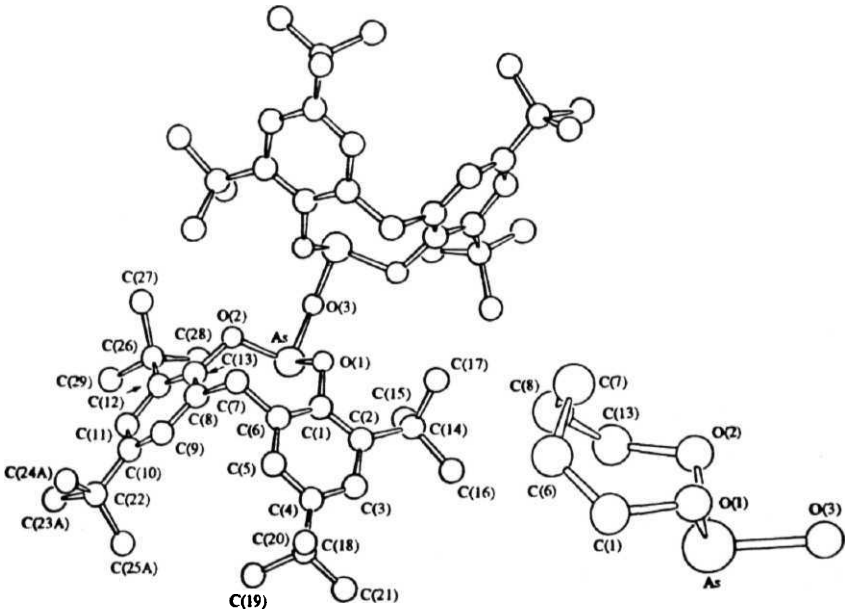


Fig. 12. Molecular structure of 47

Table 5. Selected bond lengths (A) and bond angles (°) for 44 and 47 with esd's in parantheses.

Compound 44

As1-O1	1.7771(11)	O2-C1	1.431(3)
As1-O2	1.790(2)	C1-C2	1.524(4)
Asl-O3	1.767(2)	C2-C3	1.527(4)
Asl-Ol	1.7771(11)	O3-C3	1.431(3)
O3-As1-O1	95.93(8)	C3-O3-As1	117 3(2)
O3-As1-O2	96.95(9)	O2-C1-C2	113.4(2)
O1-As1-O2	95.80(8)	C1-C2-C3	109.4(2)
As1'-O1-As1	125 81(14)	O3-C3-C2	113.6(2)
C1-O2-As1	118.1(2)		

Compound 47.

As-O1	1.794(3)	C6-C7	1.525(7)
As-O2	1.799(4)	C7-C8	1.519(7)
As-O3	1.756(3)	C8-C13	1.393(7)
O1-C1	1.404(6)	C13-O2	1.413(5)
C1-C6	1.394(7)		
As-O3-As*	139.3(3)	C1-C6-C7	121.8(4)
O1-As-O2	94.4(2)	C6-C7-C8	110.8(4)
As-O1-C1	114.2(3)	C8-C13-O2	117.4(4)
O1-C1-C6	117.3(4)	C13-O2-As	114.5(3)

Symmetry transformation used to generate equivalent atoms: 1' = -x, y -z + $^1/_2$

The two arsenane rings in 44 are in a *chair* conformation in contrast to the *twist-boat* conformation found in **XXXV.**[15] In **44** the four atoms forming the base of the *chair* (0(2), 0(3), C(l), C(3)) are coplanar to within ±0.0071 A; atoms As(l) and C(2) are away from this plane by ≈ 0.75 A. The observed conformation is consistent with the solution state studies of Aksnes and the expected anomeric effects involving the oxygen lone pair of the ring.[14]

There are short intermolecular contacts in 44 involving the 0(2) and arsenic atoms (3A). This feature reflects the weak acidic (Lewis) character of the As^{III} centre.

As is observed for $(ClCH_2CMe_2CH_2O)P(O)\{(O\text{-}2,4\text{-}(t\text{-}bu)_2C_6H_2)_2CH_2\}$ (33) and for 47, the eight-membered arsocin ring in 47 has a *symmetrical anti (boat-chair)* conformation. Since the ^1H NMR spectrum of 47 in solution gives a well-separated sharp AX doublet in contrast to 33 (but similar to 79), the molecule appears to be rigid in solution also. Compound 47 to our knowledge, is the first arsocin to be structurally characterized.

An interesting difference exists between the structures of 44 and 47. Whereas the six-membered rings in 44 are on the same side as the bridgehead oxygen, the eight-membered rings in 47 are on the opposite sides; steric interactions in 47 may responsible for this difference.

II.8.2 Tetra-coordinated phosphorus compounds

Compounds for which structures have been determined: 33, 53, and 86.

These structures were performed mainly to confirm the identity of the products. The geometrical parameters around phosphorus in the structure of 33 [Fig. 12 and Table 6] compares well with that of both the conformers of **XXXVI** reported by Holmes and coworkers.[62]

A notable feature is the wider angle at phosphorus between the exocyclic oxygens [O(3)-P-O(4) 120.5°] in 33 [Table 6] when compared to those in **XXXVI** (113.9°, 113.2°) perhaps as a result of the high group electronegativity of the $-OCH_2CF_3$ group over $-OCH_2CMe_2CH_2Cl$.

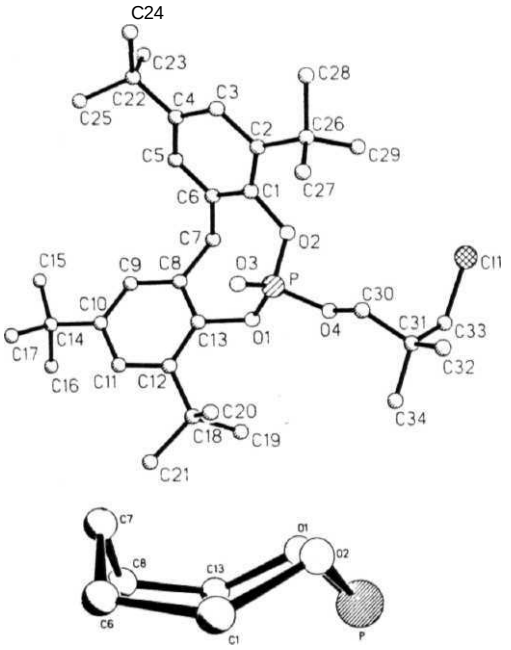


Fig. 12. Molecular structure of **33**

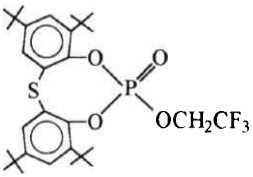
Table 6. Selected bond lengths (A) and bond angles (°) for 33 with esd's in parentheses

C1-C33	1.778(8)	P-02	1.497(4)
P-O1	1.587(5)	**P-O3**	1.457(5)
P-O4	1.580(5)	**O1-C13**	1.433(8)
O2-C1	I 424(8)	O4-C30	1.374(9)
C1-C6	**1.407(9)**	C6-C7	1.512(9)
C7-C8	1.523(9)	**C8-C13**	1.389(9)
C30-C31	1 523(9)	C31-C32	**1.525(9)**
Ol-P-02	108.3(2)	**O1-P-O3**	115.2(3)
O1-P-O4	96 8(3)	**O2-P-O3**	113.8(3)
O2-P-O4	99.9(3)	**O3-P-O4**	120.5(3)

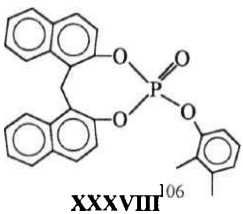
Table 6 contd

P-01-C13	122.2(4)	P-02-C1	122.3(4)
P-O4-C30	123.9(4)	O2-C1-C6	116.3(5)
O2-C1-C2	120.8(6)	O1-C13-C12	120.1(5)
O1-C13-C8	116.8(5)	O4-C30-C31	111.6(6)

A *boat-chair* conformation is observed for the eight-membered ring in **33.** This is similar to that observed for 79 and one conformer of XXXVI[62] but different from the *symmetrical tub {boat)* observed in 65 and XXXVIII.[106] However, since ^{1}H NMR spectrum of 33 shows broad signal (4.00-4.20 ppm) for bridging CH_2 protons [in contrast to the phosphite ClP{[0-2,4-(t-bu)$_2$C$_6$H$_2$]CH$_2$} (21a) which shows a well-separated AX doublet for each of the CH_2 protons] a conformational equilibrium is indicated in solution for 33.



XXXVI[62]



XXXVIII[106]

The 1,3,2-dioxaphosphorinane ring in 86 has a *chair* conformation with the P=O bond occupying an *equatorial* position [Fig 13, Table 7]; the four atoms forming the base of the *chair* [0(3), 0(4), C(13) and C(15)] are coplanar to within ±0.0086 A. The *chair* conformation is partly flattened at the O-P-O and as in 9 (see above) and **84.**[98] The relevant dihedral angles in 84 are as given below:

	Plane 1	Plane2	Dihedral angle*	Ref.
86	O(4) C(15) C(13) O(3)	0(3) P 0(4)	38.9	This work
	0(4) C(15) C(13) 0(3)	C(13) C(14) C(15)	50.2	This work
84	O(2) C(3) C(1) O(1) O(1) P 0(2)		32.2	98
	0(1) C(l) C(3) O(2) C(1) C(2) C(3)		51.6	98

*In cyclohexane this angle is 49.2 (ref. 102)

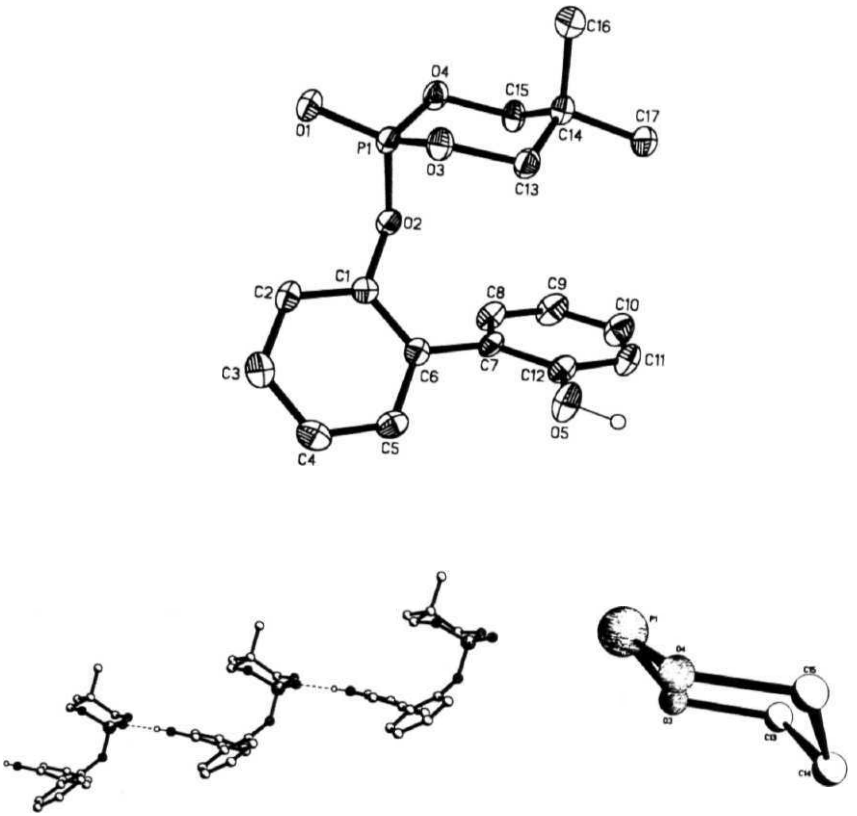


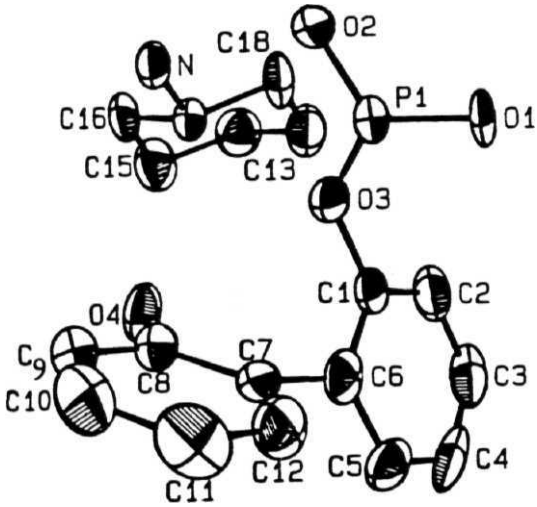
Fig. 13. Molecular structure of 86; also shown are H-bonding interactions and the conformation of the phosphorinane ring

The major difference between the structures of 84 and 86 is the type of H-bonding involved between the P=O and Ar-OH groups. In 84, it is intramolecular whereas in 86 it is intermolecular [Fig. 13]; this difference may be attributed to the proximity of the -OH group to P=O in the two compounds.

Table 7. Selected bond lengths (A) and bond angles (°) for 86 with esd's in parentheses

P(1)-O(1)	1.459(2)	O(1)-P(1)-O(3)	111.97(9)
P(1)-O(3)	1.556(2)	O(1)-P(1)-O(4)	113.45(9)
P(l)-0(4)	1.559(2)	O(3)-P(1)-O(4)	107.15(8)
P(1)-O(2)	1.583(2)	O(1)-P(1)-O(2)	115.18(8)
O(3)-C(13)	1.466(2)	O(3)-P(1)-O(2)	106.92(8)
O(4)-C(15)	1.466(3)	O(4)-P(1)-O(2)	101.32(8)
C(14)-C(15)	1.523(3)	C(1)-O(2)-P(1)	122.59(13)
C(13)-C(14)	1.522(3)	C(13)-O(3)-P(1)	117.71(13)
		C(15)-O(4)-P(1)	116.79(13)

The X-ray structure of 51 [Fig. 14; P-H not shown] confirms the structure assigned on the basis of NMR and analytical data. The P-H distance is ≈1.33Å; some bond parameters are given in Table 8.



Figs. 14. Molecular structure of **51**

Table 8. Selected bond lengths (A) and bond angles (°) for 51 with esd's in parentheses

P1-O1	1.482(5)	P1-O3	1.589(5)
P1-O2	1.471(5)	P-H	1.33
01-04	2.71(H-bonded)		
O1-P1-O2	119.8(3)	O2-P1-O3	104.3(3)
O1-P1-O3	110.6(3)	C1-03-P1	124.3(4)

II.8.3 Penta-coordinated phosphoranes

Compounds for which structures have been determined: 59, 60, 65. $\frac{1}{2}Et_2O$ and **79.**$\frac{1}{2}H_2O$.

Molecular structures of 59, 60, 65 and 79 are shown in Figs 15-18; the conformation of the six-, seven and eight-membered rings are shown alongside. Selected bond parameters are given below the plots as Tables 9-12.

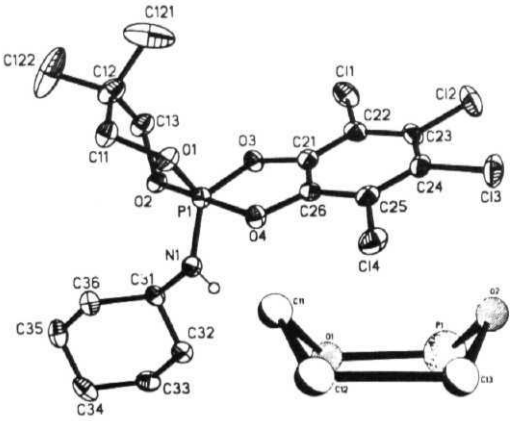


Fig. 15. Molecular structure of 59. The conformation of the phosphorinane ring is also shown

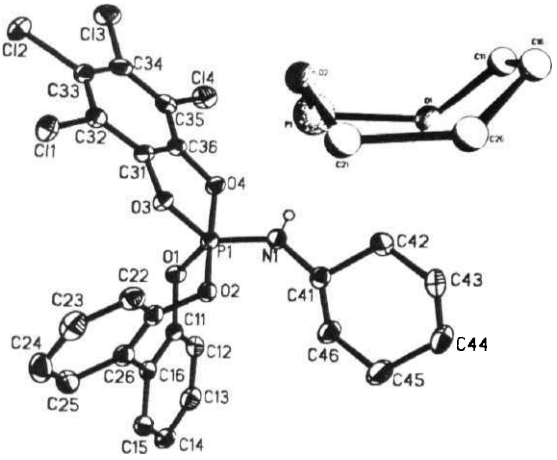


Fig. 16. Molecular structure of 60. The conformation of the seven-membered ring is also shown

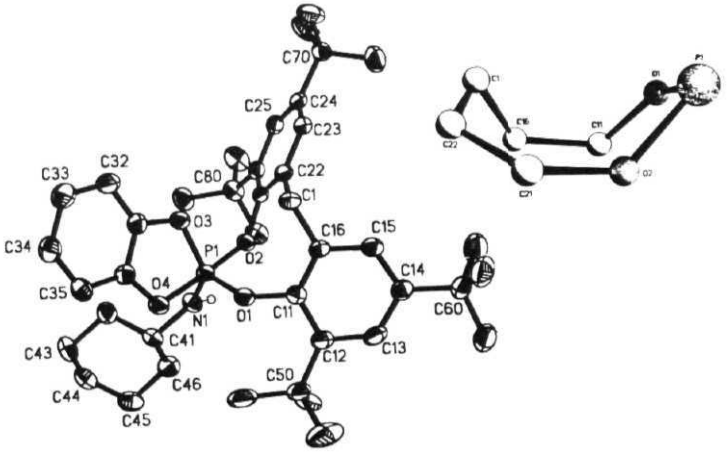


Fig. 17. Molecular structure of 65. The conformation of the eight-membered ring is also shown

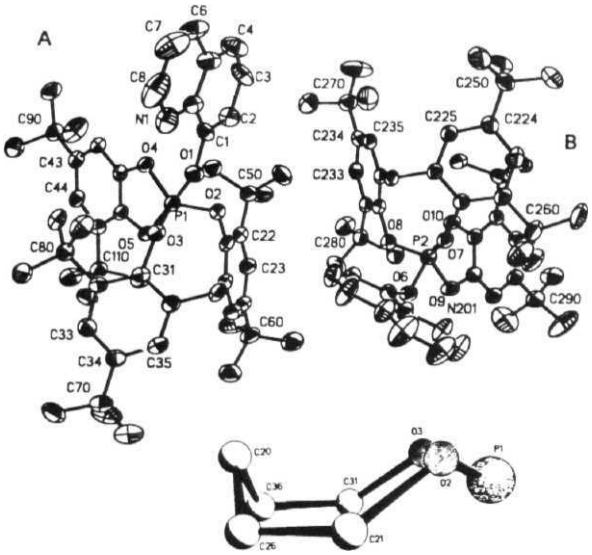


Fig. 18. Molecular structure of 79. The conformation of the eight-membered ring is also shown

Table 9. Selected bond lengths (A) and bond angles (°) for 59 with esd's in parentheses

P(1)-O(1)	1.593(2)	O(1)-P(1)-N(1)	123 82(11)
P(l)-N(l)	1.619(2)	O(1)-P(1)-O(2)	9705(10)
P(1)-O(20	1.622(2)	N(1)-P(1)-O(2)	92.01(11)
P(1)-O(3)	1.657(2)	O(1)-P(1)-O(3)	112 45(10)
P(1)-O(4)	1.784(2)	N(1)-P(1)-O(3)	122 90(11)
O(2)-C(13)	1.435(3)	O(2)-P(1)-O(3)	90.09(9)
C(13)-C(12)	1.523(4)	O(1)-P(1)-O(4)	85.34(9)
C(12)-C(l 1)	1.517(4)	N(1)-P(1)-O(4)	86 95(10)
N(l)-C(31)	1.471(3)	O(2)-P(1)-O(4)	177.58(10)
N(l)-H(l)	083(2)	O(3)-P(1)-O(4)	88 65(9)
		C(21)-O(3)-P(1)	115.0(2)

Table 9 contd

C(26)-O(4)-P(1)	1116(2)
	119.9(2)
	119.8(2)
	130 9(2)

Table 10. Selected bond lengths (A) and bond angles (°) for 60 with esd's in parentheses.

P(1)-O(1)	**1.604(2)**	O(1)-P(1)-N(1)	**123.15(11)**
P(])-N(l)	] 618(2)	O(1)-P(1)-O(2)	9759(9)
P(1)-O(2)	1 635(2)	N(1)-P′1)-O(2)	9094(10)
P(1)-O(3)	1.654(2)	O(1)-P(1)-O(3)	107 31(9)
P(1)-O(4)	1.759(2)	N(1)-P(1)-O(3)	128 97(11)
O(1)-C(11)	1.404(3)	O(2)-P(1)-O(3)	89.49(9)
O(2)-C(21)	1.390(3)	O(1)-P(1)-O(4)	87 65(9)
C(ll)-C(16)	1.384(3)	N(1)-P(1)-O(4)	86.32(10)
C(16)-C(26)	1.480(4)	O(2)-P(1)-O(4)	174 75(9)
C(21)-C(26)	1.384(4)	O(3)-P(1)-O(4)	88 76(8)
N(l)-H(l)	0 83(2)	O(11)-O(1)-P(1)	126.6(2)
N(l)-C(41)	1.472(3)	C(21)-O(2)-P(1)	122.3(2)
		C(41)-N(l)-P(l)	130 9(2)
		C(31)-O(3)-P(1)	114 2(2)
		C(36)-O(4)-P(1)	111 4(2)

Table 11. Selected bond lengths (A) and bond angles (°) for 65 with esd's in parentheses

P(1)-O(1)	1 606(2)	O(1)-P(1)-N(1)	118 09(12)
P(l)-N(l)	1.629(2)	O(1)-P(1)0(3)	116 60(11)
P(1)-O(3)	1.636(2)	N(1)-P(1)-O(3)	**125.18(13)**
P(1)-O(2)	1.669(2)	O(1)-P(1)-O(2)	95 67(10)
P(1)-O(4)	1.716(2)	N(1)-P(1)-O(2)	89 02(11)
O(1)-C(11)	1.396(3)	O(3)-P(1)-O(2)	89 41(10)
O(2)-C(21)	1.392(3)	O(1)-P(1)-O(4)	85 80(10)
C(11)-C(16)	1.393(4)	N(1)-P(1)-O(4)	90 16(11)

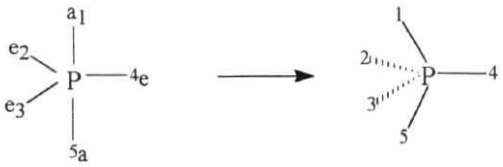
Table 11 contd

C(l)-C(16)	1 510(4)	O(3)-P(1)-O(4)	9006(10)
C(l)-C(22)	1 506(4)	O(2)-P(1)-O(4)	178 53(11)
C(21)-C(22)	**1.397(4)**	C(11)-O(1)-P(1)	**131.6(2)**
N(1)-H(1)	**0.86(2)**	C(21)-O(2)-P(1)	1326(2)
N(l)-C(41)	1.472(4)	C(31)-O(3)-P(1)	114.4(2)
		C(36)-O(4)-P(1)	112 7(2)
		C(41)-N(l)-P(l)	131.4(2)

Table 12. Selected bond lengths (A) and bond angles (°) for 79 with esd's in parentheses.

P(1)-O(3)	1.590(3)	O(3)-P(1)-O(2)	**118.50(13)**
P(1)-O(2)	1 603(2)	O(3)-P(1)-O(4)	**123.43(13)**
P(1)-O(4)	1 625(2)	O(2)-P(1)-O(4)	117 88(13)
P(1)-O(1)	1.647(2)	O(3)-P(1)-O(1)	**85.35(13)**
P(1)-O(5)	**1.713(2)**	O(2)-P(1)-O(1)	**91.39(13)**
O(2)-C(21)	**1.412(4)**	O(4)-P(1)-O(1)	89.08(12)
O(3)-C(31)	**1.412(4)**	O(3)-P(1)-O(5)	91.51(12)
C(21)-C(26)	1 383(5)	O(2)-P(1)-O(5)	**93.03(12)**
C(20)-C(26)	**1.515(5)**	O(4)-P(1)-O(5)	8988(12)
C(20)-C(36)	1.516(5)	O(1)-P(1)-O(5)	17543(13)
C(31)-C(36)	1.383(5)	C(1)-O(1)-P(1)	133.3(4)
		C(21)-O(2)-P(1)	126 1(2)
		C(31)-O(3)-P(1)	128.0(2)
		C(41)-O(4)-P(1)	**115.0(2)**
		C(46)-O(5)-P(1)	113 **3(2)**

(a) Geometry: The basic structure in all the four compounds studied is a tngonal bipyramid (TBP). The distortion from TBP (δ_{24} = 53.1°) towards a

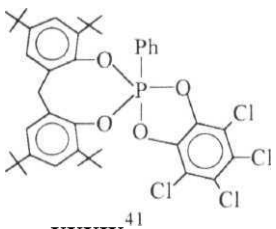


TBP **SP**

square pyramid [SP, δ_{24} = 0°] by fixing one of the equatorial atom as pivot is shown below:

Compound	Pivotal	δ_{24}(°)	TBP→SP (%)[a]
	0(1)	47.3	10.94
60	N	40.78	23.22
65	0(1)	46.68	12.09
79	0(2)	45.09	15.09 (for molecule A)
	0(8)	46.11	13.16 (for molecule B)

I (%) = [100 x (53.1 - δ)]÷53.1



XXXIX[41]

In the structures, the five-, six- and seven-membered rings span an *apical-equatorial* disposition in a TBP geometry. The eight-membered rings span an *apical-equatorial* arrangement in 65 and a *diequatorial* arrangement in 79. It is interesting to note that the cyclohexylamino (NHC_6H_{11}) group in 65 is *equatorial* whereas the phenyl group in Holmes' compound **XXXIX**[41] is *apical.*

The group electronegativities of the -Ph and -NHC_6H_{11} groups can be expected to be close [-Ph: 2.58, -NMe_2: **2.61,** -$C_6H_{11}NH$ value not available] on Pauling's scale.[107] Thus the presence of -NHC_6H_{11} to be *equatorial* may be because of the π-interaction involving the lone pair on nitrogen and an unused d-orbital on phosphorus. The sum of the bond angles around nitrogen N(1) in 65 is ~359° showing planarity and hence possible π-interaction with phosphorus.

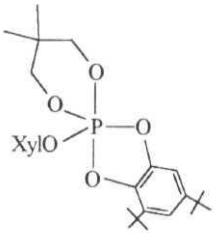
(b) Bond **lengths and bond angles:** For the rings spanning an ***apical-equatorial*** disposition in a TBP, the *apical* P-O bonds are longer than the *equatorial* P-O bonds as expected. The *apical* P-O bond of the five membered ring is the longest [1.71-1.78Å] in all the cases.

The P-N bonds in 59 [1.619(2)Å] and 65 [1.629(2)A] are shorter, ***albeit*** *marginally*, than those in 9 [mean: 1.656A] and 24 [1.635(3)A] respectively. The average (P-O)ring bond lengths are again shorter in the penta-coordinated compounds 59 (mean: 1.608A) and 65 (mean: 1.638A) relative to the respective P^{III} compounds 9 [mean: 1.634A] and 24 [mean: 1.666A]. These features may be related to the greater acidity of phosphorus in the penta-coordinated compounds pulling the electron density from the connecting atoms towards P.

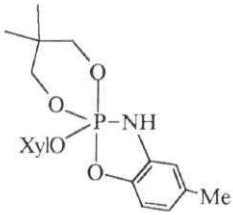
The P-N distance in 79 is 3.853A for the ordered molecule and 3.736 and 4.154Å respectively for the disordered second one. A comparison with the sum of the van der Waals radii (3.44 A) shows that there is no interaction between phosphorus and nitrogen.

(c) **Ring conformations:** The conformation of the 1,3,2-phosphorinane ring in 59 is that *of* a *boat;* the four atoms [P, 0(1), C(12), C(13)] forming the base are coplanar to within ± 0.298 A.. This kind of *boat* conformation has earlier been found for a large number of penta-oxyphosphoranes,[37(f),37(h)] and is in accord with Trippett's suggestion that it is the most favourable conformation for a saturated 1,3,2-dioxaphosphorinane ring in a TBP arrangement.[26]

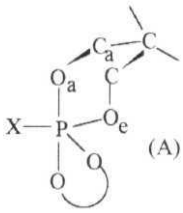
The four atom base of the boat in **59** and **XXXX** are tipped from the cyclohexylamino (59) or xylyloxy **(XXXX)** group respectively as shown **in** diagram (A) given below. By contrast, in the case of **XXXXI** the four atom base is tipped towards the xylyloxy group and away from the nitrogen of the 2-aminophenoxy group [as in (B) below].



XXXX[37(h)]



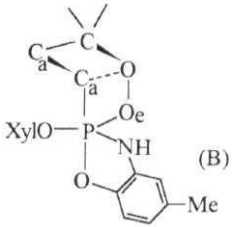
XXXXI[40]



(A)

X =NHC_6H_{11} **59**, Torsion angle Y-P-O_a-C_a = 62.9°

X= OXyl (XXXX, torsion angle 63.5°)



(B)

XXXXI

Torsion angle N-P-O_a-C_a 167.4

In contrast to the tri-coordinated derivatives 9 and 24, compounds 59, 60 and 65 did not show any H-bonding involving the NHC_6H_{11} hydrogens. This is a bit surprising because in compounds of the type XXXXI, the NH of the five-membered ring participates in H-bonding, leading to interesting structural and NMR features.[40]

The conformation of the seven-membered ring in 60 is that of a *row-boat* which is similar to some known structures.[37(c,g,h)] The four atoms [P(l), 0(1), C(21) and C(26)] forming the base of the *boat* are coplanar to within ± 0.0064 A.

The **eight-membered** ring in 65 has a *tub* conformation [Fig. 18], whereas the same ring in 79 has a *boat-chair* conformation. In 65, the atoms P, O(1), C(22) and C(l) are away from the mean atoms plane containing O(2)-C(11)-C(16) and C(21) to an extent of -0.138, -0.110, 0.047 and -0.110Å respectively. In 79, for molecule 1 (disordered, not shown), the atoms C(20), 0(2), 0(3) and P(l) are away from the mean plane containing C(26), C(21), C(31) and C(36) to an extent of 0.78, 0.74, 0.70 and 0.39A respectively; for molecule 2 (shown) in 79, the atoms O(7), O(8), C(220) and P(2) are away from the mean plane containing C(231), C(236), C(226) and C(221) to an extent of -0.77, -0.70 -0.44 and -0.76 A respectively.

Comparing the conformation of the 1,3,2-phosphocin ring in 65 and 79 with those known in the literature[37(a,e)] suggests that this ring prefers the *tub* conformation when it is positioned *apical-equatorial* [3 structures] and *boat-chair* conformation when it is *diequatorial* [5 structures] in a TBP geometry.

The five-membered rings in all these structures are planar.

Finally, the absence of N→P coordination in 79 is most likely due to steric factors, since in several other cases [next section] such a feature is present.

II.8.4 Hexa-coordinated phosphoranes and arsoranes

Compounds for which structures have been determined: 32, **73**.CH_2Cl_2, 75, **76**.CH_2Cl_2 and 78. $^1/_6Et_2O$ [The structure of 42 is incomplete].

The molecular structures of 32, 73, 75, 76 and 78 are shown in Figs 19-23; selected geometrical parameters are given in Tables 13-17.

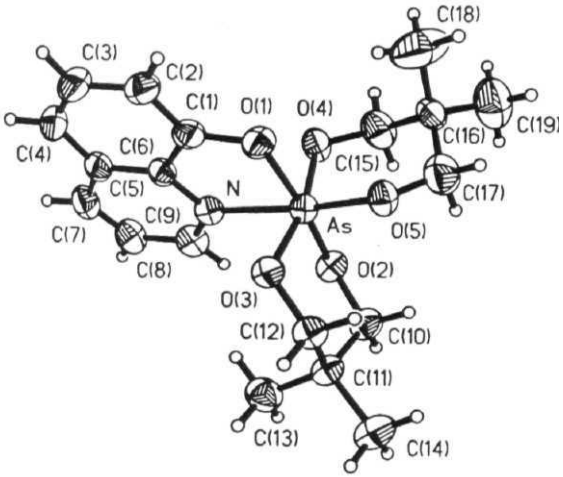


Fig. 19. Molecular structure of 32

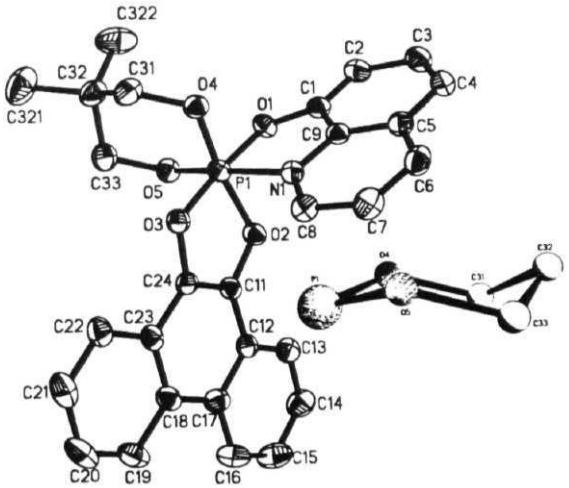


Fig. 20. Molecular structure of 73

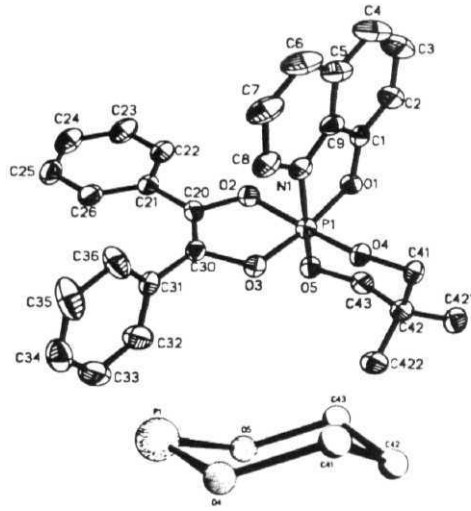


Fig. 21. Molecular structure of 75

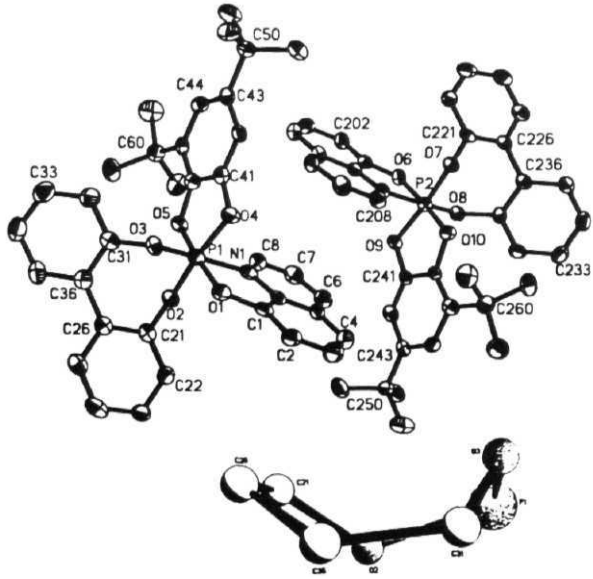


Fig. 22. Molecular structure of 76

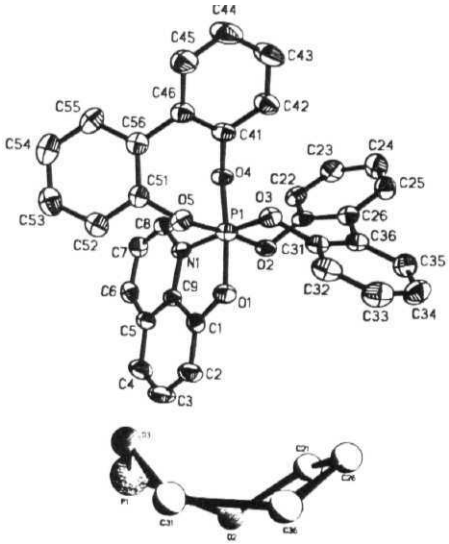


Fig. **23** Molecular stmcture of 78

Table 13. Selected bond lengths (A) and bond angles (°) for 32 with esd's in parentheses

As-0(5)	**1.771(3)**	As-O(4)	1.781(5)
As-0(3)	1 782 (4)	As-O(2)	1.789(3)
As-O(l)	1 883 (3)	As-N	2.045(4)
O(1)-C(1)	**1.317(5)**	**N-C(6)**	**1.341(5)**
O(2)-C(10)	1.432(5)	O(3)-C(12)	1.426(5)
O(4)-C(15)	**1.398(6)**	O(5)-C(17)	1.434(7)
C(l)-C(6)	1.412(6)	**C(10)-C(ll)**	1 501 (6)
C(11)-C(12)	1 516 (6)	**C(15)-C(16)**	1.510(7)
C(16)-C(17)	1.474(8)		
O(5)-As-O(4)	97.8(2)	O(5)-As-O(3)	**94.5(2)**
O(4)-As-O(3)	166 30(13)	O(5)-As-O(2)	98 4(2)
O(4)-As-O(2)	90.3(2)	O(3)-As-O(2)	93.9(2)
O(5)-As-O(1)	89.9(2)	O(4)-As-O(1)	88.1(2)
O(3)-As-O(1)	85 8(2)	O(2)-As-O(l)	171 69 (12)

O(5)-As-N	171 79 (13)	O(4)-As-N	82 6(2)
O(3)-As-N	84 4(2)	O(2)-As-N	89.8(2)
O(1)-As-N	81.9 (2)	C(10)-O(2)-As	119.4(3)
C(12)-O(3)-As	119 4(3)	C(15)-O(4)-As	**121.4(3)**
C(17)-O(5)-As	120.5(3)	O(2)-C(10)-C(11)	114.5(3)
C(10)-C(11)-C(12)	108.7(4)	O(3)-C(12)-C(11)	112.8(3)
O(4)-C(15-C(16)	114.5(4)	C(17)-C(16)-C(15)	108.8(4)
O(5)-C(17)-C(16)	116.0(5)		

Table 14. Selected bond lengths (A) and bond angles (°) for 73 with esd's in parentheses

P(1)-O(5)	1.623(2)	O(5)-P(1)-O(4)	99 90(8)
P(1)-O(4)	1.640(2)	O(5)-P(1)-O(3)	96 82(8)
P(1)-O(4)	1 705(2)	O(4)-P(1)-O(3)	90.06(8)
P(1)-O(1)	1.709(2)	O(5)-P(1)-O(1)	89.53(8)
P(1)-O(2)	**1.741(2)**	O(4)-P(1)-O(1)	91.18(8)
P(l)-N(l)	1.956(2)	O(3)-P(1)-O(1)	173.23(8)
O(4)-C(31)	1.433(3)	O(5)-P(1)-O(2)	90.85(8)
O(5)-C(33)	1.431(3)	O(4)-P(1)-O(1)	169.12(8)
		O(3)-P(1)-O(2)	90.32(7)
O(1)-P(1)-O(2)	87.21(7)	O(5)-P(1)-N(1)	172.58(8)
O(4)-P(1)-N(1)	85.11(8)	O(3)-P(1)-N(1)	88 61(7)
O(1)-P(1)-N(1)	84.87(7)	O(2)-P(1)-N(1)	84.03(7)
C(11)-O(2)-P(1)	110.29(13)	C(24)-O(3)-P(1)	111.16(13)
C(1)-O(1)-P(1)	117.33(13)	C(31)-O(4)-P(1)	121.92(14)
C(33)-O(5)-P(1)	121.49(14)		

Table 15. Selected bond lengths (A) and bond angles (°) **for 75 with** esd's in parentheses

P(1)-O(5)	1.621(2)	O(5)-P(1)-O(4)	98 71(10)
P(1)-O(4)	1.654(2)	O(5)-P(1)-O(3)	96.60(10)
P(1)-O(3)	1.678(2)	O(4)-P(1)-O(2)	86.93(10)
P(1)-O(2)	1.700(2)	O(5)-P(1)-O(2)	9231(10)
P(1)-O(1)	1.721(2)	O(4)-P(1)-O(2)	16879(9)
P(l)-N(l)	2.026(2)	O(3)-P(1)-O(2)	89 80(10)
O(4)-C(41)	1.429(3)	O(5)-P(1)-O(1)	91.61(10)
O(5)-C(43)	1.434(3)	O(4)-P(1)-O(1)	94.23(10)
C(41)-C(42)	1.525(4)	O(3)-P(1)-O(1)	171.44(9)

Table 15 contd

C(42)-C(43)	1.518(4)	O(2)-P(1)-O(1)	87 46(10)
O(4)-P(1)-N(1)	85.40(10)	O(5)-P(1)-N(1)	173 94(9)
O(2)-P(1)-N(1)	83 77(10)	O(3)-P(1)-N(1)	88.03(10)
C(1)-O(1)-P(1)	118.8(2)	O(1)-P(1)-N(1)	83.61(10)
C(30)-O(3)-P(1)	112 8(2)	C(20)-O(2)-P(l)	112 7(2)
C(43)-O(5)-P(1)	**122.7(2)**	C(41)-O(5)-P(1)	**121.1(2)**

Table 16. Selected bond lengths (A) and bond angles (°) for **76** with esd's in parentheses

P(1)-O(3)	1.652(4)	O(3)-P(1)-O(2)	95.9(2)
P(1)-O(2)	**1.655(3)**	O(3)-P(1)-O(5)	97.3(2)
P(1)-O(5)	1.692(3)	O(2)-P(1)-O(5)	87 8(2)
P(1)-O(4)	**1.696(3)**	O(3)-P(1)-O(4)	**91.5(2)**
P(1)-O(1)	1.710(4)	O(2)-P(1)-O(4)	172.6(2)
P(l)-N(l)	**1.959(4)**	O(5)-P(1)-O(4)	91.6(2)
O(2)-C(21)	**1.387(6)**	O(3)-P(1)-O(1)	88.8(2)
O(3)-C(31)	1.385(6)	O(2)-P(1)-O(1)	93 6(2)
C(21)-C(26)	1.392(7)	O(5)-P(1)-O(1)	173.6(2)
C(26)-C(36)	**1.477(7)**	O(4)-P(1)-O(1)	86.2(2)
C(31)-C(36)	**1.379(7)**	O(3)-P(1)-N(2)	**174.5(2)**
		O(2)-P(1)-N(1)	85.8(2)
		O(5)-P(1)-N(1)	88.0(2)
		O(4)-P(1)-N(1)	86.8(2)

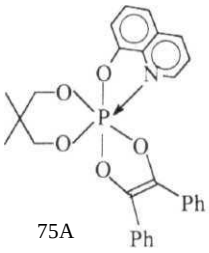
Table 17. Selected bond lengths (A) and bond angles (°) for **78** with esd's in parentheses

P(1)-O(3)	**1.637(2)**	O(3)-P(1)-O(4)	96 41(9)
P(l)-0(4)	1.662(2)	O(3)-P(1)-O(2)	95.63(9)
P(l)-0(2)	1673(2)	O(4)-P(1)-O(2)	91.14(8)
P(l)-0(5)	1681(2)	O(3)-P(1)-O(5)	90.15(9)
P(1)-O(1)	**1.725(2)**	O(4)-P(1)-O(5)	92 79(9)
P(l)-N(l)	1.938(2)	O(2)-P(1)-O(5)	172.61(10)
O(2)-C(21)	**1.374(3)**	O(3)-P(1)-O(1)	91 79(9)
O(3)-C(31)	**1.383(3)**	O(4)-P(1)-O(1)	171.78(10)
O(4)-C(41)	1.386(3)	O(2)-P(1)-O(1)	87.54(8)
O(5)-C(51)	1.370(3)	O(5)-P(1)-O(1)	87.67(9)

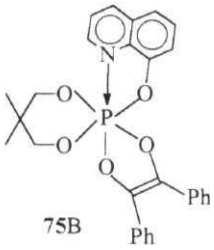
Table 17 contd

C(3)-C(36)	1.392(4)	O(3)-P(1)-N(1)	177.39(9)
C(26)-C(36)	1.476(4)	O(4)-P(1)-N(1)	86.04(9)
C(41)-C(46)	1.383(4)	O(2)-P(1)-N(1)	83.41(9)
C(46)-C(56)	1.476(4)	O(5)-P(1)-N(1)	90.61(9)
C(41)-C(46)	1.383(4)	O(1)-P(1)-N(1)	85.75(9)
		C(1)-O(1)-P(1)	116.1(2)
C(2)-O(2)-P(1)	121.8(2)	C(31)-O(3)-P(1)	**125.5(2)**
C(41)-O(4)-P(1)	**124.5(2)**	C(51)-O(5)-P(1)	126.3(2)

(a) Geometry: In all these compounds phosphorus [or arsenic in 32] is octahedrally coordinated by cyclic ligands. It can be readily recognized that for 75, 76 and 78 at least two geometrical isomers are possible; these are shown for **75** However only one isomer in which the oxinate nitrogen is *trans* to an oxygen of the six-membered ring [75 or 70] or of the seven-membered ring (77) is isolated. No evidence is found for the other isomer [^{31}P NMR in solution for the reaction mixtures and products].



75A



75B

Based on Holmes' formalism, the % age displacement from the square pyramidal (SP) geometry (with an O-P-O *trans* basal angle of 150°) toward octahedron can be calculated [Table 18 , keeping the P atom at 0.431 A from the base of the SP].[69(b)] For arsenic systems such data are not available and hence they are not included. It can be noted that a correlation of P-N distance to % O_h is not observed; this is in contrast to Holmes' compounds wherein a correlation of S-P distance to % O_h exists.[108]

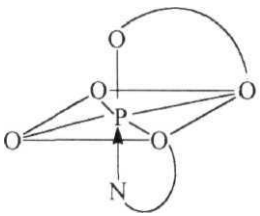


Table 18: Comparison of bond parameters for P-N coordination in cyclic penta-oxyphosphoranes

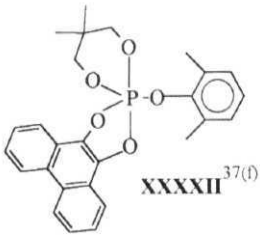
Compound	P-N(A)	P-O(Å)	N-P-0 trans (O)	Displacement (d)	%O_h*
73	**1.956(2)**	**1.623(2)**	172.58(8)	0.181	58.0
75	**2.026(2)**	**1 621(2)**	**173.94(9)**	**0 142**	**67.1**
76	**1.959(4)**	**1.652(4)**	**174.5(2)**	**0** 100	**76 8**
	1.963(4)	**1.658(3)**	**174.7(2)**	0.103	**76.1**
78	**1.938(2)**	1.637(2)	17739(9)	0 103	76 1

• **%** $O_h = [(0.431 - \mathbf{d}) \times \mathbf{100}] + 0.431$

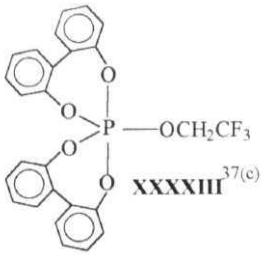
(c) Bond lengths and bond angles

Even after hexa-coordination, the As-0 bond lengths to the oxygens of the six-membered ring in 32 are surprisingly very close to that of the tetra-coordinated compound 8b. The endocyclic angle for the five-membered ring [O(1)-As-N: 81.9(2)°] is more acute than those involving six-membered rings [O(2)-As-O(3)]: 93.9(2)°; O(4)-As-O(5): 97.8(2)°]. To our knowledge, compound 32 has the shortest N→As donor acceptor bond (2.04 A) [The N→As distances in 8b, $MeN(CH_2CH_2O)_2AsMe(O_2C_6Cl_4)$[68] and $Me_3N{\rightarrow}AsCl_3$[103] are 2.60, 2.18 and 2.28 A respectively].

For the phosphorus compounds the endocyclic O-P-N angles lie between 84.0 and 85.9°. The greatest deviation from 90° is exhibited by the six-membered ring system in 73 (99.9°). The O-P-O angles in the seven-membered rings are closer to 90° [95.9° and 95.5° for 78 and 92.8° for 79] probably because of less ring strain. Such a feature is also discernible in the closely analogous penta-coordinated structures **XXXXII**[37(f)] and **XXXXIII**[37(c)] in which the O-P-O angle



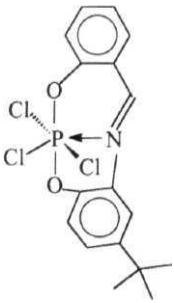
XXXXII[37(f)]



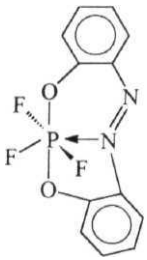
XXXXIII[37(c)]

for the six-membered ring [97.4(1)°] is larger than that observed for the seven-membered ring **[94.2(2)** and 93.3(2)°].

The P-O bond lengths differ depending on the ring size. In the five membered rings the mean P-0 distance is 1.711 A whereas it is 1 648 A in the larger rings. The mean P-0 bond distances in the 1,3,2-dioxaphosphorinane [1.631 A for 73, 1.63 A for 75] or in the phosphepin ring (1.663 A) are longer, *albeit marginally*, than those observed in the analogous penta-coordinated structures **XXXXII** (mean: 1.612 **A)** or **XXXXIII** (mean: 1.633 A) respectively, as expected. The P-N distances in 73, 75, 78 and 79 are in the range 1.938 A [for 78] - 2.026 A [for 75] [These values probably suggest varying Lewis acidities at the phosphorus centres; the two unsaturated seven-membered rings in 78 induce stronger acidic character on phosphorus]. These values are longer than those observed in **XXXXIV** (mean: 1.867 A) and **XXXXV** (mean: 1.91 A) reported



XXXXIV[109]



XXXXV[109]

recently by Cavell and coworkers.[109]

The five membered 1,3,2-dioxaphospholene rings are nearly planar in all the structures. The seven-membered ring in 76 and 78 shows a *row-boat* conformation and is analogous to our other structures [sections II.8.1 and **II.8.3**] and those reported by Holmes and coworkers.[16,37(c,g,h)]

The six-membered rings assume a *chair* conformation in 32, 73 and 75. Details are given in Table 19. As the only examples of hexa-coordinated phosphoranes with a saturated six-membered ring, compounds 73 and 75 are useful for comparing the variation in geometrical parameters and conformations in compounds with coordination numbers varying from 3 to 6.

Table 19. Details pertaining to the choice of the mean plane [of the base] in determining the conformations of the rings in 32, 73, 75, 76 and 78.

Compound	Ring Size	Conformation	Four atoms forming the base	Planarity to within A
32	six	chair	$O_2O_3C_{10}C_{12}$	±0.013
73	six	chair	$O_4O_5C_{31}C_{33}$	±0.014
75	six	chair	$O_4O_5C_{41}C_{42}$	±0.00033
76	seven	Row-boat	$P_1C_{31}C_{30}O_2$	±0.091
78	seven	Row-boat	$PO_2C_{31}C_{36}$	**±0.13**

There are weak interactions between the solvent and the molecule in structures 73 and 76; however since they do not affect the structures significantly they are not discussed any further.

II.9 *Summary and Outlook*

[1] Several interesting reactivity differences between cyclic phosphites and arsenites have been observed mainly as a result of the reluctance of arsenic to achieve the +5 oxidation state.

[2] Although the NH proton of the cyclohexylamino group participates in H-bonding in cyclic phosphites, it refuses to do so in penta-coordinated phosphoranes.

[3] The eight-membered 1,3,2-dioxaphosphocin ring prefers a *tub* conformation when it is located *apical-equatorial* and a *boat-chair* conformation when it is located *diequatorial* in a TBP structure.

[4] A novel series of hexa-coordinated phosphoranes have been structurally characterized. Although isomerism is possible, it is not detected. An air stable hexa-coordinated arsorane, $(OCH_2CMe_2CH_2O)_2As(OC_9H_6N)$ has also been structurally characterized.

Future work may involve the search for isomeric hexa-coordinated phosphoranes and arsoranes. The utility of the chloro compound $(OCH_2CMe_2CH_2O)_2AsCl$ in the synthesis of substituted arsoranes with As-I, As-$OSiMe_3$ and As-As bonds may also be explored.

CHAPTER III

EXPERIMENTAL SECTION

Chemicals and solvents were procured from Aldrich/ Fluka or from local manufacturers. Further purification was done according to standard procedures[110] whenever required All operations, unless otherwise specified, were carried out under dry nitrogen atmosphere using standard Schlenck techniques.[111] ^{1}H and ^{13}C NMR spectra were recorded on JEOL 100 MHz or on a Brucker 200 MHz spectrometer; $^{31}P\{^{1}H\}$ NMR spectra were recorded on Brucker 200 MHz [operating at 80.7 MHz] NMR spectrometer. ^{1}H, ^{13}C and $^{31}P\{^{1}H\}$ NMR were recorded in $CDCl_3$ (unless stated otherwise), with shifts referenced to $SiMe_4$ (^{1}H, ^{13}C; 5 = 0) or ext. 85% H_3PO_4 (5= 0); J values are in Hz. IR spectra were recorded on either a Perkin-Elmer 1310 spectrophotometer or on a JASCO FT/IR 5300 spectrophotometer. Elemental analyses were carried out on a Perkin-Elmer 240C CHN analyzer. Mass spectra were recorded on a CEC-21-110B double focusing mass spectrometer operating at 70 eV using direct inlet system. Melting points were determined on a SUPEREIT hot stage apparatus.

The following known compounds were prepared by literature methods.

Sl. No.	Compounds	M.p. (°C) or B.p./mm Hg.	$\delta(^{31}P)$ (ppm)	Ref.
1	N-chlorodiisoproplylamine (NCDA)	131/360 mm	-	112
2	$CH_2((t\text{-}bu)_2C_6H_2OH)_2$	147-149 5		76
3	$(Et_2N)_2AsCl$	53/1 mm	-	113
4	$(OCH_2CH_2O)PCl$ (1)	66-8/4-7 mm	-	71
5	$(OCH_2CH_2O)P(OC_9H_6N)$ (3)	136/1 mm	130	63(b)
6	$(1,2\text{-}C_6H_4O_2)PCl$ (**4a**)	91/18 mm	173 2	71
7	$(1,2\text{-}C_6H_4O_2)AsCl$ (**4b**)	130	-	72
8	$(1,2\text{-}C_6H_4O_2)P(OC_9H_6N)$ (**5a**)	83	125 1	63b
9	$(OCH_2CMe_2CH_2O)PCl$ (7a)	32/1 mm	120 8	8
10	$(OCH_2CMe_2CH_2O)P(NEt_2)$ (**10**)	65/0 5 mm	146 4	73
11	$(OCH_2CMe_2CH_2O)P(OPh)$ (13a)	115/0.5 mm	114 8	8(b)
12	$(OCH_2CMe_2CH_2O)As(OPh)$ (**13b**)	136/1 mm	-	14
13	$(OCH_2CMe_2CH_2O)P(O\text{-}2,6\text{-}Me_2C_6H_3)$ (14a)	129/0 8 mm	117 6	37(h)
14	$(2,2'\text{-}OC_6H_4C_6H_4O)PCl$ (**16a**)	195/12 mm	178 9	74
15	$(2,2'\text{-}OC_6H_4C_6H_4O)AsCl$ (16b)	98	-	75
16	$[CH_2\{2,4\text{-}(t\text{-}bu)_2C_6H_2O\}_2]PCl$ (**21a**)	213-218	136 3	76
17	$[CH_2\{(2\text{-}t\text{-}bu)(4\text{-}Me)\text{-}C_6H_2O\}_2]PCl$ (**23**)	189-192	-	77
18	$(OCH_2CMe_2CH_2O)P(O)Cl$ (26)	102-103	-3 4	78
19	$(OCH_2CMe_2CH_2O)P(O)H$ (29)	52-55	2.3	8
20	$(OC_6H_4CO_2)PCl$ (35)	80/1 5 mm	147 7	114

III.1 *Preparation of the P^{III} and As^{III} derivatives*

Arsenic trichloride[115] was prepared by adding sulphuric acid (150 mL) to a mixture of arsenic trioxide (60 g) and conc. hydrochloric acid (210 mL); the two liquid layers formed were separated and the lower layer distilled to give the pure compound **[95** g, 86%, b.p. 133°C].

The known arsenane $(OCH_2CMe_2CH_2O)AsCl$ (7b)[14] was prepared in a better yield using the following procedure:

A mixture of $AsCl_3$ (22.00 g, 0.12 mol) and 2,2-dimethyl-1,3-propanediol (12.50 g, 0.12 mol) was heated under reflux in dry dichloromethane (60 mL) till evolution of HC1 ceased (*ca* 5h). After removal of the solvent, the residue was heated at 110°C for 1h and then distilled *in vacuo* to give **7b.** Yield: 24.17 g (95%). B.p. 40°C/0.4 mm Hg)[14]. ^1H and ^{13}CNMR were identical to literature values except that in the ^{13}CNMR the two methyl carbons were resolved [21.7 and 22.88 ppm(s each, 2C, **CH3)].**

The cyclic aminophosphorus compounds 2, 6, 9, 18, 19, **24** and **25** (structures are shown in Chart 1, Section **II.**1) were prepared by treating the corresponding chloro precursor with two mole equivalents of the amine. The alkoxy/ aryloxy derivatives 5a, 8a, 8b, **11a**, **12b, 14b, 17a, 17b** and 20 were prepared by reacting the appropriate cyclic chloro phosphite/ arsenite with the required alcohol/ phenol in the presence of triethylamine. The procedure for the syntheses of 10, **11** and 36 are given below as representative examples. For the remaining compounds, experimental details are summarized in Table 17 physical and analytical data for all the compounds follow Table 17.

(a) **Synthesis** of $(OCH_2CMe_2CH_2O)P(OC_9H_6N)$ (8a): To **7a (3.47** g, 20.66 mmol) in toluene (50 mL) was added a mixture of 8-hydroxy quinoline (3.00 g, 20.66 mmol) and triethylamine (2.33 g, 23 mmol) in toluene (30 mL) over

a period of 10 mm. The mixture was stirred for 6h, filtered and solvent was removed. The residue was purified by vacuum distillation (B.p. 220°C/lmm Hg). Yield: 4.5 g (78%). Physical data follow Table 17.

(b) Synthesis of **$(OCH_2CMe_2CH_2O)P(NHC_6H_{11})$** (9): To 7a **(1.75** g, 10.40 mmol) in ether (60mL) were added cyclohexylamine **(2.06** g, 20.80 mmol) in ether (30 mL) over a period of 15 min. The mixture was stirred for 10h, filtered and solvent was removed. The residue was crystallized from n-heptane (2 g/ 1 mL). Yield: 1.83 g (76%). The compound could be purified by sublimation also (bath temp. 150°C at 0.5mm Hg). Physical data follow Table 17.

(c) Synthesis of **$[CH_2\{(2,4\text{-}t\text{-}bu)_2C_6H_2O]_2]AsCl$** (21b): To a mixture of arsenic trichloride (1.0 g, 5.5 mmol) in benzene (30 mL) [CAUTION: Benzene is a carcinogen] was added a mixture of $CH_2((t\text{-}bu)_2C_6H_2OH)_2$, (1.86 g, 4.4 mmol) and triethylamine (3 mL) in benzene (10 mL) and the whole then stirred for 4h. The mixture was filtered, solvent removed from the filtrate and the residue crystallized from benzene to give **21b.** Yield: 2.29 g (94% based on diol). Physical data follow Table 17.

Table 17. Experimental details for the synthesis of cyclic phosphites/ arsenites and phosphates

Chloro-precursor (mmol)	mmol of appropriate amine/ alcohol or phenol .3	Stirring time (h)	Product (Yield)	Crystallization solvent[b] (ratio).
1(23.72)	47 45	5	2(78%)	
1(59.77)	59.77[d]	4	3(79%)	

contd...

Table 17. contd....

4b (190)	1 90S	5	**5b** (40%)	DCM+hexane (1 1)
4a (40.70)	81.45	6	**6** (83 %)	
7b (7 33)	7.33[c]	4	**8b** (66 %)	ether+hexane (1:3)
7a (25.56)	25 56[c]	**5**	**11a (80%)**	
7b (10.50)	10 50[c]	**8**	**11b (75%)**	
7a (10.50)	10.50[c]	4	**12a** (85 %)	
7b (9.35)	9 35[c]	8	**12b** (78 %)	
7b (12.46)	12 46[c]	8	**14b** (55 %)	
7a (30.10)	30 10[c]	5	15(76%)	
16a (12.60)	12.60[c]	10	**17a** (77 %)	DCM+hexane (1:2)
16b (2 59)	2 59[c]	10	**17b** (78%)	DCM+hexane (1 1)
16a (22 99)	45 98	10	18(85%)	
16a (69.44)	138 87	44	**19(66%)**	
16a (16 35)	16.35[c]	11	**20** (72%)	
21a (2 52)	2 52[c]	38	**22a** (66 %)	ether+hexane (1 4)
21b (7 33)	7 33[c]	10	**22b** (67%)	ether+hexane (1 2)
21a (7.25)	14 51	12	**24** (80%)	hexane (2g/1mL)
23(45 51)	91 03	10	25 (85%)	hexane (1g/1mL)
26[d] (27 **10**)	54.20	**15**	**27**[e] (67 %)	DCM+hexane (1:2)
26[d] (14 42)	14.42[c]	16	**28**[f] (40 %)	DCM+hexane (1 2)

[a]Amine/ alcohol was added drop-wise to the chloro precursor through an additional funnel, [b]DCM. Dichloromethanc, [c]Equimolar quantity of triethylamine was used, [d]Chlorophosphate; [e] Phosphoramidate; [f] Phosphate ester

III.2 *Analytical and Physical Data for the Phosphites/Arsenites and Phosphate Esters.*

2 B.p. 125°C/0.5 mm [Found C, 50.71; H, 8.30; N, 7.81. Calc. for $C_8H_{16}NO_2P$: C, 50.79; H, 8.47; N, 7.41]. ^1H NMR: 1.01-2.10 (m, **11H,** cyclohexyl-C$\underline{H}_2$+N$\underline{H}$), 2.95 (br, 1H, NCH), 3.80-4.20 (m, 4H, OC$\underline{H}_2$). ^{13}C NMR: 25.3 (s, **3C,** cyclohexyl-$\underline{C}H_2$), 37.1 (s, **2C,** NC$\underline{C}H_2$), 49.8 (s, NH$\underline{C}$), **63.5** (d, ^2J(P-C) = 9.0 Hz, O$\underline{C}H_2$). ^{31}P NMR: 133.50.

3 B.p. 136°C/0.5 mm. [Found: C, 56.25; H, 4.41; N, 6.33. Calc.for $C_{11}H_{10}NO_3P$: C, 56.17; H, 4.26; N, 5.96]. ^{31}P NMR: 130.0[63b]

5a M.p. 83°C. [Found: C, 63.64; H, 3.48; N, 5.15. Calc. for $C_{15}H_{10}NO_3P$: C, 63.60; **H,** 3.53; **N,** 4.95]. ^1H NMR: 6.90-9.10 (complex, 10H, H(Ar)). ^{31}P NMR: 124.9.

5b M.p. 210°C. [Found: C, 55.78; H, 3.14; N, **4.36.** Calc. for $C_{15}H_{10}AsNO_3$: C, 55.05; H, 3.06; N, 4.28]. ^1H NMR: 6.75-9.00 (complex, 10H, H(Ar)).

6 B.p. 150°C/0.5 mm. [Found: C, 60.31; H, 6.61; N, **5.95.** Calc. for $C_{12}H_{16}NO_2P$: C, 60.76; H, 6.75; N, 5.91]. ^1H NMR: 0.90-1.88 (m, 10H, cyclohexyl-$\underline{H}$), 2.77 (br, ^1H, NH), 3.53 (m, ^3J(H-H) = 10 Hz, ^3J(P-H) =32 Hz, NCH), 6.75-7.06 (m, complex 4H, H(Ar)). ^{13}C NMR: 24.8 (s, 2C, $\underline{C}H_2$, cyclohexyl-$\underline{C}H_2$), 25.1 (s, 1C, cyclohexyl-$\underline{C}H_2$), 36.4 (s, 2C, NC$\underline{C}H_2$), 49.8 (d, ^2J(C-P) = 10 Hz, NCH), 111.4, 121, 7 and 146.3 (all C (Ar)). ^{31}P NMR: 139.8.

8a M.p. 50°C. [Found: C, 60.38; H, 5.65; N, 5.00. Calc. for $C_{14}H_{16}NO_3P$: C, 60.65; H, 5.78; N, 5.05]. ^1H NMR: 0.67 (s, 3H, CH3), 1.20 (s, 3H, CH3), 3.36 (t, 2H, $C\underline{H}_AH_B$), 4.40 (dd, 2H, ^3J(P-H) = 14 Hz, ^2J(H-H) = 11 Hz, 2H, $CH_A\underline{H}_B$), 7.20-8.90 (complex, 6H, H(Ar)). ^{31}P NMR. 113.5.

8b M.p. 80°C. [Found: C, 52.84; H, 5.11; N, 4.54. Calc. for $C_{14}H_{16}AsNO_3$: C, **52.35; H,** 4.98; **N,** 4.36]. ^1H NMR (C_6D_6): 0.41 **(s,** 3H, CH3), 1.35 **(s,** 3H, C$\underline{H}_3$),

3.48 (d, ^{2}J(H-H) = 8.0 Hz, 2H, $OC\underline{H}_AH_X$), 4.48 (d, 2H, $OCH_A\underline{H}_X$), 6.70-8.85 (m, 6H, H(Ar)). ^{13}C NMR: 21.8, 22.9 (s each, $\underline{C}H_3$), **33.2** (s, $\underline{C}Me_2$), **71.2** (s, $O\underline{C}H_2$), 110.6, **117.8, 121.2, 121.6,** 127.5, 128.0, 136.0, 147.7, 147.7 and **153.3** (all C (Ar)).

9 M.p. 78°C (B.p. 136°C/0.5 mm). [Found: C, **57.01;** H, 9.50; N, 6.51. Calc for $C_{11}H_{22}NO_2P$: **C, 57.14 H, 9.52; N, 6.06].** ^{1}H NMR: 0.92 (s, 3H, CH_3), **1.02** (s, 3H, CH_3), 1.00-2.04 (m, 10H, cyclohexyl-$\underline{H}$), 2.95 (br s, NH), 3.20 (br s, NCH), 3.60-3.90 (m, 4H, $OC\underline{H}_2$). ^{13}C NMR: 21.9 (s, $\underline{C}H_3$), 22.8 (s, CH3), 25.4 (s, 2C, cyclohexyl-CH2), 25.6 (s, 1C, cyclohexyl-$\underline{C}H_2$), 32.8 (d, ^{3}J(P-C) = 6.5 Hz, $\underline{C}Me_2$), 37.3 (d, 3J(P-C) = 6 Hz N-C-CH), 49.7 (d, ^{3}J(P-C) = 15.5 Hz, CNH), **72.1** (s, **OCH2). ^{31}P NMR: 132.1.**

11a B.p 60°C/0.5 mm. [Found: C, 50.20; H, 8.80. Calc. for $C_8H_{17}O_3P$: C, 50.00; H, 8 85] ^{1}H NMR: 0.73 (s, 3H, **CH3),** 1.24 (s, 3H, CH3), 1,28 (d, ^{3}J(H-H) = 6.0 Hz, 6H, $CH(C\underline{H}_3)_2$), 3.30 (dd, ^{3}J(P-H) = 11.0 Hz, ^{2}J(H-H) = 11.0 Hz. 2H. $OC\underline{H}_ACH_B$), 4.10 (d, ^{3}J(P-H) = **11.0** Hz, 2H, $OCH_A\underline{H}_B$), 4.30 (m, 1H, $C\underline{H}Me_2$). ^{31}P NMR: 119.9.

11b B.p. 60°C/0.5 mm. [Found: C, 40.25; H, **7.10.** Calc. for $C_8H_{17}O_3As$: C. 40.69; H, 7.20]. ^{1}H NMR (C_6D_6): 0.41 (s, 3H, $C(C\underline{H}_3)_2$), 1.16 (d, ^{3}J = 6 0 Hz, 6H, $CH(C\underline{H}_3)_2$), **1.25** (s, 3H, $C(C\underline{H}_3)_2$), 3.35 (d, ^{2}J(H-H) = 14.0 Hz, 2H $OC\underline{H}_2$), 4.10 (m, 1H. $C\underline{H}Me_2$), 4.35 (d, 2H, $OC\underline{H}_2$). ^{13}C NMR (C_6D_6):21.6 (s, $\underline{C}H_3$), 22.7 (s, **CH3),** 25.7 (s, CH3), 33.2 (s, $\underline{C}Me_2$), 65.9 (s, $\underline{C}HMe_2$), 70.9 (s, $O\underline{C}H_2$).

12a B.p. 41°C/2 mm. [Found: C, 36.15; H, 5.17. Calc. for $C_7H_{12}F_3O_3P$: C, 36.21; H, **5.17].** ^{1}H NMR: 0.75 (s, 3H, **CH3),** 1.25 (s, 3H, CH3), 3.36 (t, 2H, $OC\underline{H}_AH_B$), 4.10 (qrt, 2H, $OC\underline{H}_2CF_3$), 4.20 (m. 2H, $OCH_A\underline{H}_B$). ^{31}C NMR: 22.2 (s, $\underline{C}H_3$), 22.5 (s, **CH3),** 32.6 (s, $\underline{C}Me_2$), 60.9 (d qrt, $\underline{C}H_2CF_3$), 69.2 (s, OCH_2), 123.7 (qrt, ^{1}J = 275 Hz, $\underline{C}F_3$). ^{31}P NMR: 122.5.

12b B.p. 51°C/0.5 mm. [Found: C, 30.20; 4.21. Calc. for $C_7H_{12}AsF_3O_3$: C, 30.43; H, 4.34]. ^1H NMR: 0.72 (s, 3H, CH3), 1.23 (s, **3H, CH3),** 3.40 (d, ^2J(H-H) = 11 Hz, 2H, $OC\underline{H}_2$), 4.14 (qrt, ^3J = 8 Hz, $C\underline{H}_2CF_3$), 4.24 (d, 2H, $OC\underline{H}_2$). ^{13}C NMR: 21.6 (s, CH3), 22.9 (s, **CH3),** 33.2 (s, $\underline{C}Me_2$), **61.3** (qrt, ^2J(C-F) = 35.0 Hz, $O\underline{C}H_2CF_3$), 71.3 (s, $O\underline{C}H_2$), 125.4 (qrt, ^1J = 275 Hz, CF3).

14b B.p. 200°C/0.5 mm. [Found: C, 52.45; H, 6.70. Calc. for $C_{13}H_{19}AsO_3$: C, 52.35; H, 6.38]. ^1H NMR: 0.77 (s, 3H, CH3), 1.37 (s, 3H, CH3), 2.37 (s, 6H, Ar-CH3), 3.70 (d, ^2J(H-H) = 11.6 Hz, 2H, $OC\underline{H}_AH_B$), 4.55 (d, ^2J(H-H) = **11.6** Hz, 2H, $OCH_A\underline{H}_B$), 6.80-7.00 (m, 3H, H (Ar)). ^{13}C NMR: 17.5 (s, Ar-$\underline{C}H_3$), 21.9 (s, **CH3),** 23.2 (s, **CH3),** 33.5 (s, $\underline{C}Me_2$), 71.5 (s, $O\underline{C}H_2$), **120.9,** 128.6, 128.8, **130.1** and 152.4 (all C(Ar)).

15 B.p. 110°C/0.5 mm. [Found: C, 62.69; H, 7.81. Calc. for $C_{14}H_{21}O_3P$: C, 62.87; H, 7.83]. ^1H NMR: 0.82 (s, 3H, CH3), 1.38 (s, 3H, **CH3), 2.26(s,** 9H, Ar-CH3), 3.46 (t, 2H, $2C\underline{H}_AH_B$), 4.44 (d, ^3J(P-H) = 10 Hz, 2H, $CH_A\underline{H}_B$), 6.63 (s, 2H, H(Ar)). ^{31}P NMR: 132.3.

17a M.p. 145°C. [Found: C, 70.10; 3.80; N, 3.70. Calc. for $C_{21}H_{14}NO_3P$: C, 70.19; H, 4.00; N, 4.00]. ^1H NMR: 7.20-9.16 (m, 14H, H (Ar)). ^{31}P NMR: 139.6.

17b M.p. 138°C. [Found: C, 62.40; H, 3.60; N, 3.56. Calc. for $C_{21}H_{14}AsNO_3$: C, 62.52; H, 3.49; N, **3.47].** ^1H NMR: 7.00-8.90 (m, 14H, H (Ar)). ^{13}C NMR: 110.0-152.3 (all $\underline{C}$ (Ar)).

18 B.p. 190°C/0.5 mm [Found: C, 69.30; H, 6.43; N, 4.63. Calc. for $C_{18}H_{20}NO_2P$: C, 69.00; H, 6.40; N, 4.47]. ^1H NMR: 1.00-2.13 (m, 10H, (cyclohexyl-$C\underline{H}_2$), 3.25 (br, 2H, NH+NCH), 7.18, 7.55 (m, 8H, H (Ar)). ^{31}P NMR: 151.0.

19 B.p. 175°C/0.5 mm. [Found: C, 66.81; H, 6,75; N, 5.00. Calc. for $C_{16}H_{18}NO_2P$: C, 67.00; H, 6.27, N, 4.88]. ^1H NMR: 1.00 (t, 6H, CH3), 3.08 (qrt, 4H, $C\underline{H}_2$), 7.52 (m, 8H, H (Ar)). ^{31}P NMR: 149.6.

20 B.p. 210°C/0.5 mm. ^{1}H NMR: 2.24 (s, 3H, $C\underline{H}_3$), 2.37 (s, 6H, $2C\underline{H}_3$), 6.85 (s, 2H, H (Ar)). ^{31}PNMR: 146.8.

21b M.p 225-227°C. [Found: C, 65.40, H, 7.90. Calc. for $C_{29}H_{42}AsClO_2$: C, 65.36, H, 7.89]. ^{1}H NMR: 1.31 (s, 18H, t-bu-H), 1.42 (s, 18H, t-bu-H), 3.59 (d. ^{2}J(H-H) = 13 Hz, 1H, $C\underline{H}_AH_B$), 4.40 (d, 1H, C H A H B), 7.23-7.40 (d, 2H, (Ar)H), 7.34-7.36 (m, 2H, H (Ar)). ^{13}C NMR: 30.1 (s, $\underline{C}H_3$), 31.7 (s, $\underline{C}H_3$), 34.4 (s, $\underline{C}Me_3$), 34.7 (s, $\underline{C}Me_3$), **122.8,** 127.3, 139.9, 143.2 and **150.2** (all C (Ar)). $\underline{C}H_2$ not located.

22a M.p. 185°C. [Found: C, 76.45; H, 7.96; N, **2.45.** Calc. for $C_{38}H_{48}NO_3P$: C, 76.38, H, 8.04; N, 2.34]. ^{1}H NMR: **1.30** (s, 18H, t-bu-H), **1.32** (s, 18H, t-bu-H), 3.58 (d, ^{2}J(H-H) = 19 Hz, 1H, $C\underline{H}_AH_B$), 4.49 (dd, ^{5}J(P-H) = 2 Hz, ^{2}J(H-H)= 19 Hz, $CH_A\underline{H}_B$), 7.28-9.05 (m, 10H, H(Ar)). ^{31}P NMR: 131.2.

22b M.p. 88°C. [Found: C, **71.10;** H, 7.45; N, 2.45. Calc. for $C_{38}H_{48}AsNO_3$ C, 71.12; H. **7.54;** N, 2.18]. ^{1}H NMR: 1.29 (s, 18H, t-bu-H), **1.33** (s, 18H, t-bu-H), 4.06 ((AB)qurt, 2H, $C\underline{H}_2$), 7.15-8.85 (m, 10H, H (Ar)). ^{13}C NMR: 30.0 (s. C $C(\underline{C}H_3)_3$), 31.8 (s, $\underline{C}H_2$), 34.4 (s, $\underline{C}(CH_3)_3$), 35.1 (s, $\underline{C}(CH_3)_3$), 110.0-154.6 (many lines, C (Ar)).

24 M.p. 212°C. [Found: C, 76.03; H, 9.85; N, 2.63. Calc. for $C_{35}H_{54}NO_2P$: C, 76.22; H, 9.80; N, 2.54]. ^{1}H NMR: 1.32 (s, 18H. t-bu-H), 1.45 (s, 18H, t-bu-H). 1.32-2.25 (m, 10H, cyclohexyl-CH2), 2.90 (dd, ^{2}J(P-H)= 30 Hz, ^{3}J(HNCH)= 15 Hz, NH), **3.73** (br, NCH),3.95 (d, ^{2}J(H-H)= 14 Hz, $CH_A\underline{H}_B$ (bridging methylene)), 4.45 (dd, ^{5}J(P-H)= 4 Hz, ^{2}J(H-H)= 13 Hz, $CH_A\underline{H}_B$). 7.20-7.40 (m, 4H, H_(Ar)). ^{13}C NMR: 25.2, 25.8 (s each, cyclohexyl-CH2), 31.0, 31.1 (two s, $C(\underline{C}H_3)_3$), **31.5** (s, $C(\underline{C}H_3)_3$), 34.4 (s, $\underline{C}(CH_3)_3$), 35.1, 35.5 (two s, $\underline{C}(CH_3)_3$), 36.9 (s, cyclohexyl-$\underline{C}H_2$), 49.2 (d, ^{3}J = 4 Hz, **NCH),** 122.6, 124.8, 135.9, 141.0, 145.9, 148 (all $\underline{C}$ (Ar)). ^{31}P NMR: 140.9.

25 M.p. 155-160°C. [Found: C, 47.52; H, 8.95; N, **3.20.** Calc. for $C_{29}H_{42}O_2NP$: C, 47.46; H, 9.00, N, 3.00]. ^1H NMR: **1.15-2.30** (m. 10H, cyclohexyl-CH2), **1.40** (S, 18H, t-bu-H), 2.30 (s, 6H, **CH3),** 2.72 (dd, ^2J(P-H) = 28 Hz, ^3J(HNCH) = 9 Hz, 1H, NH), 3.34 (d, ^2J(H-H) = 18 Hz, $C\underline{H}_AH_B$), 3.72 (br, 1H, NCH), 4.38 (dd, 1H, $CH_A\underline{H}_B$), 7.05-7.15 (m,4H,H(Ar)). ^{31}P NMR: 141.4.

27 M.p. 172°C. [Found: C, 53.50; H, 8.90; N, 5.93. Calc. for $C_{11}H_{22}NO_3P$: C, 53.44; H, 8.91; N, **5.67].** ^1H NMR: 0.88 (s, 3H, CH3), **1.20** (s, 3H, CH3), 0.88-2.12 (m, 10H, cyclohexyl-$C\underline{H}_2$), 2.72 (m, 1H, NH), 3.10 (br m, 1H, NCH), 3.80 (dd, ^3J(P-H) = 24 Hz, ^2J(H-H)= 12 **Hz,** 2H, $C\underline{H}_AH_B$), **4.30 (dd,** ^3J(P-H) $^-$**2 Hz,** ^2J(H-H) = 12 Hz, 2H, $CH_A\underline{H}_B$). ^{31}P NMR: 4.1.

28 M.p. 104-6°C (lit. m. p. 118-119°C[7c]). ^{31}P NMR: -14.1.

III.3 *Preparation of **Phosphoranes/ Arsoranes***

III.3.1 General methods and representative examples:

Two general methods (A) and (B) were employed for the synthesis of phosphoranes/ arsoranes. **Method** (A) utilizes the oxidative addition of a 1,2-diketone with a phosphite/ arsenite whereas Method (B) involves the reaction of the phosphite/ arsenite with a diol in the presence of N-chlorodiisopropylamine (NCDA). The synthesis of I, 30, and 43 are given below as representative procedures. The preparations of 36, 42, 71, 77 and 78 involve significant modifications and hence these are also described. Experimental details for the other compounds are summarized in Table 18; analytical and physical data follow Table 18.

A(l) Synthesis of the phosphorane **43:**

To a solution of phosphite **14** (0.29 g, 0.97 mmol) in benzene (5 mL) was added o-chloranil (0.24 g, 0.97 mmol) slowly (5 min) and stirred for 10 min. The

solvent was removed and the residue was crystallized from ether-hexane (1:2). Yield: 0.42 g (86%). Physical data follow **Table 18.**

A(2) Synthesis of the phosphorane 43:

A mixture of phosphite **14** (0.32 g, 1.26 mmol) and o-chloranil (0.31 g, 1.26 mmol) was heated at 130°C (oil bath) for 7 min. The product was crystallized from a mixture of ether and hexane (1:2). Yield 0.57 g (91%). Physical data follow **Table** 18

B(l) Synthesis of the Phosphorane I:

To a mixture of 15 (1.88 g, 7.05 mmol) and biphenol (1.31 g, 7.05 mmol) in ether (60 mL) maintained at -60°C was added NCDA (0.96 g, 8.90 mmol) in ether (35 mL) over a period of 15 min with continuous stirring. The mixture was brought to 30°C, stirred overnight and filtered. Solvent was removed *in vacuo* and the residue crystallized from a mixture of dichloromethane and hexane (2:1). Yield: 2.39 g (75%). Physical data follow Table 18.

B(2) Synthesis of the phosphorane 30:.

To **7a** (2.33 g, 14 mmol) in ether (30 mL) maintained at -60°C was added a solution of 2,2'-dimethyl-l,3-propanediol (1.44 g, 14 mmol) and NCDA (1.88g, 14 mmol) in ether (40 mL) over a period of 20 min with continuous stirring. The mixture was brought to 30°C, stirred for 3h and filtered. Solvent was completely removed from the filtrate and the residue crystallized from a mixture of dichloromethane-hexane (1:2). Yield: 2.25 g (60%). M.p. 76°C. Physical data follow Table 18.

B(3) Reaction of chlorosalicylate 35 with salicylic acid-NCDA:

The procedure was the same as for the synthesis of the phosphorane 30 using chlorosalicylate ($(O_2CC_6H_4O)PCl$ (35) (1.70 g, 8.40 mmol), salicylic acid (1.16 g, 8.40 mmol) and NCDA **(1.14** g, 8.40 mmol). The residue was crystallized from a mixture of chloroform and hexane (1:2 ratio) to give a solid formulated as

$(OH)(O)P(O_2CC_6H_4O)$ (36). Yield: 0.3 g (18%). M.p. 80°C. [Found: C, 42.0; H, 3.03. Calc for $C_7H_5O_5P$: C, 42.0; H, 2.50]. ^1H NMR: 7.00-8.3 (m, 4H, aromatic). ^{31}P NMR: -8.73 ppm (another major peak present in the reaction mixture showed a $\delta(^{31}P)$ of -20.8 ppm].

(C) Synthesis of **the** phosphorane 42

To a mixture of 8a (0.992g, 3.58 mmol) and 2.2-dimethyl-l,3-propanediol **(0.37** g, 3.58 mmol) in toluene (35 mL) maintained at -60°C was added NCDA (0.485 g, 3.58 mmol) in toluene (25 mL) over a period of 15 min with continuous stirring. The mixture was brought to 30°C, stirred for 10h and filtered. Solvent was evaporated from the filtrate to lead to a mixture of products [^{31}P NMR: -66.8 (40%). -13.8 (5%), -8.3 (30%), -6.7 (10%) and -1.5 (15%)]. The signal at -66.8 ppm was attributed to the penta-coordinated derivative $(NC_9H_6O)P(OCH_2CMe_2CH_2O)_2$ (IV) (without N→P coordination); however on attempted crystallization from dichloromethane-hexane, it led to the air-sensitive crystalline compound 42 in low yields (*ca* 0.2 g) with $\delta(^{31}P)$ = -127.0 ppm. Physical data follow Table 18.

An attempt to prepare compound 42 was also made by reacting 8a (2.54 g, 9.17 mmol) with two moles of 8-hydroxy quinoline (2.66 g, 18.34 mmol) in the presence of NCDA (1.24 g, 9.17 mmol) in toluene (60 mL total) using the same conditions as above. The ^{31}P NMR of the reaction mixture showed a single peak at -111.5ppm. However this compound could not be isolated; only the hydrolysed product with $\delta(^{31}P)$ = -14.1 ppm was observed in an attempted crystallization.

(D) Synthesis of phosphorane 71.

A mixture of etheylene glycol (0.42 g, 6.71 mmol) and NCDA (0.91 g, 6.71 mmol) in ether (30 mL) was added to phosphite 9 (1.55 g, 6.71 mmol) in ether (40 mL) maintained at -60°C over a period of 15 min with continuous stirring. The mixture was brought to 30°C, stirred overnight and filtered. The residue was

crystallized from dichloromethane-hexane (1:2) to give initially $(OCH_2CH_2O)_2POCH_2CMe_2CH_2OP(OCH_2CH_2O)_2$ (71) (which was too susceptible to hydrolysis) and later $(OCH_2CMe_2CH_2O)P(O)(NHC_6H_{11})$ (27). These compounds were isolated by fractional crystallization from the reaction mixture. The yield of 71 was 0.2 g (7.4%). M.p. 145°C. [Found: C, 40.18; H, 7.11. Calc for $C_{13}H_{26}O_{10}P_2$: C, 38.61; H, 6.44]. ^{1}HNMR: 0.93 (s, CH3), 3.65-3.95 (m, 20H, OCH_2). ^{31}PNMR: -28.1. For compound 27 (yield: 0.3 g, 20%), physical data are identical to that reported above.

(E) Preparation of $(OCH_2CMe_2CH_2O)(2,2'\text{-}OC_6H_4\text{-}C_6H_4O)P(OC_9H_6N)$ (77) and $[2,2'\text{-}OC_6H_4C_6H_4O]_2P(OC_9H_6N).^1/_6Et_2O$ (78)

To a mixture of 8a (1.87 g, 6.74 mmol) and biphenol (1.26 g, 6.74 mmol) in dry ether (40 mL) maintained at -60°C was added NCDA (0.91 g, 6.74 mmol) in ether (30 mL) over a period of 15 min with continuous stirring. The mixture was brought to 30°C, stirred overnight and filtered. Compound 77 was obtained by fractional crystalliztion of the solid portion (which also contained diisopropylamine hydrochloride) using CH_2Cl_2-n-heptane mixture. Yield: 1.5 g (48%). Physical data follow Table 18.

Compound 78 was isolated by evaporating the solvent from the filtrate and crystallizing the residue from ether-hexane (1:3) mixture. Yield: 0.12 g (6.6%). Yield of 78 could be significantly improved when a 1:2 molar ratio of 8a to 2,2'-biphenol was used; thus by using (1.21 g, 4.35 mmol) of 8a and (1.62 g, 8.71 mmol) of 2,2'-biphenol, 0.7 g (27%) of 78 was obtained [For an alternative route, see the reaction of 81 with 8-hydroxy quinoline given below]. Physical data follow Table 18.

Table 2. Experimental details for phosphoranes/ arsoranes.

Sl. No	phosphite/ arsenite (g, mmol)	Diol/ Diketone (g, mmol)[a]	Product Yield (g, %)	Crystallization Solvent ratio	Method used
1-	**7b** (1.81, 8.50)	**E (0.88,** 8.50)[b]	**31(1.07,40)**	**toluene (1** g/0.5 mL)	A(2)
2-	**7a** (1.16, 6.90)	G (2.92, 6.90)[b]	**33(2.7,65)**	DCM+hexane(1:2)	A(2)
3-	**7a** (2.19, 13.00)	**F** (2.42, 13.00)[b]	**34**[d]		A(2)
4-	**4a(2.26, 13.0)**	**D (1.42,** 13.0)[b]	37(2.6,65)	DCM+hexane(1:2)	A(2)
5-	**7a** (0.84, 3.50)	**J** (0.78, 3.50)	**38(0.46,35)**	toluene+hexane(1:1)	B(2)
6-	**7a(0.84,5.0)**	**A (0.49, 5.0)**	**39(0.7,80)**	toluene (1g/2mL)	B(2)
7-	4a (026. 0.15)	**K** (0.03, 0.15)	**40**[d]		B(2)
8-	**4a** (0.37, 2.14)	**I** (0.53, 2.14)	*41i*		**B(2)**
9-	**6** (0.90, 3.79)	**I** (0.93, 3.79)	58(1.1,60)	**DCM+hexane(l;2)**	B(l)
10-9(0.36,1.58)		**I (0.39, 1.58)**	**59(0.45,60)**	DCM+hexane(1:2)	B(l)
11-	**18(0.63,2.02)**	**I** (0.50, 2.02)	**60(0.7,54)**	DCM+hexane(2:1)	B(l)
12-25(1.34,2.88)		**I** (0.71, 2.88)	61(1.1,54)	DCM+hexane(1:1)	B(l)
13-9(0.76,3.31)		**A(0.69,3.31)**	62(0.9,62)	DCM+hexane(1:1)	B(l)
14-	**18(3.29, 10.51)**	**A** (2.19, 10.51)	**63** (3.5, 64)	DCM+hexane(1:1)	B(l)
15-	**6** (1.25, 5.28)	**G** (2.24, 5.28)[b]	**65(2.5,72)**	DCM+hexane(l:2)	A(l)
16-18(1.25,3.99)		**F** (0.74, 3.99)[b]	66(1.5,79)	DCM+hexane(2:l)	A(l)
17-	5a (0.55, 195)	**K** (0.43, 1.95)	72(06,61)	DCM+hexane(1:1)	B(l)
18-	**8a** (0.6, 2.18)	**A** (0.45, 2.18)	73(0.6,57)	DCM+hexane(l:5)	B(l)
19-	8a (0.6, 2.18)	**K** (0.45, 2.18)	74(0.55,50)	DCM+hexane(1:4)	B(l)
20-	8a (0.53, 1.92)	J (0.40, 1.92)	75(0.42,45)	DCM+hexane(1:1)	B(l)
21-	**17a** (0.69, 1.95)	**K** (0.41, **1.95**)	76(02,41)	DCM+hexane(1:5)	B(l)

contd

22-	**22a** (0.38, 0.63)	K (0.14, 0.63)	79(0.30,58)	hcxanc (1g/1 mL)	B(l)
23-	10(295,1438)	F (2 68, 14 38)[b]	81 gum[e]		A(l)
24-	**10(2** 93, 14 26)	**A** (2 97, 14 26)	**82** (4 48, 76)	DCM+hcxanc(l:5)	B(2)

[a]A: 9,10-Phenanthrene quinone; B: Pinacol; C: Tetrachlorocatechol; D: Catechol; E: 2,2-Dimethyl-1,3-propanediol; F: 2,2'-Biphenol; G: 2,2'Methylene bis(4,6-di(tert)-butylphenol); H: 2,2'-Methylene bis(4-chlorophenol); 1: o-Chloranil; J: Benzil; K: 3,5-Di(t-butyI)-o-benzoquinone; L: Ethylene glycol.

[b]Equimolar quantity of N-chlorodiisopropylamine (NCDA) was used.

[c]DCM: Dichloromethane

[d]Although the compounds were formed in >80 % yield, analytically pure product could not be obtained

[e]The product was pure [^{31}P and ^{1}HNMR].

III.3.2 Analytical and physical data for phosphoranes/ arsorane

I **M.p.** 195°C. [Found: C, 69.20; H, 6.47. Calc. for $C_{26}H_{29}O_5P$: C, 69.03; H. 6.42]. ^{1}H NMR: 1.05 (s, 6H, CH3), 2.08 (s, 6H, CH_3-(Ar)), 2.18 (s, 3H, CH3), 3.95 (d, ^{3}J(P-H) = 19 Hz, 4H, OCH_2), 6.70 (s, 2H, H (Ar)), 7.15-7.56 (m, **10H,** H (Ar)). ^{31}P NMR: -60.3.

30 M.p. 76°C. [Found: C, 44.27; H, 7.63. Calc. for $C_{10}H_{20}ClO_4P$: C, 44.34; H, 7.39]. ^{1}H NMR: 0.91 (s, 3H, CH3 (ring)), 1.06 (s, **6H,** CH3), 1.25 (s, 3H, CH3 (ring)), 3.46 (s, **2H,** CH_2Cl), 3.91 (d, ^{3}J(P-H) = 4.0 Hz, 2H, OCH_2), 3.85-4.20 (m, 4H, OCH_2(ring)). ^{13}CNMR: 20.44 (s, CH3 (ring)), 21.5 (s, CH3 (ring)), 22.2 (s, CH3 (open)), 32.2 (d, ^{3}J (P-C) = 5.0Hz, CMe_2), 36.69 (d, ^{3}J(P-C) = 6.0 Hz.

$\underline{C}Me_2$ (ring)), 51.4 (s, $\underline{C}H_2Cl$), 71.6 **(d,** ^2J(P-C) = **5 Hz,** $O\underline{C}H_2$), 77.8 **(d,** ^2J(P-C) = **7.0** Hz, $O\underline{C}H_2$ (ring)). ^{31}P NMR: -8.7.

31 M.p. 37°C. [Found: C, 41.08; H, 8.34. Calc. for $C_{10}H_{20}AsClO_4$: C, 38.17; H, 6.36. However it agrees reasonably well with the hydroxy arsorane $(OCH_2CMe_2CH_2O)_2As(OH)$ (Calc. for $C_{10}H_{21}AsO_5$: C, 40.54; H, **7.10)].** ^1H NMR: 0.94 (s, 12H, $C\underline{H}_2$), 3.78 (s, 8H, $OC\underline{H}_2$). ^{13}C NMR: 21.6 (s, $\underline{C}H_3$), 36 0 (s, $\underline{C}Me_2$), 74.2 (s, $O\underline{C}H_2$).

33 M.p. MOT. [Found: C, 68.53; H, 9.18. Calc. for $C_{34}H_{52}ClO_4P$: C. 69.10; H, 8.81]. ^1H NMR: 1.13 (s, 6H, $C(C\underline{H}_3)_2$), 120 (s, 18H, $C(C\underline{H}_3)_3$), **1.44** (s, 18H, $C(C\underline{H}_3)_3$), 3.52 (s, 2H, $C\underline{H}_2Cl$), 4.00-4.20 (br s, 2H, $C\underline{H}_2$-Ar), 4 28 (d, 2H, ^3J(P-H) = 4 Hz, $OC\underline{H}_2$). ^{13}C NMR: 22.4 (s, $\underline{C}(CH_3)_2$), 27.3 (s, $\underline{C}H_2$-(Ar)), **51.2** (s, $\underline{C}H_2Cl$), 74.2 (d, ^2J(P-C) = 7.0 Hz, $O\underline{C}H_2$), 124.1, **125.8, 131.3,** 140.2, **146.1, 147.8, (all C** (Ar)). ^{31}P NMR: -12.7.

34. ^1H NMR: 1.03 (s, $C(C\underline{H}_3)_2$), 3.82 (s, $C\underline{H}_2Cl$), 4.15 (d, ^3J(P-H) 4 Hz, $OC\underline{H}_2$), 6.80-7.50 (m, 8H, H (Ar)). ^{13}C NMR: 22.1 (s, $C(\underline{C}H_3)_2$), 37.0 (br s, $\underline{C}Me_2$), 51.1 (s, $\underline{C}H_2Cl$), 75.50 (s, $O\underline{C}H_2$), 116.0-132.0 (m, C (Ar)). ^{31}P NMR: 0.4. Pure product could not be isolated; other minor products (*ca 15* %) were also present along with the expected one. [^{31}P NMR: -15.0, -8.5, -8.4,-8.0].

37 M.p. 180°C. ^{31}P NMR: -31.0 [lit. 5 (^{31}P) =-30.0 ppm[74]].

38 M.p. 78°C. [Found: C, 59.65; H, **5.10.** Calc. for $C_{19}H_{20}ClO_4P$: C, 60.25, H, 5.30]. ^1H NMR: 1.08 (s, 6H, **CH3),** 3.45 (s, 2H, $C\underline{H}_2Cl$), 4.10 (d, ^3J(P-H) = 4.5 Hz, 2H, $OC\underline{H}_2$), 7.30-8.00 (m, 10H, H (Ar)). ^{13}C NMR: 21.9 (s, $C(\underline{C}H_3)_3$), 36.73 (s, $\underline{C}(CH_3)_3$), 51.50 (s, $\underline{C}H_2Cl$), 72.57 (d, ^2J(P-C) = 5 Hz, $O\underline{C}H_2$), 128.0-134.0 (m, $\underline{C}$ **(Ax)).** ^{31}P NMR: 9.4.

39 M.p. 100°C. [Found: C, 60.20; H, 4.78. Calc. for $C_{19}H_{18}ClO_4P$: C, 60.57; H, 4.78]. ^1H NMR: 1.07 (s, 6H, $C\underline{H}_3$), 3.45 (s, 2H, $C\underline{H}_2Cl$), 4.14 (d, ^3J(P-H)= 6.8 Hz, 2H, $OC\underline{H}_2$), 7.60-8.80 (m, 8H, H (Ar)). ^{13}C NMR: 22.1 (s, $\underline{C}H_3$), 37.0 (s, C

$(CH_3)_2$), **51.0** (s, $\underline{C}H_2Cl$), 74.0 (s, $O\underline{C}H_2$), 120.0-128.0 (m, C (Ar)). ^{31}P NMR: 13.7.

40 MS: m/Z(%): 396(8), 394(3), $[M]^+$, 359 (100) $[M\text{-}Cl]^+$. ^1H NMR: 1.52 (s, 9H, $C(C\underline{H}_3)_3$), 1.78 (s, 9H, $C(C\underline{H}_3)_3$), 6.90-7.40 (m, 4H, H (Ar)). ^{13}C NMR: 30.1, 32.0 (s each, $C(\underline{C}H_3)_3$), 32.0, 34.9 (both $\underline{C}(CH_3)_3$), 107.1 , 107.8, 111.6, 112.3, 117.4, 123.5, 123.7, 128.8, 134.6, 135.2, 138.8, 139.0, 143.0, 143.2, 146.4, (all C (Ar)). ^{31}P NMR (C_6D_6): -31.0 (a penta-oxyphosphorane, *ca* 2%), -10.4 (-10.8 in $CDCl_3$, **40,** *ca* 90%) and 173.0 (4a, *ca 5%).*

41 MS: m/Z(%): 252(10), 250(45), 248(100), 246(80), $[M\text{-}C_6H_4ClO_2P+2H$ (?)$]^+$, 156(60) $[(C_6H_4O_2)P(OH)]^+$, 139(30). ^1H NMR (C_6D_6): 6.70-7.20 (m, 4H, H(Ar)), ^{13}C NMR (C_6D_6): 110.8, 111.2, 113.9, 122.9, 123.1, 124.1, 139.8, 142.7 (all C (Ar)). ^{31}P NMR (C_6D_6): -30.4 (a penta-oxyphosphorane, *ca* 15%), -9.2 (-8.9 in $CDCl_3$, 41, *ca* 70%), 173.0 (4a, *ca* 15%).

42 M.p. 174°C. [Found: C, 68.92; H, 5.14; N, 10.07. Calc. for $C_{32}H_{28}N_3O_5P$: C, 68.00; H, 5.0; N, 7.40]. ^1H NMR: 1.08 (br s, 6H, $C\underline{H}_3$), 4.22 (d, $^3J(P\text{-}H) = 20$ Hz. 4H. $C\underline{H}_2$). 7.00-8.98 (m. 18H, H (Ar)). ^{31}P NMR: -127.0. A small peak *(ca* 5 %) at -14.1 ppm was also seen.

43 M.p. 183°C. [Found: C, 45.5; H, 3.75. Calc. for $C_{19}H_{19}Cl_4O_5PC$, 45.62; H, 3.80]. ^1H NMR: 1.04 (s, 3H, $C\underline{H}_3$), 1.14 (s, 3H, $C\underline{H}_3$), 2.25 (s, 6H, Ar ($C\underline{H}_3$)), 3.90-4.20 (ABX m, 4H, $OC\underline{H}_2$), 6.95 (s, 3H, H (Ar)). ^{13}C NMR: 16.4 (s, Ar (CH3)), 24.4 (s, CH3), 24.5 (s, $\underline{C}H_3$), 32.8 (d, ^3J (P-C) = 5.0 Hz, $\underline{C}Me_2$, 76.7 (d, $^2J(C\text{-}P)$ = 8 Hz, $O\underline{C}H_2$), 114.5, 124, 128.6, 128.9, 140.1 and 150.7 (all C (Ar)). ^{31}P NMR: -50.4.

55 M.p. 130°C. [Found: C, 70.10; H, 6.39. Clac. for $C_{28}H_{31}O_5P$: C, 70.29; H, 6.48]. ^1H NMR: 1.11 (s. 3H, CH3), 1.28 (s, 3H, CH3), 2.34 (s, 3H, $C\underline{H}_3$-(Ar)). 2.97 (s, 6H, $C\underline{H}_3$-(Ar)), 4.15 (m, 4H, $OC\underline{H}_2$), 6.86 (s, 2H, H (Ar)), 7.17 (br m 10H, benzil). ^{31}P NMR: -54.0.

58 M.p. 182°C. [Found: C, **44.53;** H,3.29; N, 3.76 Calc. for $C_{18}H_{16}Cl_4NO_4P$: C, 44.74; H, 3.31; N, 2.90]. ^1H NMR: 1.05-1.95 (m, 10H, cylohexyl-C$\underline{H}_2$) **3.10-3.35** (m, 2H, **NH+NCH).** ^{31}P NMR: -29.4. 1R (cm^{-1}): 3368 (sharp (v(NH)).

59 M.p. 127°C. [Found: C, 42.61; H, 4.60; N, 3.00. Calc. for $C_{17}H_{22}Cl_4NO_4P$: C, 42.78; H, 4.61; N, 2.94]. ^1H NMR: 1.00, 1.05(s, each, 6H, **CH3),** 0.90-2.10 (m, 10H, cyclohexyl-C$\underline{H}_2$), 3.03 (m, 1H, NH) 3.32 (br, 1H, NCH), 3.94 (d, ^3J(P-H) = 20 Hz, OC$\underline{H}_2$). ^{31}P NMR: -45.7. IR (cm^{-1}): 3437 (sharp, (v(NH)).

60 M. p. 170°C. [Found: C, 51.46; H, 3.51; N, 2.60. Calc. for $C_{24}H_{20}Cl_4NO_4P$: C, 51.54; H, 3.58; N, 2.51]. ^1H NMR: 0.81-1.85 (m, 10H, Cyclohexyl-C$\underline{H}_2$), 3.20-3.40 (m,2H, NH+NCH), 7.15-7.48 (m, 8H, H(Ar)). ^{31}P NMR: **-34.7.**

61 M.p. 118°C. [Found: C, 73.41; H, 7.30; N, 2.62. Calc. for $C_{41}H_{42}Cl_4NO_4P$: C, 73.56; H, 7.36; N, 2.45]. ^1H NMR: 0.72-2.42 (m, 34H, cyclochexyl-C$\underline{H}_2$)+C$\underline{H}_3$), 3.25-3.70 (m, 3H, C$\underline{H}_A\underline{H}_B$+N$\underline{H}$+NC$\underline{H}$), 4.55 (d, ^2J(H-H) = 14 Hz, 1H, C$\underline{H}_A$H$_B$), 6.75-7.15 (m, 4H, H (Ar)). ^{31}P NMR: -54.6. 1R (cm^{-1}): 3366 (sharp, (v(NH)).

62 M.p. 158°C. [Found: C, 68.21; H, 6.75; N, 3.50. Calc. for $C_{25}H_{30}NO_4P$: C, 68.34; H, 6.83; N, 3.20]. ^1H NMR: 1.02, 1.08 (s each, 6H, CH3), 1.00-2.20 (m, 10H, cyclohexyl-C$\underline{H}_2$), 3.21 (m, 1H, NCH), 3.90-4.20 (m, 4H, C$\underline{H}_A\underline{H}_B$), 7.40-8.65 (m, 8H, H(Ar)). ^{31}P NMR: -46.2. IR (cm^{-1}): 3350 (sharp, (v(NH)).

63 M.p. 185°C. [Found: C, 73.17; H, 5.46; N, 3.13. Calc. for $C_{32}H_{28}NO_4P$: C, 73,70; H, 5.37; N, 2.69). ^1H NMR: 0.90-2.20 (m, 10H, cyclohexyl-C$\underline{H}_2$), (m, 2H, NH+NCH), 7.27-8.72 (m, 16H, H(Ar)). ^{31}P NMR: **-34.4.** IR (cm^{-1}): 3381 (sharp (v(NH)).

65 M.p. 173°C. [Found: C, 73.93; H, 9.05; N, 2.10. Calc. for $C_{41}H_{58}NO_4P$: C, 74.6; H, 8.80; N, 2.12]. ^1H NMR: 1.03-2.03 (m, 46H, (cyclohexyl-C$\underline{H}_2$)+C$\underline{H}_3$), 3.32 (br, 1H, NCH), 3.32-3.52 (br, 2H, NH+NCH), 4.07 (br d, 1H, C$\underline{H}_A$H$_B$), 4.60

(br d, 1H, $CH_A\underline{H}_B$), 6.72-7.35 (m, 8H, H (Ar)). ^{31}P NMR: **-56.3,** 56.8 (two peaks).

66 M.p. 209°C. [Found: C, 72.42; H, 6.03; N, 2.57. Clac. for $C_{30}H_{28}NO_4P$: C, 72.43; H, 5.63; N, 2.82]. ^1H NMR: 0.80-2.10 (br m, 10H, cyclohexyl-$C\underline{H}_2$), 3.35 (br, **2H,** NH+NCH), 6.90-7.65 (m, 16H, H (Ar)). ^{31}P NMR: **-39.6.**

72 M.p. 198°C. [Found: C, 69.05; H, 5.76; N, 2.70. Clac. for $C_{29}H_{30}NO_5P$: C, 69.18; H, 5.96; N, 2.78]: ^1H NMR: **1.25** (s, 18H, $C(C\underline{H}_3)_3$), 6.75-9.08 (m, **12H,** H(Ar)). ^{31}P NMR:-88.3.

73 M.p 265°C. [Found: C, 69.06; H, 4.80; N, 2.65. Calc. for $C_{28}H_{24}NO_5P$: C, 69.28; H, 4.95; N, 2.89]. ^1H NMR: 1.14 (s, 3H, $C\underline{H}_3$), 1,22 (s, 3H, $C\underline{H}_3$), 4.09 (d, ^3J(P-H) = 17Hz, 4H, $OC\underline{H}_2$), 5.20 (variable, $C\underline{H}_2Cl_2$), 7.15-8.68 (m, 14H, H (Ar)). ^{31}P NMR:-100.5.

74 M.p. 172°C. [Found: C, 67.35; H, 7.10; N, 2.58. Calc. for $C_{28}H_{36}NO_5P$: C, 67.60; H, 7.24; N, 2.82]. ^1H NMR: **1.05** (s, 3H, **CH3),** 1.16 (s, 3H, $C\underline{H}_3$), 1.21 (s, **9H,** $C(C\underline{H}_3)_3$), 1.46 (s, 9H, $C(C\underline{H}_3)_3$). 3.80-4.40 (m, 4H, $OC\underline{H}_2$), 6.60-8.60 (m, **8H,** H(Ar)). ^{31}P NMR:**-101.0.**

75 M.p 175°C. [Found: C, 68.84; H, 5.30; N, 2.81. Calc. for $C_{28}H_{26}NO_5P$: C, 68.99, H, 5.34; N, 2.87]. ^1H NMR: **1.05,** 1.26 (s each, 6H, **CH3),** 3.85-4.25 (m, 4H, $6C\underline{H}_2$), 7.12-8.62 (m, 10H, H(Ar)). ^{31}P NMR: -101.8.

76 M.p. 246°C. [Found: C, 72.33; H, 5.56; N, 2.15. Calc. for $C_{35}H_{34}NO_5P$: C, 72.54; H, 5.87; N, 2.42]. ^1H NMR: 1.26 (s, 9H, $C(C\underline{H}_3)_3$), 1.43 (s, 9H, $C(C\underline{H}_3)_3$), 5.20 (s. $C\underline{H}_2Cl_2$, variable), 6.48-8.84 (m, 16H, H (Ar)). ^{31}P NMR: -89.3

77 M.p. 155°C. [Found: C, 67.89; H, 5.14; N, 2.98. Calc. for $C_{26}H_{24}NO_5P$: C, 67.68; H, 5.21; N, 3.04]. ^1H NMR: 0.97 (br s, 3H, **CH3),** 1.35 (br s, 3H, $C\underline{H}_3$), 3.50-4.60 (br m, 4H, $C\underline{H}_2$), 6.55-8.82 (m, 4H, H (Ar)). ^{31}P NMR: -107.9.

78 M.p. 251°C. [Found: C, 73.14; H, **4.18;** N, 2.40 Calc. for $C_{33}H_{22}NO_5P$: **C,** 72.93; H, 4.05; N, 2.58]. ^1H NMR: 5.22-8.83 (m,, H (Ar)). ^{31}P NMR: -94.8.

79 M.p. 142°C. [Found: C, 76.32; H, 8.25; N, 1.65. Calc. for $C_{52}H_{68}NO_5P$: C, 76.38; H, 8.32; N, **1.71].** ^1H NMR: 0.29 (s, 9H, $C(C\underline{H}_3)_3$), 1.11 (s, **18H, C** $(C\underline{H}_3)_3$), 1.25 (s, 9H, $C(CH_3)_3$), 1.29 (s, 18H, $C(C\underline{H}_3)_3$), 3.45 (d, ^2J **(H-H)=** 15.0 Hz, $C\underline{H}_A H_B$), 4.55 (dd, ^5J (P-H)= 3 Hz, ^2J (H-H) = 15 Hz, 1H, $CH_A\underline{H}_B$), 6.15-9.05 (m, 15H, H (Ar)). ^{31}P NMR:-56.3.

81 Gum. [Found: C, 65.32; H, 7.46; N, 2.91. Calc. for $C_{21}H_{28}NO_4P$: C, 64.78; H, 7.20; N, 3.60]. ^1H NMR: 0.90-1.40 (many lines $C\underline{H}_3$), 3.15-3.30 (m, 4H, NCH2), 3.60-3.80 (d, $^2J \approx$ 18.0Hz, 4H, $OC\underline{H}_2$), 7.10-7.65 (m, 8H, H (Ar)). A second $NC\underline{H}_2$ signal (quartet) at 2.65 ppm was also observed over a period of time. ^{31}P NMR:-50.1.

82 M.p. 155°C. [Found: C, 66.52; H, 6.50; N, 3.45. Clac. for $C_{23}H_{28}NO_4P$: C, 66.83; H, 6.78; N, 3.39]. ^1H NMR: 1.02 (s, 3H, $C\underline{H}_3$), 1.09 (s, 3H, $C\underline{H}_3$), 1.13 (t, ^3J(H-H)= 6.8 Hz, 6H, $CH_2C\underline{H}_3$), 3.25 (m, ^3J(P-H)= 13.6 Hz, ^3J(H-H)= 6 8 Hz, 4H, $NC\underline{H}_2$), 3.97 (d, $J \approx$ 18 Hz, 4H, $OC\underline{H}_2$), 7.42-8.76 (m, 8H, H (Ar)). ^{31}P NMR: -40.6. A second signal for $NC\underline{H}_2$ at ca 2.85 slowly developed over a period of time.

(F) The following compounds could not be isolated in a pure state [as they were too susceptible to hydrolysis and/or too soluble in the solvent used].

Sl No.	Reaction mixture	Method	^{31}P (intensity)	Assignment
1-	9+ 1,2-O_2-3,4-(t-bu)$_2C_6H_2$	B(l)	-48 8(85%)	XXVI
			121.1(15%)	9
2-	18+ 1,2-O_2-3,4-(t-bu)$_2C_6H_2$	B(l)	-36 6(100%)	64
3-	**18** + Benzil	B(l)	-39 4(100%)	XXVII

4-	18 + $HOCH_2CMe_2CH_2OH$ + $ClN(i\text{-}Pr)_2$	A(2)	-54.2(90%) -46.0 (5%) 7.5(5%)	68 Not assgnd Not assgnd
5-	9 + $CH_2((t\text{-}bu)_2C_6H_2OH)_2$ + $ClN(i\text{-}Pr)_2$	A(2)	-70.3 (55%) -13.7(45%)	**69** Not assgnd
6-	**18** + $CH_2((t\text{-}Bu)_2C_6H_2OH)_2$ + $ClN(i\text{-}Pr)_2$	A(1)	-58 8(85%) 11.0 (15%)	70 Not assgnd
7-	**5a** + Catechol + $ClN(i\text{-}Pr)_2$	A(l)	**-89.5** (>50%) -84.8(30%) -8.0, **10.5** (~15%)	**XXI** {[$P(O_2C_6H_4)_3$]-(?)} Not assgnd
8-	8a + Catechol + $ClN(i\text{-}Pr)_2$	A(l)	**-102.4(85%)** -12.3(15%)	**XVII** Not assgnd
9-	8a + $HOCMe_2CMe_2OH$	A(l)	-58 5(35%) 10 0 to -25.0 (many peaks)	**XXIII**
10-	**5a** + Methylene bis(4-chloro phenol)+ $ClN(i\text{-}Pr)_2$	A(l)	-106.7(100%)	**XXII**
11-	**8a** + Methylene bis(4-chloro phenol)+ C1N(/-Pr)2	A(l)	-127.1(50%) -14.8(50%)	**XVIII** 87
12-	**22a** + 9,10-Phenanthrenequinone	B(1)	-56.1(15%) -13 7(40%), 131.2(45%)	**XXIV** Not assgnd Not assgnd
13-	**14a** + $HOCH_2CMe_2CH_2OH$ $ClN(i\text{-}Pr)_2$	A(2)	-68 8(40%) **-66.9(35)**	**XXV** **XXV**
14	**15** + Biphenol+ Et_3N+ N-Bromo succinimide	A(l) (Solvent was DCM)	-60 3(<5%) 132 3(95%)	I **1S(S.M.)**

III.3.3 Reactions of the chloroarsorane 31 and the arsenite 14b

(1) **Preparation of $(OCH_2CMe_2CH_2O)_2As(OC_9H_6N)$ (32):**

To **7b** (3.44 g, 10.17 mmol) in ether (40 mL) maintained at -60°C was added a mixture of 2,2-dimethyl-l,3-propanediol (5.68 g, 16.17 mmol) and NCDA (2.20 g, 16.17 mmol) in ether (40 mL) over a period of 15 min with continuous stirring. The mixture was brought to 30°C, stirred overnight and filtered. The precipitate was washed with ether (10 mL) and the washings added to the filtrate. To this solution, a mixture of 8-hydroxy quinoline (2.38 g, 16.17 mmol) and triethylamine (1.67 g, 16.17 mmol) in ether was added. The mixture was stirred for 3h and filtered. Solvent was removed from the filtrate and the residue obtained was crystallized from CH_2Cl_2-hexane mixture (1:4) to afford **32.** Yield: 4.5 g (65%). M.p. 187-192°C. [Found: C, 53.85; H, 6.00; N, 3.20. Calc. for $C_{19}H_{26}AsNO_5$: C, 53.90; **H,** 6.15; **N, 3.31].** ^{1}H NMR: 0.71 (s, 3H, CH3), 1.01 (s, 6H, $C\underline{H}_3$), 1.11 (s, 3H, CH3), 1.16 (s, 3H, CH3), 3.38-4.76 (m, 8H, $OC\underline{H}_2$), 7.22-9.34 (m, **16H,** H (Ar)). ^{13}C NMR: 22.0, 22.2, 22.6, 23.5 (s each, CH3), 71.6, 76.0, 78.7, 78.9, (s each, $OC\underline{H}_2$), 111.0, 114.5, 121.5, 127.0, 130.9, 140.7 and 151.0 (All C (Ar)).

(2) **Attempted preparation of $(OCH_2CMe_2CH_2O)_2As(O\text{-}2,4,6\text{-}Me_3\text{-}C_6H_2)$:**

The procedure was the same as for compound **32** using 7b (3.10 g, 14.58 mmol), 2,2'-dimethyl-1,3-propanediol (1.52 g, 14.58 mmol), NCDA (1.98 g, 14.58 mmol), 2,4,6-trimethylphenol (1.99 g, 14.58 mmol), and triethylamine (1 mL). The required amount of salt was obtained; however the product was too hygroscopic to characterize further.

(3) **Attempted preparation of $(OCH_2CMe_2CH_2O)(C_6Cl_4O_2)As(O\text{-}2,6\text{-}Me_2C_6H_3)$:**

Method B(2) was applied using the following quantities: arsenite **14b** (0.29 g, 0.97 mmol) and o-chloranil (0.24 g, 0.97 mmol). The reaction did-not take place

at 30°C. When was heated strongly; the ^1H NMR spectrum of the product showed it to be a mixture including the starting material; no pure compound was isolated.

III.4 *Hydrolysis and Related Reactions of Cyclic Phosphites and Arsenites*

III.4.1 Hydrolysis of **aminophosphites:**

(1) Hydrolysis of **$(OCH_2CH_2O)P(NHC_6H_{11})$** (2): Compound 2 was mixed with water (1.09 g, 5.29 mmol). After 10 min excess of water was evaporated and the residue extracted with dichloromethane to gave 48 (viscous liquid) in quantitative yield (^{31}P NMR). [Found: C, 39.85; H, 9.2; N, 5.8. Calc. for $C_8H_{22}NO_5P$: C, 39.51; H, 9.05; N, 5.76]. ^1H NMR: 1.05-2.20 (m, 10H, cyclohexyl-C$\underline{H}_2$), 3.05 (br s, 1H, NCH), 3.45 (s, 2H, OC$\underline{H}_2$), 3,73 (m, 2H, C$\underline{H}_2$OH), 3.95 (m, 2H, C$\underline{H}_2$OP), 6.83 (d, ^1J(P-H) = 620 Hz, P$\underline{H}$), 8.30 (br s, 3H, RN^+H_3). ^{13}C NMR: 24.5 (s, 2C, $\underline{C}H_2$), 24.9 (s, 1C, CH3), 31.0 (s, 2C, $\underline{C}H_2$), 50.2 (s, NCH), 62.0 (d, ^2J(P-C) = 3 Hz, O$\underline{C}H_3$), 65.7 (d, ^2J(P-C) < 3 Hz, O$\underline{C}H_2$). ^{31}P NMR: 4.6. 1R (cm^{-1}): 2363 ν(PH), 1199 (ν(P=O)), 1076 (ν(P=O)).

(2) Hydrolysis **of $(OCH_2CMe_2CH_2O)P(NHC_6H_{11})$** (9): (1) Water (0.037 g, 2.05 mmol) was added to a solution of 10 (0.16 g, 0.68 mmol) in THF (10 mL) and the mixture stirred overnight. It was then evaporated and the residue crystallized from dichloromethane-hexane (1:3) to give 49. Yield 0.19g. (>95%) M.p. 145-150°C. [Found: C, 48.3; H, 10.1; N, 5.2. Calc. for $C_{11}H_{26}NO_4P$: C, 49.40; H, 9.74; N, 5.24]. The sample contained variable amounts of water in different preparations; ^1H NMR: 0.84 (s, 6H, CH3), 1.05 (m, 10H, cyclohexyl-C$\underline{H}_2$), 2.95 (br m, 1H, NCH), 3.29 (s. 2H, HOCH_2), 3.56 (d, ^2J (H-H)= 10.0 Hz. 2H, POCH_2), 4.10 (br, *ca* 1.5H, H20), 6.72 (d, ^1J(P-H) = 621.0 Hz), 8.40 (s, 3H, $^+NH_3$). ^{13}C NMR: 21.4 (s, 1C, CH3), 24.5 (s, 2C, $\underline{C}H_2$), 24.8 (s, 1C, $\underline{C}H_2$), 31.1 (s. 2C, 2CH_2), 36.9 (s, 1C, $\underline{C}Me_2$), 50.1 (s, 1C, NCH), 67.0 (s, HO$\underline{C}H_2$), 68.7 (s,

$PO\underline{C}H_2$, J< 2.0 Hz). ^{31}P NMR: 4.8. IR (cm^{-1}): 3435, 3400, 2940vs, 2374 ν(P-H), 2183, 1639, 1545, 1452, 1180vs (ν(P=O)), 1051vs (ν(P=O)), 827.

(ii) Keeping 9 (0.5g, 2.12 mmol) in open air for > 6h also led to 49 [^{31}P NMR], but a crystalline product was not obtained.

(iii) Even when compound 9 (0.5 g, 2.12 mmol) was mixed with water (0.38 g, 2.12 mmol) and after 10 min, excess of water was evaporated and the residue crystallized from dichloromethane-hexane (1:3) to give 49 in quantitative yield. M.p., ^{1}H and ^{31}P NMR were identical to those reported above. Different batches varied only in the sharpness of $^{+}N\underline{H}_3$ and $O\underline{H}_2$ peaks (^{1}H NMR). The ^{31}P NMR results were identical for all the samples.

(3) **Identification** of the intermediate VII: Compound 9 was either (i) exposed to moist air for 3h on a watch glass or (ii) stirred with water (3 mol equiv.) in THF for 25 min after which the solvent was removed immediately. The ^{1}H NMR spectrum for the oily product VII obtained from routes (i) and (iii) were identical. ^{1}H NMR: 0.84 (s, 6H, CH3), 1.00-2.00 (m, 10H, cyclohexyl-$C\underline{H}_2$), 2.95 (m, 1H, NCH), 3.29 (AB qrt, 2H, $OC\underline{H}_A\underline{H}_B$) 3.50 (t, J=10.0, 11.0 Hz, 1H, OCH_2), 3.70 (t, J= 10.0, 11.0 Hz, 1H, $OC\underline{H}_2$), 4.70 (variable, $O\underline{H}_2$), 6.90 (d, ^{1}J(P-H) = 640 Hz, 1H). ^{13}C NMR: 21.2 (s, 2C, CH3), 24.9 (s, 2C, $\underline{C}H_2$), 25.2 (s, 1C, $\underline{C}H_2$), 35.6 and 35.8 (AB qrt, ^{3}J(P-C) = 4.5 Hz, 2C, $\underline{C}H_2$), 36.8 (d, ^{3}J(P-C)= 5 Hz, $\underline{C}Me_2$), 49.5 (s, NCH), 66.9 (s, $H\underline{C}H_2$), 68.2 (d, ^{2}J = 2.2 Hz, $PO\underline{C}H_2$). ^{31}P NMR: 12.1. This sample VII when kept for > 6h gave compound 49 quantitatively (^{1}H, ^{31}P and ^{13}C NMR).

(4) Hydrolysis of **$(OCH_2CMe_2CH_2O)P(NEt_2)$** (10) [method as in (1) above]: The compound 50 was obtained by using 10 (1.0 g, 4.87 mmol) and water (2 mL). Yield was quantitative [^{31}P NMR]. The product was purified by extracting it from water using hexane whereby 50 was obtained as a viscous liquid. [Found: C, 39.05; H, 9.00; N, 4.20. Calc. for $C_9H_{28}NO_6P$: C, 38.99; H, 8.66; N,

5.05]. ^{1}H NMR: 0.85 (s, 6H, $C(C\underline{H}_3)_2$), 134 (t, 6H, ^{3}J=7.2 Hz, $CH_2C\underline{H}_3$), **2.91** (m, 4H, $NC\underline{H}_2$), 3.30 (s, 2H, $OC\underline{H}_2$), 3.59 (d, ^{3}J(P-H) = 10.8 Hz, 2H, $OC\underline{H}_2$), 3.75 (br s, 4H, $OC\underline{H}_2$), 6.77 (d, ^{1}J(P-H) = 626.0 Hz, 1H, PH), 9.70 (br s, 2H, $^{+}N\underline{H}_2$). ^{13}C NMR: 11.0 (s, $CH_2\underline{C}H_3$), 21.4 (s, $C(CH_3)_2$), 36.9 (d, ^{3}J(P-C) = 35 Hz, $\underline{C}Me_2$), 41.8 (s, $N\underline{C}H_2$), 67.2 (s, $O\underline{C}H_2$), 68.6 (d, ^{2}J = 4.7 Hz, $PO\underline{C}H_2$) ^{31}P NMR: 4.2 ppm. IR (cm^{-1}): 2361 (ν(P-H)), 1197vs (ν(P=O)), 1053vs (ν(P=O)).

(5) **Hydrolysis** of **$(OC_6H_4C_6H_4O)P(NHC_6H_{11})$ (18)** [method as in (1)]. Water (3 mL) was added directly to 18 (1.30 g, 4.15 mmol) to give 51. Needle shaped crystals grew over a period of time (3 days) from the aqueous solution. Yield: 1.35 g (93%). M.p. 180°C. [Found: C, 62.48; H, 7.25; N, 4.09. Calc. for $C_{18}H_{24}NO_4P$: C, 61.89; H, 6.88; N, 4.01] ^{1}H NMR: (DMSO-d_6): 1.00-2.00 (m, 10H, cyclohexyl-$C\underline{H}_2$), 2.85 (m, **NCH),** 3.10-4.20 (br, $O\underline{H}_2$), 6.82 (d, ^{1}J(P-H)= 606 Hz. P$\underline{H}$). 6 70-7.40 (m, 8H, H (Ar)), 8.10 (s, 3H, $^{+}NH_3R$). ^{13}C NMR: 23.8 (s, 2C, $\underline{C}H_2$), 24.6 (s. $\underline{C}H_2$), 30.2 (s, **2C,** $\underline{C}H_2$), 49.1 (s, NCH), 115.8, 116.9, 118.6. 121.2. 122.2. 125.9, 127.8, 128.0, 128.2, **131.1,** 131.4, 137.6, 154.5 and 154.8 (all C (Ar)). ^{31}P NMR: 2.98. IR (cm^{-1}): 2391 (ν(PH)), 1200vs (ν(P=O)), **1068vs (ν(P=O)).**

(6) Hydrolysis of **1,3,2-Benzodioxaphosphole** 6 [method as in (1)] A single product was obtained [^{31}P NMR] using 6 (1.0 g, 4.22 mmol) and water (3 mL). The product was crystallized from dichloromethane-hexane (1:3). Yield: 1.1 g (96%). M.p. 115-125°C. [Found: C, 48.7; H, 7.8; N, 4.9. Calc. for $C_{12}H_{22}NO_6P$: C, 49.48; H, 7.56; N, 4.81]. ^{31}P NMR: (DMSO-d_6). 2.6 ppm. The P-H signal could not identified in the ^{1}H NMR spectrum. The product was formulated as $(1,2\text{-}HOC_6H_4O)P(O)(O^{-})(H)N^{+}H_3C_6H_{11}$) on the basis of elemental analysis.

(7) **Attempted** hydrolysis of 24: Hydrolysis did not take place even in boiling water.

III.4.2 Reaction of $(OCH_2CMe_2CH_2O)P(O)H$ (29) with aqueous **amine solutions.**

(1) A mixture of 29 (0.5 g, 3.33 mmol) and dimethylamine solution (3 mL) (w/v) (35-40%) was stirred for 10 min. The solvent was removed completely to afford $(HOCH_2CMe_2CH_2O)P(O)(O^-)(H)^+NH_2Me_2$ (54) in quantitative yield as a viscous liquid. ^1H NMR: **0.78** (s, 6H, $C\underline{H}_3$), **2.65** (s, 6H, NCH3), 3.22 (s, 2H, $HOC\underline{H}_2$), 3.5 (d, ^3J(P-H) = 1 1Hz, 2H, $C\underline{H}_2$), 6.67 (d, ^1J(P-H) = 620 Hz) 6.4 (br, H_3^+N-$OC\underline{H}_2$). ^{31}P NMR: 4.9.

(2) Reaction of 21 (0.5 g, 3.33 mmol) with a mixture of cyclohexylamine (3 nL) and water (0.5 mL) afforded 49 [^1H and ^{31}P]. Physical data are given above.

III.4.3 Cyclization of ring cleaved phosphonate **salts**

Upon heating compounds 54 or 49 individually at 220°C/0.5 mm with proper cooling of the receiver, 29 was obtained in 40-50% yield, B.p. (7070.5 run) [^1H and ^{31}P NMR]. The identity of the product was also confirmed by heating a mixture of equimolar quantities of the resulting product 29 and g-chlorobenzaldehyde in benzene to afford the known derivative $(OCH_2CMe_2CH_2O)P(O)CH(OH)C_6H_4$-p-Cl. [M.p.(174-175°C), ^1H and ^{31}P (5 = **12.9 ppm**) NMR were identical].[90]

III.4.4 Effect of CsF/ **KF** on the hydrolysis **of** aryloxy/ **aminophosphites.**

(1) To a mixture of $(OCH_2CMe_2CH_2O)P(NHC_6H_{11})$ (9) (0.31 g, 1.34 mmol) and CsF (1.0 g, 6.7 mmol) was added (2 mL) of water. The obtained mixture was stirred for 7h, water was removed *in vacua* (0.5 mm Hg) and the resulting products were extracted with $CDCl_3$ (1 mL) using a syringe. ^{31}P and ^1H NMR spectra showed that the extract *(ca* 0.2 g) was mainly 9 (> 95 %).

(2) To a mixture of $(OCH_2CMe_2CH_2O)P(OPh)$ **(13a)** (0.5 g. 2.21 mmol) and KF (0.7 g, 12.05 mmol) was added water (5 mL). The mixture was stirred overnight, water was removed *in vacuo* (0.5mm Hg) and the resulting products were extracted with $CDCl_3$ (1 mL) using a syringe. ^{31}P and ^{1}H NMR of the extract showed that the extract *(ca* 0.3 g) was mainly **(13a)** (> 95%).

(3) To a mixture of $(OCH_2CMe_2CH_2O)P(OCH(CH_3)_2)$ **(11a)** (0.32 g, 1.67 mmol), and CsF (0.44 g, 6.20 mmol) was added water (0.06 g, 3.33 mmol) in THF (5 mL). The mixture was heated under reflux for 12h, solvent removed *in vacuo* (0.5mm Hg) and the resulting products were extracted with $CDCl_3$ (1mL) using a syringe. ^{31}P NMR spectrum of the extract *(ca* 0.1 g) showed it to be exclusively **11a**

1II.4.5 Hydrolysis of aryloxy/ alkoxy phosphites/ arsenites.

These reactions were carried out by mixing stoichiometric quantities of the cyclic phosphites/ arsenites and water in the presence or absence of cyclohexylamine. Solvents used were toluene benzene, ether, THF or water (as shown in each case). The products were identified by $^{1}H/^{31}P$ NMR spectroscopy and wherever feasible, by isolation. Details are presented below:

(a) Hydrolysis of 8a (Synthesis of **52)** Following the same procedure as in section **III.4.1,** method 2(i), using 8a (1.0 g, 3.61 mmol) and water (0.20 g, 0.82 mmol) in THF (5 mL) gave 52 (viscous liquid). Yield *(ca* 0.97 g, > 95%). ^{1}H NMR: 0.87 (s, 6H, CH3), 3.40 (s, 2H, $C\underline{H}_2$), 3.78 (d, ^{3}J(P-H) = 10 Hz, 2H, $C\underline{H}_2OP$), 7.05 (d. ^{1}J(P-H) = 645 Hz, 1H, P-H). ^{13}C NMR: 21.4 (s, 1C, CH3), 37.0 (d, ^{3}J(P-C) = 5 Hz, $\underline{C}Me_2$), 67.3 (s, 1C, $\underline{C}H_2$), 69.2 (d, ^{2}J = 5 Hz, $\underline{C}H_2OP$), 114.1, 117.5, 121.4, 129.5, 129.6, 122.5, 141.1, 145.0and 151.0, (all **C (Ar)).** ^{31}P NMR: **5.6.**

(b) Hydrolysis of 17a. (Synthesis of 53): Following the same procedure as in section **III.4.1,** method 2(i), using **17a** (1.5 g, **4.17** mmol) and water (0.32 g, 12.52 mmol) in THF (7 mL) gave 53 (1.6 g, 97%). M.p. 146°C [Found: C, 63.3; H, 4.46; N, 3.70. Calc. for $C_{21}H_{18}NO_5P$: C, 63.80; H, 4.56; N, 3.87]. ^1H NMR: (DMSO-d_6): 6.78 (d, ^1J(P-H) = 640 Hz, 1H, PH), 6.70-8.90 (m, 14H, H (Ar)). ^{31}P NMR: 4.4.

(c) Synthesis of **$[(OCH_2CMe_2CH_2O)As]_2O$** (44): (i) To a stirred solution of 7a (1.5 g, 7.05 mmol) in toluene (30 mL), a mixture of cyclohexylamine (0.7 g, 7.05 mmol) and water (0.06 g, 3.52 mmol) was added dropwise over a period of 0.5h at 20°C. After 12h of stirring the mixture was filtered, the solvent evaporated from the filtrate and the residue crystallized from hexane to give **44** (0 78 g, 60%). M.p. HOT. [Found: C, 37.3; H, 5.65 Clac. for $C_{10}H_{20}As_2O_5$: C, 32.43; H, 5.41]. ^1H NMR: 0.72 (s, 12H, CH3), 3.44 (d, ^2J(H-H) = 10.6 Hz, OCH_AH_X), 4.25 (d, 4H, OCH_AH_X). ^{13}C NMR: 21.9 (s, 1C, CH3), 32.2 (s, 1C, CH3), 33.5 (s, 1C, CMe_2) and 71.1 (s, OCH_2). IR (cm^{-1}): 2981, 2820, 1465, 1380, 1350, 1035vs, 765vs.

(ii) Compound **44** was also prepared by heating under reflux a mixture of As_2O_3 (2.0 g, 10.11 mmol) and 2,2'-dimethylpropane-1,3-diol (2.10 g, 20.22 mmol) in toluene (30 mL) for 2h with azeotropic removal of water. The residue was crystallized from hexane to give **44** (3.18 g, 86%). IR as well as ^1H and ^{13}C NMR spectra were identical to those given above.

(d) Synthesis of **$((OC_6H_4C_6H_4O)As)_2O$** (46): (i) Procedure was the same as in **III.4.5** c(i) above; using 29 (0.46 g, 1.58 mmol) cyclohexylamine (0.31 g, 3.16 mmol) and water (0.03 g, 1.59 mmol) 46 (insoluble in $CDCl_3$) was obtained. Yield: 0.59 g, (35%). M.p. 160°C (lit. M.p. 168°C).[88] [Found: C, 54.2; H, 3.1. Calc. for $C_{24}H_{16}As_2O_5$: C, 55.91; H, 3.0].

Compound 46 was also isolated in an attempt to prepare $(OC_6H_4C_6H_4O)AsCl$ by starting with $(Et_2N)_2AsCl$. The procedure is given below:

(ii) To a stirred solution of $(Et_2N)_2AsCl$ (1.63 g, 6.41 mmol) in toluene (15 mL) was added biphenol (1.15 g, 6.41 mmol) in toluene (2 mL). The mixture was stirred for 2h and solvent was removed. Attempts to crystallize the product from ether-hexane led only to 46. Yield (1.1 g, 65%). M.p. and analytical data were the same as given above.

(e) Synthesis of $((CH_2((t\text{-}bu)_2C_6H_2O)_2)As)_2O$ (47): Procedure was the same as in section **III.4.5 c**(i), using **21b** (1.05 g, 1.97 mmol), cyclohexylamine (0.39 g, 3.94 mmol) and water (0.035 g, 1.97 mmol). The residue was crystallized from toluene. Yield: 0.5 g (50%). M.p. 258°C. [Found: C, 69.0; H, 8.4. Calc. for $C_{58}H_{84}As_2O_5$: C, 68.92; H, 8.32]. ^1H NMR: 1.31 (s, 36H, $C(C\underline{H}_3)_3$), 1.45 (s, 36H, $C(C\underline{H}_3)_3$), 3.50 (d, $^2J(H\text{-}H) = 13$ Hz, 2H, $C\underline{H}_A H_B$), 4.70 (d, $^2J(H\text{-}H) = 13$ Hz, 2H, $CH_A\underline{H}_B$), 7.30 (m, 8H, H (Ar)). ^{13}C NMR: 30.4 (s, $\underline{C}H_2$(?)), 31.2 (s, C $(\underline{C}H_3)_3$), 31.6 (s, $C(\underline{C}H_3)_3$), 34.5 (s, $C(CH_3)_3$), 35.4 (s, $\underline{C}Me_3$), 122.7, 125.4, 136.4, 141.7, 145.9 and 147.8, (all C (Ar)). IR (cm^{-1}): 2850, 1440, 1250, 780, 720.

(f) **Hydrolysis** of **$(OCH_2CMe_2CH_2O)PCl$** (7a): Procedure was similar to **III.4.5** c(i), using **7a,** cyclohexylamine and water using 2:2:1 or 2:4:1 stoichiometry in toluene or benzene (30 fold excess) under reflux conditions to give compound 29 in (>50%) Yield. No other product was identified. When the stoichiometry was **1:1:1,** 29 was exclusively formed. [^1H, ^{31}P NMR].

(g) Hydrolysis of other **phosphites/arsenites.** These reactions are summarized below.

(i) Compound **16a** + $C_6H_{11}NH_2$ + H_2O (2:4:1 or 1:2:1 benzene/ reflux). Procedure similar to **III.4.5** (c)(i). Products 18 (60%) + A (40%). The structure

($OC_6H_4C_6H_6O$)P(O)H was assigned for the product A. ^1H NMR: 7.21 (d, ^1J(P-H) = 634Hz, PH). ^{31}P **NMR:-2.2.**

(ii) **Compound 21a** + $C_6H_{11}NH_2$+H_2O **(1.2:0.5** benzene/ 25°C). Products B + others [$\delta(^{31}P)$: **-12.1, 0.5** and **2.0** (not identified)]. ^1H NMR: 7.20 (d, ^1J(P-H) = 644 Hz, PH); ^{31}P NMR: **2.0** ppm The structure **(CH2((t-bu)$_2C_6H_2O)_2$)**P(O)H is assigned for B.

(iii) Compound **13a** + H_2O (1:1 and 1:3/ THF/25°C). Product 29 (>80%).

(iv) Compound **11a** + H_2O (1:3/ THF/ 25°C). Products **11a** (80%), 29 (10%) and others.[^{31}P NMR].

(v) Compound **13b** + H_2O (1:3/ THF/ 25°C). Insoluble material (As_2O_3, 10-30%, IR), PhOH, diol, and 44 (20-50%) [^1H NMR].

(vi) Compound **11b** + H_2O (1:1/ THF/ 25°C). Insoluble material (As_2O_3, IR) isopropyl alcohol, diol and 44 (50%). [^1H NMR].

III.4.6 Hydrolysis of spirophosphoranes [preparation of phosphate esters]:

(1) **Preparation** of **the phosphate esters** 84 and 89. (i) Compound ($OCH_2CMe_2CH_2O$)P(OPh)(9,10-$O_2C_{14}H_8$) (88)" (1.00 g, **2.3** mmol) was dissolved in chloroform (1 mL)-ether (3 mL) mixture and kept in open air till all the solvent evaporated. The residue was crystallized from dichloromethane-n-heptane (1:1) to obtain 84. Yield 0.55 g, (67%). M.p. 162°C. [lit. m.p. 162-164°C].[98] ^1H NMR: 1.00 (s, 3H, CH3), 1.35 (s, 3H, $C\underline{H}_3$), 4.05 (dd, ^3J(P-H) = 14.3Hz, $OC\underline{H}_AH_B$), 4.50 (d, ^3J(P-H) = MHz, 2H, $OCH_A\underline{H}_B$), 7.50-8.70 (m, 8H, H(Ar)). 9.50 (br, 1H, OH). ^{31}PNMR:-10.2. IR (cm^{-1}): 3185 (ν(OH))

(ii). The same compound 84 was obtained [^1H, ^{31}P] when compound 73 (1.0 g) was dissolved in chloroform (5 mL) and kept aside for 2 days in open air. Although the product was pure by ^{31}P NMR; it could not be obtained free of 8-

hydroxy quinoline. Upon washing this product with hot water, the double hydrolysis product 89 (which could be crystallized from CH_2Cl_2-n-heptane (1:1)) was obtained. Yield: 0.4 g (39%). [Found: C, 63.47; H, 5.45; N, 2.85. Calc. for $C_{28}H_{28}NO_7P$ $1/2H_2O$. C, 63.39; H, 5.45; N, 2.64]. ^1H NMR: 0.74 (s, 6H, CH_3), 3.23 (s, 2H, 6CH2), 3.80 (d, $^3J(P\text{-}H)$ = 20.0 Hz, 2H, $POCH_2$), 4.45 (br, variable intensity, OH_2(?)), 7.30-8.80 (m, 14H, H (Ar)). ^{31}P NMR:-0.6.

(2) Preparation of **the phosphate ester** 85: (i) To a mixture of 8a (1.33 g, 4.79 mmol) and catechol (0.53 g, 4.79 mmol) in dry ether (40 mL) maintained at -60 C° was added (NCDA) (0.65 g, 4.79 mmol) in ether (30 mL) over a period of 15 min with continuous stirring. The mixture was brought to 30°C, stirred overnight and the precipitated solid filtered. The ^{31}P NMR of the solid showed two products with chemical shifts -102.4 **(XVII,** 90%) and -12.3 **(85,** 10%). The solid was given a water wash (2x5 mL) and dried *in vacua.* The product was crystallized from dichloromethane-n-heptane (2:1) to afford 85. Yield 0.7 g (57%). M.p. 142°C IR (cm^{-1}): 3202 (ν(OH)).

Instead of a water wash, when a D_2O wash was given, a band at 2390 cm^{-1} (ν(O-D)) in the IR was observed for the solid; this band was also observed for the H_2O washed product after dissolving it in $CDCl_3$ and evaporating all the solvent. The following data is for the water-washed product. [Found: C, 51.74; H, 6.17. Calc. for $C_{11}H_{15}O_5P$: C, 51.16; H, 5.81]. ^1H NMR: 0.96 (s, 3H, CH3), 1.35 (s, 3H, CH_3), 1.35 (s, 3H, CH3), 4.04 (qrt, 2H, OCH_AH_B), 4.36 (d, 2H, OCH_AH_B), 6.80-7.70 (m, 4H, H(Ar)). ^{31}P NMR ($CDCl_3$): -11.5 (triplet of equal intensity due to $^2J(P\text{-}O\text{-}D)$ = 22.2 Hz). The precipitate when kept in open air for three days without giving a water wash exhibited a peak at -12.7 in the ^{31}P NMR.

(ii) When the reaction of $(C_6H_4O_2)P(OC_9H_6N)$ (5a) (1.17 g, 4.12 mmol) with 2,2-dimethyl-1,3-propanediol (0.43 g, 4.12 mmol) and NCDA (0.56 g. **4.12** mmol) was carried out, the same product 85 [^1H, ^{31}P] was observed.

(3) Preparation of the phosphate ester 86: Following the same procedure as in (2) (i) above, the precipitate obtained by treating 8a (2.37 g, 8.42 mmol), 2,2'-biphenol (1.57 g, 8.42 mmol) and NCDA (1.14 g, 8.42 mmol) was washed quickly with water and dried *in vacua.* The residue was crystallized from a mixture of dichloromethane-n-heptane (3:1) to obtain 86. Yield: 1.1 g (39%). M.p. 182°C. [Found: C, 61.00; H, 5.55. Calc. for $C_{17}H_{19}O_5P$: C, 61.08; H, 5.69]. ^1H NMR: 0.40 (s, 3H, CH3), 1.10 (s, 3H, CH3), 3.35-3.62 (m, 4H, OCH2), 5.4 (br, 1H, OH), 6.81-7.65 (m, 8H, H (Ar)). ^{31}P NMR: -15.1 ppm. IR (cm^{-1}): 3292 ν(OH).

(4) Preparation of the phosphate ester 87. Following the same procedure as in (2)i, the precipitate obtained by using 3.73 mmol each of 8a, 2,2'-methylen-bis(4-chlorophenol) and NCDA [^{31}P NMR: -127.1 XVIII, (40%), -14.8 87 (40%), and -13.4 (20%)] was crystallized from dichloromethane-n-heptane (1:2) in open air to obtain 87. Yield: 0.3 g (19%). M.p. 175°C. [Found: C, 51.80; H, 4.81. Calc. for $C_{18}H_{19}Cl_2O_5P$: C, 51.81; H, 4.56]. ^1H NMR (DMSO-d_6 + $CDCl_3$): 0.52 (s, 3H, CH3), 1.03 (s, 3H, CH3), 3.50-3.80 (m, 4H, OCH_2), 4.35 (s, 2H, CH_2 (Ar)), 6.56-7.28 (m, 6H, H (Ar)). ^{31}P NMR: -14.8 ppm.

III.5 *Preparation of* ***2,2'-Isopropylidenedioxy*** *bis(5,5-dimethyl-l,3,2-dioxarsenocin)* (45)

To a solution of 7b (1.76 g, 8.3 mmol) in toluene (20 mL), cyclohexylamine (1.64 g, 16.6 mmol) in toluene (10 mL) was added dropwise (0.5h) at 20°C. The mixture was stirred for 2h after which it was filtered and the solvent evaporated from the filtrate. The residue (A) was distilled *in vacua* (0.2 mm Hg, bath temp. 240°C) to give a liquid (B) with 45 as the major compound *{ca* 80%). The ^1H NMR spectra of liquids (A) and (B) were identical. ^1H NMR: 0.67 (s, 6H, CH3), 0.96 (s, 6H, CH3), 1.23 (s, 6H, CH3), 3.34 (d, ^2J(H-H)= 10 Hz, ring OCH_2), 3.61

(s, 4H, bridge $OC\underline{H}_2$), 4.23 (d, $^2J(H\text{-}H)$ = 10.0 Hz, 4H, ring $OC\underline{H}_2$); the spectrum was the same in C_6D_6. Additional signals at 1.00-2.60 (cyclohexyl-$C\underline{H}_2$) were also observed.

Compound 45 was prepared in a pure state by treating **22** with sodium (see below).

III.6 *Action of Sodium on Chlorophosphites/Arsenites*

(1) **Preparation of $((OCH_2CMe_2CH_2O)_2As)_2(OCH_2CMe_2CH_2O)$ (45):**

A mixture of 7b (1.75 g, 8.25 mmol) and sodium (1.90 g, 8.25 mmol) in toluene (20 mL) was heated under reflux for 20h. The mixture was then filtered, solvent evaporated from the filtrate and the residue distilled *in vacua* to give 45. Yield: 0.5 g (40%) (based on the diol) B.p. 170°C/2mm Hg. [Found: C, 39.8; H, **6.65.** Calc. for $C_{15}H_{30}As_2O_6$: C, 39.47; H, 6.58]. ^1H NMR: 0.67 (s, 6H, CH3), 0.96 (s, 6H, CH3), **1.23** (s, 6H, CH3), 3.34 (d, $^2J(H\text{-}H)$ = 10 Hz, 4H, $OC\underline{H}_2$(ring)), **3.61** (s, 4H, $OC\underline{H}_2$(bridge)), 4.23 (d. $^2J(H\text{-}H)$ = 10 Hz, 4H, $OC\underline{H}_2$(ring)). ^{13}C NMR: 21.7, 22.0, (s each, 4C, $\underline{C}H_3$(ring)), (s, **2C,** $\underline{C}H_3$(bridge)), 33.6 (s, 2C, $\underline{C}Me_2$(ring)), 38.2 (s, $\underline{C}Me_2$(bridge)), 68.3 (s, 2C, $O\underline{C}H_2$(bridge)), **71.2** (s, 4C, $O\underline{C}H_2$(ring)).

(2) **Preparation of $((OCH_2CMe_2CH_2O)_2P)_2(OCH_2CMe_2CH_2O)$ (55)**

Same procedure as for 45 by procedure (1) above was followed using (2.27 g, 13.48 mmol) of 7a and sodium (0.31 g, 13.48 mmol). Yield: 4.2 g (55%) B.p. 115/0.5 mm. ^1HNMR: 0.75 (s, 6H, CH3), 1.00 (s, 6H, CH3), 1.27 (s, 6H, CH3), 3.31 (t, $^3J(P\text{-}H) = {}^3J(H\text{-}H)$ = 10 Hz, 4H, $OC\underline{H}_2$(ring)), 3.60 (d, ^3J = 6 Hz, 4H, $OC\underline{H}_2$(bridge)), 4.15 (d, $^3J(P\text{-}H)$ = 10 Hz, 4H, $OC\underline{H}_2$(ring)). ^{13}CNMR: 21.3 (s, **2C,** CH3, (bridge)), 22.3, 22.6 (s each, 2C, $\underline{C}H_2$(ring)), 32.6 (d, $^3J(P\text{-}C)$= 4.5 Hz, $\underline{C}Me_2$(ring)), 36.8 (t, $^3J(P\text{-}C)$ =6 Hz, $\underline{C}Me_2$(bridge)), 67.3 (d, $^2J(P\text{-}C)$ = 17 Hz,

2C, O<u>C</u>H$_2$(bridge)), 67.6 (s, 4C, O<u>C</u>H$_2$(ring)). ^{31}P NMR: 121.3 (lit. ^{31}P NMR: **121.7**[93]**].** MS (m/z): 368 $[M]^+$

(3) Preparation of **[(CH$_2$((t-bu)$_2$C$_6$H$_2$O)$_2$As]$_2$** (57): Same procedure as for 45 was followed using (1.64 g, 3.08 mmol) of 21b and sodium (0.07 g, 3.08 mmol). The product was crystallized from n-heptane. Yield 1.35 g (46%). M.p. 226°C. [Found: C, 69.78; H, 8.98. Calc. for $C_{58}H_{84}As_2O_4$: C, 70.02; H, 8.45]. ^{1}H NMR: 1.38 (s, 36H, C(C<u>H</u>$_3$)$_3$), 1.44 (s, 18H, C(C<u>H</u>$_3$)$_3$), 3.52 (d, ^{2}J(H-H)= 14 Hz, 1H, C<u>H</u>$_A$H$_B$), 4.64 (d, ^{2}J(H-H) = 14 Hz, 1H, CH$_A$<u>H</u>$_B$), 7.35 (m, 4H, H(Ar)). ^{13}C NMR: **31.1, 31.6** (s each, 4C, C(<u>C</u>H$_3$)$_3$), 34.6, 35.5 (s each, 2C, <u>C</u>Me$_3$), 122.4, 125.7, 136.5, 140.9, 145.9, 154.6 (all C(Ar)).

(4) **[CH$_2$((t-bu)$_2$C$_6$H$_2$O)$_2$PO(C$_6$H$_2$(t-bu)$_2$-2,4)CH$_2$(C$_6$H$_2$(t-bu)$_2$-2,4)OP-(O$_2$C$_6$H$_2$-(t-bu)$_2$CH$_2$)]** (56): Same procedure as for 45 was followed using (0.49 g, 1.01 mmol) of 21a and sodium (0.023 g, 1.01 mmol). The product was crystallized from dichloromethane and acetonitrile (1:1.5). Yield (35%). M.p. 299°C. ^{1}H NMR: 1.12, 1.17, 1.24, 1.28, 130, 1.5 (s each, 108H, C(C<u>H</u>$_3$)$_3$), 3.25 (d, ^{2}J(H-H) - 9 Hz, 2H, C<u>H</u>$_A$H$_B$(ring)), 4.43 (d, J(H-H)= 7 Hz, 2H, CH$_A$<u>H</u>$_B$(ring)), 4.75 (br s, 2H, C<u>H</u>$_2$(bridge)), 7.23-7.47 (m, 12H, H(Ar)). ^{31}P NMR: 136.8; the mother liquor showed an additional peak at 185.5 ppm (50%).

II I.7 *Reactivity of (N-P) Bond in* P^{III} *and* P^V *Compounds*

(1) Reaction of **(OCH$_2$CMe$_2$CH$_2$O)P(NHC$_6$H$_{11}$)** (9) with 8-hydroxy quinoline: A mixture of (OCH$_2$CMe$_2$CH$_2$O)P(NHC$_6$H$_{11}$) (9) (^{31}P NMR: 132.0 ppm) (0.19 g, 8.83 mmol) and 8-hydroxy quinoline (0.12 g, 0.83 mmol) in dry toluene (10 mL) was heated under reflux for 5h. The mixture was then brought to 25°C and subjected to ^{31}P NMR analysis after complete removed of the solvent. The resulting product was identified as (OCH$_2$CMe$_2$CH$_2$O)P(OC$_9$H$_6$N) (8a) (100 %) [^{3} lp NMR: 113.8] and could be purified by vacuum distillation.

(2) Reaction of $(OCH_2CMe_2CH_2O)P(O)(NHC_6H_4)$ with 8-hydroxy quinoline: The same procedure as in (1) above was followed using the same molar quantities to give the starting material [^{31}P NMR: 4.1 ppm]. Even on using p-xylene and prolonged refluxing (24h), there was no reaction.

(3) **Reaction of compound 62 with 8-hydroxy quinoline:** The same procedure as for 9 above was followed using the same molar quantities as in (1). The resulting product was identified as the starting material 45 [^{31}P NMR]. However using p-xylene as the solvent and prolonged refluxing (24h) led to a mixture of products [^{31}P NMR: -78.7 (10 %),-46.1 (62, 55%), -10.2 (84, 10 %), 8.6 and 14.8 ppm].

(4) **Reaction of the phosphite 18 with 8-hydroxy quinoline:** A mixture of $(OC_6H_4C_6H_4O)P(NHC_6H_{11})$ (18) (52 g, 1.67 mmol) and 8-hydroxy quinoline (0.24 g, 1.67 mmol) in dry p-xylene (20 mL) was heated under reflux for 10h. **The** resulting products were mainly $(OC_6H_4C_6H_4O)P(OC_9H_6N)$ (17a) and **18.** ^{31}P NMR: 151.0(18, 80%), 140.1 **(17a,** 15%), 11.6(5%).

(5) **Reaction of $(OC_6H_4C_6H_4O)P(NHC_6H_{11})(O_2$-2,4-(t-Bu)$_2C_6H_4)$ (64) with 8-hydroxy quinoline:** The procedure, conditions and molar quantities are the same as in (4) above. There was no sign of any significant reaction. ^{31}P NMR: **-36.3 (64,** 95%), -13.5 (5%).

(6) **Reaction of the aminophosphorane 82 with 8-hydroxy quinoline:**

A mixture of **82** (0.43 g, 1.05 mmol) and 8-hydroxy quinoline (0.15 g, 1.05 mmol) was heated under reflux in dry toluene (10 mL) overnight. After removal of the solvent, product **73** could be crystallized from dichloromethane-hexane (1:1). NMR data and m.p. were identical to that given above.

(7) **Reaction of 82 with 2,4,6-trimethylbenzoic acid:** A mixture of **82** (0.55 g, 1.34 mmol) and 2,4,6-trimethylbenzoic acid (0.22 g, 1.74 mmol) was heated under reflux in dry p-xylene (5 mL) overnight, the solvent removed

completely and the residue crystallized from CH_2Cl_2-hexane (1:2) to give $(OCH_2CMe_2CH_2O)P(O)(O\text{-}(2,4,6\text{-}Me_3\text{-}C_6H_2C(O)\text{-}O)C_{14}H_8)$ (83). Yield: 0.4g (59%) M.p. 160°C. [Found: C, 68.45; H, 5.81. Calc. for $C_{29}H_{29}O_6P$: C, 69.05; H, 5.75]. ^1H NMR: 0.73 (s, 3H, $C\underline{H}_3$), 1.22 (s, 3H, $C\underline{H}_3$), 2.40 (s, 3H, $C\underline{H}_3$(Ar)), 2.75 (s, 6H, $C\underline{H}_3$ Ar)), 3.85 (dd, 2H, $CH_A\underline{H}_B$), 4.20 (d, 2H, $CH_A\underline{H}_B$), 7.06-8.80 (m, 10H, H (Ar)). ^{31}P NMR: -14.4. IR. (cm^{-1}): 1742 ν(C=O) of the ester), [ν (C=O) for the parent carboxylic acid observed at 1686 cm''], 1607; no ν(OH) band observed].

(8) **Reaction of 82 with benzoic acid:** Procedure was the same as in (7) above. The known compound $(OCH_2CMe_2CH_2O)P(O)\text{-}O(OH)C_{14}H_8$) **84** was isolated. M.p. ^1H and ^{31}P NMR were identical to that reported above in section **III.4.6** (1).

(9) Reaction of 81 with 8-hydroxy quinoline: Compound 81 (0.70 g, 1.80 mmol) and 8-hydroxy quinoline (0.23 g, 1.62 mmol) were heated together in p-xylene (5 mL) under reflux for 12h. The solvent was removed and the residue crystallized from ether-n-heptane (1:1) mixture to afford pure **78.** Yield: 0.2 g (23% based on 8-hydroxy quinoline) [physical data are given in **(III.3.2)** for 78]. The ^{31}P NMR soectrum of the mother-liquor after removing **78** showed a large number of peaks in the tetra-coordinated region [10 to -20 ppm].

III.8 *X-ray Crystallography*

The X-ray data were obtained from the following sources:

a) Compounds 9, 24, 42 (partially solved), **59, 60, 65.½Et_2O, 73.CH_2Cl_2, 75, 76.CH_2Cl_2, 78.Et_2O, 79.½H_2O** and **86:** Gottingen, Germany.

b) Compounds 8(b), **17(b), 22(b),** 32 and **47:** Saarbrücken, Germany.

c) Compounds **44** and **51:** Indian Institute of Technology, Madras, India.

d) Compound 33: Indian Institute of Chemical Technology, Hyderabad

For compounds described in (a) data were collected at -120°C; for those described in (b) and (c)[116] data were collected after inserting the crystal inside a Lindemann capillary. The compound 33 was stable in air and hence data were collected by mounting it on a glass fibre.[117] All the structures were solved by standard programmes.[118] Some details of structure solution and data refinement are given in Appendix 2; the coordinates of only the atoms relevant to the present study are given in Appendix 3. Further analysis of the structures was done by using a hpplot programme.

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Part B

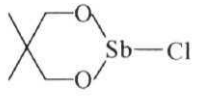
Antimnony Cages

CHAPTER IV

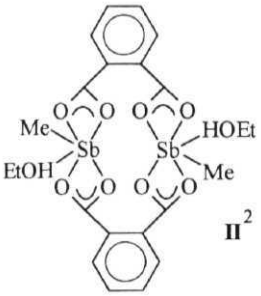
INTRODUCTION

IV. 1. *Organoantimony(V) Compounds:*

The greater tendency of Sb(V), when compared to P(V) or As(V) compounds, to achieve higher coordination numbers (six, seven) makes its chemistry quite different from that of P and As. Even antimony (III) compounds are quite acidic and hence in the presence of donor atoms (O, S, Cl, etc.), they get involved in donor acceptor bonds. Our attempts to utilize the antimony compound (I)[1] in a manner analogous to its arsenic or phosphorus counterpart [Part A Chapter 2, *cf.* compounds 7a & 7b] were not successful because of the insolubility of the compound, most likely due to polymerization *via* Sb←O interaction. An interesting example in this regard is the compound $[MeSb\{(O_2C)_2C_6H_4\}]_2[EtOH]_2$ II[2] obtained by the reaction of phthalic acid with $MeSb(OEt)_2$ at low temperature in ethanol solution; the trivalent antimony is hexa-coordinated in compound II.



I[1]



II[2]

Recognizing that antimony and tin in their respective higher oxidation states of +4 and +5 can be expected to achieve coordination numbers of six and seven readily in the presence of oxo/hydroxo group and bidentate ligands like carboxylates and phosphinates, a variety of structures with similar skeletons and possibly related

chemistry must be possible. In this context it is pertinent to note that the "crown" structure observed for tin[3-4] in III is close to that observed for (IV) reported by Sowerby *et. al.*[5] [Fig 1]. However,

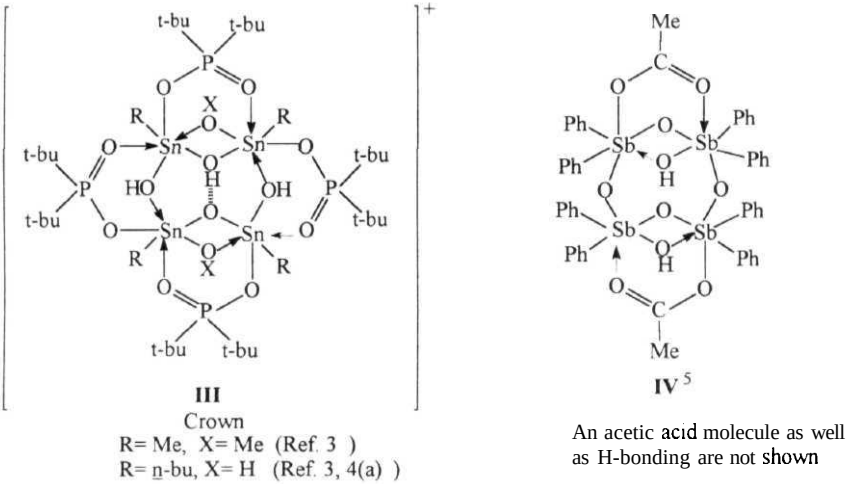


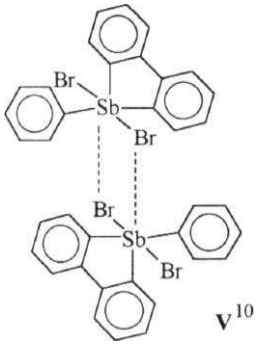
Fig. 1 Structures of III and IV showing the similarity in the skeleton.

compared to the large number of structurally diverse oxo-carboxylate and phosphinate cages known for tin,[3,4] only a few analogous species for antimony have been reported. The present study is aimed at developing antimony(V) chemistry and the literature pertinent to this is reviewed in the following section.

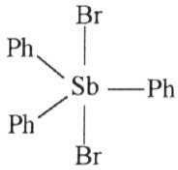
IV.2 *Organoantimony(V)* Halides:

Organoantimony(V) halides R_4SbX (R = alkyl, aryl; X= F, I),[6-7] R_3SbX_2 (R = Me, X = Cl;[8] R= Ph; X = Cl, Br, F[6,9]), $(2,2'\text{-}C_6H_4\text{-}C_6H_4)(Ph)SbBr_2$,[10] Ph_2SbX_3 (X = Br, F, Cl),[11] and $(2'\text{-}Cl\text{-}C_6H_4\text{-}C_6H_4)_2SbCl_3$[11] and $PhSbCl_4$[12,14]

are known; X-ray structures of some of these have also been reported.[9-11,13] These studies have revealed a square pyramidal geometry in (biphenyl-2,2'-diyl)phenylantimony dibromide (V)[10] and a TBP geometry in Ph_3SbBr_2 (VI)[9] for antimony. However, what is important from our point of view is that in V there is



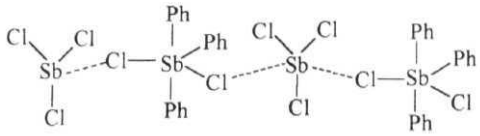
V[10]



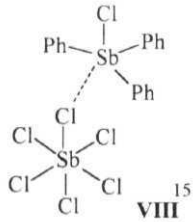
VI

a residual interaction between a bromine atom of one compound with the antimony of a second one leading to dimerization in the solid state. The compounds Me_2SbCl_3[13] and Ph_2SbCl_3[14] are both dimeric with two chlorine bridges and six-fold coordination around antimony; by contrast, bis(2'-chloro-biphenyl-2-yl)antimony trichloride is a penta-coordinated monomer.[11]

An interesting case of the donor characteristic (via chlorine) of triphenyl antimony dichloride towards $SbCl_3$ (structure VI) and $SbCl_5$ (structure VII) has been shown by Sowerby and co-workers.[15] From these structures it appears that both $SbCl_3$ and $SbCl_5$ are stronger Lewis acids than



VII[15]

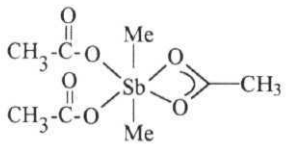


VIII[15]

IV.3 *Organoantimony(V)* ***Carboxylates*** *and Related Compounds:*

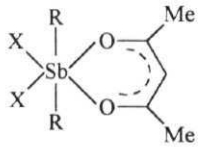
IV.3.1 Monomeric organoantimony(V) carboxylates and P-diketonates:

Meinema and Noltes[16] first prepared thermally stable monomeric dimethyl antimony(V)triacetate, $Me_2Sb(OAc)_3$ (IX); the identity of IX was also confirmed later by Stevens and Troomster.[17] The molecule is monomeric with octahedral geometry in which only one acetate group is bidentate.



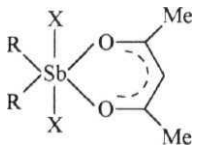
IX[16]

Diorganoantimony(V) ß-diketonates of type R2Sb(R'COCHCOR")X2 are monomeric;[18] IR and ^1H NMR studies show that $Ph_2Sb(acac)Cl_2$ exists exclusively in the hexa-coordinated form. Thus, assuming an octahedral geometry, three possible forms **[XI-XIII]** car. be considered for compounds of type $R_2Sb(acac)X_2$:[13]



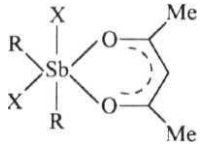
XI

Trans-diorgano



XII

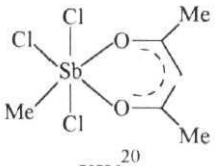
Cis-diorgano



XIII

On the basis of the equivalence of the acac-Me groups and their peak separations in the ^1H NMR spectra, it has been shown that these compounds exist as mixtures of symmetrical forms XI and **XII**[19] in varying proportions. However, X-ray structural studies on $Me_2Sb(acac)Cl_2$ and $Ph_2Sb(acac)Cl_2$ show that the organic groups on antimony occupy *trans* positions.[13, 21]

For the monorgano antimony compound MeSb(acac)Cl3 **XIV** the X-ray structure shows that the methyl group is *trans* to an oxygen of the acetyl acetonato group;[20] this result is in agreement with the studies of Meinema *et. al.*[18] but in contrast to those reported earlier.[13]



XIV[20]

Compared to diphenylantimony(V), and related triphenylantimony(V) systems, reactions utilizing PhSbCl4 have been less studied, probably because of disproportionation (eq. 1).[22] However, Wieber *et. al.* could isolate $PhSb(OAc)_4$

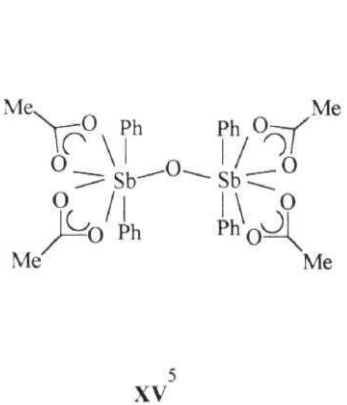
$$2PhSbCl_4 \rightarrow Ph_2SbCl_3 + SbCl_3 + Cl_2 \qquad \rightarrow(1)$$

by reacting phenyldichloroantimony successively with sulfuryl. chloride and silver acetate at low temperature (-70 C); the X-ray structure for this compound reveals hexa-coordination by chelation of one bonded acetate group[12].

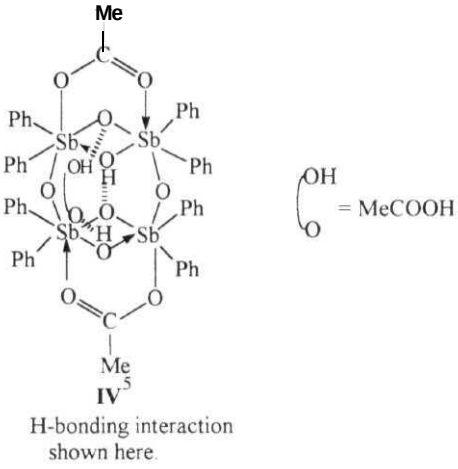
IV.3.2 Di- and poly-nuclear organoantimony(V) carboxylates and related compounds:

While attempting to isolate $Ph_2Sb(OAc)_3$, Sowerby and co-workers[5] obtained two interesting oxo-bridged compounds **IV** *(vide supra)* and XV. The structure of **XV** is unusual in that the coordination number of each antimony

is raised to seven by the presence of two chelating acetate groups. Attempts to



XV[5]



IV[5]

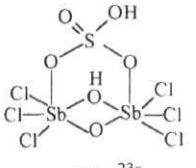
H-bonding interaction shown here.

crystallize the original triacetate from dichloromethane with no precautions against hydrolysis resulted in compound IV being isolated. Here the antimony is hexa-coordinated with octahedral geometry. Despite the novelty, there does not appear to be further studies on these systems; many questions remain unanswered, for example, (i) Whether products such as IV or XV are formed for all the carboxylates or not? (ii) What is the effect of using a phosphinate in place of the acetate? (iii) Whether any interconversion between IV and XV, similar to that observed for tin,[4(b)] is possible or not?

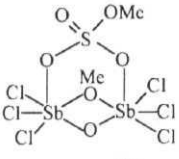
Schmidt and co-workers[23,24] have concentrated on antimony(V) chloro systems containing no Sb-C bonds. They have isolated the triply bridged dinuclear compounds **XVI-XIX**.

The preparation of XVI involves the reaction of $SbCl_5.H_2O$ with sulfinic acid; compound XVII can be prepared either by reacting $SbCl_5$ with H_2SO_4 in

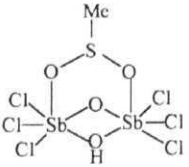
methanol or by treating $[Cl_4Sb(OMe)]_2$ with the acid in dichloromethane. Analogous routes are adopted for XVIII and XIX.



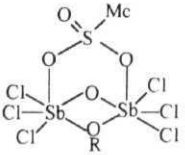
XVI[23a]



XVII[23b]



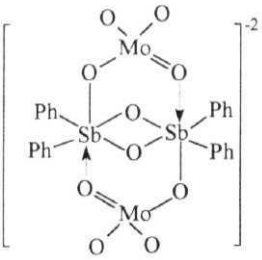
XVIII[24]



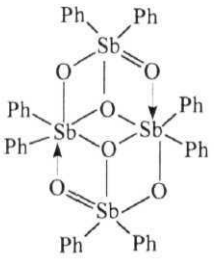
XIX[24]

Liu and coworkers have reported the structure of the tetra-n-butyl ammonium salt of the novel quadruply bridged dianion **XX;** this compound was obtained by the reaction of Ph_2SbI_3 with excess of tetra-n-butyl ammonium molybdate.[25]

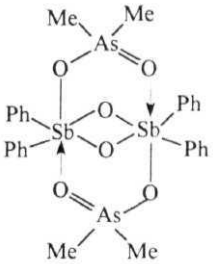
The neutral tetranuclear cluster $Ph_8Sb_4O_6$ **(XXI),** with two **triply** connected oxygens has been structurally characterized by Doak and co-workers.[26] The dimethyl arsenate compound **XXII** reported by Sowerby *et. al.*[27] is similar in



XX[25]



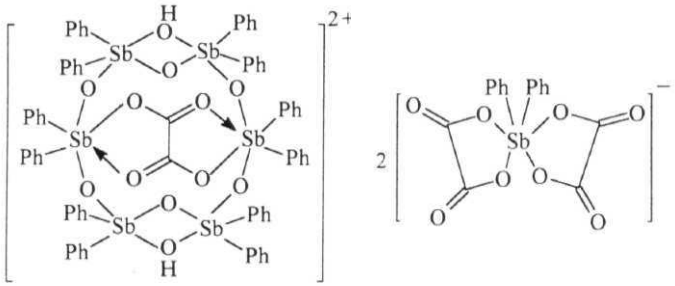
XXI[26]



XXII[27]

skeleton to **XX** but neutral; this compound was prepared by treating $(Ph_2SbBrO)_2$ with sodium dimethyl arsenate. Although phosphinates can also form compounds analogous to **XXI,** none has been reported (prior to this work).

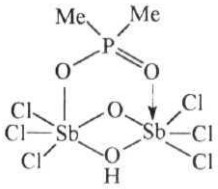
The reaction of equimolar quantities of $[Ph_2SbBrO]_2$ and silver oxalate in refluxing benzene leads to the ionic compound $[Ph_{12}Sb_6O_6(OH)_2(O_2C_2O_2)]^{2+}$ $2[Ph_2Sb(O_2C_2O_2)]^-$ XXIII[28]; the structure of the cation and anion are shown in Fig. 2 The unique feature of this compound is the presence of a previously unknown twelve-membered Sb_6O_6 ring system. It can be noted that the final stoichiometry of the product is not 1:1 [Sb: oxalate], and it would have been difficult to predict its formation *a priori.*



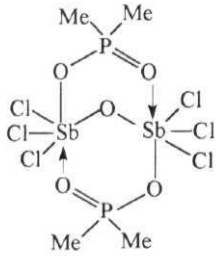
XXIII[28]

Fig. **2.** The structures of the anionic and cationic portions of the oxalate compound XXIII.

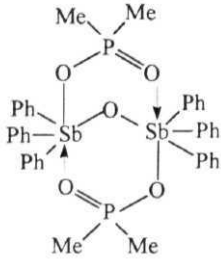
As far as phosphinates are concerned, compounds **XXIV-XXVI**[29] have been prepared by Schmidt and co-workers. Structurally these compounds are different from the carboxylates in that chelation is not observed in these phosphinates. Even in $Me_3Sb(OSPPh_2)_2$ wherein a good possibility of chelation through "S" exists, the thio-phosphinate is monodentate [structure **XXVII**].[8]



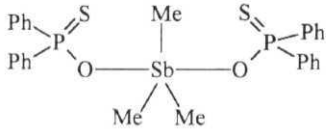
XXIV[29]



XXV[29]



XXVI[29]



XXVII[8]

IV.4. *Methods of Preparation of* ***Organoantimony Carboxylates/*** *Phosphinates*

General routes to antimony carboxylates/ phosphinates are given below:

1) By exchanging of alkoxy groups.[16]

(i) $R_2Sb(OMe)_3 + AcOH(excess) \rightarrow R_2Sb(OAc)_3 + 3MeOH$

2) By substitution reaction of halides[3,13,27].

(i) $R_3SbX_2 + 2R'COOH + 2Et_3N \rightarrow R_3Sb(O_2CR')_2 + 2Et_3N.HX$

(11) $Ph_2SbCl_3 + 3AgO_2CCH_3 \xrightarrow{(water)}$ dimer (IV) + tetramer (XV) + 3AgCl

(iii) $(Ph_2SbBrO)_2 + 2Me_2AsO_2Na \rightarrow [Ph_2Sb(O_2AsMe_2)O]_2 + 2NaCl$

(iv) $(Ph_3SbBr)_2O + 2Me_2PO_2Ag \rightarrow [Ph_3Sb(O_2PMe_2)]_2O +$ **2AgCl**

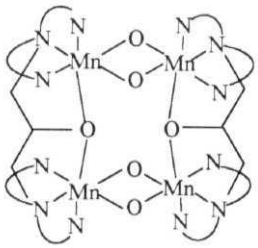
3) By elimination of water:[13]

$R_3SbO + 2R'COOH \rightarrow R_3Sb(O_2CR')_2 + H_2O$

IV.5 *Structural Comparison*

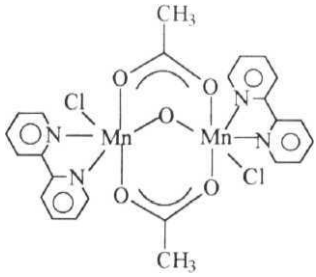
Hexa-coordinated (and to a limited degree hepta-coordination) is quite prevalent for oxo-carboxylates/ phosphinates of organotin(lV) and transition metal species. A knowledge of these relationships is useful in understanding the reaction chemistry and probably predicting new structural types.

The similarity between the tetranuclear cages of tin (structure III) and antimony (structure IV) has been pointed out before (Sec. **IV.3.2**). A similar skeleton can be found for the cationic manganese cage XXIII having the multi-dentate ligand N,N,N',N'-tetrakis (2-pyridyl methyl)-2-hydroxo-propane-1,3-diamine (tphpn)[30]. Similarly the skeleton found in **XXV-XXVI** is observed for **XXIX**.[31]



Structure of $[(Mn_2O_2)_2(tphpn)_2]^{4+}$

XXVIII[30]



XXIX[31]

OBJECTIVE OF THE PRESENT WORK

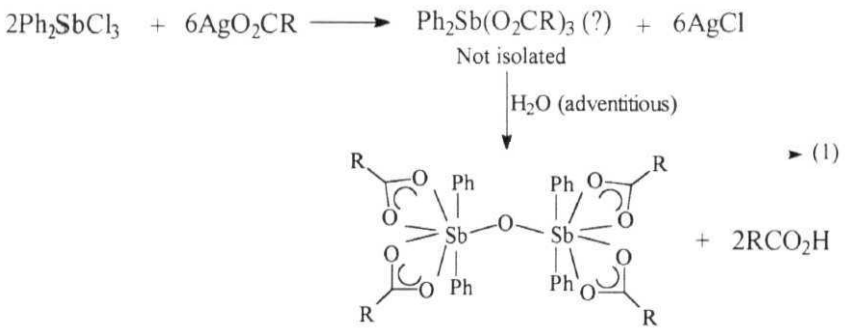
The main objective of the present work is to uncover new oxo-carboxylate/ phosphinate cages of antimony and correlate the structures of these compounds with those of analogous tin compounds.

CHAPTER V

RESULTS AND DISCUSSION

V. 1 *Synthesis and Spectroscopy*:

V.I.I **Diphenylantimony carboxylates.** The oxo-bridged carboxylates $[Ph_2Sb(O_2CR)_2]_2O$ [R = Ph (2), $CHPh_2$ (3), 2,4,6-$Me_3C_6H_2$ (4), 2-MeC_6H_4 (5), 4-MeC_6H_4 (6)] were readily obtained when Ph_2SbCl_3 (1) was treated with 3 mole equivalents of the respective silver carboxylates (eq. 1). Compounds 2-6 can be crystallized from a mixture of dichloromethane and hexane (or n-heptane).



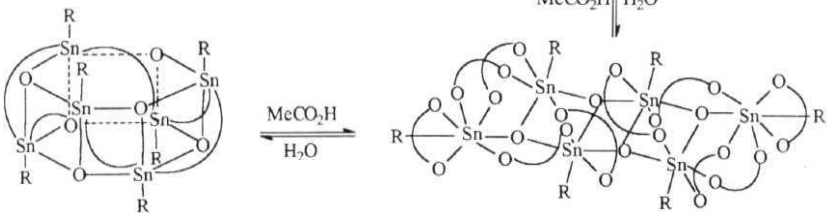
This contrasts with the reaction of Ph_2SbCl_3 with silver acetate[5] where recrystallization from dichloromethane afforded the tetranuclear cage $Ph_8Sb_4O_6.3MeCO_2H$ (IV); isolation of the oxo-bridged compound $[Ph_2Sb(O_2CMe)_2]_2O$ (XV) required a solvent containing a water scavenger (acetic acid + acetic anhydride]. Thus it is likely that the initially formed product XV underwent hydrolysis during recrystallization from dichloromethane to give

IV. This prompted us to examine the hydrolysis of our compounds 2-4. Indeed upon hydrolysis of 2 we obtained a solid 2a, m.p. 179-183°C, which analysed as $Ph_8Sb_4O_6$ $3PhCO_2H$ (*cf.* compound IV above). The ^1H NMR spectrum of the product from the hydrolysis of 4 corresponded to the analogous compound $Ph_8Sb_4O_6$ $3(2,4,6\text{-}Me_3C_6H_2CO_2H)$ However, the diphenyl acetate derivative 3 was resistant to hydrolysis.

The formulae for compounds XV and IV as well as 2 and 2a suggest that an interconversion similar to that observed for the tin carboxylates (Scheme 1*) is feasible.[4(b)] Since removal of the excess of acid and monitoring by ^1H NMR spectroscopy is easier for the interconversion between XV and IV, this pair was chosen for study. Thus the dinuclear compound $[Ph_2Sb(O_2CMe)_2]_2O$ (XV) was converted into the tetranuclear cage $Ph_8Sb_4O_6.3MeCO_2H$ (IV) by exposing a dichloromethane solution of the former to air. More interestingly, it was possible to convert IV into XV by heating it with excess (>30 fold) of acetic acid-anhydride [eq. 2].

*

Scheme 1



C = O_2CMe, R= n-Bu

$[SnR(O)(O_2CMe)]_6$
Prismane

$[(SnR(O)O_2CMe)_2.(SnR(O_2CMe)_3)]_2$
Ladder

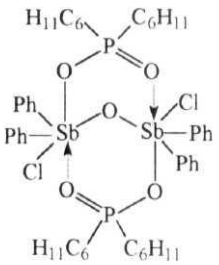
$$XV \underset{+5MeCO_2H,\ -4H_2O\ [+\ excess\ (MeCO)_2O]}{\overset{+4H_2O,\ -5MeCO_2H}{\rightleftharpoons}} IV \qquad (2)$$

Three crystalline chloro derivatives $Ph_2SbCl(O_2CR)_2$ (R= Ph (7), 2-MeC_6H_4 (8) or 4-MeC_6H_4 9) were also synthesized by the 1:2 stoichiometric

$$Ph_2SbCl_3 + 2AgO_2CR \longrightarrow \text{Cl—Sb(Ph)(O}_2\text{CR)}_2 + 2AgCl \qquad (3)$$

reaction (eq. 3) The separation of the most intense bands in the IR spectra ascribable to the carbonyls for sodium benzoate, 2 and 7 are 143, 129 and 87 cm^{-1} respectively; on this basis[32] we assign a seven co-ordinated monomeric structure with chelating carboxylates for the chloro compound 7 (and hence for 8 and 9). For compound 8 the assigned structure has been confirmed by an X-ray analysis. These chloro carboxylates do not undergo any appreciable hydrolysis in $CDCl_3$ solution as shown by their ^1H NMR spectra recorded ovtr a period of several days. This feature is in contrast to that of the oxo-bndged derivatives 2, 4 and 6 which underwent hydrolysis.

V.1.2 Diphenylantimony phosphinates. In the reaction of diphenyl antimony trichloride (1) with 2 mole equivalents of silver dicyclohexylphosphinate we were able to isolate only $\{Ph_2SbCl[O_2P(C_6H_{11})_2]\}_2O$ (10) [$\delta(^{31}P)$: 54.6 ppm]



^{31}P 56.6 ppm

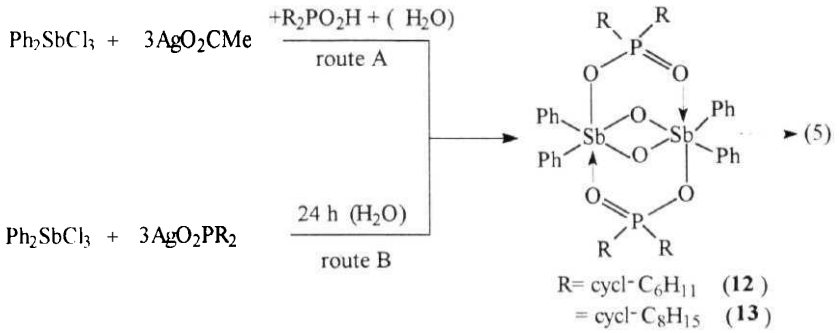
10

although the reaction mixture suggests the presence of a second compound [$\delta(^{31}P)$: 60.3] in significant quantity (*ca.* 20%). It is known that Ph_2SbCl_3 takes up water readily; this upon heating could lead to $(Ph_2SbCl_2)_2O$[33] The formation of the oxo-bridge in our case could have occurred after the reaction with the phosphinate (eq 4). A similar reaction with silver dicyclooctylphosphinate also afforded a crystalline product 4 [$\delta(^{31}P)$: 58.6] which we

$$2Ph_2SbCl_3 + 2AgO_2P(C_6H_{11})_2 \xrightarrow[-2HCl]{H_2O} \{Ph_2SbCl[O_2P(C_6H_{11})_2]\}_2O + 2AgCl \quad (4)$$

formulate as $[Ph_2SbCl\{O_2P(C_8H_{15})_2\}]_2O$ on the basis of elemental analysis and the ^1H N'MR spectrum. The compound is very soluble in common organic solvents Attempts to obtain crystals suitable for X-ray analysis resulted in partial hydrolysis.

The dimeric compounds $\{Ph_2Sb(O_2PR_2)O\}_2$ [R = cycl-C_6H_{11} (**12**), cycl-C_8H_{15} (13)] have been synthesized by two different routes (eq.5). The ^{31}P NMR



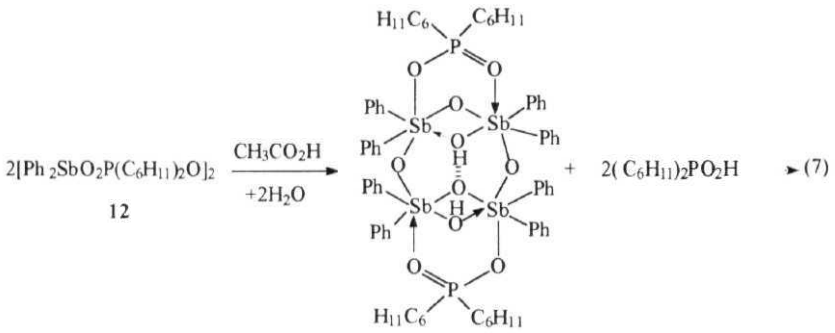
spectra of 12 and 13 show a single resonance at 64.3 and 69.6 ppm respectively and are consistent with a dimeric structure in solution with a single phosphorus environment. For both the compounds the route (A) utilizing silver acetate affords the best yields of the pure products. In this route the initially formed acetate $Ph_2Sb(O_2CMe)_3$ is very moisture sensitive and presumably hydrolyzes to give $[Ph_2Sb(O_2CMe)_2]_2O$ as reported in the literature.[5] Upon addition of the phosphinic acid, two of the acetates may be replaced to give a mixed acetate-phosphinate; in fact, in the case of dicyclohexylphosphinic acid, when the reaction time after adding the acid was reduced, we have been able to isolate the mixed acetate phosphinate $Ph_2Sb(O_2CMe)\{O_2P(C_6H_{11})_2\}]_2O$ (14) [$\delta(^{31}P)$: 53.1 ppm]. Product 14, although isolatable, is moisture sensitive. If the reaction is allowed to continue for a longer time or if 14 is crystallized in open air, adventitious moisture is sufficient to hydrolyze this intermediate to 12 (eq. 6). Such a feature is observed for other antimony carboxylates also.[5]

$$\underset{\textbf{14}}{[Ph_2Sb(O_2CMe)(O_2P(C_6H_{11})_2)]_2O} \xrightarrow[-2CH_3CO_2H]{H_2O} \underset{\textbf{12}}{[Ph_2SbO_2P(C_6H_{11})_2O]_2} \qquad (6)$$

In the second route (route B) for the synthesis of 12, the chloro compound $[Ph_2SbCl(O_2PC_6H_{11})_2]_2O$ (10) was a minor product [$\delta(^{31}P)$: 54.6 ppm]; indeed if the reaction is not allowed to continue for longer than 2h, this chloro compound becomes the major product.

Both the compounds 12 and 13 are fairly stable in air; however, when 12 is heated with a mixture of acetic acid and water, the tetrameric cage $Ph_8Sb_4O_4(OH)_2(O_2P(C_6H_{11})_2).CH_3COOH$(**15** without CH_2Cl_2) is obtained in

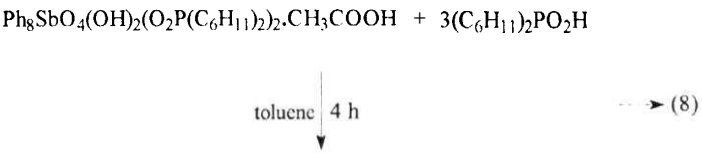
good yields (eq. 7) this compound was initially obtained in attempt to crystallize



15.CH_3CO_2H

the products from the reaction shown in equation 5 (route A). Compound 15 also exhibits a single resonance in the ^{31}P NMR spectrum at 57.7 ppm showing that the two phosphinates are in an identical chemical environment (see later for structure). Under similar experimental conditions compound 13 does not hydrolyze to any significant extent.

What is perhaps more interesting is the observation that we were able to convert the tetrameric cage 15 back to the dimer 12 by heating the former with an excess of dicyclohexylphosphinic acid (eq. 8). The ^{31}P NMR spectrum of the



reaction mixture showed compound 12 to be the major product [5 = 64.3 ppm; > 85%]; two minor products [8= 53.8 and 45.9 ppm with total intensity <15%)| were also observed. The interconversion between the two carboxylates $[Ph_2Sb(O_2CMe)_2]_2O$ (XV) and $Ph_8Sb_4O_6(HO_2CMe)_3$ (IV) has been demonstrated earlier (see above Sec. V.I.I). Thus it appears that the [Sb-O] bonds in these (oxo)carboxylates/ phosphinates are quite labile; such a feature is reminiscent of the interconversion observed in n-butyltin (oxo)carboxylates/ phosphinates.[4(b)]

V.1.3 Phenylantimony(V) compounds. We have tried to obtain $PhSb(O_2CCHMe_2)_4$ (XX) as a crystalline solid; however, the air-sensitive crystalline product 17 obtained by reacting PhSbCl4 with 4 mole equivalents of AgO_2CCHMe_2 (eq. 8) showed only one isobutyrate per phenyl group [^{1}H NMR]; there was also a broad peak at 7.90 ppm corresponding to one proton. The

$$PhSbCl_4 + 4AgO_2CCHMe_2 \xrightarrow[\text{(adventitious(?))}]{H_2O} \underset{17}{[PhSb(O)(OH)(O_2CCHCMe_2)]_n} \quad (9)$$

spectrum changed with time, [with the intensity of isobutyrate signal going down], perhaps due to hydrolysis. The compound was too moisture sensitive (upon slight exposure to air it became a liquid) to obtain a satisfactory analysis [an X-ray structure still awaited]. On the basis of ^{1}H NMR and allowing for neutralization of charges the formula $[PhSb(O)(OH)(O_2CHMe_2)]_n$ is assigned for 17.

Since in the present work, dicyclohexylphosphinates gave more stable derivatives we attempted a replacement reaction as shown in (eq. 10). The ^{1}H NMR spectrum of the crystalline product 18 thus obtained showed one

$$PhSb(O_2CMe)_4 + HO_2P(C_6H_{11})_2 \xrightarrow[\text{(adventitious (?))}]{H_2O} [PhSb(O)(OH)(O_2P(C_6H_{11})_2] \quad \text{(10)}$$

18

phosphinate per phenyl group [the acetate (or acetic acid) methyl signal was too low in intensity]. The ^{31}P NMR showed two peaks of nearly equal intensity at 52.8 and 64.3 ppm; thus although the formula can be nearly the same as shown in (eq. 9), the structure should show two kinds of phosphinates. Since it becomes too speculative (without an X-ray structure) no further comment is made.

V.2 *Structural Aspects*

The structure of the carboxylate compound $[Ph_2Sb(O_2CPh)_2]_2O$ (2) (Fig. 3) is similar to that of the corresponding acetate $[Ph_2Sb(O_2CMe)_2]_2O$ (XV)

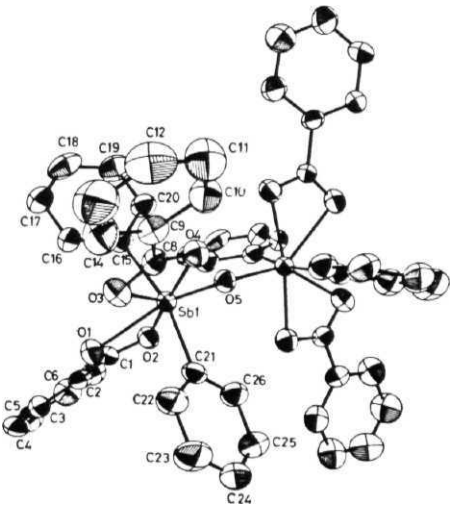


Fig. 3 An ORTEP diagram of compound 2

with a distorted pentagonal-bipyramidal geometry around antimony. The Sb-0 distances (Table 1) show two sets of four with mean values of 2.188 and 2.418 A° respectively (2.16 and 2.47 A^0 in XV) moving towards each other more closely than in the acetate. The five equatorial oxygen atoms and the antimony are coplanar to within ± 0.09 A° (± 0.05 A^0 in XV). The diaxial disposition of the less

Table 1 Selected bond distances (A) and bond angles (°) for compound **2.**

Sb91)-0(l)	2.406(2)	Sb(l)-C(21)	2 119(5)
Sb(1)-O(2)	2 187(3)	O(1)-C(1)	1 239(5)
Sb(1)-O(3)	2 429(4)	O(2)-C(1)	1.268(4)
Sb(1)-O(4)	2 189(3)	O(3)-C(8)	1.222(6)
Sb(1)-O(5)	1.923(1)	O(4)-C(8)	**1.305(4)**
Sb(1)-C(15)	2 115(4)		
C(15)-Sb(1)-C(21)	1637(2)	O(2)-Sb(1)-O(3)	**131.7(1)**
O(5)-Sb(1)-C(21)	98 3(1)	O(1)-Sb(1)-C(21)	81.7(1)
O(5)-Sb(1)-C(15)	979(1)	O(1)-Sb(1)-C(15)	84 8(2)
O(4)-Sb(1)-C(21)	93 3(2)	O(1)-Sb(1)-O(5)	141.2(1)
O(4)-Sb(1)-C(15)	89 1(2)	O(1)-Sb(1)-O(4)	1320(1)
O(4)-Sb(1)-O(5)	868(4)	O(1)-Sb(1)-O(3)	75 9(1)
O(3)-Sb(1)-C(21)	856(2)	O(1)-Sb(1)-O(2)	55 9(1)
O(3)-Sb(1)-C(15)	82.4(2)	Sb(1)-O(1)-C(1)	87.8(2)
O(3)-Sb(1)-O(5)	142.9(1)	Sb(1)-O(2)-C(1)	97 2(2)
O(3)-Sb(1)-O(4)	56 1(1)	Sb(1)-O(3)-C(8)	87 8(3)
O(2)-Sb(1)-C(21)	905(2)	Sb(1)-O(4)-C(8)	96 7(2)
O(2)-Sb(1)-C(15)	89 4(2)	O(1)-C(1)-O(2)	119.1(4)
O(2)-Sb(1)-O(5)	85 3(1)	O(3)-C(8)-O(4)	119 4(4)
O(2)-Sb(1)-O(4)	171.7(1)	Sb(1)-O(5)-Sb(1)	173 9(2)

electronegative phenyl groups in the pentagonal bipyramid contrasts with the expected diequatorial disposition in a trigonal bipyramidal structure.

An X-ray investigation showed that the compound $Ph_2SbCl(O_2C\text{-}2\text{-}Me\text{-}C_6H_4)_2$ **8** (Fig. 4) has seven coordination around antimony with two asymmetrically chelating carboxylate groups. The Sb-0 (carboxylate) distances (Table 2) fall into two sets with mean values of 2.217 and 2.292 A. These values

are comparable to those in 2 and XV where Sb-0 distances are 2.188, 2.418 and 2.16, 2.47 A respectively. The geometry around antimony in 8 is distorted pentagonal bipyramidal.

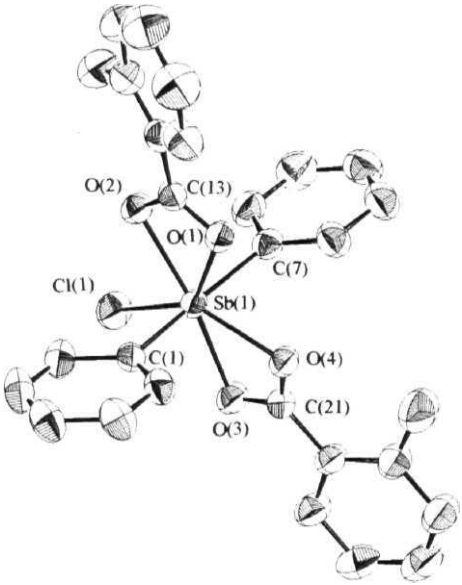


Fig. 4 An ORTEP diagram of compound **8**

Table 2. Selected bond lengths (A) and bond angles (°) for compound 8*

Sb(1)-O(1)	2 296(3)	Sb(l)-C(21)	2.628(4)
Sb(l)-0(2)	2.222(3)	Sb(l)-C(13)	2 642(4)
Sb(l)-0(3)	2.213(3)	O(1)-C(13)	1.265(5)
Sb(l)-0(4)	2.288(3)	O(2)-C(13)	1.283(5)
Sb(l)-C(7)	2.128(4)	O(3)-C(21)	1.273(5)
Sb(l)-C(l)	2.121(4)	O(4)-C(21)	1.258(5)
Sb(l)-Cl(l)	2.4020(13)		

Table 2 contd

C(l)-Sb(l)-C(7)	1684(2)	C(l)-Sb(l)-C(21)	**91.63(14)**
C(1)-Sb(1)-O(3)	9302(14)	C(7)-Sb(l)-C(21)	86 70(14)
C(7)-Sb(1)-O(3)	91 04(14)	O(3)-Sb(1)-C(21)	28.91(12)
C(1)-Sb(1)-O(2)	89.14(14)	O(2)-Sb(1)-O(4)	136 96(11)
C(1)-Sb(1)-O(1)	83.83(14)	O(2)-Sb(1)-C(21)	165.39(12)
C(7)-Sb(1)-O(1)	85.79(14)	O(4)-Sb(1)-C(21)	28.61(12)
O(3)-Sb(1)-O(1)	136 86(11)	O(1)-Sb(1)-C(21)	108 00(12)
O(2)-Sb(1)-O(1)	57 58(11)	Cl(l)-Sb(l)-C(21)	110 82(10)
O(4)-Sb(1)-O(1)	79.41(10)	C(1)-Sb(1)-C(13)	85 78(14)
C(l)-Sb(l)-Cl(l)	95.49(12)	C(7)-Sb(1)-C(13)	87.57(14)
C(7)-Sb(l)-Cl(l)	95.81(13)	O(3)-Sb(1)-C(13)	16546(12)
O(3)-Sb(1)-Cl(1)	81.95(8)	O(2)-Sb(1)-C(13)	28.98(12)
O(4)-Sb(1)-Cl(1)	139.41(8)	O(4)-Sb(1)-C(13)	108.00(12)
O(1)-Sb(1)-Cl(1)	141.18(8)	O(1)-Sb(1)-C(13)	28.60(12)
Cl(l)-Sb(l)-C(13)	112 59(10)	C(21)-Sb(l)-C(13)	136 57(13)

"Symmetry transformations used to generate equivalent atoms

The phosphinates in $\{Ph_2SbCl[O_2P(C_6H_{11})_2]\}O$ 10 act only as bridging ligands and the structure (Fig. 5) can be compared to that of $[SbCl_3(O_2PMe_2)]_2O$ (XXV).[29] The Sb-Cl and Sb-O(P) bond distances (Table 3) [2.428 and 2.093 A^0 (mean) respectively] are longer than those observed for $[SbCl_3(O_2PMe_2)]_2O$ [2.333 and 2.010 A^0 (mean) respectively] possibly due to the presence of less electronegative phenyl groups in 10. The bridging phosphinates are *cis* to each other as is observed for $[Ph_2Sb(O_2CMe)_2]_2O$ (XV) as well as $[SbCl_4(O_2PRR')]_2$ (R = R' = OMe or NMe_2, R = OMe, R' = NMe_2).[35] The three oxygens connected to antimony are *facial*, a feature common to numerous oxo-bndged bimetallic compounds.[35-38]

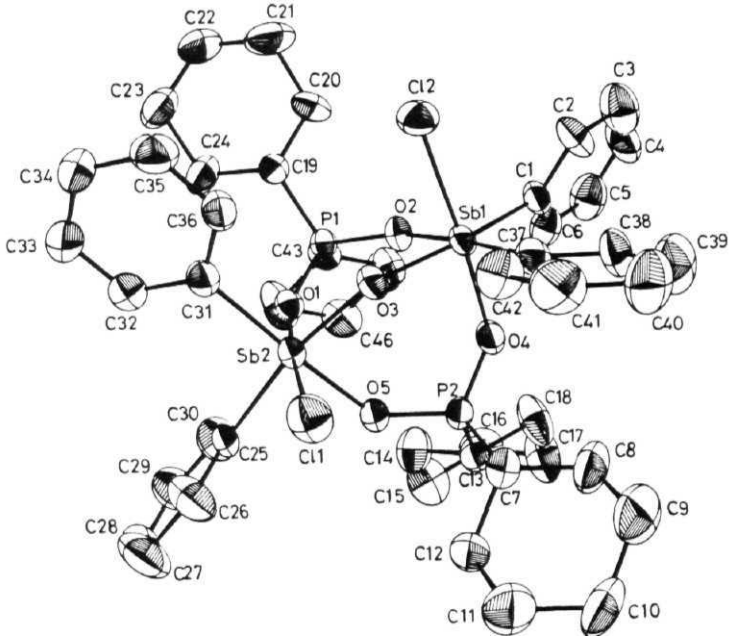


Fig.5 An ORTEP diagram of compound 10

Table 3 Selected bond distances (A) and angles (°) for compound **10.**

Sb(l)-Cl(2)	2.428(2)	Sb(2)-C(25)	**2.155(5)**
Sb(l)-0(2)	2.119(4)	Sb(2)-C(31)	2 131(6)
Sb(l)-0(3)	1.938(4)	P(1)-O(1)	1.528(4)
Sb(l)-0(4)	2.070(4)	P(1)-O(2)	1.526(4)
Sb(l)-C(l)	2.124(6)	P(l)-C(43)	1.829(6)
Sb(1)-C(37)	2.130(6)	P(l)-C(19)	1.805(6)
Sb(2)-Cl(1)	2.425(2)	P(2)-O(4)	1.531(4)
Sb(2)-O(1)	2.098(4)	P(2)-O(5)	**1.549(5)**
Sb(2)-O(3)	1.936(4)	P(2)-C(7)	**1.793(6)**
Sb(2)-O(5)	2.085(4)	P(2)-C(13)	1.820(6)

Table 3. contd

C(1)-Sb(1)-C(37)	100.8(2)	O(3)-Sb(2)-C(25)	167 1(2)
O(4)-Sb(1)-C(37)	91.3(2)	O(3)-Sb(2)-O(5)	86.0(2)
O(4)-Sb(1)-C(1)	88.5(2)	O(1)-Sb(2)-C(31)	89.9(2)
O(3)-Sb(1)-C(37)	92.4(2)	O(1)-Sb(2)-C(25)	88.2(2)
O(3)-Sb(1)-C(1)	166.7(2)	O(1)-Sb(2)-C(5)	85.7(2)
O(3)-Sb(1)-O(4)	89.7(2)	O(l)-Sb(2)-O(3)	88.2(2)
O(2)-Sb(1)-C(37)	175.7(2)	Cl(1)-Sb(2)-C(31)	94.0(1)
O(2)-Sb(1)-C(1)	82.1(2)	Cl(l)-Sb(2)-C(25)	95.1(2)
O(2)-Sb(1)-O(4)	85.5(2)	Cl(1)-Sb(2)-O(5)	90.4(1)
O(2)-Sb(1)-O(3)	84.7(2)	Cl(l)-Sb(2)-O(3)	87.6(1)
Cl(2)-Sb(l)-C(37)	93.4(2)	Cl(1)-Sb(2)-O(1)	174.4(1)
Cl(2)-Sb(l)-C(l)	93.0(2)	O(1)-P(1)-O(2)	113 5(2)
Cl(2)-Sb(1)-O(4)	174.7(1)	O(4)-P(2)-O(5)	113.0(3)
Cl(2)-Sb(1)-O(3)	87.7(1)	Sb(2)-O(1)-P(1)	**131.3(2)**
Cl(2)-Sb(1)-O(2)	89 7(1)	Sb(1)-O(2)-P(1)	135 5(3)
C(25)-Sb(2)-C(31)	99.6(2)	Sb(1)-O(4)-P(2)	**133.2(3)**
O(5)-Sb(2)-C(31)	175.4(2)	Sb(2)-O(5)-P(2)	137.4(2)
O(5)-Sb(2)-C(25)	81.4(2)	Sb(1)-O(3)-Sb(2)	144 7(2)
O(3)-Sb(2)-C(31)	92.8(2)		

The Sb-O-P-O-Sb-O rings have a boat conformation (Fig. 6) with phosphorus at one of the 'prow' positions;[39] it appears from molecular models

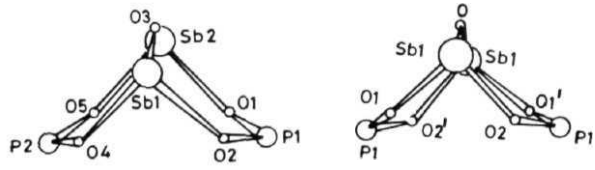


Fig. 6 The boat conformation of the Sb-O-P-O-Sb-O rings in compounds 10 and $[SbCl_3(O_2PMe_2)]_2O$ **(XXV)**

that the chair conformation leads to greater steric interaction between substituents on the two phosphinate ligands. Given the boat conformation for the six-

membered rings and *facial* arrangement for the three oxygens on antimony, four geometrical isomers are possible for 10 (Fig 7). It can be seen that steric interactions between the phenyl and cyclohexyl groups on a particular phosphorus are minimized in the observed structure A.

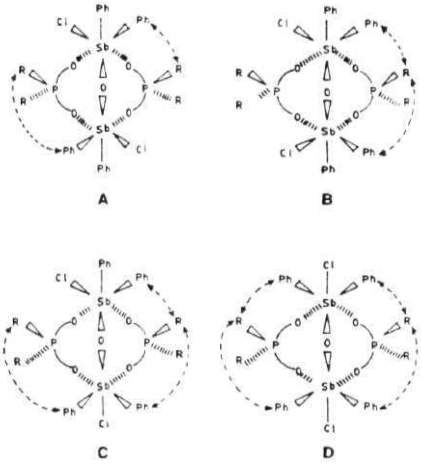


Fig. 7 Possible geometrical isomers for $[Ph_2SbCl\{O_2P(C_6H_{11})_2\}]_2O$ (10); R = C_6H_{11} in the diagram.

Surprisingly, the Sb-0 (oxo) distance in compound 2 is shorter than that observed in 10 or $\{SbCl_3(O_2PMe_2)\}_2O$ [Table 4]. despite the fact that antimony is hepta-coordinated in 2 and hexa-coordinated in 10. All these distances are shorter than the non-oxo Sb-0 bonds [(mean) 2.083 in 10 and 2.30 A^0 in 2]. Table 4 also gives data for oxo-bridged complexes of titanium, iron and gallium. The shortening of the Sb-0 (oxo) bonds may result from the partial ionic character $M^{\delta+}$ $O^{\delta-}$ as suggested by Cowley *et al.*[40] for the galloxane complound

Table 4. M-0 (oxo) distances (A^0) and M-O-M angles (°) in selected compounds.

Compounds[a]	M-0	M-O-M	Ref.
10	1.937	144.7	This work
$SbCl_3(O_2PMe_2)]_2O$ (XXV)	1.942	136.0	29
2	1.923	173.9	This work
XV	1.911[b]	163.8b	5
$[\{Fe(O_2PPh_2)[HB(pz)_3]\}_2O]$	1.812(short)	130.6	38
$[\{TiCl_2(O_2CCMe_3)HO_2CCMe_3)\}_2O]$	1.766(short)	138.3	36
$\{(2,4,6\text{-}Bu^t_3C_6H_2)GaMn(CO)_5\}_2O$	1.786(short)	150.2	40

[a]pz= pyrazolyl. [b]Calculated using atomic coordinates

$\{(2,4,6\text{-}Bu^t_3C_6H_2)GaMn(CO)_5\}_2O$. Unlike in the case of titanium[36] or iron[37-38] complexes where the participation of the d orbitals can be invoked[37] to explain the short M-0 (oxo) bonds, it is doubtful whether such a participation exists for antimony compounds.

The molecular structures of the compounds 12, **13** and 15 are depicted in Figs. 8-10. Selected bond distances and bond angles are provided in Tables 5-7. All the three compounds possess four membered Sb-O-Sb-0 rings with bridging phosphinates and hexa-coordinated antimony. In 15 the two Sb_2O_2 rings are connected through oxo bridges between the antimony atoms to form an Sb_4O_6 cage and the structure can be described as a "crown".[3,4,41] The bridging phosphinates in 12, **13** and 15 are *cis* to the phenyl groups on antimony. Thus the three compounds represent new structural types for antimony phosphinates.

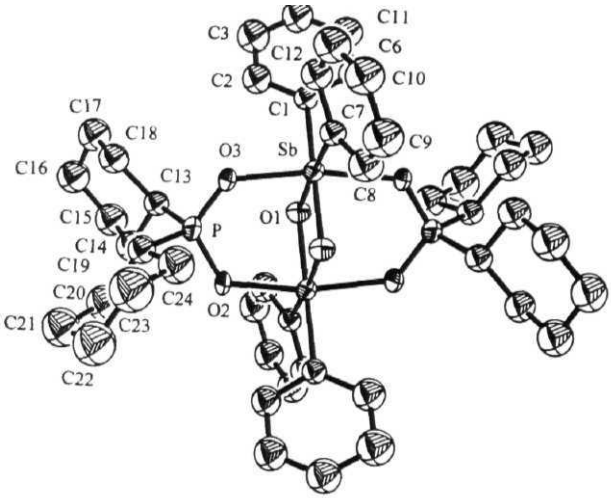


Fig. 8. Molecular structure of 12; H-atoms and the solvent molecule are not shown.

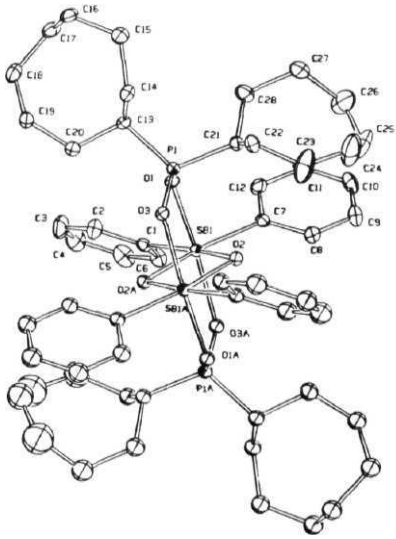


Fig. 9. Molecular structure of 13; H-atoms and the solvent molecule are not shown.

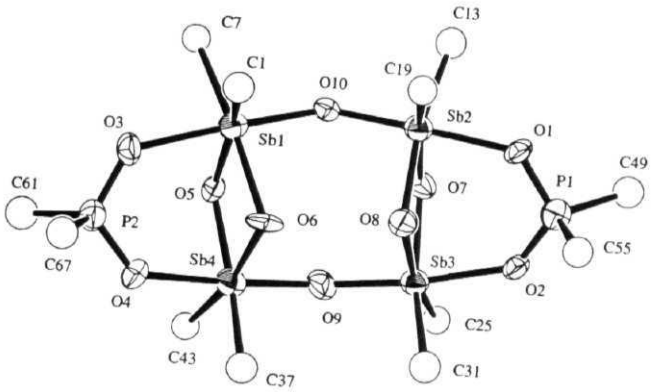


Fig. 10. Molecular structure of 15. showing the skeleton. C atoms of the phenyl, cyclohexyl, acetic acid and solvent as well as H atoms are omitted for clarity.

Table 5. Selected bond lengths (A) and bond angles (°) with e.s.d.s in parentheses for 12 (atoms related by a centre of symmetry are given the suffix A).

Sb(l)-0(2)	1.975(2)	P(l)-0(3)	1.542(2)
Sb(l)-0(2A)	1.977(2)	**P(l)-C(13)**	1.812(3)
Sb(1)-O(3A)	2 132(2)	P(l)-C(21)	1811(3)
Sb(1)-C(l)	2.134(3)	Sb(l)..Sb(lA)	3.0142(5)
Sb(l)-C(7)	2 137(3)		

Table 5. contd

O(1)-Sb(1)-O(2)	85.97(8)	O(3A)-Sb(1)-C(1)	94 1(1)
O(1)-Sb(1)-O(2A)	85.74(8)	O(3A)-Sb(1)-C(7)	92.3(1)
O(1)-Sb(1)-O(3A)	168.99(8)	C(l)-Sb(l)-C(7)	98.7(1)
O(1)-Sb(1)-C(1)	92.2(1)	O(1)-P(1)-O(3)	**115.5(1)**
O(1)-Sb(1)-C(7)	**95.7(1)**	O(1)-P(1)-C(13)	104.2(1)
O(2)-Sb(1)-O(2A)	80.6(1)	O(1)-P(1)-C(21)	106.4(1)
O(2)-Sb(1)-O(3A)	86.51(8)	O(3)-P(1)-C(13)	107.9(1)
O(2)-Sb(1)-C(1)	171.6(1)	O(3)-P(1)-C(21)	110.0(1)
O(2)-Sb(1)-C(7)	89.7(1)	C(13)-P(1)-C(21)	112.9(2)
O(2A)-Sb(1)-O(3A)	85.10(8)	Sb(1)-O(1)-P(1)	123.7(1)
O(2A)-Sb(1)-C(1)	**91.1(1)**	Sb(1A)-O(3)-P(1)	123.0(1)
O(2A)-Sb(1)-C(7)	170.1(1)	Sb(1)-O(2)-Sb(1A)	99.4(1)

Table 6. Bond lengths (A) and bond angles(°) with e.s.d.s in parentheses for 13 (atoms related by a centre of symmetry are given the suffix A)

Sb-O(1)	**1.986(5)**	P-O(2)	**1.530(5)**
Sb-O(1A)	1.982(5)	P-O(3)	1.538(5)
Sb-O(2A)	2 115(5)	**P-C(13)**	1.794(8)
Sb-0(3)	2 112(5)	P-C(19)	1.805(8)
Sb-C(l)	2.147(8)	Sb-Sb(A)	3.019(4)
Sb-C(7)	2.129(8)		

O(1A)-Sb-O(1)	80.9(2)	O(2A)-Sb-C(1)	92.0(3)
O(1A)-Sb-O(3)	86.6(2)	C(7)-Sb-C(l)	99.4(3)
O(1)-Sb-O(3)	85.6(2)	O(3)-Sb-C(1)	95.4(3)
O(1A)-Sb-O(2A)	84.6(2)	O(2)-P-O(3)	116.7(3)
O(1)-Sb-O(2A)	86.3(2)	O(2)-P-C(13)	108.6(3)
O(1A)-Sb-C(7)	91.7(3)	O(2)-P-C(19)	106.3(3)
O(3)-Sb-C(7)	93.9(3)	O(3)-P-C(13)	106.2(3)
O(3)-Sb-O(2A)	168.9(2)	O(3)-P-C(19)	107.0(3)
O(1)-Sb-C(7)	**172.7(2)**	C(13)-P-C(19)	112.2(4)
O(2A)-Sb-C(7)	93.1(3)	Sb(A)-O(1)-Sb	99 1(2)
O(1)-Sb-C(1)	87.9(3)	P-O(2)-Sb(A)	126.8(3)
O(1A)-Sb-C(1)	168.5(2)	P-O(3)-Sb	125 6(3)

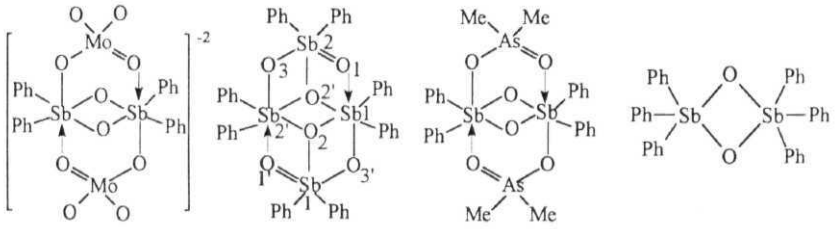
Table 7 Selected interatomic distances (A) and bond angles (°) with e.sd.s in parenthesis for **15**

Sb(l)-0(5)	2.00(1)	Sb(2)-C(19)	**2.14(2)**	**Sb(4)-C(37)**	2 13(2)
Sb(1)-O(6)	**2.17(1)**	Sb(3)-O(8)	**2.02(1)**	Sb(4)-C(43)	**2.13(2)**
Sb(1)-O(3)	**2.19(1)**	Sb(3)-O(7)	**2.11(1)**	O(1)-P(1)	1.52(1)
Sb(1)-O(10)	1.94(1)	Sb(3)-O(2)	**2.12(1)**	P(1)-O(2)	**152(1)**
Sb(l)-C(l)	**2.17(2)**	Sb(3)-O(9)	**1.93(1)**	0(3)-P(2)	1 52(1)
Sb(l)-C(7)	2.18(2)	Sb(3)-C(25)	**2.14(2)**	P(2)-O(4)	1 53(1)
Sb(2)-O(8)	2.01(1)	Sb(3)-C(31)	**2.11(2)**	Sb(l)-Sb(4)	**3.257(2)**
Sb(2)-O(7)	2.13(1)	Sb(4)-O(5)	2.02(1)	Sb(2)-Sb(3)	**3.270(2)**
Sb(2)-O(1)	2 12(1)	Sb(4)-O(6)	2 09(1)	O(11). 0(12)	2.71(3)[a]
Sb(2)-O(10)	1.93(1)	Sb(4)-O(4)	2 13(1)	O(6) 0(8)	2.80(2)
Sb(2)-C(13)	2.10(2)	Sb(4)-O(9)	**1.95(1)**		

O(3)-Sb(1)-O(5)	**82.3(5)**	O(2)-Sb(3)-O(7)	**82.3(5)**
O(3)-Sb(1)-O(6)	**89.5(5)**	O(2)-Sb(3)-O(8)	**86.3(5)**
O(3)-Sb(1)-O(10)	1765(4)	O(2)-Sb(3)-O(9)	172.5(5)
O(3)-Sb(1)-C(1)	83.7(6)	O(2)-Sb(3)-C(25)	87 8(6)
O(3)-Sb(1)-C(7)	886(6)	O(2)-Sb(3)-C(31)	86 3(6)
O(5)-Sb(1)-O(6)	**75.0(4)**	O(7)-Sb(3)-O(8)	74.9(5)
O(5)-Sb(1)-O(10)	**94.2(5)**	O(7)-Sb(3)-O(9)	90.3(5)
O(5)-Sb(1)-C(1)	158.9(6)	O(7)-Sb(3)-C(25)	89 6(6)
O(5)-Sb(1)-C(7)	95.0(6)	O(7)-Sb(3)-C(31)	162.9(6)
O(6)-Sb(1)-O(10)	89.0(5)	O(8)-Sb(3)-O(9)	93.2(5)
O(6)-Sb(1)-C(1)	89 1(6)	O(8)-Sb(3)-C(25)	164.0(6)
O(6)-Sb(1)-C(7)	170.0(6)	O(8)-Sb(3)-C(31)	91.6(6)
O(10)-Sb(1)-C(1)	99.4(6)	O(9)-Sb(3)-C(25)	90.7(6)
O(10)-Sb(1)-C(7)	92.3(6)	O(9)-Sb(3)-C(31)	101.2(7)
C(l)-Sb(l)-C(7)	1005(7)	C(25)-Sb(3)-C(31)	102 8(8)
O(1)-Sb(2)-O(7)	86.8(5)	O(4)-Sb(4)-O(5)	85 6(5)
O(1)-Sb(2)-O(8)	84.6(5)	O(4)-Sb(4)-O(6)	84.3(5)
O(1)-Sb(2)-O(10)	1753(4)	O(4)-Sb(4)-O(9)	176.6(5)
O(1)-Sb(2)-C(13)	862(6)	O(4)-Sb(4)-C(37)	83.9(6)
O(1)-Sb(2)-C(19)	87 1(6)	O(4)-Sb(4)-C(43)	**91.2(6)**
O(7)-Sb(2)-O(8)	747(5)	O(5)-Sb(4)-O(6)	76.4(5)
O(7)-Sb(2)-O(10)	88.5(5)	O(5)-Sb(4)-O(9)	92.6(5)
O(7)-Sb(2)-C(13)	89.7(6)	O(5)-Sb(4)-C(37)	163.3(6)
O(7)-Sb(2)-C(19)	168 1(6)	O(5)-Sb(4)-C(43)	92 9(6)
O(8)-Sb(2)-O(10)	94.9(5)	O(6)-Sb(4)-O(9)	92.6(5)
O(8)-Sb(2)-C(13)	**162.2(6)**	O(6)-Sb(4)-C(37)	89.7(6)
O(8)-Sb(2)-C(19)	945(6)	O(6)-Sb(4)-C(43)	168.7(6)
O(10)-Sb(2)-C(13)	93 1(6)	O(9)-Sb(4)-C(37)	97 3(6)
O(10)-Sb(2)-C(19)	97.6(6)	O(9)-Sb(4)-C(43)	**91** 7(6)
C(13)-Sb(2)-C(19)	100.1(7)	C(37)-Sb(4)-C(43)	100 2(7)

i Intermolecular distance.

The Sb-O-Sb-0 rings in 12 and 13 are nearly planar; however the angles at the oxygen atoms are wider (99.1(2)° for 12 and 99.4(1)° for 13) at the expense of those at antimony (81.9(2)° for 12 and 80.6(1)° for 13) in both the dinuclear compounds. The latter values are comparable to those in $[Ph_2Sb(O_2AsMe_2)O]_2$ (**XXII**) [mean O-Sb-O 79.5°].[27] It is interesting to note that diminution of the angle at antimony is found even at penta-coordinated antimony in $[Ph_3SbO]_2$



XX[25] XXI[26] XXII[27] XXXI[42]

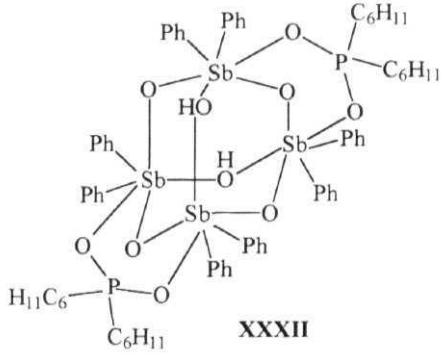
XXXI (77.4°)[42] and the fused ring system in $Ph_8Sb_4O_6$ (**XXI**) (≈76°)[26] both of which contain the Sb_2O_2 ring system. The Sb-0 distances within the four membered ring in 15 [mean 1.976 A^0] are shorter than the Sb-0 distances to the bridging phosphinates but are longer than the Sb-0 (oxo) distances in 10 [mean 1.937 A^0] and $[Cl_3Sb(O_2PMe_2)]_2O$ [mean 1.942(2) A°].[29] The *transoidal* orientation of phosphinates in 12 and 13 as compared to *cisoidal* in 10 is most likely due to a restriction imposed by the formation of the Sb_2O_2 ring.

An interesting structural correlation exists between **XXI** and our compounds 12 and 13. Removal of the two bonds Sb(2)-O(2) and Sb(l)-0(2) from **XXI** will lead to the same skeleton as that observed for 12 and 13, with the antimony atoms Sb(2) and Sb(l') (in **XXI)** being replaced by the phosphorus atoms (in 12 and 13). In fact in the original paper the authors suggest such a canonical structure for **XXI.**

In compound 15, charge balance would require the formula for the unsolvated molecule to be written as $Ph_8Sb_4O_4(OH)_2(O_2P(C_6H_{11})_2)_2$ In the actual structure, an acetic acid molecule, unconnected to the antimony cage even by H-bonding is also present. On the basis of the bond length data (Table 7) we propose that the oxygen atoms 0(6) and 0(7) of the cage are protonated; it can be readily seen that Sb-0 distances to these oxygen atoms are longer than the other nonphosphinate Sb-0 distances [to 0(5), 0(8), O(9) and 0(10)].

Compared to 12, the Sb_2O_2 rings in 15 are slightly nonplanar with a maximum deviation of atoms being < 0.1 A from the mean plane. What is more interesting in 15, however, is the dihedral angle between the two Sb_2O_2 rings [Sb(4)-O(5)-Sb(1)-O(6) and Sb(2)-O(7)-Sb(3)-O(8)] which is 30°. This makes the atoms 0(6) and 0(8) come closer [2.80 A^0]; simultaneously, 0(5) and 0(7) move farther apart [4.18 A°]. The O(6)-O(8) distance is appropriate for a proton to sit in between. In the X-ray structure of the acetate analogue $Ph_8Sb_4O_6(HO_2CMe)_3.CH_2Cl_2$ (IV) of 15, which has been described briefly in a communication,[5] a proton resides between the atoms corresponding to 0(6) and 08 [O....O distance in IV: 2.63 A^0]. However, in the acetate cage IV an acetic acid molecule bridges the oxygen corresponding to 0(5) and 0(7) by H-bonding; such a feature is absent in compound 15. The acetate group in 15 exists as acetic acid and is neutral; this conclusion is based on the intermolecular H-bond between the two oxygens [O(11)....0(12) = 2.71(3) A^0] of the acetic acid.

In connection with the Sb_4O_6 skeleton that we observed in 15, it is instructive to note that a second alternative structure XXXII with an "adamantane" type of skeleton is possible. From the molecular models at least, there does not appear to be any severe strain in such a structure. Since such a cage for

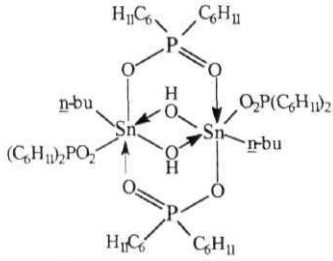


XXXII

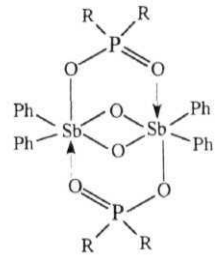
hexa-coordinated manganese has already been found,[43] we believe that the "crown" structure observed for 15 is a result of the reaction pathway rather than any special preference for the observed structure.

V.3 *Analogy to Tin Structures:*

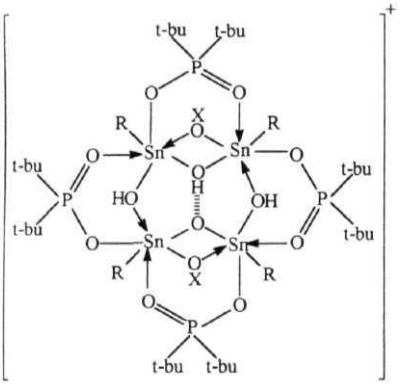
In hexa-coordinated systems, five covalent and one coordinate bond would make antimony(V) electronically equivalent to tin(IV) with four covalent and two coordinate bonds. Hence structural analogies can be expected between Sn(lV) and Sb(V) derivatives Thus compounds 12, 13 and 15 are structurally equivalent to the "butterfly" (XXXII)[44] and crown (III)[3,4] structures reported for tin.



"Butterfly"
XXXII (Ref. 44)



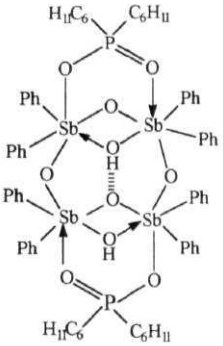
R= cycl-C_6H_{11} (12)
= cycl-C_8H_{15} (13)



III

Crown

R= Me, X= Me (Ref 3)
R= n-bu, X=H (Ref. 3. 4(a))



15

V.4 *Summary*

[1] Novel dimeric and tetrameric diphenylantimony (oxo)phosphinate cages have been synthesized and characterized.

[2] Structural interconversion similar to those observed for n-butyltin (oxo)carboxylates/ phosphinates have also been found for antimony (oxo)carboxylates/ phosphinates.

[3] A stable monomeric hepta-coordinated chloro carboxylate, $Ph_2SbCl(O_2C\text{-}2\text{-}Me\text{-}C_6H_4)_2$, nas been structurally characterized.

CHAPTER VI

EXPERIMENTAL SECTION

Dicyclohexyl phosphinic acid was prepared by a literature method,[45] the unknown dicyclooctylphosphinic acid (m.p. 118°C; $\delta(^{31}P)$: 66.2 ppm) was also prepared using the same method.[46] Silver salts of phosphinic/carboxylic acids were prepared using stoichiometric amounts of the acid, sodium hydroxide and silver nitrate; a typical procedure is illustrated for $AgO_2P(C_8H_{15})_2$ in (c) below. Chlorine and antimony were determined by known procedures.[47] Ph_2SbCl_3 (1) and $PhSbCl_4$ (16) were prepared following a modified version of the literature procedure;[14] $PhSb(O_2CMe)_4$ (XX) was also prepared by a literature method.[12]

(a) Preparation of Ph_2SbCl_3 (1): Freshly sublimed antimony trichloride (2.134 g, 9.30 mmol) was added to triphenyl antimony (6.6 g, 18.70 mmol). The mixture was left aside for 2h to yield Ph_2SbCl. This was taken in 100 mL of dry dichloromethane and then chlorinated following a standard procedure.[48] Three times the required amount of $KMnO_4$ and HCl (for generating Cl_2) was used to ensure the completion of the reaction. The volume of the solvent was reduced to half after filtration and then 10 mL of n-hexane was added. The solution upon keeping at **0°C** for 24h yielded Ph_2SbCl_3 (yield: 6.4g, 60%) M.p. 169°C [lit. m. p. 175°C[14]].

(b) Preparation of $PhSbCl_4$ (16)[14]: The same procedure as for Ph_2SbCl_3 (1) was followed using $SbCl_3$ (5.47 g, 23.89 mmol) and Ph_3Sb (4.23 g, 11.99 mmol). An air sensitive grey coloured product was obtained (yield: 4.3 g, 35%).

(c) Preparation of $AgO_2P(C_8H_{15})_2$: To a solution of NaOH (0.47 g, 11.75 mmol) in 15 mL of water was added dicyclooctyl phosphinic acid (3.37 g, 11.77 mmol), the solution stirred for 15 min and silver nitrate (2.0 g, 11.78 mmol) in 5 mL of water was added. The precipitate formed was collected, washed with 5 mL of methanol and dried *in vacuo* (yield: 3.9 g, 85%).

VI. 1. *Reactions of Diphenylantimony Trichloride with Silver Carboxylates*

$[Ph_2Sb(O_2Ph)_2]_2O$ (2). A mixture of Ph_2SbCl_3 (1) (0.85 g, 2.24 mmol) and AgO_2CPh (91.54 g, 6.72 mmol) in toluene (70 mL) was heated under reflux overnight and then filtered. The solvent was completely removed and the residue crystallized from dichloromethane-hexane (1:2). Yield 1.3 g, (55%). M.p. 198°C [Found: C, 59.50; H, 3.95. Calc. for $C_{52}H_{40}O_9Sb_2$: C, 59.30; H, 3.81%]. ^1H NMR: 7.00-8.40 (m, aryl H): ^{13}C NMR: 128.2-133.8 (aryl C). Major IR bands: 1599, 1531vs, 1448, 1402vs, 872, 835, 721 and 686 cm^{-1}.

When a solution of compound 2 in dichloromethane was recrystallized in air a less-soluble compound 2a was obtained; this was washed with ether to remove residual benzoic acid. Yield ≈ quantitative. M.p. 179-183°C [Found:C, 52.25; H, 3.20; Sb, 30.50. Calc. for $C_{69}H_{56}O_{12}Sb_4$: C, 52.95; H, 3.60; Sb, 31.15].

Compounds 3-6 were similarly prepared.

$[Ph_2Sb(O_2CCHPh_2)_2]_2O$ (3). Quantities used: Ph_2SbCl_3 (1) (1.27 g, 3.33 mmol), AgO_2CCHPh_2 (3.20 g, 10 mmol). Recrystallization from dichloromethane-hexane. Yield 2.0 g (42.5%). M. p. 195°C. [Found: C, 68.15; H, 4.55; Sb, 17.05. Calc. for $C_{80}H_{64}O_9Sb$: C, 68.00, H, 4.55; Sb, 17.25%]. ^1H NMR: 4.95 (s, 4H, $C\underline{H}Ph_2$), 6.90-7.90 (br m 60H, aryl H); ^{13}C NMR: 57.4 ($\underline{C}HPh_2$), 126.9-138.4 (many lines, aryl C) 147.8 (aryl C) and 178.8 (CO). Major IR bands: 1555vs, 1493, 1400vs, 860, 802, 687, 644 and 461 cm^{-1}.

Upon exposure of a solution of compound 3 in dichloromethane-acetone to air no significant change in the ^1H NMR spectrum was observed except a broadening of the CH signal; the m.p. of the solid remained the same.

$[Ph_2Sb(O_2C\text{-}2,4,6\text{-}Me_3C_6H_2)]_2O$ (4). Quantities used: Ph_2SbCl_3 (1) (0.53 g, 1.38 mmol), $Ag(O_2C\text{-}2,4,6\text{-}Me_3C_6H_2)$ (1.5 g, 5.54 mmol). Recrystallization was done from dichloromethane-heptane. Yield 1.10 g (65%). [Found: C, 62.30; H, 5.50; Sb, 19.10. Calc. for $C_{64}H_{64}O_9Sb_2$: C, 62.95; H, 5.25; Sb, 19.95%]. ^1H NMR: 1.84, 2.17 (two s, 30H, CH_3) and 6.60, 8.60 (many peak, 28H, aryl H). Major IR bands : 2970 (br), 1684, 1609, 1435vs, 1294vs, 1178, 1097, 856, 779, 603 and 453 cm^{-1}.

Exposure of a solution of compound 4 in dichloromethane-acetone to air and washing the residue with benzene after complete evaporation of the solvents afforded a solid, m.p. 181°C. The ^1H NMR spectrum of this solid showed a large number of methyl peaks (5 1.92, 1.98, 2.02, 2.15, 2.18, 3.46 and 3.64) along with $2,4,6\text{-}Me_3C_6H_2CO_2H$; however the integrated intensities (CH_3: aryl H) were consistent with the formulation $Ph_8Sb_4O_6.3(2,4,6\text{-}Me_3C_6H_2CO_2H)$.

$[Ph_2Sb(O_2C\text{-}2\text{-}Me\text{-}C_6H_4)]_2O$ (5). Quantities used: Ph_2SbCl_3 (1) (0.60 g, 1.58 mmol), $AgO_2C\text{-}2\text{-}Me\text{-}C_6H_4$ (1.17g, 4.78 mmol). Recrystallized from dichloromethane-hexane. Yield 1.0 g (56.4%) M.p. 205°C. [Found: C, 60.50; H, 4.20; Sb, 22.65. Calc. for $C_{56}H_{48}O_9Sb_2$: C, 60.70; H, 4.35; Sb, 22.00%]. ^1H NMR: 2.60 (s, 12H, CH_3) and 7.00-8.40 (many lines, aryl C). Major IR bands: 1687, 1604, 1579, 1510vs [ν(C=O)], 1479, 1444vs, 1394vs, 881, 833, 734, 688, 669 and 439 cm^{-1}.

$[Ph_2Sb(O_2C\text{-}4\text{-}Me\text{-}C_6H_4)]_2O$ (6). Quantities used: Ph_2SbCl_3 (1) (0.64 g, 1.68 mmol) $AgO_2C\text{-}4\text{-}Me\text{-}C_6H_4$ (1.17 g, 4.81 mmol). Recrystallized from dichloromethane-hexane. Yield 0.9 g(51%). M.p. 185-190°C. [Found: C, 61.40; 4.35; Sb, 22.35. Calc. for $C_{56}H_{48}O_9Sb_2$: C, 60.70; H, 4.35; Sb, 22.00%]. ^1H

NMR: 2.38, 2.45 (two s, 12H, CH3) and 7.05-8.25 (many lines, 36H, aryl H); ^{13}C NMR: 21.6, 21.8 (s each, CH3) 126.8-138.6 (many lines, aryl C), 170.3, 172.2(both (C=O)). Major IR bands: 1680, 1635, 1610, 1574, 1418, 1325vs, 1288vs, 1180, 758, 733, 688, 623, 461 and 417 cm^{-1}.

A solution of compound 6 in dichloromethane on evaporation in air afforded a solid which showed two CH3 peaks at 5 2.37 (major) and 2.44 (minor) in *ca.* 1:5 intensity ratio.

$Ph_2SbCl(O_2CR)_2$ (R= Ph (7), 2-Me-C_6H_4 (8) or 4-MeC_6H_4 (9)). These compounds were prepared by a procedure similar to that for 2 using a 1:2 stoichiometry of Ph_2SbCl_3 (1) (*ca.* 1.5 mmol) to AgO_2CR. They were recrystallized from dichloromethane-hexane.

Compound 7. Yield (70%); m.p. 168°C. [Found: C, 56.40; H, 3.60; Cl, 6.80; Sb, 21.50. Calc. for $C_{26}H_{20}ClO_4Sb$: C, 56.45; H, 3.65; Cl, 6.40; Sb, 22.00%]. ^1H NMR: 7.20-8.50 (m); ^{13}C NMR: 128.7-134.3 (many lines, aryl C) and 190.0 (C=O). Major IR bands: 1601, 1504vs [ν(C=O)], 1417[ν(C=O)], 875, 717, 684 and 445 cm^{-1}.

Compound 8. Yield 78%; m.p. 192°C. [Found: C, 57.85; H, 4.10; Cl, 6.0; Sb, 21.45. Calc. for $C_{28}H_{24}ClO_4Sb$: C, 57.80; H, 4.15; Cl, 6.10; Sb 20.95%]. ^1H NMR: 2.6 (s, 6H, CH3) and 7.10-8.45 (m, 18H, aryl H); ^{13}C NMR: 22.1 (CH_3), 126.0-133.5, 141.8, 152.0 (all aryl C), 196.0 (very weak, C=O). Major IR bands: 1602, 1498vs [ν(C=O)], 1413vs [ν(C=O)], 885, 733 and 682 cm^{-1} (up to 600 cm^{-1}).

Compound 9. Yield 73%; m.p. 198°C. [Found: C, 57.45; H, 4.05; Cl, 5 95; Sb, 21.85. Calc. for $C_{28}H_{24}ClO_4$ Sb: C, 57.80; H, 4.15; Cl, 6.10; Sb, 20.95%] ^1H NMR: 2.37 (s, 6H, CH3) and 7.15-8.40 (m, 18H, aryl H); ^{13}C NMR: 21.8 (CH3) 125.0, 129.2, 131.1, 131.1, 132.5, 145.4, 152.8(all aryl C). Major IR bands:

1610, 1520, 1494, 1477, 1437 [ν(C=O)], 1178, 887, 762, 733, 683, 629, 459, and 419 cm^{-1}.

VI. 1.1 Interconversion of compounds **XV** and IV. Compound XV (0.200 g) was dissolved in dichloromethane (30 mL). Upon crystallization in air IV. CH_2Cl_2 was formed quantitatively. ^1H NMR (after drying *in vacua* for 2h): 1.76 (s, 3H, CH3), 1.90 (s, 6H, CH3), 6.40-8.00 (m, *ca.* 43H, aryl H + OH).

Compound IV (0.150 g) was heated under reflux with acetic acid-acetic anhydride (5+5 mL) for 24h. Upon reducing the volume of the solvent XV (120 mg) was obtained as a crystalline solid. ^1H NMR: 1.98 (s, 12H, CH_3), 7.15-8.2 (m, 20H, aryl H).

VI.2 *Reactions of Diphenylantimony Trichloride with Silver Phosphinates.*

$[Ph_2SbCl\{O_2P(C_6H_{11})_2\}]_2O$ (10) A mixture of Ph_2SbCl_3 (1) (0.39 g, 1 mmol) and $AgO_2P(C_6H_{11})_2$ (0.68 g, 2 mmol) was heated in dry toluene 50 mL for 2h under reflux and then filtered. The solvent was completely removed from the filtrate and the residue crystallized from dichloromethane-hexane (1:5). Yield 0.7 g (65%). M. p. 235°C. [Found: C, 52.6; H, 5.8. Calc. for $C_{48}H_{64}Cl_2O_5P_2Sb_2$: C, 52.5, H, 5.8%]. ^1H NMR: 1.18-2.50(br m, 44H, C_6H_{11}), 7.19-8.30 (m, 20H, aryl H). ^{13}C NMR: 26.0-26.9 (many lines, C_6H_{11}, except PC), 37.8 [d, ^1J (P-C)= 99.6, PC), 39.6 [d, ^1J(P-C)= 94.0Hz, PC], 127.7-133.6 (many lines, aryl C) and 152.6 (aryl C). ^{31}P NMR: 54.7. Major IR bands: 2930, 1433, 1084 [ν(P=O)], 1014,981, 758, 731, 688, 551, and 459 cm^{-1}.

$[Ph_2SbCl\{O_2P(C_8H_{15})_2\}]_2O$ (11). The same procedure as for compound 10 was followed using Ph_2SbCl_3 (1) (0.37 g, 0.98 mmol) and $AgO_2P(C_8H_{15})_2$ in toluene 50 mL. The product was recrystallized from dichloromethane-hexane (1:10; 4d). Yield 0.5g (43%). M.p. 221°C. [Found: C, 56.50; H, 6.65; Cl, 5.50;

Sb, 20.90. Calc. for $C_{56}H_{80}Cl_2O_5P_2Sb_2$: C, 55.60; H, 6.60; Cl, 5.85; Sb, 20.15%]. ^1H NMR: 0.85-2.35 (br m, 60H, C_8H_{15}), 7.23-8.40 (m, 20H, aryl H). ^{31}P NMR: 58.6. Major IR bands: 2922, 1477, 1433, 1080. [ν(P=O)], 995, 731, 688, and 461 cm^{-1}.

$[Ph_2Sb(O_2P(C_6H_{11})_2O)]_2$ (12). **Route** (A). A mixture of Ph_2SbCl_3 (1) (1.01 g, 2.66 mmol) and silver acetate (1.77 g, 0.63 mmol) was heated in dry toluene 50 mL for 3h under reflux and then filtered. The precipitate was washed with 10 mL of dry toluene , and the washing was added to filtrate. To this filtrate dicyclohexylphosphinic acid (1.2 g, 2.66 mmol) was added and the mixture heated overnight under reflux. The ^{31}P NMR spectrum of the reaction mixture showed a major peak at 64.3 ppm (> 70%) and two minor peaks at 61.1 and 54.2 ppm. The solvent was completely removed from the mixture and the residue crystallized from dichloromethane-hexane (1:3) Yield: 1.5 g (54 %), m. p. 284°C [Found: C, 51.34,; H, 5.81. Calc. for $C_{49}H_{66}Cl_2O_2P_2Sb_2$: C, 52.20; H, 5.86]. ^1H NMR: 0.70-2.20 (br m, 44H, C_6H_{11}),7.20-8.00 (m, 20H, H (Ar)). ^{31}PNMR: -64.3 ppm.

Route (B). A mixture of 1 (0.39 g, 1.06 mmol) and $AgO_2P(C_6H_{11})_2$ (2.65 g, 7.87 mmol) was heated under reflux in dry toluene (60 mL) for 24h and filtered. The solvent was removed from the filtrate and the residue crystallized from dichloromethane-hexane in air to obtain 12. Yield 0.44 g, (40%). M.p., IR, and ^{31}P NMR of the crystalline product were identical to that obtained by route A.

$[Ph_2Sb(O_2P(C_8H_{15})_2)O]_2.2CH_2Cl_2$ (12). The procedure was similar to that for 12 (route A or B). **Route (A):** The following quantities were used: 1 (1.97 g, 5.17 mmol), silver acetate (2.5 g, 15.5 mmol), dicyclooctylphosphinic acid (2.96 g, 10.33 mmol). The ^{31}P NMR spectrum of the reaction mixture shows a major peak at 69.6 ppm (>70%) and two minor peaks at 66.1 and 60.5 ppm. The product was crystallized from dichloromethane-hexane. Yield 2.5 g (38.6%). M.p. 255°C. [Found: C, 57,75; H, 7.08. Calc. for $C_{56}H_{80}O_6P_2Sb_2$: C, 58 26; H, 6.94.

^{1}H NMR: (after drying): 0.90-2.30(br m, 60H, $C_8\underline{H}_{15}$), 7.08-7.95(m, 20H, H (Ar)). [A peak for dichloromethane solvent is observed at 5.3 ppm if the sample is not dried]. ^{31}P NMR: 69.6. IR (major peaks): 1039 ν(P=O) and 960 cm^{-1}. The same compound could be obtained from route B in 40% yield.

$[Ph_2Sb(O_2P(C_6H_{11})_2)(O_2CMe)]_2O$ (14): A mixture of Ph_2SbCl_3 (1) (0.50 g, 1.31 mmol) and silver acetate (0.875 g, 5.25 mmol) was heated in dry toluene (20 mL) for 3h under reflux and filtered. To the filtrate dicyclohexylphosphinic acid (0.30g, 1.31 mmol) was added and the mixture heated under reflux for 5h. Then the solvent was removed and the residue crystallized from dichloromethane-heptane (1:7) with stringent precautions against the ingress of moisture. Yield: 0.40g, (27%). M.p. 218°C. [Found: C, 54.10, H, 6.23. Calc. for $C_{52}H_{70}O_9P_2Sb_2$, C, 54.60; H, 6.12]. ^{1}H NMR (after drying): 0.70-2.00 (br m, 44H, $C_6\underline{H}_{11}$), 2.05 (s, 6H, $C\underline{H}_3$), 7.23-8.15 (m, 20H, H (Ar)). ^{31}P NMR: 53.3. IR (major bands only): 1680 ν(C=O), 1278, 1091 [ν(P=O)], 1014 and 981cm^{-1} Compound 14 is moisture sensitive and gives either **12** or **15** upon hydrolysis depending on the conditions. Thus crystals of 15 suitable for X-ray were grown while an attempt was made to crystallize 14 from dichloromethane-hexane.

Tetrameric cage $Ph_8Sb_4O_4(OH)_2\{O_2P(C_6H_{11})_2\}_2.(HO_2CMe).CH_2Cl_2$ (15). A mixture of the dimer 12 (0.50 g, 0.48 mmol), acetic acid (3 mL) and water (0.2 mL) was heated under reflux for 2h. Acetic acid was removed and the compound was crystallized from dichloromethane-hexane (1:5). Yield 0.60 g (69%). M.p. 248°C. [Found: C, 51.45; H, 5.05. Calc. for $C_{74}H_{90}O_{12}P_2Sb_4$: C, 51.69; H, 5.28]. ^{1}H NMR (after evacuation and removal of solvent): 0.63-2.15 (br m, 44H, 3H, $C_6\underline{H}_{11}$+CH3), 3.50-3.90 (br, 2H, OH), 6.97-8.00 (m, 40H, H (Ar)). One solvent molecule (CH_2Cl_2; δ(^{1}H): 5.2 ppm) per tetrameric cage is observed if

no evacuation is done. ^{31}P NMR: 57.7. IR (major bands only): 1761, 1705 [ν (C=O)] and 1072 [ν(P=O)] cm^{-1}.

VI.2.1 Conversion of the tetrameric cage 15 to the dimer 12. A mixture of **15** (0.05 g) and dicyclohexylphosphinic acid (0.02 g) was heated under reflux in toluene (7 mL) with azeotropic removal of water for 12h. The solvent was completely removed and ^{31}P NMR recorded for the mixture; it showed compound **12** [$\delta(^{31}P$: 64.2 (>85%)]. Two other minor products [$\delta(^{31}P)$: 53.8, (>5%), **45.9** (5%)] and the excess of the phosphinic acid [$\delta(^{31}P)$: 59.9] were also present

VI.3 *Reactions of* $PhSbCl_4$

(i) With silver isobutyrate. A mixture of PhSbCl4 (0.93 g, 2.72 mmol) and silver isobutyrate (2.70 g, 13.61 mmol) was heated under reflux in toluene (60 mL) for 12h, and then filtered. The solvent was completely removed from the filtrate and the residue crystallized from dichloromethane-hexane (1:3) to get a crystalline solid $PhSb(O)(OH)(O_2CCHMe_2)$(?) (17). Yield 0.55 g (66%, based on $PhSbCl_4$). M.p. 155°C. ^1HNMR: 1.15 (d, ^1J= 10Hz, 6H, CH3), 2.40 (m, 1H, CH), 6.90-7.60 (m, 5H, H (Ar)) 7.90(br s, 1H (?)). The product was very moisture-sensitive; the ^1H NMR changed with time [additional peaks at 0.93 (d, J=10 Hz, CH3). and 5.2 ppm developed; the integral intensity ratio of carboxylate: phenyl became <1.

(ii) With silver acetate followed by dicyclohexylphosphinic acid. A mixture of PhSb(C>2CMe)4[12] (2.24 g, 5.15 mmol) and $(C_6H_{11})_2PO_2H$ (1.19 g, 5.15 mmol) was heated under reflux for 5h in toluene (50 mL) and filtered. The solvent was completely removed from the filtrate and the residue crystallized from dichloromethane-hexane (1:2) to give $PhSb(O)(OH)(O_2P(C_6H_{11})_2)$ (?) (18). Yield 1.5g (63%, based on $PhSb(O_2CMe)_4$). M.p. 168°C. ^1H NMR: 0.73-1.90 (m, 22H, $C_6\underline{H}_{11}$), 2.1 (s, (variable), CH3), 4.95 (br s, *ca.* 1H, OH(?)), 5.2 (s, (variable), $C\underline{H}_2Cl_2$), 7.05-8.00 (m, 5H, H (Ar)). ^{3}lp NMR: 52.8, 64.3.

VI.4 *X-ray Crystallography*

X-ray structures were obtained from I. I. Sc. (Bangalore, India) [for 2, 8 (in part) and 10], Texas A & M University (for 13 and 15) or Universitat des Saarlandes (for 12). Analysis was performed using a hpplot program. Some details on crystal data, structure solution etc are given in Appendix 2; important atomic coordinates are given in Appendix 3. More information for all compounds except 8 are available in references 49 and 50.

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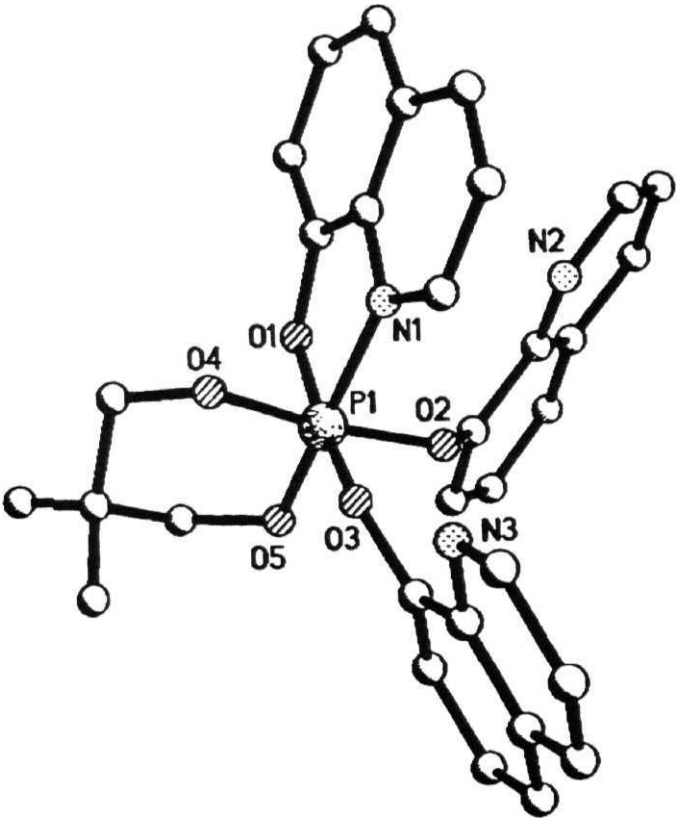
APPENDIX 1



Molecular structure of compound 42.

APPENDIX 2

SELECTED CRYSTALLLOGRAPHIC DATA

Part- A: Phosphorus and arsenic compounds

Compound	9	44	47
formula	$C_{28}H_{26}NO_2P$	$C_{10}H_{20}As_2O_5$	$C_{58}H_{84}As_2O_5$
fw	**231.27**	370.1	1011.09
cryst system	orthorhombic	Monoclinic	Monoclinic
Space group	$Pna2_1$	C2/c	C2/c
a/ *k*	18.287(2)	18.874(4)	22.60(3)
b/ A	15.157(1)	9.896(2)	17.85(2)
c/ Å	18.541(3)	8.651(2)	16.21(2)
p7°	90	116.45(3)	122.68(7)
V/A^3	5139.1(11)	1446.7(5)	5505(11)
Z	16	4	4
μ, mm"^{1}	0 198	4 626	1.259
F(000)	2016	744	2152
20-range (°)	7-45	2-50	2-45
Refl collected	8219	1252	3607
Indep. reflections	6689	1215	3607
R_1 (I > 2 σ (I))	0.0584	0.0222	0.0395
[illegible]	[illegible]	1210 0 0528 0	1120

Compound	8b	17b	22b
formula	$C_{14}H_{16}AsNO_3$	$C_{21}H_{14}AsNO_3$	$C_{38}H_{48}AsNO_3$
fw	321.2	403 25	6'1.69
space group	P1	$P2_1$	P1
al A	10.013(7)	10.469(7)	11.320 (6)
bl A	10.501(8)	7.126(4)	12.749(7)
c/ Å	**13.553(9)**	11.837(6)	14.257(8)
α/ °	86.40(6)	-	116.50(3)
p/°	83.54(6)	95.14(5)	97.21(4)
γ/ °	86.87(6)	-	102.62(4)
V/A^3	1412(2)	879.5(9)	1737(2)
Z	4	2	2
μ, cm^{-1}	24 11	19 53	10 14
F(000)	656	408	680
20 range (°)	3.0-45	3.5-45	3.3-45
Refl collected	3859	2518	4553
Indep reflections	3683	2295	4548
R1 (I > 2 σ (I))	**0.0375**	0 0284	0.0348
wR2 (all data)	0 0827	0 0715	0 0787

Compound	33	**51**	86
formula	$C_{34}H_{52}O_4ClP$	$C_{18}H_{24}NO_4P$	$C_{17}H_{19}O_5P$
fw	**591.2**	34935	334 29
cryst system	Monoclinic	Orthorhombic	Monoclinic
space group	P2]/c	$Pca2_1$	Cc
n/A	12.0337(2)	30.992(17)	**15.372**
bl A	14.797(2)	8.613(4)	9.725(1)
c/ Å	20.302(3)	6.721(11)	10.678(1)
β/ °	94 44(2)	-	97.23(1)
V/ A^3	3604.0(9)	1794.0(31)	1583.6(2)
Z	4	4	4
μ, mm^{-1}	1.784	0 17	0.197
F(OOO)	1280	744	704
2θ-range (°)	3.0-45	2.3-50	7-50
Refl collected	5238	1705	2810
Indep reflections	4734	1309	2805
R1 (I > 2σ(I))	(R = 0.050)	0 0525	0.0280
wR2 (for all data)	(R_w = 0.089)	0.2072	0.0677

Compound	59	**60**	**65**.1/2Et_2O
Formula	$C_{17}H_{22}Cl_4NO_4P$	$C_{24}H_{20}Cl_4NO_4P$	$C_{41}H_{58}NO_4P$.1/2Et_2O
fw	477.1	559 18	696.91
cryst system	Monoclinic	Monoclinic	Monoclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a/ A	9.845(1)	14.256(2)	9.499(1)
bl A	17.923(4))	1.253(2)	18.971(2)
c/ Å	12.344(2)	15.193(2)	23.478(1)
β/ °	10747(1)	11428(1)	95.93(1)
V/ A^3	2077.7(6)	23797(6)	4208.3(6)
Z	4	4	4
μ, mm^{-1}	0.67	0.598	0 105
F(000)	984	1144	1516
2θ-range (°)	4-50	5-50	7-50
Refl collected	4945	7974	9259
Indep rencctions	3681	4223	7458
R1 (I > 2σ(I))	0.0382	0 0373	0.0634
\vR2 (for all data)	0.1107	0.0877	0 1864

IV

Compound	73CH_2Cl_2	76CH_2Cl_2	781/6 Et_2O	791/2 H_2O
formula	$C_{28}H_{24}NO_5P$ CH_2Cl_2	$C_{35}H_{34}NO_5P$ CH_2Cl_2	$C_{33}H_{22}NO_5P$ 1/6 Et_2O	$C_{52}H_{68}NO_5P$ 1/2 H_2O
fw	570.38	664.53	**555.84**	827.05
crystal system	monoclinic	orthorhombic	rhombohedral	triclinic
space group	$P2_1/c$	Pna2]	R3	P1
a [A|	10.582(1)	17 463(5)	36.021(2)	10.988(3)
b [Å]	27 900(3)	**12.558(2)**	36 021(2)	21 980(5)
c [A]	9.255(1)	30 426(7)	**10.646(2)**	**22.108(5)**
|°1	90	90	90	110.05(1)
[°]	106.57(1)	90	90	101.77(2)
[°]	90	90	120	92.94(1)
V[A^3]	2619.0(5)	6672(3)	11963(2)	4868(2)
Z	4	8	18	4
[mm^{-1}]	**0.351**	0.286	0 150	0 103
F(000)	1184	2784	5202	1784
2 range	8-50	4-45	7-45	7-50
reflect. collected	5991	9105	6273	17857
Indep reflections	4612	8723	3498	17492
R1 [I>2(I)]	0 0420	0 0461	0 0410	**0.0732**
vvR2 [all data)	0.1011	0.1141	0.0989	0.2256

Compound	75	32
Formula	$C_{28}H_{26}NO_5P$	$C_{19}H_{26}AsNO_5$
fw	487.47	423.33
Space group	P1	P1
a/ Å	9.17(6)	9.631(12)
b/ A	11.484(7)	9 969(13)
c/ Å	12 168(8)	11.34(2)
α/ °	107 00(5)	114.38(10)
p/°	100.86(4)	106 25(10)
y/°	95.17(3)	93.18(10)
V/A^3	1189 5(13)	934(2)
Z	2	2
μ, cm^{-1}	15.6	18.5
F(000)	512	440
Refl collected	4796	3286
Indep reflections	3107	3286 (Rint = 0 0000)
Final R indices	Rl - 0 0416	Rl = 0 0445
(I > 2 σ (I))	vvR2 = .01105	wR2 = 0.1211

Part- B Antimony comounds

Compound	2	8	10
Empirical formula	$C_{52}H_{40}O_9Sb_2$	$C_{28}H_{24}ClO_4Sb$	$C_{48}H_{64}Cl_2O_5P_2Sb_2$
Formula weighl	1052 4	581.67	1097 5
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	Pbcn	$P2_1/n$	$P2_1/n$
Z	4	4	4
a/A	11.827(44)	**8.791(3)**	13.989(8)
b/A	18.209(18)	21.687(3)	20 588(5)
c/A	21016(8)	13.488(4)	17 156(3)
|V	9000	103.78(2)	94.95(3)
V/A'	4526(5)	2497.5(12)	4923(13)
F(000)	1972	1168	2192
μ(Mo-Kα)/cm^{-1}	9.32	12.4	12.85
2θ rangc/°	2-50	2-50	2-50
Tota, reflections	4599	4702	9379
Obsd reflcns	3336 (F_o>5σ(F_o))	3575 (F_o>4σ(F_o))	6911(F_o>5σ(F_o))
R	0.037	0.0353	0.046
R'	0 053	0.1028	0 054
w	$1/[\sigma^2(F) + 0.008488F^2]$		$1/[\sigma^2(F) + 0.000414F^2]$

For 2 and 10, $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

Compound	12	**13**	15
Empirical formula	$C_{50}H_{68}Cl_4O_6P_2Sb_2$	$C_{29}H_{42}Cl_2O_3PSb$	$C_{75}H_{92}Cl_2O_{12}P_2Sb_4$
Formula weight	1212.28	662.28	1805 43
Crystal svstem	Triclinic	Monoclinic	Monoclinic
Space group	**P1**	P2j/a	$P2_1/n$
Z	1	4	4
a/A	10.520(12)	**12.119(2)**	15.111(2)
b/A	11.609(10)	**19.739(3)**	27 860(5)
c/A	13.35(2)	13 155(2)	18.669(2)
α/°	6465(8)		
β/°	71.86(9)	11221(1)	101.10(1)
γ/°	68.70(8)		
V/A^1	1350(3)	2913.4(8)	7712(2)
F(000)	616	1360	3624
μ(Mo-Kα)/cm^{-1}	**13.03**	12.19	15.52
T/°C	20	**-110**	23
2θ rangc/°	3.44-34 88	50 1 (max)	50.1 (max)
Total reflections	1713	5615	14492
Unique reflections	1713	5349	13936
Obsd reflcns	1673(I >2σ(I))	4372 (I >3σ(I))	4637 (I >3σ(I))
Final R indices	R_1= 0.0335 (I >2σ(I))	R^a= 0.028 (I >3σ(I))	R^a= 0.061 (I >3σ(I))
	wR_2= 0.0836	$R_w{}^a$= 0.037	$R_w{}^a$= 0.053

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_w = \{\Sigma w(|F_o| - |F_c|^2/\Sigma wF_o{}^2\}^{1/2}$.

APPENDIX 3

Selected Atomic Coordinates for Compounds

PART A: 8b, 9, 17b, 22b, 24, 32, 33, 44, 47, 51, 59, 60, 65, 73, 75, 76, 78, 79 and **86**

PART B 2, 8, 10, 12, 13 and **15.**

PART A ***Phosphorus and Arsenic Compounds***

Compound 8b

Atom	x	y	z
As(l)	.1547(1)	1873(1)	.4398(1)
O(1)	.1163(3)	.3486(3)	.4678(2)
0(2)	.3062(3)	.2118(3)	**.3588(3)**
0(3)	0607(3)	.1824(4)	3319(2)
N(l)	**-.0939(4)**	**.1544(4)**	**.5109(3)**
C(l)	**.1387(5)**	.4474(5)	.3899(4)
C(2)	**.2829(5)**	.4474(5)	.3402(4)
C(3)	**3166(5)**	.3225(5)	.2916(4)
C(6)	**-.0743(5)**	1703(5)	.3341(4)
C(14)	**-.1569(5)**	**.1547(5)**	.4264(3)
As(2)	**.0799(1)**	1080(1)	.8914(1)
0(4)	2294(3)	**.1901(4)**	.9014(2)
0(5)	0513(3)	.1690(3)	7708(2)
0(6)	-.0203(3)	2285(4)	**.9643(3)**
N(2)	-.1705(4)	.0524(4)	.8908(3)
C(15)	**.2408(5)**	**.3189(6)**	8608(4)
C(16)	.2203(5)	3344(5)	.7520(4)
C(17)	.0779(5)	.2976(5)	.7394(4)
C(20)	-.1563(5)	2445(5)	9717(4)
C(28)	-.2371(5)	.1546(5)	9337(3)

Compound 9

Atom	x	y	z
P(l)	.5048(1)	2638(1)	4379(1)
0(1)	5727(2)	.3160(3)	3987(2)
0(2)	4469(2)	2655(3)	.3715(3)
N(l)	5382(3)	1627(3)	.4437(3)
C(17)	5956(3)	2917(4)	.3271(3)
C(18)	5328(4)	2964(4)	2738(3)
C(19)	4696(4)	.2397(5)	3005(4)
P(2)	.7593(1)	7604(1)	3500(1)
N(2)	7256(3)	6590(3)	.3477(3)
0(3)	6911(2)	.8137(3)	3871(2)
0(4)	8176(2)	.7639(3)	4169(3)
C(27)	.6681(3)	7916(4)	4591(3)

Compound 9 Contd

C(28)	7311(4)	7992(4)	5134(3)
C(29)	.7934(3)	.7415(4)	.4877(4)
P(3)	6769(1)	5104(1)	5312(1)
0(5)	6074(2)	5100(3)	5861(2)
O(6)	.6404(2)	.5658(2)	.4645(2)
N(3)	.6831(3)	4119(3)	.4943(3)
C(37)	5685(3)	.5436(4)	.4385(4)
C(38)	5115(3)	.5452(4)	.4982(4)
C(39)	5361(3)	4862(4)	5593(4)
P(4)	.5803(1)	1.0083(1)	.2629(1)
N(4)	.5762(3)	.9076(3)	2993(3)
0(7)	.6221(2)	1.0624(2)	.3272(2)
0(8)	.6451(2)	1.0068(3)	.2024(2)
C(47)	.6968(3)	1.0405(4)	**.3455(4)**
C(48)	7478(3)	1.0434(4)	2816(4)
C(49)	.7172(3)	.9829(5)	.2240(4

Compound 17b

Atom	x	y	z
As	5398(1)	**.9271(1)**	**.6895(1)**
0(1)	.5310(2)	8468(4)	8329(2)
0(2)	.6994(2)	8265(4)	.6772(2)
0(3)	.4694(2)	7183(4)	6219(2)
N	.3108(3)	.9675(4)	.7028(3)
C(l)	.6338(3)	8914(5)	**.9105(3)**
C(2)	.7457(3)	7892(5)	9139(3)
C(7)	7589(3)	6285(6)	8372(3)
C(8)	.7295(3)	6511(6)	.7189(3)
C(13)	.3425(3)	.6759(6)	**.6183(3)**
C(21)	.2569(4)	8073(6)	6587(3)

Compound **22b**

Atom	x	y	z
As	.1034(1)	8524(1)	1734(1)

Compound **22b** Contd

O(1)	**.1193(2)**	.8461(2)	.2979(2)
0(2)	-.0664(2)	.8056(2)	.1316(2)
0(3)	**.0869(2)**	6935(2)	.0795(2)
N	**.3231(3)**	**.8358(3)**	.1970(2)
C(l)	**.0201(3)**	.8144(3)	**.3381(2)**
C(6)	-.0662(3)	8798(3)	**.3543(2)**
C(7)	-.0422(3)	.9960(3)	.3451(2)
C(8)	**-.1125(3)**	.9897(3)	.2441(2)
C(9)	-.1218(3)	.8967(3)	.1406(3)
C(14)	.1853(3)	.6533(3)	**.0480(3)**
C(22)	.3088(3)	.7268(3)	.1093(3)

Compound 24

Atom	x	y	z
P(l)	0.6029(1)	0.1480(1)	0.1641(1)
N(l)	0.6619(3)	0.1477(2)	0.0639(2)
0(1)	0.5307(2)	0.0229(2)	0.1377(2)
C(ll)	0.4910(3)	-0.0281(2)	0.2115(2)
C(16)	**0.3575(3)**	-0.0156(2)	0.2292(2)
C(10)	0.2616(3)	0.0527(2)	0.1726(2)
0(2)	0.4577(2)	0.2066(2)	0.1311(2)
C(21)	0.3818(3)	0.2394(2)	0.2002(2)
C(26)	0.2844(3)	0.1654(2)	0.2220(2)

Compound 32

Atom	x	v	7.
As	.3686(1)	.2137(1)	.2222(1)
0(1)	.2473(3)	.2079(3)	.3253(3)
N	.4124(3)	.0220(3)	.2376(3)
0(2)	.4893(3)	.1939(3)	.1239(3)
0(3)	.5138(3)	.3066(3)	.3831(3)
0(4)	.2232(3)	.0847(3)	.0720(3)
0(5)	.3154(3)	.3817(3)	.2243(3)
C(l)	.2556(4)	.1004(4)	.3644(4)
C(6)	.3453(4)	-.0029(4)	.3176(4)
C(10)	.6022(5)	.3186(5)	.1630(4)
C(ll)	.7076(5)	.3783(5)	.3070(4)
C(12)	**.6210(5)**	.4269(4)	.4055(4)
C(15)	.1627(6)	.1181(6)	-.0376(5)
C(16)	.1129(5)	.2669(5)	.0022(5)
C(17)	.2415(6)	.3880(6)	.0985(6)

Compound **33**

Atom	\	v	/.
Cl	**0.7463(1)**	-0.1356(1)	0.6332(2)
P	**0.9533(2)**	0.0741(1)	0.7977(1)

Compound **33** Contd

O(1)	1.0253(3)	0.0294(3)	**0.8579(2)**
O(2)	0.8249(3)	0 0683(3)	0.8123(2)
0(3)	0.9889(3)	01641(3)	0 7792(2)
O(4)	0.9598(3)	-00078(3)	0 7483(2)
C(1)	0 7704(5)	0.1390(4)	0 8448(3)
C(6)	0.7961(5)	0 1465(4)	0.9133(3)
C(7)	0.8723(5)	0.0796(4)	**0.9506(3)**
C(8)	0.9948(5)	0.1062(4)	**0.9592(3)**
C(13)	1.0693(5)	0 0811(4)	0.9137(3)
C(30)	0.9476(4)	0.0007(4)	0.6807(4)
C(31)	0.9696(5)	-0.0884(4)	0 6464(4)
C(33)	0.8883(6)	-0.1623(6)	0.6555(4)

Compound 44

Atom	x	y	z
As(1)	.0801(1)	.0202(1)	.2331(1)
O(1)	.0000	1020(2)	2500
O(2)	.0679(1)	.1055(2)	.0403(2)
0(3)	**.1548(1)**	1267(2)	.3805(2)
C(1)	0631(2)	2498(3)	.0368(3)
C(2)	.1347(2)	.3176(3)	.1801(4)
C(3)	.1430(2)	.2694(3)	.3551(3)

Compound 47

Atom	x	v	/.
As	.4363(1)	.2501(1)	.1333(1)
0(1)	4193(2)	.3369(2)	1726(2)
O(2)	4991(2)	.2770(2)	.1031(2)
O(3)	5000	.2159(3)	2500
C(l)	.3598(2)	.3753(3)	.0989(3)
C(6)	3672(2)	.4170(3)	.0323(3)
C(7)	.4370(2)	.4212(3)	.0386(3)
C(8)	.4391(2)	.3645(3)	**-.0295(3)**
C(13)	4695(2)	.2940(3)	.0031(3)

Compound 51

Atom	x	y	z
P(l)	.08667(5)	0991(2)	**-.0076(6)**
O(1)	.09098(14)	.0696(6)	.2088
O(2)	.04366(14)	.0984(6)	-.1003(10)
0(3)	.11318(13)	-.0257(5)	-.1317(9)
O(4)	.15340(14)	.0227(5)	-.5157(10)
N	4583(2)	9383(6)	0164(11)
C(1)	.1538(2)	-.0800(7)	**-.0794(11)**
C(2)	1567(2)	-.2178(8)	.0205(13)
C(3)	1972(3)	-.2751(10)	.0712(13)

Compound 51 Contd

C(4)	.2328(3)	- 1940(9)	0264(13)
C(5)	.2300(2)	**-.0573(10)**	**-.0743(12)**
C(6)	.1904(2)	.0048(8)	**-.1320(11)**
C(7)	1885(2)	1497(8)	**-.2492(12)**
C(8)	1700(2)	.1566(8)	**-.4378(11)**
C(9)	1692(2)	2942(8)	**-.5411(14)**
C(10)	1874(3)	**.4253(10)**	-.4636(17)
C(ll)	.2071(3)	4202(9)	-2812(16)
C(12)	.2073(3)	.2836(9)	-1768(14)
C(13)	.4360(3)	**.5299(10)**	.2129(15)
C(14)	4451(3)	4405(8)	.0210(16)
C(15)	4297(3)	.5303(10)	**-.1592(15)**
C(16)	4489(3)	6918(9)	-.1640(12)
C(17)	.4390(2)	.7789(7)	**.0268(11)**
C(18)	4563(3)	6915(9)	.2046(12)

Compound 59

Atom	x	v	z
P(I)	0.7613(1)	0.1157(1)	0.3522(1)
O(3)	0.6201(2)	0.1604(1)	0.2705(1)
O(4)	0.7738(2)	**0.0673(1)**	2293(1)
C(21)	0.5844(3)	0.1429(2)	0 1578(2)
C(22)	0.4746(3)	0.1739(2)	**0.0752(2)**
C(23)	0.4502(3)	0.1483(2)	-0.0366(2)
C(24)	0.5384(3)	0 0943(2)	**-0.0595(2)**
C(25)	0 6516(3)	0.0642(2)	0.0262(2)
C(26)	0.6736(3)	0.0892(1)	0.1364(2)
N(l)	0.7514(2)	0.0346(1)	0.4070(2)
0(2)	0.7431(2)	0 1584(1)	0.4630(2)
0(1)	0.9071(2)	0.1543(1)	0 3523(2)
C(13)	0.7566(3)	0.2380(2)	04715(3)
C(12)	09005(3)	0.2656(2)	0 4656(3)
C(ll)	0.9854(3)	0.1984(2)	0.4486(2)

Compound 60

Atom	x	y	z
P(l)	09814(1)	0.7080(1)	0.1902(1)
0(1)	0 8626(1)	0.6794(1)	0.1620(1)
0(2)	1.0301(1)	0.6346(1)	02894(1)
C(ll)	0 8233(2)	0.5805(2)	0 1821(2)
C(16)	08393(2)	0.5499(2)	0 2750(2)
C(21)	1.0030(2)	06520(2)	0.3663(2)
C(26)	0.9109(2)	0.6095(2)	0 3617(2)
0(3)	10082(1)	0.8226(1)	02559(1)
0(4)	0.9406(1)	0.7908(1)	0.0858(1)
C(31)	0.9691(2)	0.9172(2)	0.2038(2)
C(36)	0.9310(2)	0.8970(2)	0 1059(2)
N(l)	**1.0514(2)**	0 6424(2)	0 1461(2)

Compound 65

Atom	x	v	z
P(l)	0.1708(1)	0.4834(1)	0 2394(1)
O(1)	0.2819(2)	**0.4890(1)**	0.1925(1)
0(2)	0.1826(2)	0.5678(1)	0.2594(1)
0(3)	0.2346(2)	**0.4601(1)**	0.3041(1)
0(4)	01551(2)	**0.3963(1)**	**0.2199(1)**
N(l)	0.0037(3)	04957(1)	**0.2183(1)**
C(l)	0.4851(3)	05569(2)	02716(1)
C(ll)	**0.3540(3)**	0.5466(2)	0 1724(1)
C(16)	0.4570(3)	**0.5795(2)**	**0.2098(1)**
C(21)	0.2572(3)	06017(1)	**0.3057(1)**
C(22)	0 4051(3)	0 5998(2)	0.3115(1)
C(31)	0 2534(3)	0.3882(2)	**0.3115(1)**
C(36)	02073(3)	0.3520(2)	0.2622(1)

Compound 73

Atom	x	y	z
P(l)	1557(1)	**.4125(1)**	.7769(1)
0(2)	.2795(1)	3827(1)	.9115(2)
0(3)	0393(1)	**.3874(1)**	.8481(2)
0(1)	2782(2)	**.4415(1)**	.7249(2)
0(4)	.0443(1)	**.4489(1)**	6736(2)
0(5)	.1549(2)	.3711(1)	6536(2)
N(l)	1816(2)	**.4623(1)**	**.9314(2)**
C(ll)	.2258(2)	3515(1)	.9907(2)
C(24)	.0934(2)	.3534(1)	**.9539(2)**
C(l)	.3215(2)	4832(1)	7938(2)
C(9)	.2700(2)	.4949(1)	**.9131(2)**
C(33)	0346(2)	3548(1)	**.5502(3)**
C(32)	-0452(2)	.3952(1)	4583(2)
C(31)	-.0732(2)	**43.4(1)**	**.5675(3)**

Compound 75

Atom	x	y	/
P(l)	.0894(1)	.2384(1)	4175(1)
0(1)	.1550(2)	2359(2)	2935(2)
0(2)	2646(2)	.3071(2)	4980(2)
0(3)	0413(2)	2244(2)	5400(2)
0(4)	-0699(2)	1467(1)	**.3429(2)**
0(5)	0332(2)	.3699(2)	4258(2)
C(l)	.2349(3)	.1472(2)	.2513(2)
N(l)	.1788(2)	0808(2)	4018(2)
C(9)	2492(3)	0595(2)	3119(2)
C(20)	.2838(3)	.3147(2)	.6151(2)
C(30)	.1588(3)	.2687(2)	6388(2)

Compound 76

Atom	x	y	z
P(l)	1677(1)	.5936(1)	.0969(1)
0(1)	1494(2)	.7041(3)	.1280(1)
0(2)	0943(2)	.5263(3)	.1173(1)
0(3)	1196(2)	6491(3)	0561(1)
0(4)	2495(2)	.6561(2)	0816(1)
0(5)	1937(2)	.4811(3)	.0702(1)
N(l)	.2248(2)	.5413(3)	.1479(1)
C(l)	.1837(3)	.7089(5)	1679(2)
C(9)	.2260(3)	.6180(4)	.1796(2)
C(21)	.0221(3)	5703(4)	.1233(2)
C(26)	-.0265(3)	.5825(4)	.0874(2)
C(31)	.0724(3)	.5922(4)	.0281(2)
C(36)	-.0001(3)	.5596(4)	.0422(2)
C(41)	.2885(3)	.5987(4)	.0507(2)
C(46)	.2574(3)	.4976(4)	.0441(2)
P(2)	.5864(1)	4055(1)	.2400(1)
0(6)	.6039(2)	.2940(3)	.2093(1)
0(7)	.6587(2)	.4735(3)	.2177(1)
0(8)	.6377(2)	.3529(3)	.2804(1)
0(9)	.5049(2)	.3427(2)	.2572(1)
0(10)	.5605(2)	.5186(2)	.2666(1)
N(201)	.5264(2)	.4550(3)	.1894(1)
C(201)	.5692(3)	.2890(5)	.1698(2)
C(209)	.5251(3)	.3779(4)	1585(2)
C(221)	.7310(3)	4285(4)	.2109(2)
C(226)	.7814(3)	.4194(4)	.2458(2)
C(231)	.6860(3)	4126(4)	.3066(2)
C(236)	.7574(3)	.4446(4)	.2913(2)
C(241)	.4672(3)	.4015(4)	.2882(2)
C(246)	.4959(3)	.5029(4)	.2928(2)

Compound 78

Atom	x	v	z
P(l)	.2315(1)	.0549(1)	.2778(1)
N(l)	2261(1)	.0187(1)	.4193(2)
0(1)	.2861(1)	.0782(1)	.3002(2)
0(2)	.2339(1)	.0167(1)	.1949(2)
0(3)	.2383(1)	.0860(1)	.1575(2)
O(4)	.1783(1)	.0279(1)	2729(2)
0(5)	.2327(1)	.0922(1)	.3754(2)
C(l)	.2986(1)	.0614(1)	.3923(3)
C(9)	.2653(1)	.0277(1)	.4594(2)
C(21)	.2083(1)	-.0020(1)	.0919(3)
C(26)	.2193(1)	.0189(1)	-.0231(3)
C(31)	.2658(1)	.0935(1)	.0578(3)
C(36)	.2570(1)	.0624(1)	-.0332(3)
C(41)	.1531(1)	0459(1)	.2459(3)
C(46)	.1445(1)	0676(1)	.3382(3)

Compound 78 Contd

C(51)	.2069(1)	.0847(1)	.4778(3)
C(56)	.1644(1)	.0753(1)	4638(3)

Compound 79

Atom	x	y	/.
P(l)	-0.1724(1)	0.2811(1)	0.0819(1)
0(1)	-0.1046(2)	0.3177(1)	00413(1)
C(l)	0.0156(7)	03466(4)	00515(3)
N(l)	0.0193(6)	0.2847(3)	-0.0608(3)
C(l')	-0.0038(8)	03697(4)	0 0760(5)
0(4')	0.2009(9)	0 4664(5)	0.1348(6)
0(5')	0.0802(7)	0 4843(4)	0 1242(4)
N(l')	-0.1452(6)	0.4504(3)	0 0797(3)
0(2)	-0.1996(2)	03496(1)	0.1302(1)
0(3)	-0.2703(2)	02449(1)	00129(1)
CM)	-0.0404(2)	0 2554(1)	0.1036(1)
0(5)	-0.2434(2)	0.2373(1)	0.1190(1)
C(20)	-0.4549(4)	0.3185(2)	0.0610(2)
C(21)	-0.2890(3)	0.3584(2)	0 1691(2)
C(26)	-0 4138(3)	0.3405(2)	0 1358(2)
C(31)	-0.3891(3)	0.2095(2)	0 0011(2)
C(41)	-0.0435(3)	0.2169(2)	0 1419(2)
C(46)	-0 1625(3)	0 2064(2)	0 1502(2)
P(2)	0.6274(1)	07039(1)	0.3430(1)
O(6)	0 5077(2)	0.6504(1)	0 2918(1)
0(7)	0.6620(2)	0.7196(1)	0.2825(1)
0(8)	0.6929(2)	0.6479(1)	0.3623(1)
0(9)	0.5212(2)	0.7372(1)	0.3806(1)
O(10)	0.7401(2)	0.7639(1)	0.3999(1)
C(201)	0.5099(3)	0.6060(2)	0.2306(2)
C(202)	0.5732(4)	0.5533(2)	0.2241(2)
C(203)	0.5725(4)	0.5092(2)	**0.1607(2)**
C(204)	0.5085(5)	0.5176(3)	**0.1057(2)**
C(205)	0.4396(4)	0.5710(2)	0.1112(2)
C(206)	0.3672(5)	0.5814(3)	0.0562(2)
C(207)	0.2992(5)	0.6322(3)	0.0650(2)
C(208)	03058(5)	0.6731(2)	0.1267(2)
N(201)	0 3708(3)	0.6667(2)	0 1830(2)
C(220)	0.8787(3)	0.6559(2)	0.2913(2)
C(221)	0.7751(3)	0 7546(2)	0.2839(2)
C(226)	0.8822(3)	0.7242(2)	0 2893(2)
C(231)	0.8193(3)	0.6490(2)	0 3943(2)
C(236)	0.9095(3)	0.6529(2)	0.3599(2)
C(241)	05671(3)	0.7930(2)	04361(2)
C(246)	0.6935(3)	0.8080(2)	0.4474(2)

Compound 86

Atom	x	y	z
P(l)	4850(1)	.1934(1)	**.6570(1)**
0(1)	.4097(1)	.1525(2)	.7189(1)
0(2)	**.5762(1)**	1324(1)	.7174(1)
0(3)	4957(1)	3524(1)	.6536(1)
0(4)	4804(1)	1411(2)	5183(1)
C(l)	.6179(1)	**.1744(2)**	8358(2)
0(5)	7953(1)	4563(2)	.7717(2)
C(13)	**.5587(1)**	.4088(2)	5750(2)
C(14)	5435(1)	.3539(2)	.4406(2)
C(15)	.5451(2)	.1973(2)	.4424(2)

Part B ***Antimony Compounds***

Compound 2

Atom	X/a	Y/b	Z/c
Sb(l)	0.15911(2)	0.13581(1)	023181(1)
0(1)	0.2934(2)	0.1090(2)	0.1491(1)
0(2)	0.1154(2)	0 0837(2)	0.1414(1)
0(3)	0.3398(3)	0.1716(2)	0.2777(2)
O(4)	0.1791(2)	0.1822(2)	0.3273(1)
0(5)	0	0.1303(2)	0.2500(2)
C(l)	0.2145(3)	0.0817(2)	0.1184(2)
C(8)	0.2889(3)	0.1889(2)	0.3255(2)
C(15)	0.2058(4)	0.0319(2)	0.2684(2)
C(21)	0 1611(3)	0.2402(2)	0 1874(2)

Compound 8

Atom	x	y	z
Sb(l)	**.1870(1)**	.0375(1)	2673(1)
Cl(l)	.1737(2)	.444(1)	4428(1)
O(1)	.2497(4)	-.0305(1)	.1527(2)
0(2)	.2732(4)	-.0573(1)	.3112(2)
0(3)	.1018(4)	1336(1)	2649(2)
0(4)	1409(3)	.973(1)	.1235(2)
C(l)	-.0421(5)	0013(2)	.2134(3)
C(7)	.4226(5)	0685(2)	.2918(3)
C(13)	.2855(5)	**-.715(2)**	.2211(3)
C(21)	1060(5)	.1425(2)	.1723(3)

Compound 10

Atom	X	Y/	Z/
Sb(l)	0 06435(2)	0.21376(2)	0.90504(2)

Compound 10 Contd

Sb(2)	0.17316(2)	0 28387(2)	0.73555(2)
Cl(l)	0.14365(13)	0.39781(8)	0.75995(11)
Cl(2)	020595(12)	020147(8)	0.99610(9)
P(l)	0.18537(10)	0.12701(6)	0.77814(8)
P(2)	-0.06548(10)	0.25912(8)	0.74365(8)
0(1)	0.1868(3)	0.1833(2)	0.7202(2)
O(2)	0.1117(3)	0.1355(2)	0.8380(2)
0(3)	0 1413(3)	0.2668(2)	0 8412(2)
0(4)	-0.0492(3)	0.2202(2)	0.8197(2)
0(5)	0.0277(3)	02696(2)	0 7026(2)
C(7)	-0.1144(4)	0.3375(3)	0 7625(4)
C(13)	-0.1486(4)	0.2144(3)	0.6761(4)
C(43)	0.1549(4)	0 0523(3)	0.7239(3)
C(19)	0 3038(4)	**0.1166(3)**	0 8272(3)
C(l)	-0.0103(4)	0 1380(3)	0 9580(3)
C(37)	0.0143(4)	0 2963(3)	0 9644(3)
C(25)	0.1765(4)	0 2948(3)	06109(3)
C(31)	0.3228(4)	0.2903(2)	0.7704(3)

Compound **12**

Atom	x	y	z
Sb	0.1267(1)	-0.1114(1)	0 4865(1)
P	0.1778(2)	0.1633(3)	0.4558(2)
0(1)	0.0053(5)	0 0492(4)	**0.3926(4)**
0(2)	0.0201(50	02101(4)	0 4897(4)
0(3)	0.2393(5)	00167(5)	0 4862(4)
C(l)	0.2392(8)	-0.1512(7)	0.3352(6)
C(7)	0.2404(8)	-0 2767(7)	0.6051(6)
C(13)	02276(8)	0.2568(7)	0.3098(6)
C(19)	02514(9)	0.1903(7)	0 5466(6)

Compound 13

Atom	x	y	z
Sb(l)	0.03043(2)	006823(1)	0.05497(2)
P(l)	0 06911(7)	0 04775(4)	-0 17255(7)
O(1)	0.1017(2)	0.0884(1)	-0.0647(2)
0(2)	-0.1011(2)	00229(1)	-0 0639(2)
0(3)	0.0464(2)	-0.0285(1)	-0.1639(2)
C(l)	0.1872(3)	0.1041(2)	0.1840(3)
C(7)	-0.0741(3)	0 1586(2)	0 0273(3)
C(13)	0.1988(3)	0 0563(2)	-0 2086(3)
C(21)	-0 0626(3)	0.0875(2)	-0 2711(3)

Compound **15**

Atom	x	y	z
Sb(l)	0 32519(9)	0 27922(5)	0 73455(7)

Compound **15** Contd			
Sb(2)	0.33668(8)	0.14653(5)	0.73456(8)
Sb(3)	**0.50527(8)**	0.15003(5)	0.64789(8)
Sb(4)	0.48313(8)	0.28194(6)	0.63807(7)
P(l)	0.3984(4)	00460(2)	0.6604(3)
P(2)	0.3599(4)	0.3815(2)	0.6472(3)
0(1)	0.3395(7)	0.0735(4)	0.7039(6)
0(2)	0.4779(7)	0.0753(4)	0 6462(6)
0(3)	0.3118(8)	0.3541(4)	0 6990(6)
0(4)	0.4243(8)	0 3507(4)	06129(6)
O(5)	0.4558(7)	0.2925(4)	0 7386(6)
O(6)	0.3495(8)	0.2590(5)	0.6277(6)
0(7)	0.4804(7)	0.1440(5)	0.7549(7)
0(8)	0.3709(8)	0.1593(4)	0.6377(7)
0(9)	0.5306(7)	0.2176(5)	0.6629(6)
0(10)	0.3448(7)	0.2130(5)	0.7654(6)
O(11)	0.478(1)	0.4651(9)	0.414(1)
0(12)	**0.575(1)**	0.4527(6)	0.5203(10)
C(l)	0 181(1)	0.2767(7)	0.691(1)
C(7)	**0.325(1)**	0.3034(7)	0.8454(10)
C(13)	**0.338(1)**	0.1210(7)	0.841(1)
C(19)	**0.195(1)**	0.1450(7)	0.692(1)
C(25)	0.644(1)	0.1330(7)	0.6879(10)
C(31)	0.494(1)	0 1445(7)	0.534(1)
C(37)	0.472(1)	0.2764(7)	**0.5230(10)**
C(43)	**0.614(1)**	0.3128(6)	0.6671(10)
C(49)	0.441(1)	-0.0070(7)	**0.713(1)**
C(55)	**0.335(1)**	0.0321(7)	0.572(1)
C(61)	**0.423(1)**	0.4323(7)	0.692(1)
C(67)	0.275(1)	0.4053(7)	0.572(1)
C(73)	0.551(2)	**0.393(1)**	0.421(2)
C(74)	**0.541(2)**	0.440(1)	0.459(2)