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

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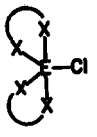
Abstract: The phosphorinane ring opens when $ClP(OCH_2CMe_2CH_2O)$ **(1)** is treated with diols and N-chlorodiisopropylamine (NCDA) or with quinones. X-ray structure of one such product, the phosphocin oxide, $(ClCH_2CMe_2CH_2O)P(O)\{(O\text{-}(2,4\text{-}(t\text{-}bu)_2C_6H_2)_2CH_2\}$ **(3)** reveals a 'symmetrical anti' (chair) conformation of the eight membered ring. The phenylene phosphorochloridite $ClP(O_2C_6H_4)$ by contrast gives pentacoordinated phosphoranes in similar reactions. The arsorinane $ClAs(OCH_2CMe_2CH_2O)$ **(9)** on treatment with 2,2-dimethyl-1,3-propanediol-NCDA affords an arsorane formulated as $ClAs(OCH_2CMe_2CH_2O)_2$; no reaction was apparent when 9 was treated with quinones.

In our investigations on the chemistry of phosphorus and arsenic we have been interested in species of type **(A)**.



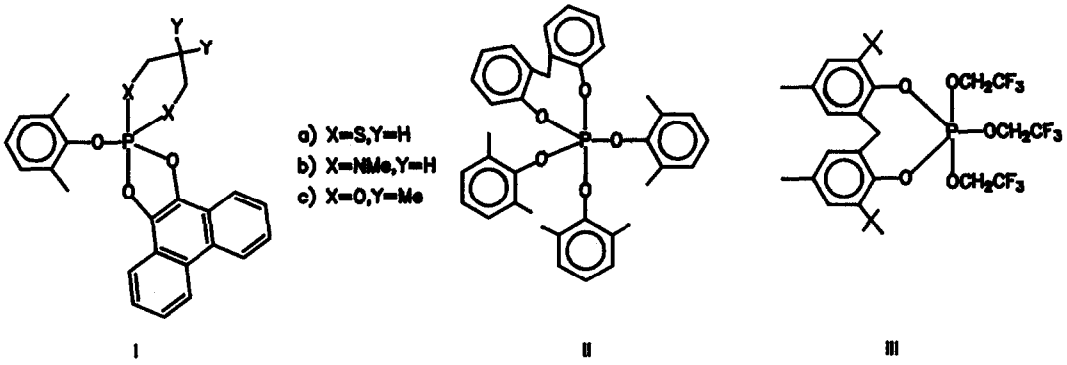
(A)

E = P, As

X = O, NR, S

Well-authenticated compounds of type **(A)** include $ClP(O_2C_6H_4)_2$[1] and $ClP[MeNC(O)NMe]_2$.[2] Interest in such species stems from the utility of the chloro group for further derivatization as is demonstrated by the isolation of the first iodophosphorane.[2a] Both of these chlorophosphoranes were obtained by starting with phosphorus pentachloride and hence other routes may be desirable, particularly when the two rings are different. It has been amply demonstrated that oxidative addition reactions of cyclic phosphites with either (i) o-quinones,[3-5] or (ii) diols in the presence of N-chlorodiisopropylamine[6-8] (NCDA) afford novel cyclic phosphoranes with six- and higher membered rings in good yields as exemplified by the synthesis of **I-III.** Extension of these routes by employing cyclic chlorophosphites could lead to cyclic chlorophosphoranes and possibly to chloroarsoranes by using suitable precursors.

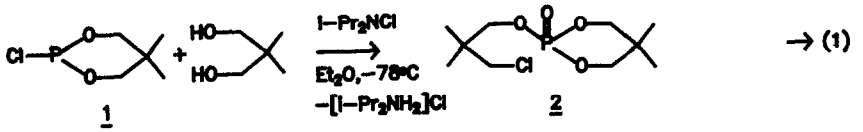
In this paper, we report our results on the reactions of cyclic chlorophosphites and arsenites with (a) diols-NCDA and (b) quinones. In several of these cases ring cleavage occurs and this is a point we would like to emphasize. Since conformational studies are scant for seven and higher membered rings, we also report the X-ray structure of one of the products, the phosphocin $(ClCH_2CMe_2CH_2O)P(O)\{(O\text{-}2,4\text{-}(t\text{-}bu)_2C_6H_2)_2CH_2\}$ **(3)**.



I II III

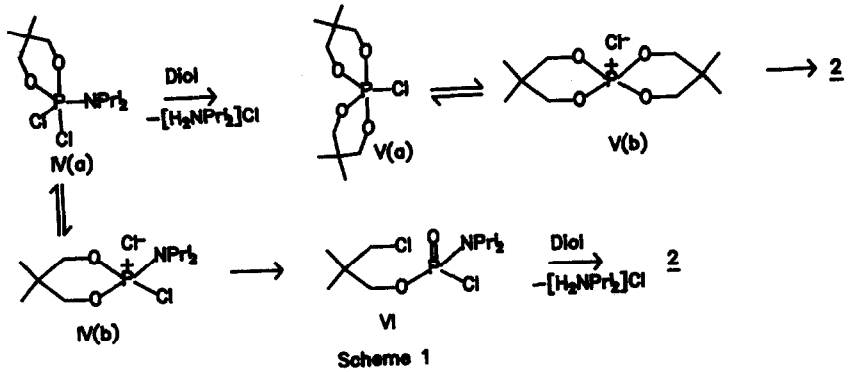
RESULTS AND DISCUSSION

The reaction of I with 2,2-dimethyl-1,3-propanediol in the presence of NCDA affords the ring cleavage (modified Arbuzov) product 2 in good yield (eqn. 1). Compound 2 is readily characterized by its ^{1}H NMR spectrum which shows a multiplet pattern for $OC\underline{H}_A\underline{H}_B$ protons (3.88-4.20 ppm) and two singlets for $C\underline{H}_3$ 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 $C\underline{H}_3$ protons. ^{13}C and ^{31}P NMR as well as the elemental analysis confirm the identity of this product.



1 2

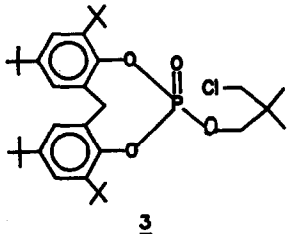
Since Denney and coworkers[9] have already demonstrated the intermediacy of the pentacoordinated species $(1,2\text{-}C_6H_4O_2)P(OEt)Cl(NEt_2)$ in the reaction of $(1,2\text{-}C_6H_4O_2)P(OEt)$ with N-chlorodiethylamine, an analogous species is likely to be involved in our reactions also [Scheme 1].



Scheme 1

Ring cleavage, in principle, could occur from both **IV** and **V**. When the cyclic phosphite $(OCH_2CMe_2CH_2O)P(O\text{-}2,6\text{-}Me_2C_6H_3)$ is treated with various diols in the presence of NCDA, intermediate $(OCH_2CMe_2CH_2O)P(O\text{-}2,6\text{-}Me_2C_6H_3)(NPr^i_2)(Cl)$ similar to **IV** is involved; in these reactions only pentaoxyphosphoranes, and not cleavage products with $ClCH_2CMe_2CH_2O$-group, are observed.[4,7,10] Hence we conclude that in our reactions ring opening occurs from **V** and not from **IV**. It can also be readily seen that the formation of **2** from **V(b)** is analogous to the elimination of ethyl chloride from $[(1,2\text{-}C_6H_4O_2)P(OEt)(NEt_2)]^+Cl^-$ to afford $(1,2\text{-}C_6H_4O_2)P(O)\text{-}(NEt_2)$ by Arbuzov reaction.[9]

It is known that ring cleavage takes place upon treatment of organosulfenyl chloride[11] or $ROC(O)N(R')Cl$[11] or chlorine[12] with cyclic chlorophosphites, 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 **3** by our route in high yields:

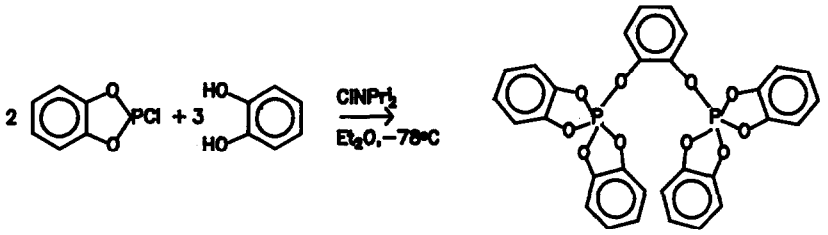


3

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

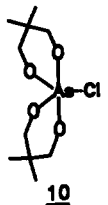
However, not all the reactions gave clean products. When **1** was reacted with 2,2'-biphenol-NCDA, although the product $(ClCH_2CMe_2CH_2O)P(O)(O_2C_{12}H_8)$ (**4**) is readily identified, other products are certainly formed (^1H, ^{31}P NMR). In the reaction of the chlorosalicylate $ClP\text{-}(O_2CC_6H_4O)$ with salicylic acid two products were observed [$\delta(^{31}P)$: -8.70, -2.83 ppm]; only the product with downfield chemical shift [$\delta(^{31}P)$ = -8.70] could be isolated. This has been identified as $(HO)(O)P(O_2CC_6H_4O)$ (**8**) by elemental analysis. Obviously some hydrolysis must have occurred during the course of the reaction to lead to **8**.

Diphosphorane $(C_6H_4O_2)_2P(OC_6H_4O)P(O_2C_6H_4)_2$ (**6**) and not the chlorophosphorane $ClP\text{-}(O_2C_6H_4)_2$ is the product isolated when o-phenylenephosphorochloridite (**5**) is reacted with catechol-NCDA (eqn. 2). No trace of chlorophosphorane was observed even with 1:1:1 stoichiometry of the reactants; the reaction mixture shows only **5** and **6** (^{31}P NMR) when this stoichiometry is used. Compound **6** can be readily isolated from the mixture. We also conducted the reaction by first adding NCDA to **5** 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 **6** in significant quantities.[13] Our approach offers an alternative route to **6**.



5 **6**

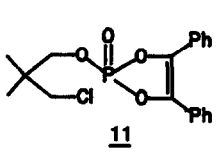
A crystalline (moisture sensitive) product with mp 37°C is obtained readily by reacting ClAs(OCH_2CMe_2O) (**9**) with 2,2-dimethyl-1,3-propanediol-NCDA. The chloroarsorane structure (**10**) is assigned to this from the following considerations: (a) Required amount of diisopropylamine hydrochloride was obtained. (b) ^1H NMR spectrum (25°C) is similar to that of the fast exchanging [Berry pseudorotation] phosphorane PhP($OCH_2CMe_2CH_2O)_2$.[4] Only one signal each with no apparent coupling was observed in (**10**) for $OC\underline{H}_2$ and $OC\underline{H}_3$ protons. In the starting material (**9**) as well as its alkoxy/aryloxy derivatives[10] two doublets for OCH_AH_X protons are observed. (c) Reaction of (**10**) 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_2-$CMe_2CH_2O)_2$ which presumably is formed during handling.



10

Reaction of **9** 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,[7] oxidation does occur with catechols. Indeed a blank reaction of catechol or tetrachlorocatechol with NCDA (in ether or benzene) 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 **1** with the o-diketones benzil and 9,10-phenanthrene quinone; the products (**11**) ($\delta(^{31}P)$: 9.43 ppm) and (**12**) ($\delta(^{31}P)$: 13.73 ppm) are formed readily via an intermediate similar to **V** (Scheme 1).



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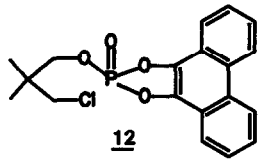

12

Both these compounds can be easily isolated. By contrast, the reaction of **1** with the more reactive 3,5-di-t-butyl-o-benzoquinone and o-chloranil gives several other products in addition to ring opened products of type **12**; a notable feature however is that in the former case a peak at -28.00 ppm [^{31}P NMR] corresponding to a chlorophosphorane can be observed in an NMR tube experiment.

Better results are achieved in the reaction of phenylenephosphorochloridite **5** with 3,5-di(t-butyl)-o-benzoquinone and o-chloranil. The chlorophosphoranes $ClP(O_2C_6H_4)(O_2\text{-}3,5\text{-}(t\text{-}bu)_2C_6H_2)$ **(13)** ($\delta(^{31}P)$ = -8.92 ppm) and $ClP(O_2C_6H_4)(O_2C_6Cl_4)$ **(14)** ($\delta(^{31}P)$ = -10.80 ppm) are formed in yields of >70%, the only other observed product is pentaoxyphosphorane (<15%) with low intensity [$\delta(^{31}P)$ = -31.0 ppm]. No unreacted quinone was present in the reaction mixture. It should now be possible to obtain analytically pure chlorophosphoranes **13** and **14** by changing the reaction conditions; currently we are exploring these possibilities. The chloroarsenite **9** did not under go any perceptible reaction under the conditions employed here due to its reluctance to undergo oxidation.[14]

The observed ^{31}P NMR chemical shifts of -12.67, -8.70, 0.35, 9.43 and 13.73 ppm for **3, 2, 4, 11** and **12** respectively are in an order similar to that observed for pentacoordinated phosphoranes.[4,5,7,10] Thus on the basis of available data we make the observation that analogous derivatives possessing five or seven membered rings containing phosphorus (connected to the oxygens in the ring) exhibit ^{31}P NMR signals downfield to those containing six or eight membered rings. The ^{31}P NMR chemical shift values of **13** and **14**, which are close to that observed for $ClP(O_2C_6H_4)_2$ [$\delta(^{31}P)$ = -9.40 ppm][1] are not surprising since all the three compounds have two five membered rings and a chlorine substituent attached to phosphorus.[5]

X-ray structure of 3[15]

A plot of the molecular structure of **3** as well as a picture depicting the conformation of the eight-membered phosphocin ring are shown in Fig. 1. Selected bond lengths and bond angles are given in Table 1. These data compare well with those reported by Holmes and coworkers[16] recently for both the conformers of **(B)**. A notable feature is the wider angle at phosphorus between the exocyclic oxygens [03-P-04, 120.5°] in **3** when compared to those in **(B)** [113.9°, 113.2°] perhaps as a result of the high group electronegativity of $-OCH_2CF_3$ group over $-OCH_2\text{-}CMe_2CH_2Cl$.

A "symmetrical anti" (chair) conformation for **3** is observed. This is similar to one conformer of **(B)** but different from the "symmetrical tub" (boat) conformation observed for **(C)**.[17] Such a difference is possibly a consequence of the presence of bulky t-bu groups in proximity to the oxygens of the phosphocin ring in **3**. However, since the ^{1}H NMR spectrum of **3** shows a broad signal (4.00-4.20 ppm) for bridging CH_2 protons [in contrast to the phosphite $ClP^{\wedge}(O\text{-}2,4\text{-}(t\text{-}bu)_2C_6H_2)_2CH_2$ which shows a well-separated AX doublet for each of CH_2 protons][10] a conformational equilibrium is indicated in solution for **3**.

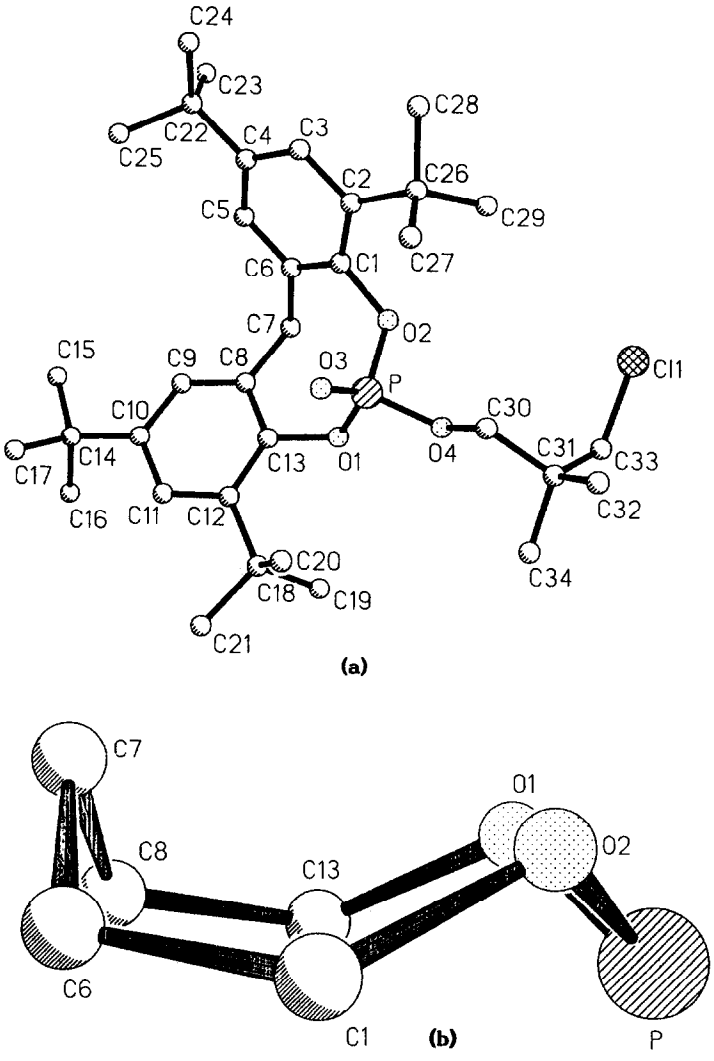

Fig. 1(a) A plot of the molecule of **3**. **(b)** Picture showing conformation of the eight-membered ring in **3**.

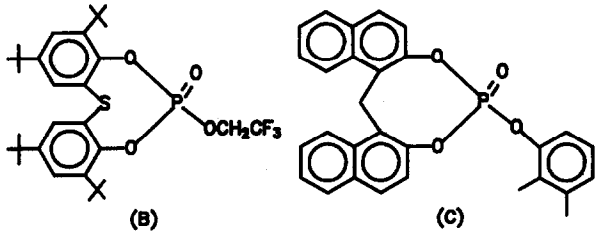

Table 1. Selected bond distances (Å) and bond angles (°)

CL-C33	1.778(8)	C1-C6	1.407(9)
P-01	1.587(5)	C6-C7	1.512(9)
P-02	1.597(4)	C7-C8	1.523(9)
P-03	1.457(5)	C8-C13	1.386(9)
P-04	1.580(5)	C30-C31	1.523(9)
01-C13	1.433(8)	C31-C32	1.525(9)
02-C1	1.424(8)	C31-C33	1.489(9)
04-C30	1.374(9)	C31-C34	1.525(9)
01-P-02	108.3(2)	C6-C7-C8	115.7(5)
01-P-03	115.2(3)	C7-C8-C13	121.7(6)
01-P-04	96.8(3)	C7-C8-C9	119.8(6)
02-P-03	113.8(3)	C9-C8-C13	118.5(6)
02-P-04	99.9(3)	C8-C13-C12	122.9(6)
03-P-04	120.5(3)	01-C13-C12	120.1(5)
P-01-C13	122.2(4)	01-C13-C8	116.8(5)
P-02-C1	122.3(4)	04-C30-C31	111.6(6)
P-04-C30	123.9(4)	C30-C31-C34	109.2(6)
02-C1-C6	116.3(5)	C30-C31-C33	116.1(6)
02-C1-C2	120.8(6)	C30-C31-C32	103.9(6)
C2-C1-C6	122.7(6)	C33-C31-C34	109.1(6)
C1-C6-C5	117.7(6)	C32-C31-C34	108.3(6)
C1-C6-C7	121.5(6)	C32-C31-C33	109.8(6)
C1-C6-C13	121.7(6)	CL-C33-C31	115.7(5)
C5-C6-C7	120.8(6)		

EXPERIMENTAL SECTION

Chemicals were procured from Aldrich/Fluka or from local manufacturers; they were purified when required. Solvents were purified according to standard procedures.[18] All operations were carried out under dry nitrogen atmosphere using standard Schlenck techniques.[19] ^{1}H and ^{13}C NMR spectra were recorded on JEOL 100 MHz and Bruker 200 MHz spectrometers; $^{31}P\{^{1}H\}$ NMR spectra were recorded on Bruker 200 MHz [operating at 80.7 MHz]. Chemical shifts [$CDCl_3$, ppm] are measured against tetramethyl silane (^{1}H, ^{13}C) or 85% phosphoric acid. IR spectra were recorded on a Perkin-Elmer 1310 spectrometer. Elemental analyses were carried out on a Perkin-Elmer 240C CHN analyser. Mass spectra were recorded on a CEC-21-110B double focussing mass spectrometer operating at 70 eV using direct inlet system.

(A) Reaction of cyclic chlorophosphites/arsenites with diols in the presence of NCDA:

(i) 2-(3-chloro-2,2-dimethyl-1-propoxy)-2-oxo-5,5-dimethyl-1,3,2-dioxaphosphorinane, ($ClCH_2$-

$CMe_2CH_2O)P(O)(OCH_2CMe_2CH_2O)$ **(2)**: To 5,5-dimethyl-2-chloro-1,3,2-dioxaphosphorinane $ClP(OCH_2CMe_2CH_2O)$ **(1)**[20] (2.33 g, 14 mmol) in ether (30 mL) maintained at -78°C was added a solution of 2,2-dimethyl-1,3-propanediol (1.44 g, 14 mmol) and NCDA[21] (1.88 g, 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 and hexane (1:2). Yield: 2.25 g (60%), mp 76°C. ^1H NMR: 0.91(s, 3H, $C\underline{H}_3$ (ring)), 1.06(s, 6H, $C\underline{H}_3$), 1.25(s, 3H, $C\underline{H}_3$(ring)), 3.46(s, 2H, $C\underline{H}_2Cl$), 3.91(d, 2H, $OC\underline{H}_2$, $^3\underline{J(P\text{-}H)}$ = 4.0 Hz)), 3.85-4.20 (m, 4H, $OC\underline{H}_2$(ring)). ^{13}C NMR: 20.44(s, $\underline{C}H_3$ (ring)), 21.52(s, $\underline{C}H_3$(ring)), 22.16(s, $\underline{C}H_3$(open)), 32.16(d, $^3\underline{J(P\text{-}C)}$ = 5.0 Hz, $\underline{C}Me_2$), 36.69(d, $^3\underline{J(P\text{-}C)}$ = 6.0 Hz, $\underline{C}Me_2$(ring)), 51.39(s, $C\underline{H}_2Cl$), 71.59(d, $O\underline{C}H_2$, $^2\underline{J(P\text{-}C)}$ = 5.0 Hz), 77.85(d, $^2\underline{J(P\text{-}C)}$ = 7.0Hz, $O\underline{C}H_2$(ring)), $^{31}P\{^1H\}$ NMR: -8.70. Anal. Calcd. for $C_{10}H_{20}ClO_4P$: C, 44.34; H, 7.39. Found: C, 44.27; H, 7.63.

(ii) The phosphocin, $(ClCH_2CMe_2CH_2O)P(O)$ $(O\text{-}2,4\text{-}(\underline{t}\text{-}Bu)_2C_6H_2)_2CH_2$ **(3)**: This compound was prepared by a procedure similar to that for **2** using 1.16 g (6.90 mmol) of **1** and 2.92 g (6.90 mmol) of 2,2'-methylene-bis(4,6-di-t-butyl phenol).[22] Yield: 2.66g (65%), mp 140-142°C. ^1H NMR: 1.13(s, 6H, $C(C\underline{H}_3)_2$), 1.29(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, $^3\underline{J(P\text{-}H)}$ = 4.0 Hz, $OC\underline{H}_2$). ^{13}C NMR: 22.35(s, $C(\underline{C}H_3)_2$), 30.94(s, $C(\underline{C}H_3)_3$), 31.02(s, $C(\underline{C}H_3)_3$), 34.50(s, $\underline{C}(CH_3)_3$), 35.30(s, $\underline{C}(CH_3)_3$), 36.88(s, $\underline{C}(CH_3)_2$), 37.30(s, $\underline{C}H_2$(Ar)), 51.24(s, $\underline{C}H_2Cl$), 74.15(d, $^2\underline{J(P\text{-}C)}$ = 7.0Hz, $O\underline{C}H_2$), 124.07, 125.83, 131.34, 140.18, 146.10, 147.80 (all $\underline{C}$(Ar)), $^{31}P\{^1H\}$ NMR: -12.67. Anal. Calcd. for $C_{34}H_{48}ClO_4P$: C, 69.10; H, 8.81. Found: C, 68.53; H, 9.18.

(iii) The phosphepin, $(ClCH_2CMe_2CH_2O)P(O)(2,2'\text{-}O_2C_{12}H_8)$ **(4)**: This is one of the products (ca. 30% by ^{31}P NMR) in the reaction of **1** with 2,2'-biphenol-NCDA. ^1H NMR: 1.03(s, $C(C\underline{H}_3)_2$), 3.82(s, $C\underline{H}_2Cl$), 4.15(d, $^3\underline{J(P\text{-}H)}$ = 4.0 Hz , $OC\underline{H}_2$) and 6.80-7.50 ($\underline{H}$(Ar)). ^{13}C NMR: 22.05(s, $C(\underline{C}H_3)_2$), 37.00(br s, $\underline{C}Me_2$), 51.12(s, $\underline{C}H_2Cl$), 75.50(s, $O\underline{C}H_2$), 116.00-132.00(m, $\underline{C}$(Ar)), $^{31}P\{^1H\}$ NMR: 0.35. Pure product could not be isolated. Other minor products were also present [^{31}P: -15.00, -8.50, -8.40, -8.00 ppm].

(iv) The diphosphorane, $(C_6H_4O_2)P(OC_6H_4O)P(O_2C_6H_4)_2$ **(6)**: This compound was readily prepared (correct C,H analysis) by procedure (i) using o-phenylene phosphorochloridite $(C_6H_4O_2)PCl$ **(5)** (2.26 g, 13 mmol), catechol (1.42 g, 13 mmol) and NCDA (1.75 g, 13 mmol). Yield 0.8 (20%), mp 180-200°C. $^{31}P\{^1H\}$ NMR: -31.00. By changing the solvent system to toluene-ether the only product found was **6** (>65%), the rest being starting material **(5)** [^{31}P NMR]. Even by changing the order of addition (NCDA first and then catechol) **6** was found to be the major product (>50%). This compound has been previously prepared using $(C_6H_4O_2)PCl_3$.[13]

(v) In the reaction of 2-chloro-4H-1,3,2-benzodioxaphosphorin-4-one, $ClP(O_2CC_6H_4O)$ **(7)** with salicylic acid-NCDA, ^{31}P NMR of the reaction mixture showed two products [^{31}P: -20.83, -8.73 ppm]. We were able to isolate only the product with the downfield chemical shift. This was identified as 2-hydroxy-2-oxo-4H-1,3,2-benzodioxaphosphorin-4-one **(8)**; this could arise from hydrolysis. Yield: 0.3g (11%), mp 80°C. ^1H NMR: 7.10-8.40 (complex). ^{13}C NMR: 119.40, 120.00, 127.10, 132.9, 139.10 (carbonyl carbon could not be located). $^{31}P\{^1H\}$ NMR: -8.73. Anal. Calcd. for $C_7H_5O_5P$: C, 42.00; H, 2.50. Found: C, 42.00; H, 3.03.

(vi) The reaction of 5,5-dimethyl-2-chloro-1,3,2-dioxaarsorinane (8.5 mmol) (**9**) [prepared by a procedure similar to that for **1**] with equimolar quantities of 2,2-dimethyl-1,3-propanediol-NCDA after removal of the required amount of amine hydrochloride afforded a product (**10**) which could be recrystallized from cyclohexane (0°C) as needles. Yield: 1.1g (40%), mp 37°C. ^{1}H NMR: 0.94(s, 12H, $\underline{CH}_3$), 3.78(s, 8H, $O\underline{CH}_2$). ^{13}C NMR: 21.64(s, $\underline{CH}_3$), 35.99(s, $\underline{C}Me_2$), 74.16(s, $O\underline{CH}_2$). Anal. Found: C, 41.08; H, 8.34 agrees reasonably well with the hydroxy asorane (OCH_2CMe_2-$CH_2O)_2$ As(OH) [Calcd. for $C_{10}H_{21}AsO_5$: C, 40.54; H, 7.10]. Hydrolysis presumably had occurred during handling for analysis. The product **10** reacted with 2,4,6-trimethylphenol in the presence of triethylamine to give the expected amount of amine hydrochloride.

(B) Reaction of cyclic chlorophosphites with quinones:

(i) The phospholene, $(ClCH_2CMe_2CH_2O)P(O)(O_2C_2Ph_2)$ (**11**): Compound **1** (0.84g, 5 mmol) and benzil (0.784g, 3.5 mmol) were heated together at 130°C for 24h. Excess of **1** was removed in vacuo and the residue was crystallized from a mixture of toluene and hexane to give **11**. Yield: 0.46g (35%), mp 78°C. ^{1}H NMR: 1.08(s, 6H, $\underline{CH}_3$), 3.45(s, 2H, $\underline{CH}_2Cl$), 4.10(d, $^{3}\underline{J(P\text{-}H)}$ = 4.5 Hz, 2H, $O\underline{CH}_2$), 7.30-8.00(m, 10H, $\underline{H}$(Ar)), ^{13}C NMR: 21.93(s, $C(\underline{CH}_3)_3$), 36.73(s, $\underline{C}(CH_3)$), 51.50(s, $\underline{CH}_2Cl$), 72.57(d, $^{2}\underline{J(P\text{-}C)}$ = 5.0 Hz, $O\underline{CH}_2$), 128.00-134.00(m, $\underline{C}$(Ar)), ^{31}P $\{^{1}H\}$ NMR: 9.43. Anal. Calcd. for $C_{19}H_{20}ClO_4P$: C, 60.25; H, 5.30. Found: C, 59.65; H, 5.10.

(ii) The phospholene $(ClCH_2CMe_2CH_2O)P(O)(O_2C_{14}H_8)$ (**12**): 9,10-phenanthrenequinone (0.49g, 23 mmol) and **1** (0.84g, 5 mmol) were heated together at 170°C for 48h. After removal of excess of **1**, the product was crystallized from toluene. Yield(based on quinone): 0.7g (80%), mp 100°C. ^{1}H NMR: 1.07(s, 6H, $\underline{CH}_3$), 3.45(s, 2H, $\underline{CH}_2Cl$), 4.14(d, $^{3}\underline{J(P\text{-}H)}$ = 6.8Hz, 2H, $O\underline{CH}_2$), 7.60-8.80(m, 8H, $\underline{H}$(Ar)). ^{13}C NMR: 22.08(s, $\underline{CH}_3$), 37.00(s, $\underline{C}(CH_3)_2$), 50.95(s, $\underline{CH}_2Cl$), 73.99(s, $O\underline{CH}_2$), 120.00-128.00(m, $\underline{C}$(Ar)). ^{31}P $\{^{1}H\}$ NMR: 13.73. Anal. Calcd. for $C_{19}H_{18}ClO_4P$: C, 60.57; H,4.78. Found: C, 60.20, H, 4.78.

(iii) (a) Reaction of **5** with o-chloranil (1:1, neat, 25°C instantaneous): Data for the colourless reaction mixture): ^{1}H NMR(C_6D_6): 6.70-7.20(m). ^{13}C NMR(C_6D_6, major peaks): 110.80, 111.16, 113.85, 122.89, 123.09, 124.05, 139.76, 142.71 (all $\underline{C}$(Ar)). ^{31}P $\{^{1}H\}$ NMR(C_6D_6): -30.35(a pentaoxyphosphorane, ca 15%), -9.18 (-8.92 in $CDCl_3$, **13**, ca 70%), 173.10 (**5**, ca 15%). MS: m/z (%):- 252(10), 250(45), 248(100), 246(80) $[M\text{-}C_6H_4ClO_2P\text{+}2H(?)]^+$, 156(60) $[(C_6H_4O_2)P(OH)]^+$, 139(30) $[C_6H_4O_2P]^+$.

(iii) (b) Reaction of **5** with 3,5-di(t-butyl)-o-benzoquinone(1:1, neat, 25°C, 5 min): Data for the colourless reaction mixture): ^{1}H NMR(C_6D_6): 1.52(9H, C($\underline{CH}_3$)), 1.78(9H, C($\underline{CH}_3$)), 6.90-7.40(6H, $\underline{H}$(Ar)). ^{13}C NMR(C_6D_6): 30.12, 32.00(both C($\underline{C}H_3$)), 32.00, 34.88(both $\underline{C}$(CH_3)), 107.12, 107.83, 111.59, 112.30, 117.42, 123.48, 123.71, 128.72, 134.60, 135.19, 138.77, 139.01, 143.01, 143.24, 146.42 (all $\underline{C}$(Ar)). ^{31}P $\{^{1}H\}$ NMR: (C_6D_6): -30.98(a pentaoxyphosphorane, ca 2%), -10.37 (-10.80 in $CDCl_3$, **14**, ca 90%), 173.03(5, ca 5%). MS: m/z(%):- 396(8), 394(3) $[M]^+$, 359 (100) $[M\text{-}Cl]^+$.

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Supplementary material: Structure determination summary, atomic coordinates with thermal parameters, full set of bond lengths and bond angles and F_o/F_c tables are deposited at Cambridge Crystallographic Data Centre, Cambridge (UK).

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