Reactivity of cyclic arsenites and phosphites: X-ray structures of bis(5,5-dimethyl-1,3,2-dioxarsenan-2-yl) ether and bis(2,4,8,10-tetra-*tert*-butyl-12*H*-dibenzo[*d*,*g*][1,3,2]dioxarsenocin-6-yl) ether

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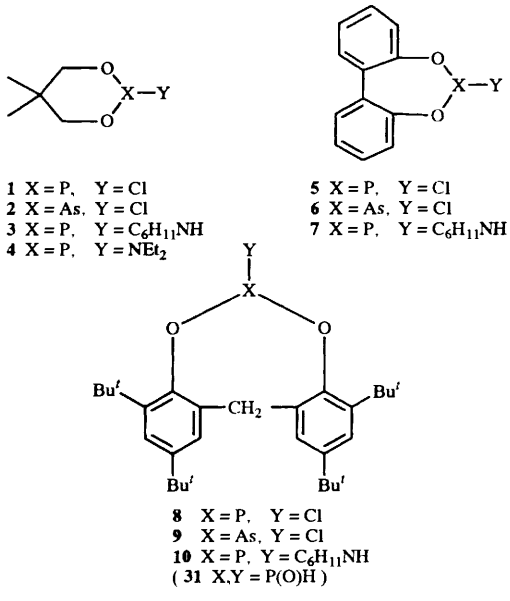
Reaction of the chlorophosphite $ClPOCH_2CMe_2CH_2O$ **1** with cyclohexylamine gave the expected product $(C_6H_{11}NH)POCH_2CMe_2CH_2O$ **3** whereas the corresponding chloroarsenite **2** led to the bridged compound **12**. When the reaction was performed in the presence of water, **1** gave the expected product $H(O)POCH_2CMe_2CH_2O$ **11** whereas **2** gave the oxo-bridged compound $(AsOCH_2CMe_2CH_2O)_2O$ **13**. The amino phosphite **3** underwent hydrolysis to afford the ring cleaved product **18** whereas the phenoxy phosphite **21** led to the ring preserved compound **11**. In contrast, the corresponding phenoxy arsenite $(PhO)AsOCH_2CMe_2CH_2O$ **25** gave the oxo-bridged compound **13**. Addition of perchloro-*o*-benzoquinone to the phosphite **23** was highly exothermic and afforded the phosphorane **29**; however the corresponding arsenonate **27** reacted very sluggishly at room temperature and when heated gave an uncharacterizable mixture of products.

The identity of the title oxy-bridged compounds **13** and **15** obtained here has been confirmed by X-ray structure determination; the six-membered rings in **13** have a 'chair' conformation and the eight-membered rings in **15** have a 'symmetrical anti' conformation.

The relative instability of arsenic pentachloride when compared to phosphorus or antimony pentachlorides is a well-documented fact and is attributed to the completion of the first (3d) transition series for arsenic.[1] We have also reported similar features in the oxidative additions of cyclic phosphites and arsenites while synthesizing analogous five-coordinated derivatives containing six-and higher-membered rings.[2] Thus, the reluctance of arsenic to achieve higher oxidation state (+5) can easily lead to different reaction paths for arsenites when compared to phosphites and this is the theme of the present study. In this context it should be noted that although the high reactivity of the As–N bond[3] and the lability of As–O bonds[4] have been made use of by several workers, a comparative assessment with respect to their phosphorus counterparts is, however, lacking. This paper focuses mainly on the behaviour of As–N and As–O bonds as compared to P–N and P–O bonds in cyclic 1,3,2-diox(a)-arsenites and -phosphites, respectively.

Furthermore, although the solution-state conformation of 1,3,2-dioxarsenanes has been investigated in depth by Aksenes and co-workers.[5] there is little structural information on the solid state.[6] We report the X-ray structures of the bridged arsenites **13** and **15** obtained in the present study.



1 X = P, Y = Cl
2 X = As, Y = Cl
3 X = P, Y = $C_6H_{11}NH$
4 X = P, Y = NEt_2

5 X = P, Y = Cl
6 X = As, Y = Cl
7 X = P, Y = $C_6H_{11}NH$

8 X = P, Y = Cl
9 X = As, Y = Cl
10 X = P, Y = $C_6H_{11}NH$
(**31** X,Y = P(O)H)

Results and discussion

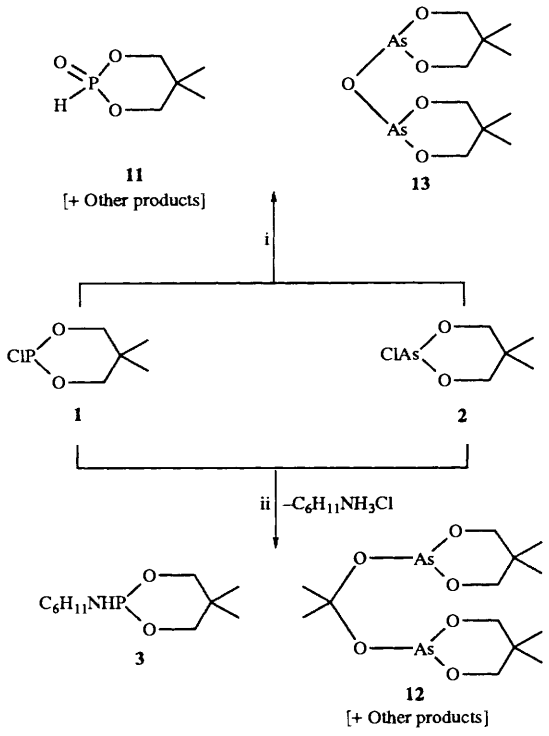
The known arsenite **2**[5] has been prepared in the present study in high yield by treating the trichloride with the diol in CH_2Cl_2 by following the same route as for **1**.[7] Synthesis of the seven- and eight-membered ring compounds **5**[8] and **6**[9] and **8**[10] and **9**, respectively, is accomplished similarly; **9** is a new cyclic arsenite.

Reaction of compounds **1** and **2** with cyclohexylamine in the presence and in the absence of water proceeds in entirely different ways (see Scheme 1). Compound **11** is formed almost exclusively from **1** when 1 mol equiv. of water is used in the presence of triethylamine[11] or cyclohexylamine; even when 0.5 mol equiv. of water is used, **11** is the only significant product observed. Under similar conditions, compounds **5** and **8** also afford products with =P(O)H linkages (^1H, ^{31}P NMR). By contrast, when the arsenic precursors **2**, **6** and **9** are used the oxy-bridged derivatives **13**, **14**[12] and **15** are obtained as crystalline compounds.

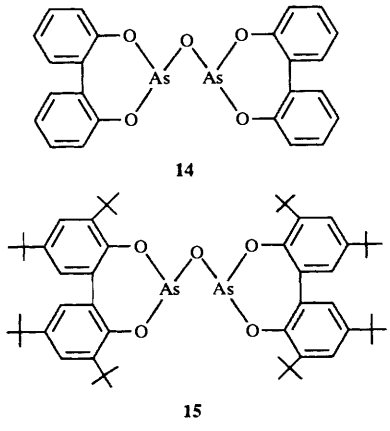
The formation of compounds **11** and **13** can be easily rationalized by invoking the reluctance of arsenic to achieve the +5 oxidation state as against the tendency of phosphorus to form P=O bonds.

Under anhydrous conditions, in contrast to the ready formation of **3**, **4**,[13] **7**, **10**, $(C_6H_{11}NH)POC_6H_4O$ **16** and $(C_6H_{11}NH)POCH_2CH_2O$ **17** chlorophosphites, the arsenite **2** afforded the bridged compound **12**; the reaction mixture

as well as the distillate showed cyclohexyl peaks (^{1}H NMR) in variable amounts indicating the presence of other products,



Scheme 1 *Reagents*: i, $C_6H_{11}NH_2$ (1–2 equiv.), water (0.5 equiv.), ii. $C_6H_{11}NH_2$ (2 equiv.)



presumably of the type $ClAs(NHC_6H_{11})_2$ or $[ClAsNC_6H_{11}]_n$. By treating **2** with sodium, pure compound **12** has been independently synthesized and characterized.[14]

Although the formation of **12** is puzzling, it has been observed that arsenanes have a tendency to oligomerize leading to bridging groups as, for example, in the case of $MeAsOCH_2CH_2CH_2O$;[15] it is possible that the intermediate amino product undergoes reorganization to lead to **12** and other As–N derivatives.

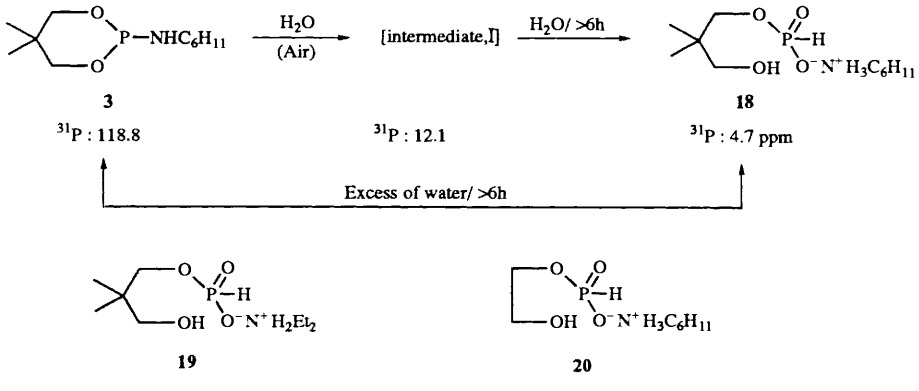
Since the arsenic analogue of **3** could be a possible intermediate in the formation of **12** (or **13**), we have explored the hydrolytic behaviour of **3** and similar phosphorus compounds **4**, **7**, **10**, **16**, **17** in more detail. The only compounds that we could characterize satisfactorily in these reactions were double hydrolysis products as their amine salts (Scheme 2). Thus compounds **18**, **19**, and **20** were obtained from **3**, **4** and **17**, respectively.

Compound **7** afforded a less-soluble product whereas **10** did not react; in the case of **16**, although the elemental analysis for the product is close to the expected values, the P–H proton was not clearly visible in the ^{1}H NMR spectrum.

The hydrolysis of compound **3** occurs in a stepwise fashion. The phosphorinane ring is cleaved in the first step to afford the intermediate **I** [compare the hydrolysis of compound **21**, Scheme 3]. In Fig. 1, the ^{1}H and ^{13}C NMR spectra of the intermediate **I** along with those of **3**, **18** and **11** (^{1}H only) are shown. The appearance of two triplets in the ^{1}H NMR and an AB pattern for the cyclohexyl N–CH–*C* carbons with ^3J(PC) 4.5 Hz in the ^{13}C NMR spectrum indicate a strongly H-bonded system involving CH_2OH and NHC_6H_{11} protons. Since no reaction occurs between cyclohexylamine and compound **11** upon mixing, the ring-cleaved product $(C_6H_{11}NH)H(O)POCH_2C(Me_2)CH_2OH$ (note that this formula corresponds to an equimolar mixture of **11** and cyclohexylamine) is a likely structure for **I**. The non-equivalence of the protons and carbons due to H-bonding, as observed for **I** is, to our knowledge, quite rare.

Synthesis of alkoxy aryloxy phosphites as well as arsenites is very straightforward; however their hydrolysis led to different types of products. For example, compound **21** leads to the cyclic phosphite **11** whereas the corresponding arsenite **25** affords **13** as the major product along with As_2O_3, 2,2-dimethylpropane-1,3-diol and phenol (Scheme 3). The same factors as explained for the behaviour of the amino 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–O bonds to obtain **13** by treating As_2O_3 with 2,2-dimethylpropane-1,3-diol (and *vice versa*).

Preservation of the phosphorinane ring in the hydrolysis of **21** (Scheme 3) and its cleavage in the case of **3** (Scheme 2) is an



Scheme 2

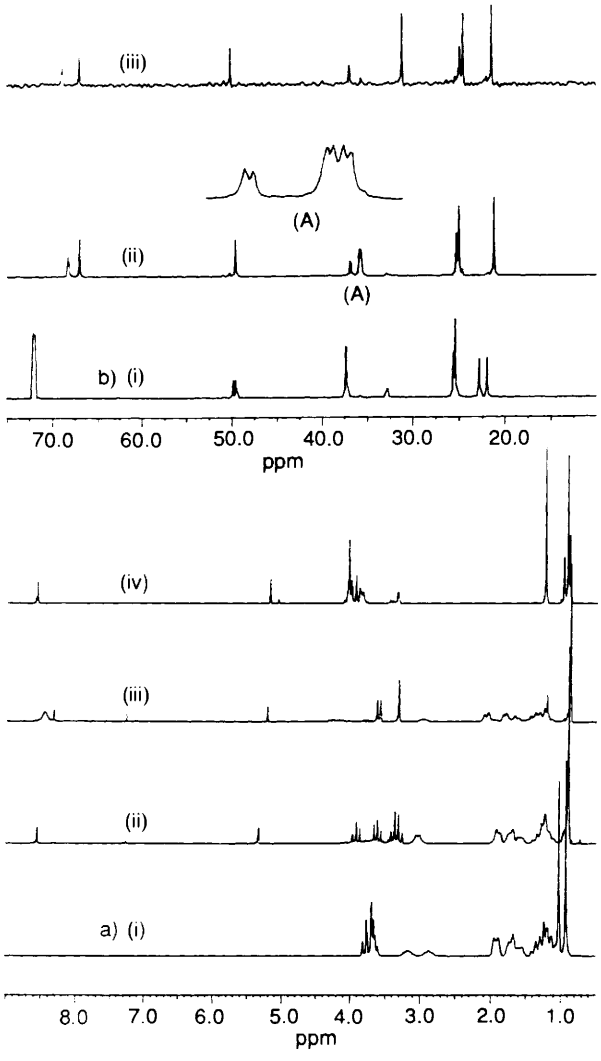


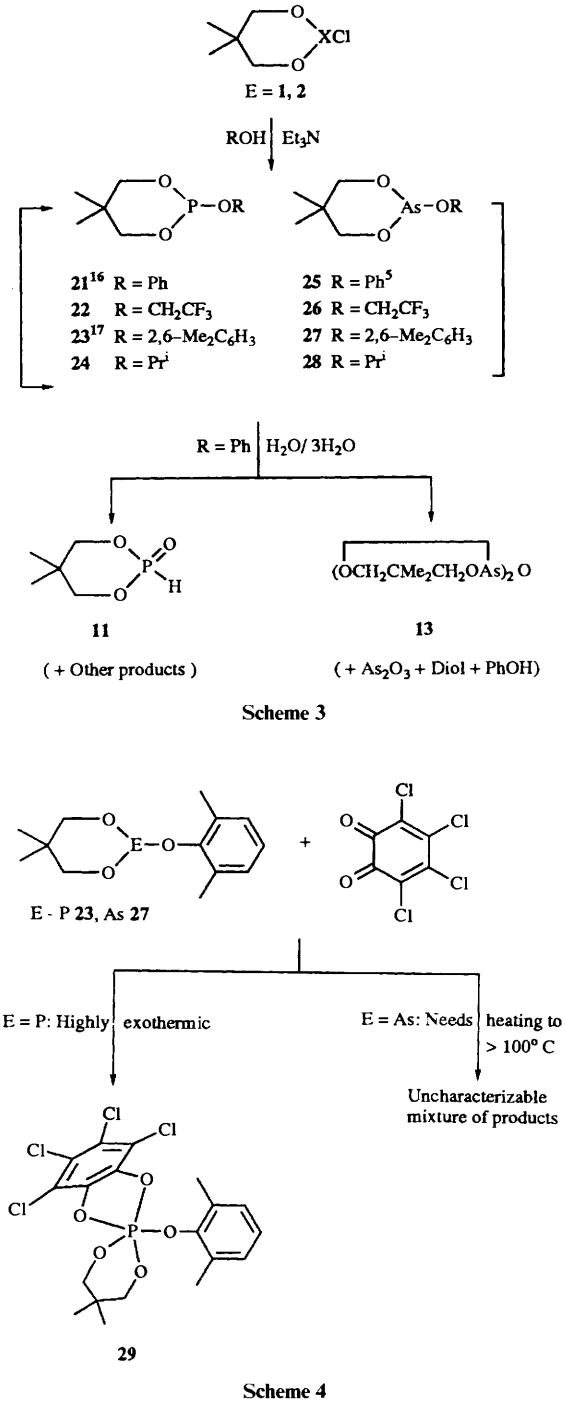
Fig. 1 (a) ^{1}H NMR spectra of (i) **3**, (ii) intermediate **I**, (iii) the amine salt **18**, and (iv) phosphonate **11**. (b) ^{13}C NMR spectra of (i) **3** (ii) intermediate **I** and (iii) **18**.

interesting contrast between aryloxy and amino phosphites and may be attributed to the difference in H-bonding in the mechanistic pathways of the two reactions.

The reluctance of arsenic to achieve five-coordination is also reflected in the behaviour of cyclic arsenites towards perchloro-*o*-benzoquinone (Scheme 4). All attempts to prepare several arsoranes with an arsenane ring from arsenites by using different quinones were unsuccessful † although the corresponding reactions with phosphites afforded phosphoranes readily.[18]

In order to compare the donor-acceptor properties of arsenites and phosphites we treated compounds **21** and **25** with [Mo(CO)$_4$(nbd)]. Although the phosphite **21** reacted readily (^{31}P NMR), the arsenite **25** gave a black residue which contained mostly starting material. Compound **13** did not react with [Mo(CO)$_4$(nbd)], bipyridyl, or 2,2-dimethylpropane-1,3-diamine, showing that it has very weak or no donor and acceptor characters.

† However, the reaction of (2,6-$Me_2C_6H_3O$)$\overline{AsOCH_2CMe_2CH_2O}$ with selenium dioxide afforded a product tentatively formulated as (2,6-$Me_2C_6H_3O$)(O)$\overline{AsOCH_2CMe_2CH_2O}$, $\delta_H(C_6D_6)$ 0.141 (s, 3 H, CH_3), 0.97 (s, 3 H, CH_3), 2.06 (s, 6 H, ArCH_3), 2.92 (d, ^3J 11.8, 2 H, OCH_2), 4.60 (d, J 11.8, 2 H, OCH_2) and 6.75–7.10 [m, 3 H, H(Ar)]. Further characterization was impracticable owing to the instability of the compound.



X-Ray structural analysis of compounds 13 and 15

The molecular structures of compounds **13** and **15** are depicted in Figs. 2 and 3; selected bond lengths and bond angles are given in Tables 1 and 2. Bond distances in both the compounds fall in the normal range[19] but are longer than those observed for Cl$\overline{As(OCMe_2CH_2CMe_2O)}$ **II** (mean: 1.74 Å);[6] even the As–O(bridging) distances in **13** (1.777 Å) and **15** (1.756 Å) are longer than the ring As–O distances in **II**. The As–O–C bond angles in **13** (mean: 117.4°) are smaller than those in **II** (mean 124.5°) most likely as a result of steric strain in the latter. Also the widening of the As–O–As angle in **15** (139.2°) when compared to **13** (125.8°) is probably a result of steric effects

rather than the interaction of orbitals containing the lone pair electrons on bridgehead oxygen with arsenic d-orbitals.[20]

The two arsenane rings in **13** are clearly in the 'chair' conformation in contrast to the 'twist-boat' conformation observed for **II**. The atoms As(1) and C(2) in **13** are away from the mean plane containing the other four ring atoms by nearly 0.75 Å. This is consistent with the solution-state studies of Aksenes and the expected anomeric effects involving the oxygen lone pairs of the ring.[20]

There are short intermolecular contacts involving O(2) and the arsenic atoms (3 Å). This feature reflects the weak acidic (Lewis) character of the arsenic(III) centres.

As was observed by us[2] for $ClCH_2CMe_2CH_2O$-$PO(C_6H_2Bu^t_2$-2,4)$CH_2(C_6H_2Bu^t_2$-2,4)O **III**, the eight-membered arsocine ring in **15** has a 'symmetrical anti' conformation; Since the ^1H NMR spectrum of **15** in solution gives a well-separated sharp AX doublet in contrast to **III**,[2] the molecule appears to be rigid. Compound **15**, to our knowledge, is the first 'arsocine' to be structurally characterized.

An interesting difference exists between the structures of **13** and **15**. Whereas the six-membered rings in **13**, are on the same side as the bridgehead oxygen, the eight-membered rings in **15** are on the opposite side; steric interactions in **15** may be responsible for this difference.

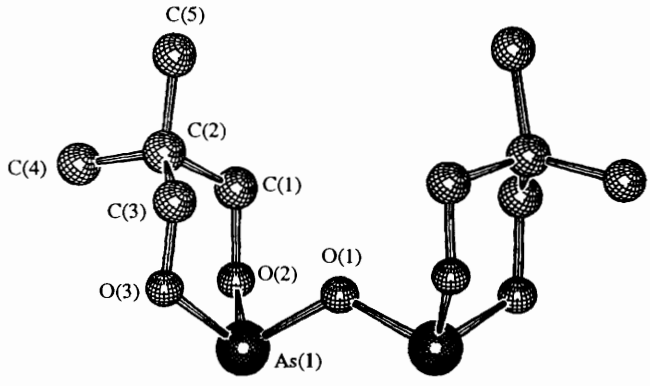


Fig. 2 Molecular structure of compound **13** (H atoms omitted)

Table 1 Selected bond lengths (Å) and bond angles (°) for compound **13** with standard deviations in parentheses

As(1)–O(1)	1.7771(11)	O(2)–C(1)	1.431(3)
As(1)–O(2)	1.790(2)	C(1)–C(2)	1.524(4)
As(1)–O(3)	1.767(2)	C(2)–C(3)	1.527(4)
As(1′)–O(1)	1.7771(11)	O(3)–C(3)	1.431(3)
O(3)–As(1)–O(1)	95.93(8)	C(3)–O(3)–As(1)	117.3(2)
O(3)–As(1)–O(2)	96.95(9)	O(2)–C(1)–C(2)	113.4(2)
O(1)–As(1)–O(2)	95.80(8)	C(1)–C(2)–C(3)	109.4(2)
As(1′)–O(1)–As(1)	125.81(14)	O(3)–C(3)–C(2)	113.6(2)
C(1)–O(2)–As(1)	118.1(2)		

Symmetry transformations used to generate equivalent atoms: 1′ = $-x, y, -z + \frac{1}{2}$.

Table 2 Selected bond lengths (Å) and bond angles (°) for compound **15** with standard deviations in parentheses

As–O(1)	1.794(3)	C(6)–C(7)	1.525(7)
As–O(2)	1.799(4)	C(7)–C(8)	1.519(7)
As–O(3)	1.756(3)	C(8)–C(13)	1.393(7)
O(1)–C(1)	1.404(6)	C(13)–O(2)	1.413(5)
C(1)–C(6)	1.394(7)		
As–O(3)–As*	139.3(3)	C(1)–C(6)–C(7)	121.8(4)
O(1)–As–O(2)	94.4(2)	C(6)–C(7)–C(8)	110.8(4)
As–O(1)–C(1)	114.2(3)	C(8)–C(13)–O(2)	117.4(4)
O(1)–C(1)–C(6)	117.3(4)	C(13)–O(2)–As	114.5(3)

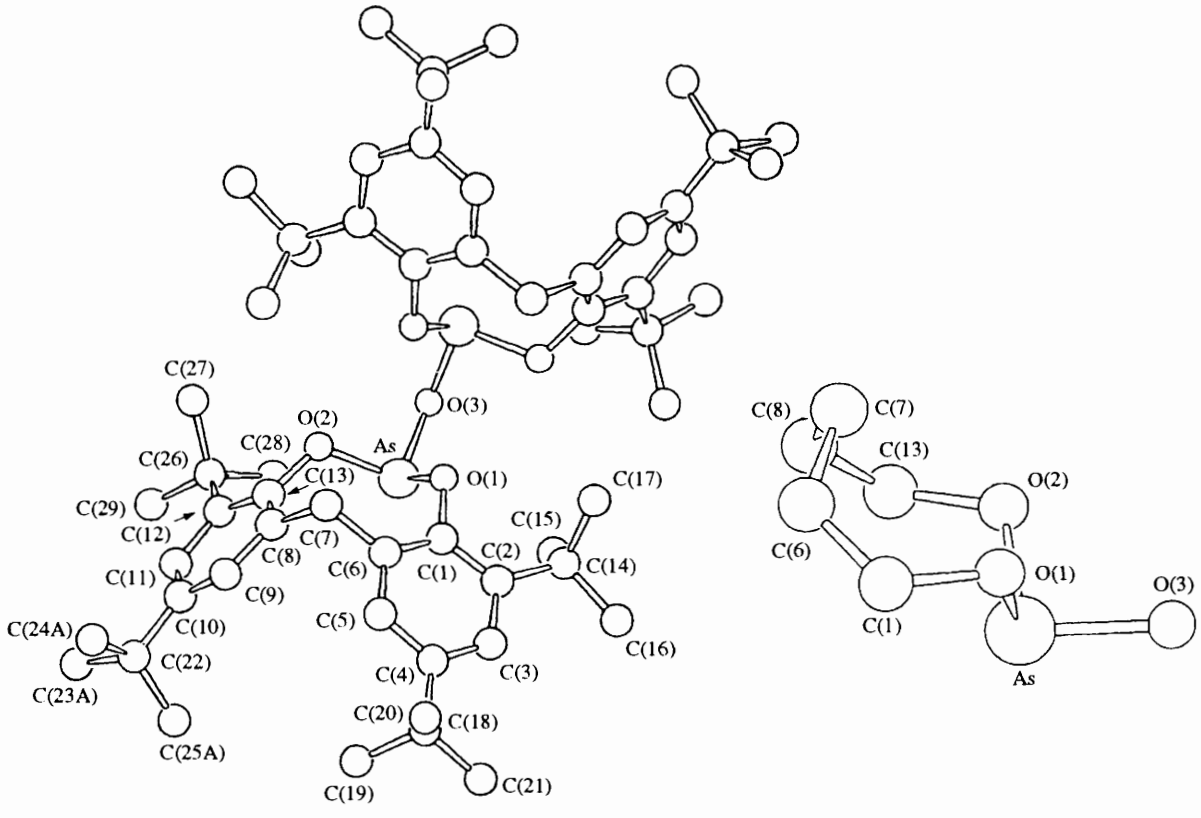


Fig. 3 Molecular structure of compound **15** (H atoms omitted). Inset shows the conformation of the eight-membered ring.

Experimental

Chemicals were procured from Aldrich/Fluka or from local manufacturers; they were purified according to standard procedures.[21] All operations, unless stated otherwise, were performed under a dry nitrogen atmosphere. ^1H, ^{13}C and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker 200 MHz spectrometer using $CDCl_3$ or C_6D_6 solution with shifts referenced to $SiMe_4$ ($\delta = 0$) or 85% H_3PO_4 ($\delta = 0$); J values are recorded in Hz. IR spectra were recorded on JASCO FT/IR-5300 spectrophotometer. Elemental analyses were carried out on a Perkin-Elmer 240C CHN analyser.

The cyclic compounds **1**,[7] **5**,[8] **6**,[9] **8**,[10] **11**,[11] **21**,[16] **23**[17] and **25** (bp 110 °C 0.5 mm Hg)[5] were prepared by literature methods. Compounds **3** (δ_p 118.8), **7** (δ_p 151.0), **10** (δ_p 140.9), 4 (δ_p 146.4), **16** (δ_p 139.8) and **17** [δ_p 133.5 ppm] were prepared by treating the corresponding cyclic chloro precursor with 2 mol equiv. of amine; details will be reported elsewhere. Compounds **22** (δ_p 122.5), **24** (δ_p 119.9), and **26–28** were obtained by treating the cyclic chloro phosphites/arsenites with the appropriate alcohols phenols in the presence of triethylamine.

(a) 2-Chloro-5,5-dimethyl-1,3,2-dioxarsenane. The same procedure as for **1**[7] was used to afford **2** in 95% yield (**WARNING**: All arsenic compounds should be treated as highly poisonous). The reaction, performed in ether, with equimolar proportions of arsenic trichloride, the diol and triethylamine gave the product in 75% yield; bp 40 °C/0.2 mmHg [lit.,[5] bp 52 °C/0.4 mmHg]; $\delta_H(C_6D_6)$ 0.57 (br s, 6 H, CH_3) and 3.71 (br s, 4 H, OCH_2); $\delta_C(CDCl_3)$ 21.7 (s, CH_3), 22.9 (s, CH_3), 33.2 (s, CMe_2) and 72.4 (s, OCH_2). The ^1H NMR ($CDCl_3$) spectrum was identical with that reported in the literature.[5]

(b) 2,4,8,10-Tetra-*tert*-butyl-6-chloro-12*H*-dibenzo[*d*,*g*][1,3,2-dioxarsenocine 9. To a solution of arsenic trichloride (1.0 g, 5.5 mmol) in benzene [**CAUTION**: Benzene is a carcinogen] (30 cm^3) a mixture of methylenebis(4,6-di-*tert*-butylphenol)[10] (1.86 g, 4.4 mmol) and triethylamine (3 cm^3) in benzene (10 cm^3) was added and the whole then stirred for 4 h. The mixture was filtered and evaporated and the residue crystallized from benzene to give **9** (2.29 g, 94% based on diol), mp 225–227 °C (Found: C, 65.4; H, 7.9. Calc. for $C_{28}H_{36}AsClO_2$: C, 66.20; H, 8.32%); δ_H 1.31 (s, 18 H, Bu^t), 1.42 (s, 18 H, Bu^t), 3.59 [d, J 13.1, 1 H, CH_2 (A)], 4.40 [d, 1 H, CH_2 (B)], 7.23–7.40 (d, 2 H, ArH) and 7.34–7.36 (m, 2 H, ArH); δ_C 30.1 (s, CH_3), 31.7 (s, CH_3), 34.4 (s, CMe_3), 34.7 (s, CMe_3), 122.8, 127.3 139.9, 143.2 and 150.2 (all ArC; CH_2 not located.

(c) 2,2′-Isopropylidenedioxybis(5,5-dimethyl-1,3,2-dioxarsenane) 12. To a solution of **2** (1.76 g, 8.3 mmol) in toluene (20 cm^3), cyclohexylamine (1.64 g, 16.6 mmol) in toluene (10 cm^3) was added dropwise (0.5 h) at 20 °C. The mixture was stirred for 2 h after which it was filtered and evaporated. The residue (A) was distilled *in vacuo* (0.2 mmHg oil-bath at 240 °C) to give a liquid (B) with **12** as the major component (*ca.* 80%). The ^1H NMR spectra of liquid (A) and (B) were identical; $\delta_H(CDCl_3)$ 0.67 (s, 6 H, CH_3), 0.96 (s, 6 H, CH_3), 1.23 (s, 6 H, CH_3), 3.34 (d, J 10.0, 4 H, ring OCH_2), 3.61 (s, 4 H bridge OCH_2), 4.23 (d, J 10.0, 4 H, ring OCH_2); the spectrum was the same in C_6D_6. Additional signals at 1.00–2.60 (cyclohexyl) were also observed.

Compound **12** was prepared pure by treating **2** (1.75 g, 8.25 mmol) with sodium (1.9 g, 8.25 mmol) in toluene (20 cm^3) for 20 h. The mixture was then filtered, evaporated and distilled *in vacuo* to give the product (0.5 g, 40% based on diol moiety), bp 170 °C 2mmHg (Found: C, 39.8; H, 6.65. Calc. for $C_{15}H_{30}As_2O_6$: C, 39.47; H, 6.58%); the ^1H NMR spectrum was the same as above, with no additional signals; δ_C 21.7, 22.0, 23.2 (all CH_3), 33.6 (CMe_2), 36.2 (bridging CMe_2), 68.3 (bridging OCH_2) and 71.2 (OCH_2).

(d) Bis(5,5-dimethyl-1,3,2-dioxarsenan-2-yl) ether 13. (i) To a solution of **2** (1.5 g, 7.05 mmol) in toluene (30 cm^3), cyclohexylamine (0.7 g, 7.05 mmol) and water (0.064 g, 3.52 mmol) were added dropwise (0.5 h) with stirring at 20 °C. After 12 h of stirring, the mixture was filtered and evaporated and the residue crystallized from hexane (needles) to give the product **13** (0.78 g, 60%), mp 110 °C (Found: C, 32.3; H, 5.65. Calc. for $C_{10}H_{20}As_2O_5$: C, 32.43; H, 5.41); δ_H 0.72(s, 3 H, CH_3), 3.44 [d, J 10.6, 2 H, OCH_2(A)] and 4.25 [d, 2 H, OCH_2(X)]; δ_C 21.9 (s, CH_3), 23.2 (s, CH_3), 33.5 (s, CMe_2) and 71.1 (s, OCH_2); ν_{max}/cm^{-1} (major bands) 2910, 2820, 1465. 1380, 1350, 1035vs and 765vs.

(ii) 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 cm^3) was heated under reflux for 2 h with azeotropic removal of water. The residue was crystallized from hexane to give the product (3.18 g, 86%); mp and IR and ^1H NMR spectra were identical with those of the compound prepared by procedure (i).

(e) Bis(12*H*-dibenzo[*d*,*g*][1,3,2]dioxarsenocin-6-yl) ether 14[2] and bis(2,4,8,10-tetra-*tert*-butyl-12*H*-dibenzo[*d*,*g*][1,3,2]dioxarsenocin-6-yl) ether 15. A similar procedure to that adopted for **10** (i) was followed. Compound **14** was insoluble in $CDCl_3$; yield 0.59 g (35%); mp 160 °C (lit.,[12] mp 168 °C) (Found: C, 54.2; H, 3.1. Calc. for $C_{24}H_{16}As_2O_5$: C, 53.95; H, 3.00%). Compound **15**: yield 50% (isolated); mp 258 °C (recrystallized from toluene) (Found: C, 69.0; H, 8.4. Calc for $C_{58}H_{84}AS_2O_5$: C, 68.92; H, 8.32%); δ_H 1.31 (s, 36 H, Bu^{t}H), 1.45 (s, 36 H, Bu^t-H), 3.50 [d, J 13.0, 2 H, CH_2(A)], 4.70 [d, J 13.0, 2 H, CH_2(B)] and 7.30 (d, 8 H, ArH); δ_C 30.4 [s, CH_2(?)], 31.2 [s, $C(CH_3)_3$], 31.6 [s, $C(CH_3)_3$], 34.5 (s, CMe_3), 35.4 (s, CMe_3), 122.7, 125.4, 136.4, 141.7, 145.9 and 147.8 [all C(Ar)]; ν_{max}/cm^{-1} (major bands) 2850, 1440, 1250, 780 and 720 cm^{-1}.

(f) Cyclohexylammonium 3-hydroxy-2,2-dimethylpropyl phosphonate hydrate 18. (i) Water (0.037 g, 2.05 mmol) was added to a solution of compound **3** (0.16 g, 0.68 mmol) in THF (10 cm^3), and the mixture stirred overnight. It was then evaporated and the residue crystallized from dichloromethane–hexane (1:3) to give the title compound (0.19 g, >95%), mp 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 samples contained variable amounts of water); δ_H 0.84 (s, 6 H, CH_3), 1.05–2.15 (m, 10 H, CH_2 cyclohexyl), 2.95 (br m, 1 H, NCH), 3.29 (s, 2 H, $HOCH_2$), 3.56 (d, J 10.0, 2 H, $POCH_2$), 4.10 (br, *ca.* 1.5 H, H_2O), 6.72 (d, $^1J_{PH}$ 621.0) and 8.40 (s, 3 H, $^+NH_3$); δ_C 21.4 (s, CH_3), 24.5 (s, $2CH_2$), 24.8 (s, $1CH_2$), 31.1 (s, $2CH_2$), 36.9 (s, CMe_2), 50.1 (s, N–CH), 67.0 (s, $HOCH_2$) and 68.7 (s, $POCH_2$, $J < 2.0$); δ_P 4.8; ν_{max}/cm^{-1} 3435, 3400, 2940vs, 2374 (PH), 2183, 1639, 1545, 1452, 1180vs ν(P=O), 1051vs (P=O) and 827. No other product was identified (^1H and ^{31}P NMR).

(ii) The same compound could be prepared quantitatively by treating **3** directly with water (evaporation followed by crystallization). Different batches varied only in the $^+NH_3$ and OH_2 region (^1H NMR). The ^{31}P NMR results were identical for all the samples.

(g) Diethylammonium 3-hydroxy-2,2-dimethylpropyl phosphonate dihydrate 19, 20 (and others). A similar procedure [(**f**)(ii)] as that for compound **18** was adopted.

Compound **19** Viscous liquid (extracted from water by hexane) (Found: C, 39.05; H, 9.0; N, 4.2. Calc for $C_9H_{28}NO_6P$: C, 38.99; H, 8.66; N, 5.05%); δ_H 0.85 [s, 6 H, $C(CH_3)_2$], 1.34 (t, 6 H, ^3J 7.2, CH_2CH_3), 2.91 (m, 4 H, NCH_2), 3.30 (s, 2 H, OCH_2), 3.59 (d, 2 H, ^3J 10.8, OCH_2), 3.75 [br s, 4 H, OH_2(?)], 6.77 (d, $^1J_{PH}$ = 624.6, 1 H, PH) and 9.70 (br s, 2 H, $^+NH_2$); δ_C 11.0 (s, CH_2CH_3), 21.4 [s, $C(CH_3)_2$], 36.9 (d, J 3.5, CMe_2), 41.8 (s, NCH_2), 67.2 (s, OCH_2) and 68.6 (d, J 4.7, $POCH_2$); δ_P 4.2; ν_{max}/cm^{-1} 3381, 2515, 2361, 1637, 1475, 1197 and 1053.

Cyclohexylammonium 2-hydroxyethyl phosphonate **20**. Viscous liquid (Found: C, 39.85; H, 9.2, N, 5.8. Calc for

Table 3 Crystallographic data for compounds **13** and **15**

Compound		**13**	**15**
Formula		$C_{10}H_{20}As_2O_5$	$C_{58}H_{84}As_2O_5$
Mol. wt.		370.10	1011.09
Crystal system		Monoclinic	Monoclinic
Space group		*C*2/*c*	*C*2/*c*
Unit cell dimensions			
a/Å		18.874(4)	22.60(3)
b/Å		9.896(2)	17.85(2)
c/Å		8.651(2)	16.21(2)
β/°		116.45(3)	122.68(7)
V/Å^3		1446.7(5)	5505(11)
Z		4	4
Density (calc.), mg m^{-3}		1.699	1.22
Crystal size(mm)		0.4 × 0.3 × 0.1	0.3 × 0.3 × 0.3
F(000)		744	2152
μ(Mo-Kα)/mm^{-1}		4.626	1.259
T/°C		23	20
Scan method		ω/2θ	ω/2θ
2θ range		2–50	2–45
Reflections collected		1252	3607
Independent reflections		1215 (R_{int} = 0.0190)	3607(R_{int} = 0.000)
Programmes used		SHELX 86 & SHELX 93	SHELX86&SHELX93
Final *R* indices ($I > 2\sigma(I)$)		R_1 = 0.0222; wR_2 = 0.0508	R_1 = 0.0395 wR_2 = 0.0990
	(all data)	R_1 = 0.0283 wR_2 = 0.0528	R_1 = 0.0651 wR_2 = 0.1129
No. parameters refined		81	296
Largest diff. peak and hole (e Å^{-3})		0.367 and −0.342	0.801 and −0.488

$C_8H_{22}NO_5P$: C, 39.51; H, 9.05; N, 5.76%); δ_H 1.05–2.20 (m, 10 H, CH_2), 3.05 (br s, 1 H, CH), 3.45 (s, 2 H, OH_2), 3.73 (m, 2 H, CH_2OH), 3.95 (m, 2 H, CH_2OP), 6.83 (d, *J* 620.0, PH) and 8.30 (br s, 3 H, RN^+H_3); δ_C 24.5 (s, $2CH_2$), 24.9 (s, $1CH_2$), 31.0 (s, $2CH_2$), 50.2 (s, NCH), 62.0 (d, *J* 3.0, OCH_2) and 65.7 (d, *J* < 3.0, OCH_2); δ_P 4.6; ν_{max}/cm^{-1} 3383, 2363, 1641, 1199vs, 1076vs and 1051vs. The 1,3,2-benzodioxaphosphole **16** upon hydrolysis also afforded a single product; mp 115–125 °C; δ_P([$^2H_6$]-DMSO) 2.66; there was no PH signal in the ^1H NMR spectrum (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%).

(h) Intermediate I. Compound **3** was either (i) exposed to air (moisture) for 6 h on a watch glass or (ii) stirred with water (3 mol equiv.) in THF for 25 min after which the solvent was evaporated. The ^1H NMR spectra for the oily product **I** obtained from routes (i) and (ii) were identical; δ_H 0.84 (s, 6 H, CH_3), 1.00–2.00 (m, 10 H, CCH_2), 2.95 (m, 1 H, N–CH), 3.29 (AB qrt, OCH_ACH_B), 3.50 (t, *J* 10.0, 11.0, 1 H, OCH_2), 3.70 (t, *J* 10.0, 11.0, 1 H, OCH_2), 4.70 (variable, OH_2), 6.90 (d, $^1J_{PH}$ 640.0); δ_C: 21.2 (s, $2CH_3$), 24.9 (s, $2CH_2$), 25.2 (s, $1CH_2$), 35.6 and 35.8 [AB qrt, ^3J 4.5 (?), $2CH_2$], 36.8 (d, ^3J 5.0, CMe_2), 49.5 (s, NCH), 66.9 (s, $HOCH_2$) and 68.2 (d, ^2J 5.5, $POCH_2$); δ_P 12.1. This sample **I** when kept for > 3 days yields compound **18** quantitatively (^1H, ^{31}P, ^{13}C NMR).

(i) 4,5,6,7-Tetrachloro-2-(2,6-dimethylphenoxy)-2,2-isopropylidenedioxy-1,3,2-benzodioxaphosphole 29. The phosphite **19** in benzene was added to a stoichiometric quantity of perchloro-*o*-benzoquinone in benzene in a highly exothermic reaction. The product was crystallized from ether–hexane and had mp 183 °C (Found: C, 45.5; H, 3.75. Calc. for $C_{19}H_{19}Cl_4O_5P$: C, 45.62; H, 3.80%); δ_H 1.04(s, 3 H, CH_3), 1.14(s, 3 H, CH_3), 2.25(s, 6 H, $ArCH_3$), 3.90–4.20(ABX m, 4 H, OCH_2) and 6.95(s, 3 H, ArH)); δ_C 16.4(s, $ArCH_3$), 24.4(s, CH_3), 24.5(s, CH_3), 32.8(d, *J* 5.0, CMe_2), 76.7(d, ^2J 8.0, OCH_2), 114.5, 124.6, 128.6, 128.9, 140.1 and 150.7 (all ArC); δ_P −50.4.

The reaction under neat conditions also afforded compound **29** in > 90% yield, but the reaction was very exothermic. The corresponding reaction with the arsenite **27** was very sluggish and needed heat; however, the ^1H NMR spectrum of the product showed it to be a mixture, no pure compound being isolated.

(j) [Mo(CO)$_n$(PhOPOCH$_2$CMe$_2$CH$_2$O)$_{6-n}$]. Compound **21** (0.2 g, 0.89 mmol) and [Mo(CO)$_4$(NBD)] (0.13 g, 0.43 mmol) were heated together in toluene (15 cm^3) under reflux for 12 h after which the volatile components were removed under reduced pressure; the residue showed: δ_P 150.4 and 157.2 (> 85%); ν_{max}/cm^{-1} 1919vs, 1489, 1047 and 993.

The corresponding reaction using **25** gave a black residue which showed mostly the starting material (> 70%, ^1H NMR), and other unidentified products.

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

(i) Compound **1** + $C_6H_{11}NH_2$ + H_2O (1:1:0.5 or 1:2:0.5; toluene or benzene/reflux). Procedure similar to **d**(i). Compound **11** was isolated in > 50% yield. No other product was identified. When the stoichiometry was 1:1:1, **8** was exclusively formed.

(ii) Compound **5** + $C_6H_{11}NH_2$ + H_2O(1:2:0.5; benzene/25 °C). Products: **7** (60%) + **30** (40%). Structure H(O)POC$_6$H$_4$C$_6$H$_4$O assigned for **30**; δ_H(PH) 7.21(^1J 634, PH); δ_P −2.2.

(iii) Compound **8** + $C_6H_{11}NH_2$ + H_2O (1:2:0.5; benzene/25 °C). Products: **31** + others (not identified); δ_H 7.20(d, ^1J 644, PH); δ_P 2.0.

(iv) Compound **21** + H_2O (1:1 and 1:3/THF/25 °C): Product: **11** (> 80%).

(v) Compound **24** + H_2O (1:3/THF/25 °C). Products: **24** (80%), **11** (10%) + others.

(vi) Compound **25** + H_2O (1:1 and 1:3/THF/25 °C): insoluble (As_2O_3, 10–30%. IR), PhOH, diol, and **13** (20–50%).

(vii) Compound **28** + H_2O (1:1/THF/25 °C): insoluble (As_2O_3, IR), **13** (50%), diol and isopropyl alcohol.

X-Ray structural analysis

Compounds **13** and **15** were crystallized from hexane and a mixture of diethyl ether–hexane, respectively. Data were collected on an Enraf-Nonius CAD 4 (compound **13**) or a Siemens four-circle AED 2 (compound **15**)[22] diffractometer. Data were collected after inserting the crystal inside a capillary. Details of data collection and structure determinations are summarized in Table 3. H atoms (as rigid groups) were fixed by geometry and their positions refined isotropically; the bond lengths are not corrected for thermal motion. Final atomic positional parameters, anisotropic thermal parameters and isotropic *B* values have been deposited with the Cambridge Crystallograph Data Centre.‡

‡ For details of the scheme, see Instructions for Authors (1995), *J. Chem. Soc., Perkin Trans 1*, 1995, Issue 1.

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