SYNTHESIS AND CHARACTERIZATION OF ORGANOARSENIC(III) DIALKYLTHIOPHOSPHATES

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Abstract

Reactions of $PhAsCl_2$ and Ph_2AsCl with $NH_4SOP(OR)_2$ in benzene at room temperature readily gave complexes of the types $[PhAs(Cl)\{SOP(OR)_2\}]$ **(1)**, $[PhAs\{SOP(OR)_2\}_2]$ **(2)** and $[Ph_2As\{SOP(OR)_2\}]$ **(3)** (R = Et, Pr^n, Pr^i, Bu^n). These complexes were characterized by elemental analysis (P, As), IR, NMR (^1H, ^{13}C, ^{31}P) and mass spectral data. Monodentate bonding through sulfur of the dialkylthiophosphate moiety to the organoarsenic(III) species has been suggested.

Introduction

There is a remarkable variation in the stereochemistry of trivalent arsenic, antimony and bismuth complexes. The geometry of these molecules is primarily influenced by the presence of a non-bonding electron pair which becomes stereochemically inactive with increasing mass of the central metal atom [1]. The structural diversity is well demonstrated in a number of coordination and organometallic complexes of these elements with sulfur ligands [2]. For example, antimony(III) complexes with anionic O^S ligands show primary bonding both through oxygen (such as $[Ph_2Sb(OSPPh_2)]$ [3], $[Sb(OSPR_2)_3]$ (R = Ph or c-Hx) [4] and sulfur (such as $[PhSb(SOCMe)_2]$ [5], $[Sb(SOCR)_3]$ (R = Me or Ph) [6]). Although a number of arsenic(III) complexes with dithio ligands, such as $As(S\hat{}S)_3$ ($S\hat{}S = SSP(OEt)_2$ [7], SSCOR [8], $SSCNEt_2$ [9]), $[PhAs(S\hat{}S)_2]$ [10] and $[Ph_2As(S\hat{}S)]$ [11], have been reported, there is paucity of data on similar complexes with O^S donor ligands [12]. In this paper, we report synthesis and characterization of organoarsenic dialkythiophosphates.

Results and Discussion

Reactions of phenylarsenic dichloride and diphenylarsenic chloride with ammonium dialkylmonothiophosphates readily gave complexes of the types $[PhAs(Cl)\{SOP(OR)_2\}]$ **(1)**, $[PhAs\{SOP(OR)_2\}_2]$ **(2)** and $[Ph_2As\{SOP(OR)_2\}]$ **(3)** (R = Et, Pr^n, Pr^i, Bu^n) (eqs. 1-3).

$$PhAsCl_2 + NH_4SOP(OR)_2 \longrightarrow [PhAs(Cl)\{SOP(OR)_2\}] + NH_4Cl \quad ----(1)$$
$$PhAsCl_2 + 2NH_4SOP(OR)_2 \longrightarrow [PhAs\{SOP(OR)_2\}_2] + 2NH_4Cl \quad ----(2)$$
$$Ph_2AsCl + NH_4SOP(OR)_2 \longrightarrow [Ph_2As\{SOP(OR)_2\}] + NH_4Cl \quad ----(3)$$

All these complexes are colourless viscous oils. They were characterized by elemental analysis (P, As), IR, NMR (^1H, ^{13}C, ^{31}P) and mass spectral data. In the IR

Table 1: NMR data for phenyl- and diphenyl-arsenic dialkylthiophosphates in $CDCl_3$

Complex	$^{31}P\{^1H\}$ δ in ppm	^{13}C NMR data		^1H NMR data [b]
		Ph-As carbons [a]	Ligands carbons b	
$PhAs(Cl)\{SOP(OEt)_2\}$	25.1	128.9 C-p 130.7 C-m 131.2 C-o 142.3 C-i	15.8 (d, 4.5 Hz, Me); 63.9 (br, OCH_2-)	1.34 (t, 6.9 Hz, OCH_2Me); 4.16 (m, OCH_2-); 7.49 (m, m+p-H), 7.86 (m, o-H) [Ph]
$PhAs(Cl)\{SOP(OPr^n)_2\}$	29.9	128.8 C-p 130.5 C-m 131.3 C-o 142.7 C-i	9.8 (s, OCH_2CH_2Me); 23.2 (d, 8 Hz, OCH_2CH_2); 69.3 (d, 6Hz, OCH_2)	0.92 (t, 7.3 Hz, OCH_2CH_2Me); 1.67 (m, OCH_2CH_2); 4.01 (m, OCH_2-); 7.46 (br,m, m+p-H) 7.84 (br,m, o-H) [Ph]
$PhAs(Cl)\{SOP(OPr^i)_2\}$	21.7	128.9 C-p 131.0 C-m + C-o (overlapping) C-i not detected	23.6 (d, 7 Hz, $OCHMe_2$), 73.2 (d, 4.5 Hz, OCH<)	1.31 (d), 1.33 (d) (each 6.5 Hz, $OCHMe_2$), 4.66 (m, OCH<); 7.47 (m, m+p-H), 7.88 (m, o-H) [Ph]
$PhAs(Cl)\{SOP(OBu^n)_2\}$	25.2	128.7 C-p 130.6 C-m 131.1 C-o 142.5 C-i	13.3 (s, Me); 18.4 (s, γ-CH_2-); 31.7 (d, 7 Hz, β-CH_2-); 67.4 (d, 6Hz, OCH_2-)	0.92 (t, 7.3 Hz, Me); 1.38 (m, $OCH_2CH_2CH_2$); 1.64 (m, OCH_2CH_2); 4.05 (m, OCH_2-); 7.48 (m, m+p-H); 7.87 (m, o-H) [Ph]
$PhAs\{SOP(OEt)_2\}_2$	27.5	128.8 C-p 130.7 C-m 131.9 C-o 141.5 C-i	15.9 ($OC-CH_3$) 63.8 (OCH_2-)	1.29(t,7Hz, OC-Me); 4.10 (m, OCH_2); 7.42 (m, m+p-H), 7.84 (br, o-H) [Ph]
$PhAs\{SOP(OPr^n)_2\}_2$	26.4	128.8 C-p 130.6 C-m 131.9 C-o 141.3 C-i	9.9(s, $OCC-CH_3$); 23.3(d, 6 Hz, $OCCH_2$-); 69.1 (d, 5 Hz, OCH_2-)	0.82 (t, 7.5 Hz,OCCMe); 1.57 (m, $OCCH_2$-); 3.88 (m, OCH_2-); 7.33 (m, m+p-H); 7.87 (m, o-H) [Ph]
$PhAs\{SOP(OPr^i)_2\}_2$	22.5	128.7 C-p 130.4 C-m 132.0 C-o 142.0 C-i	23.6 (s, $OC-Me_2$); 72.9 (s, OCH<)	1.29 (d) 1.31 (d) (each 6.5 Hz, $OC-Me_2$); 4.65 (m, OCH<); 7.42 (m, m+p-H); 7.90 (m, o-H) [Ph]
$PhAs\{SOP(OBu^n)_2\}_2$	25.6	128.6 C-p 130.5 C-m 131.8 C-o 141.4 C- i	13.3 (s,Me); 18.5 (s, γ-CH_2-); 31.8 (d, 7 Hz, β-CH_2-); 67.3 (d, 6Hz, OCH_2-)	0.90 (t, 7.3 Hz, OCCCMe); 1.36 (m, $OCCCH_2$-); 4.03 (m, OCH_2-); 7.43 (m, m+p-H), 7.88 (m, o-H), [Ph]

$Ph_2As\{SOP(OEt)_2\}$	28.0	128.6 C-p 129.4 C-m 132.6 C-o 139.5 C-i	15.7 (br, $OCH_2\underline{Me}$); 63.4 (br, OCH_2-)	1.27 (t, 7.0 Hz, $OCH_2\underline{Me}$); 4.13 (m, OCH_2); 7.36 (m, m+p-H); 7.58 (m, o-H) |Ph|
$Ph_2As\{SOP(OPr^n)_2\}$	27.6	128.7 C-p 129.5 C-m 132.6 C-o 139.9 C-i	9.9 (s, $OCH_2\underline{CH_2}Me$); 23.3 (s, br, $OCH_2\underline{CH_2}$); 69.1 (s, br, OCH_2-)	0.92 (t, 7.3 Hz, Me); 1.67 (sextet, 7Hz, $OCH_2\underline{CH_2}$-); 4.03 (m, OCH_2-); 7.39 (m, m+p-H), 7.58 (m, o-H) |Ph|
$Ph_2As\{SOP(OPr^i)_2\}$	27.0	128.7 C-p 129.4 C-m 132.8 C-o 140.0 C-i	23.6 (d, 11Hz $OCH\underline{Me}_2$); 72.6 (d, 4.5 Hz, OCH<)	1.28 (d) 1.33 (d) (each 6 Hz, $OCH\underline{Me}_2$), 4.71 (m, OCH<); 7.40 (m, m+p-H); 7.59 (m, o-H) |Ph|
$Ph_2As\{SOP(OBu^n)_2\}$	32.3	128.7 C-p 129.5 C-m 132.7 C-o 139.6 C-i	13.5 (s, Me); 18.6 (s, γ-CH_2-); 32.0 (d, 7 Hz, β-CH_2-); 67.1 (d, 6Hz, OCH_2-)	0.89 (t, 7 Hz, $OCCC\underline{Me}$); 1.35 (m, $OCCC\underline{H_2}$-); 1.61 (m, $OC\text{-}\underline{CH_2}$-); 4.02 (m, OCH_2-); 7.36 (m, m+p-H), 7.58 (m, o-H) |Ph|

a) appeared as singlets
b) d = doublet; t = triplet; m = complex pattern; br = broad

spectra of **1-3**, the (P)-O-C and P-O-(C) stretching modes have been observed in the regions 930-1170 and 740-870 cm^{-1}, respectively [13]. Medium intensity νAs-C bands are observed in the region 450-485 cm^{-1} [10,14], whereas the νAs-S bands have been observed between 370 and 390 cm^{-1} [10,15].

The ^1H NMR spectra of these complexes showed expected integration and peak multiplicities (Table1). The methyl protons of the isopropoxy group appeared as two doublets but only one multiplet was observed for OCH proton. This suggests that the methyl groups of the diisopropylphosphate ligand are anisochronous. However, in the ^{13}C NMR spectra, the methyl carbons of the isopropoxy group are not seen as anisochronous. The $^{13}C\{^1H\}$ NMR spectra exhibited a single set of resonances for phenyl arsenic and ligand carbons. The C-i of the phenyl group is progressively shielded on substituting chloride with dialkylthiophosphate moiety ($PhAsCl_2$<**1**<**2**). The ligand carbon resonances for the C-α and C-β appeared as doublets due to phosphorus coupling, however, in some cases broad signals were observed.

The ^{31}P NMR spectra displayed a single resonance in the range δ 21.7 to 32.3 ppm. The ^{31}P resonance for these complexes is significantly shielded as compared to analogous complexes of organo-germanium [16], -tin(IV) [17] and -antimomy(V) [18] (δ 46.0 to 59.8 ppm) in which primary bonding through oxygen has been suggested. Glidewell has studied a series of diisopropylthiophosphate complexes by ^{31}P NMR spectroscopy [19] and has suggested that purely S-bonded structures have δ ^{31}P < +30 ppm and O-bonded > +58 ppm. Accordingly, monodentate bonding through sulfur has been suggested in $[As\{SOP(OPr^i)_2\}_3]$ [19]. In view of this and the presence of νAs-S in

the IR spectra, the complexes **1-3** have primary bonding through sulfur and interaction with oxygen in solution, if any, must be very weak.

The mass spectra of a few representative complexes $[PhAs\{SOP(OR)_2\}_2]$ (R = Et or Bu) and $[Ph_2As\{SOP(OR)_2\}]$ (R = Et or Bu^n) showed molecular ion peaks at 490, 602, 398, 454, respectively. All these spectra exhibited a strong peak attributable to $[PhAs\{SOP(OR)_2\}]^+$ ion. The spectra of $[PhAs\{SOP(OR)_2\}_2]$ also displayed peaks due to $[As\{SOP(OR)_2\}_2]^+$ [R = Et (413) and R = Bu (525)] indicating that these complexes follow both R and L dissociation routes.

Experimental

IR spectra were recorded as neat liquids between CsI plates on a Perkin Elmer 783 spectrometer. The NMR spectra were recorded on a Varian XL-300 (^1H, ^{13}C and ^{31}P) or a Bruker AC-200 (^{13}C) NMR spectrometers in 5mm NMR tubes as a $CDCl_3$ solution. Chemical shifts are referenced to internal chloroform peak (δ 7.26 and 77.0 ppm) for ^1H and ^{13}C, respectively and external 85% H_3PO_4 for ^{31}P. Mass spectra were recorded on a VG Micromass 7070F. Arsenic and phosphorus were analysed by standard methods (Table2).

Table 2: Analytical data for phenyl- and diphenyl-arsenic compounds.

Complex	Found (required) %	
	As	P
$PhAs(Cl)\{SOP(OEt)_2\}$	20.8 (21.0)	8.4 (8.7)
$PhAs(Cl)\{SOP(OPr^n)_2\}$	19.2 (19.5)	8.0 (8.0)
$PhAs(Cl)\{SOP(OPr^i)_2\}$	19.4 (19.5)	7.9 (8.0)
$PhAs(Cl)\{SOP(OBu^n)_2\}$	18.2 (18.2)	7.3 (7.5)
$PhAs\{SOP(OEt)_2\}_2$	15.0 (15.3)	12.4 (12.6)
$PhAs\{SOP(OPr^n)_2\}_2$	13.6 (13.7)	11.2 (11.3)
$PhAs\{SOP(OPr^i)_2\}_2$	13.2 (13.7)	11.1 (11.3)
$PhAs\{SOP(OBu^n)_2\}_2$	12.1 (12.4)	10.2 (10.3)
$Ph_2As\{SOP(OEt)_2\}$	18.5 (18.8)	7.5 (7.8)
$Ph_2As\{SOP(OPr^n)_2\}$	17.3 (17.6)	7.1 (7.3)
$Ph_2As\{SOP(OPr^i)_2\}$	17.0 (17.6)	7.0 (7.3)
$Ph_2As\{SOP(OBu^n)_2\}$	16.0 (16.5)	6.5 (6.8)

All reactions were carried out in analytical grade solvents under anhydrous conditions. Phenylarsonic acid and triphenylarsine were obtained from commercial sources. Dialkylthiophosphoric acids [17], $PhAsCl_2$ and Ph_2AsCl were prepared according to literature methods [20, 23].

Preparation of $PhAsCl_2$:

$PhAsCl_2$ was obtained by reduction of $PhAs(O)(OH)_2$ with SO_2 in concentrated HCl, and distilling the resulting product *in vacuo* (120°C/10mm) [20]. Alternatively it was more conveniently obtained in 70% yield by refluxing $PhAs(O)(OH)_2$ in thionyl

chloride for 2 h, and distilling the resulting product *in vacuo* 2-3 times. ^{13}C in $CDCl_3$: δ 128.4, 129.7, 132.0, 145.0 ppm.

Preparation of Ph_2AsCl:

Attempted preparation by pyrolysis [21] of Ph_3AsCl_2 always gave a product which was contaminated with Ph_3As as revealed by ^{13}C NMR spectroscopy. Repeated distillation and fractionation did not improve the quality of product. Fairly pure Ph_2AsCl was obtained by condensation of $PhAsCl_2$ and PhAsO [22] in 1:3 stoichiometry in the presence of ZnO at 120°C [23].The product was extracted with benzene followed by distillation *in vacuo* (160-170°C/3-4 mm)(yield 46%).^{13}C NMR in $CDCl_3$: 128.8, 130.0, 131.7, 142.1 [small impurity of Ph_3As (^{13}C δ 128.4, 128.6, 133.7,139.7 ppm)was present].

Preparation of [PhAs(Cl){SOP(OEt)$_2$}] (1):

To a benzene solution (25 ml) of $PhAsCl_2$ (937 mg, 4.20 mmol) was added slowly solid $NH_4SOP(OEt)_2$ (784 mg, 4.19 mmol) with constant stirring. The reactants were stirred at room temperature for 6 h, and filtered off through a G-3 sintered funnel. The filtrate was concentrated *in vacuo* to yield a colourless oily liquid (1.449 g, 97%). The other monochlorophenylarsine complexes were prepared similarly. Reactions in 1:2 stoichiometry afford [PhAs{$SOP(OR)_2$}$_2$] **(2)** in excellent yields.

Preparation of [Ph_2As{SOP(OEt)$_2$}] (3):

To a benzene solution of Ph_2AsCl (1.044g, 3.95 mmol) was added $NH_4SOP(OEt)_2$ (741 mg, 3.96 mmol) with vigorous stirring, which was continued for an additional 8h. Precipitated ammonium chloride was filtered off through a G-3 sintered funnel. The filtrate was evaporated in vacuo (Yield 1.525g, 97%). The oily residue was dissolved in hexane (10 ml) and cooled at -10 °C, whereupon a colourless paste was settled in the flask. The solvent was decanted and the residue was washed with small quantity of cold hexane, and finally dried in vacuum to give a thick mobile liquid in about 60% yield.

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