Investigación

Bromination of (AsPh$_2$)$_2$O: The Structure of Tribromo-Diphenylarsenic (V)

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Dedicated to the memory of Dr. Jacobo Gómez-Lara, whom we greatly appreciated for his outstanding human and professional qualities

Abstract. Bromination of (AsPh$_2$)$_2$O leads to cleavage of the oxo-bridge with formation of the new organoarsenic (V) bromide, AsPh$_2$Br$_3$. A crystal structure determination shows that the compound is a trigonal bipyramidal monomer with crystallographically imposed two-fold symmetry and one shorter, equatorial, and two longer, axial bromines. There are weak C-H...π and Br...Br intermolecular interactions in the solid phase.
Key Words: Bromination, tribromophenylarsenic (V), trigonal bipyramidal monomer.

Resumen. La bromación de (AsPh$_2$)$_2$O conduce a la ruptura del puente oxo con la formación de un nuevo bromuro organoarsénico (V), AsPh$_2$Br$_3$. La determinación de la estructura cristalina muestra que el compuesto es un monómero de bipirámide trigonal con simetría cristalográfica doble, y un bromo ecuatorial y dos bromos axiales. Existen interacciones intermoleculares débiles C-H...π y Br...Br en fase sólida.
Palabras clave: Bromación, tribromofenilarsénico (V), monómero de bipirámide trigonal.

Introduction

We have recently reported [1] that oxidation of the arsenic(III) bridged compounds, (AsPh$_2$)$_2$E where E = O or S, with either *t*-butyl hydroperoxide or sulfur led to the four possible mono-oxidation products, AsPh$_2$(E)EAsPh$_2$, but the corresponding di-oxidation products were hydrolytically unstable and were not isolated. In continuation of this work we now report the results of related experiments with (AsPh$_2$)$_2$O, where the oxidising agent is elemental bromine.

Results and Discussion

Reactions
Attempts to oxidise the oxygen bridged diarsenic(III) compound (AsPh$_2$)$_2$O with one and two mols of bromine to produce, respectively, the mono- and di-oxidation products, (AsPh$_2$Br$_2$)O(AsPh$_2$) and (AsPh$_2$Br$_2$)$_2$O were unsuccessful. Reactions were carried out in dichloromethane solution and even at temperatures as low as -78°C, the As-O-As system was always cleaved and the products isolated were monoarsenic species.

Reaction with one mol of bromine gave as products dihydroxodiphenyl-arsonium bromide, [AsPh$_2$(OH)$_2$]Br **1**, and diphenylarsenic(III) bromide, AsPh$_2$Br **2**. The former must arise from partial hydrolysis, although all reasonable precautions to exclude moisture were made. As expected, one of the arsenic(III) centres has been oxidised. With two mols of bromine, the reaction course was similar but here both products were arsenic(V) species. Hydrolysis by adventitious water again led to the arsonium bromide, [AsPh$_2$(OH)$_2$]Br **1**, as one product while the second was diphenylarsenic tribromide, AsPh$_2$Br$_3$ **3**. This compound had not been previously prepared and we have characterised it by an X-ray structure determination. Although the structure of the dihydroxoarsonium bromide co-product has not been determined, it is likely to be similar to that of the chloride analogue, [AsPh$_2$(OH)$_2$]Cl [2].

A possible mechanism for the formation of the observed products via hydrolysis of the initial bromination products is shown in Scheme 1.

*Structure of AsPh$_2$Br$_3$ **3***
The X-ray crystal structure determination confirmed compound **3** as tribromo-diphenylarsenic(V) in which bromines occupy one equatorial and the two axial sites in a slightly distorted trigonal bipyramid about arsenic. Arsenic and the equatorial bromine lie on a crystallographic two-fold axis leading to equivalence of both the axial bromines and the two equatorial phenyl groups.
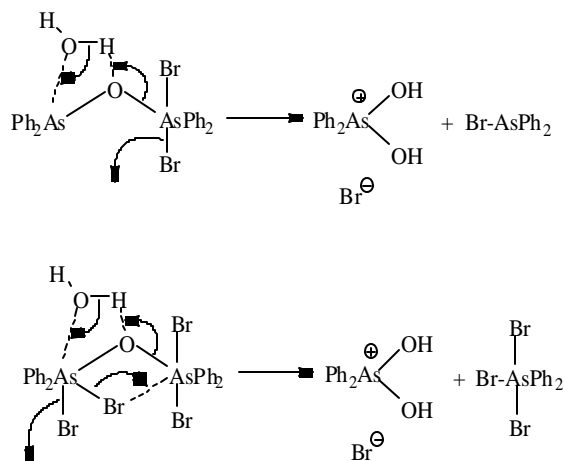
Scheme 1.

Molecular parameters are listed in Table 1 and a diagram showing the geometry and atom numbering scheme is in Fig. 1.

The axial As-Br separations are equal by symmetry [2.518(2)Å] and as usual in a trigonal bipyramid they are approximately 10% longer than the corresponding equatorial
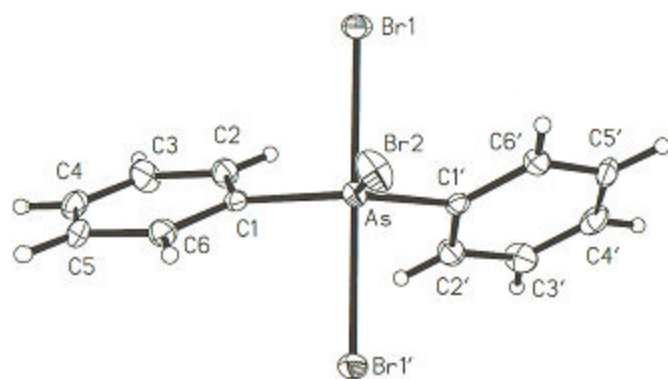

Fig. 1. A plot of **3** viewed approximately along the crystallographic two-fold axis, which passes through Br(2) and As, showing the atom numbering scheme and displacement elipsoids drawn at the 30% probability level. Primed atoms are related to their unprimed equivalents by the symmetry operation –x, y, 0.5 –z.

Table 1. Selected bond lengths (Å) and angles (°) for AsPh₂Br₃ **3**.

As-Br(1)	2.518(2)
As-Br(2)	2.286(2)
As-C(1)	1.917(7)
Br(1)-As-Br(1')	178.74(5)
Br(1)-As-Br(2)	89.37(2)
C(1)-As-Br(1')	89.66(15)
C(1)-As-Br(2)	117.39(15)
C(1)-As-C(1')	125.2(3)

Primed atoms are related to their unprimed equivalents by the symmetry operation –x, y, 0.5 –z.

As-Br distance [2.286(2)Å]. The Br-As-Br axial angle [178.74(5)°] is close to the ideal value and the major distortion of the trigonal bipyramid is in the increased C-As-C angle from 120° to 125.2(3)° at the expense of the equatorial C-As-Br angles [117.4(2)°]. The As-C distances, equivalent by symmetry, are unremarkable.

No other arsenic compounds with this stoichiometry have been crystallographically investigated and there are, in fact, few related compounds with which to make comparisons. The phosphorus compound, P(CCl₃)₂Cl₃ has trigonal bipyramidal geometry but the trichloromethyl groups are in axial sites, leaving the crystallographically equivalent chlorines to occupy equatorial positions [3]. SbR₂X₃ structures are more complicated as antimony Lewis acidity in both diphenyl- [4] and dimethyl- [5] antimony trichlorides is sufficient to give doubly chlorine bridged dimers in the solid state, increasing the coordination number and giving octahedral geometry about antimony. Steric effects appear to prevent such bridges forming in bis(p-chlorobiphenyl-2-yl) antimony(V) trichloride and discrete trigonal bipyramidal monomers are found [6]. Axial and equatorial Sb-Cl distances are 2.421 and 2.282 Å, respectively with the axial bonds *ca.* 6% longer than the equatorial one. Lewis acidity is much reduced in diphenylantimony tribromide and the mixed chloride-bromides, but is still sufficient to promote weak intermolecular interactions *via* one of the axial bromines and elongation of that bond [7]. The Sb-Br distance to the free axial bromine in SbPh₂Br₃, for example, is 2.557Å compared with the equatorial separation, 2.478Å, an elongation here of only *ca.* 3%.

There is rather more structural information on compounds with the ER₃X₂ stoichiometry and although there is a preponderance of discrete trigonal bipyramidal structures, there are alternatives. A molecular ER₃-X-X 'spoke' structure has been identified, for example, in PPh₃X₂ (X = Br or I), [8] AsMe₃X₂ (X = Br or I) [9] and AsPh₃I₂ [10] and the more classical, but still unusual, distorted square pyramidal geometry in the strained (biphenyl-2,2'-diyl)phenyl antimony dibromide and dichloride [11]. Both AsPh₃Br₂ [9] and As(neo-pentyl)₃Br₂ [12] have isolated trigonal bipyramidal molecules in which distances to the axial bromines are 2.551 and 2.564 Å, respectively, values close to the axial distances in compound **3**. (The As-Br(2) separation in the former appears to be erroneously reported [9] as 2.441 Å; the Br(1)-As-Br(2) angle should be 179.1°). The crystal structure of (cyclo-C₆H11)₃AsCl₂ has also been determined [13] with the unexpected result that the two axial As-Cl bond lengths are different [2.4957(7) Å and 2.3029(7) Å].

Molecular orbital calculations
RHF/3-21G(*) molecular orbital calculations [14] have been carried out to gain insight into the bonding in AsPh₂Br₃. According to Gillespie [15] electronegative elements prefer the axial positions in a TBP structure. However, a more elaborate picture based on the concept of apicophilicity/equatoriphilicity of substituents [16-18] shows a more complex dependence of stereochemistry on the nature of both axial and equatorial ligands. Thus, the stereochemistry of arsenic in this

system, with substituents of very similar electronegativities, *i.e.* 2.80 for bromine and 2.72 for the phenyl group [19], is particularly interesting.

RHF/3-21G(*) optimizations show that the minimum energy isomer is that with two bromine atoms in axial positions, in agreement with the structure found in the solid state. The other two isomers (one Br axial and all Br equatorial) are higher in energy by approximately 17 kcal/mol. The major geometrical parameters for the isomer with two axial bromine atoms are given in Scheme 2.

The As-C and equatorial As-Br bond lengths are well reproduced at this level of calculation, but the axial As-Br distances are somewhat underestimated. The main difference between the experimental and calculated structure concerns the relative orientations of the two phenyl rings. In the solid, the angle between the planes of these rings is 53.6° while in the calculated structure the rings are coplanar. If it is assumed that the calculated structure more nearly resembles that of isolated molecules in the gas phase, the different observed phenyl group orientations could be traced to specific crystal packing forces.

Packing in the crystal, shown in Fig. 2, leads to interlocked chains of molecules aligned approximately along the Br_{axial}-As-Br_{axial} vector and a view perpendicular to the (001) plane (Fig. 2a) shows that each chain contains alternating orientations of the equatorial As-Br bonds.

Although there are no remarkably short intermolecular contacts, crystal packing reveals peculiarities which are worthy of comment. Thus, there are a number of C-H...C(Ph) contacts of 2.966 Å (those H atoms are marked in Fig. 2a) which, according to recent studies, [20] are probably weak C-H...π bonds. A second type of interaction occurs between axial bromine atoms of two neighbour molecules of one chain with the equatorial bromine of a molecule from the adjacent parallel chain leading
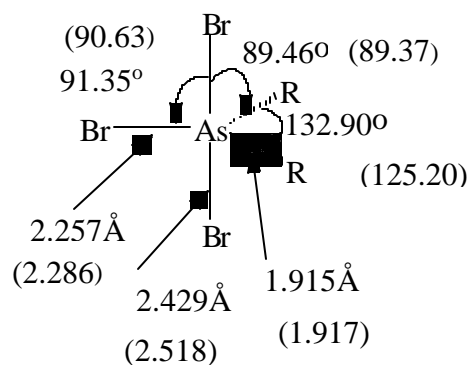
to "herring-bone" packing (see Fig. 2b). The Br_{axial}...$Br_{equatorial}$ distances are slightly lower than the sum of van der Waals radii (3.64 Å compared with 3.70 Å [21]), while the Br_{axial}...Br_{axial} distances are shorter (3.58 Å), suggesting weak intermolecular bonds along the chains. The solid state structure of $AsPh_2Br_3$ can thus be described as a supramolecular assembly, adding a new example to the few known organoarsenic architectures self-organized through secondary bonds [22].

Experimental

All experiments were carried out using a standard Schlenck line with freshly distilled anhydrous solvents. Tetraphenyl-diarsineoxide [23] was prepared according to the literature.

Reaction of (AsPh2)2O with Br2 in molar ratio 1:1. A solution of 0.95 g (2.0 mmol) of $(AsPh_2)_2O$ in 10 mL dichlorome-
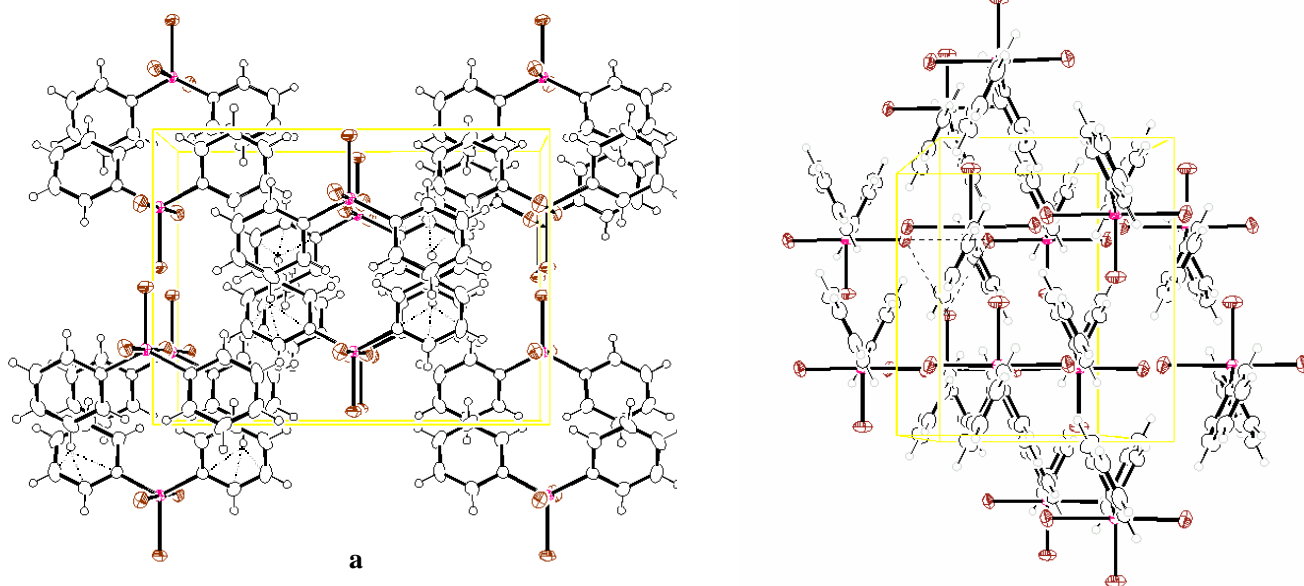
Scheme 2.

Fig. 2. Crystal packing for $AsPh_2Br_3$ viewed a) perpendicular to the (001) plane; b) perpendicular to the (100) plane. Note the C-H...π and the Br...Br contacts (dotted lines).

thane (dried over CaH_2) was treated with 0.32 g (2.0 mmol) of bromine. After stirring for three hours at room temperature, the solvent was evaporated slowly in an inert atmosphere. A syrup remained from which white crystals (m.p. 128°C) separated on standing. The crystals **1** were separated by filtration to leave a yellowish oil **2**. Analysis suggested that the white crystals were $AsPh_2(OH)_2Br$ [Found for **1**: C, 42.15; H, 3.51. Calc. for $C_{12}H_{12}O_2AsBr$: C, 42.01; H 3.53%. Mass spectrum: m/z 324 ($AsPh_2OBr$), 308 ($AsPh_2Br$), 261 ($AsPh_2O_2$), 245 ($AsPh_2O$) 229 ($AsPh_2$) 227 ($AsPh_2$-2H), 154 (Ph_2) and 152 ($AsPh$)]. The yellow oil was identified as $AsPh_2Br$ [Found for **2**: C, 46.03; H, 3.46. Calc. for $C_{12}H_{10}AsBr$: C, 46.34; H 3.89%. MS: 308 ($AsPh_2Br$), 229 ($AsPh_2$) 227 ($AsPh_2$-2H), 154 (Ph_2) and 152 ($AsPh$)].

Reaction of (AsPh₂)₂O with Br₂ in molar ratio 1:2. Bromine (0.64 g, 4.0 mmol) was added slowly *via* a syringe to a solution of 0.950 g (2.0 mmol) of ($AsPh_2$)$_2$O in 25 mL of anhydrous dichloromethane to give an immediate yellow-orange precipitate **3**. The supernatant solution was removed using a cannula and the precipitate washed with small amounts of CH_2Cl_2 (m. pt 110°C). Analysis showed compound **3** to be $AsPh_2Br_3$ [Found: C, 30.96; H, 2.56. Calc. for $C_{12}H_{10}AsBr_3$: C, 30.74; H 2.15%. Mass spectrum: 308 ($AsPh_2Br$), 229 ($AsPh_2$) 227 ($AsPh_2$-2H), 154 (Ph_2) and 152 ($AsPh$)]. Crystals suitable for X-ray diffraction were obtained by slow evaporation of a solution of the compound in dichloromethane. The filtrate was allowed to stand for several days at –20°C to give a crop of white crystals (mp: 128°C). Analysis pointed again to the formation of $AsPh_2(OH)_2Br$ **1** (Found: C, 42.15; H, 3.51. Calc for $C_{12}H_{12}O_2AsBr$: C, 42.01; H 3.53%)

Molecular orbital calculations. Full geometry optimisations have been carried out on three conformers of $AsPh_2Br_3$ (two axial bromines, two axial phenyls and one axial phenyl) at the RHF/3-21G(*) *ab initio* level using Spartan 5.1 [14].

Structure determination for 3. Crystallographic data are summarised in Table 2, which also includes details of the method of solution and the refinement conditions.

Data were corrected for Lorentz and polarisation effects, merged and systematically absent reflections removed; an absorption correction was applied. The structure was solved by direct methods (SHELXS-86 [24]) and refined by full matrix least squares (SHELXL-93 [25]); hydrogen atoms were placed at their calculated positions and refined riding on their respective carbon atoms. A further refinement of their positions has been carried out by using the molecular mechanics module from Spartan. A standard weighting scheme was applied, as was a correction for extinction.

Acknowledgement

Table 2. Crystallographic data.

Chemical formula	$C_{12}H_{10}AsBr_3$
Formula weight	468.85
Crystal size/mm	$0.31 \times 0.26 \times 0.10$
Crystal system	Monoclinic
Space group	$C2/c$
a / Å	14.855(10)
b / Å	11.030(9)
c / Å	8.469(5)
ß / °	98.04(5)
Volume / Å³	1374.0(17)
Z	4
D_c / g cm⁻³	2.266
Radiation (λ / Å)	Mo-K_α (0.71073)
μ / cm⁻¹	111.69
$F(000)$	880
θ /limits / °	2.5-25
Index ranges	$-17 < h < 17$
(for unique data)	$0 < k < 13$
	$-10 < l < 10$
Temperature / K	220(2)
Reflections collected	2404
Independent reflections	1202
R(int)	0.085
Observed reflections	
$[I > 2\sigma(I)]$	918
Absorption correction	Numerical
min /max	0.0843 / 0.327
Structure solution	Direct
Refinement	Full-matrix methods
	least squares on F^2
Data/restraints/variables	1202/8/71
R [$I > 2?(I)$]	0.0423
R_w [$I > 2?(I)$]	0.0909
R (all data)	0.0658
R_w (all data)	0.1038
Goodness of Fit (S)	1.171
Final diff. map (e Å⁻³)	+0.78, -0.64

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