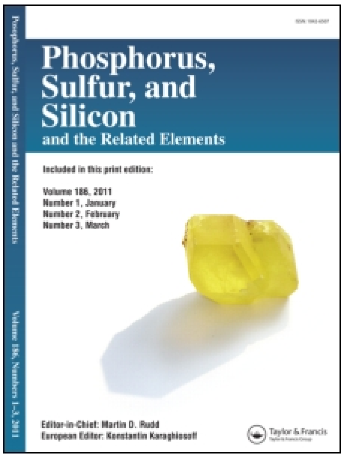

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Studies on the Air Oxidation of Some Arsenic(III) Compounds

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The air oxidation of As(III) oxides [$(PhAsO)_x$ and $Ph_2As\text{-}O\text{-}AsPh_2$] and thioesters [$Ph\text{-}As(SPh)_2$, $Ph_2As\text{-}SPh$ $Me\text{-}As(SPh)_2$, $Me_2As\text{-}SPh$], in chloroform and in methanol was studied. The air oxidation in chloroform was faster probably because the solubility of dioxygen is greater than in methanol, and it is favored by the electron-withdrawing phenyl groups bound to As(III). The products obtained were the arsonic or arsinic acids and diphenyl disulfide. In one case, diphenyl disulfide and thiophenol were produced. The results can be rationalized by assuming first hydrolysis of the As(III) compounds to arsonous or arsinous acids followed by their oxidation to arsonic and arsinic acids, which should involve the binding of dioxygen to As(III). The other hypothesis assumes first the binding of dioxygen to As(III) of these oxides and thioesters followed by the decomposition of the adducts. The binding of the ground state dioxygen to As(III) may have biochemical implications for toxicity or chemotherapy of arsenic(III) compounds.

Keywords Arsine oxides; binding; dioxygen; dithioarsonites; thioarsinites

INTRODUCTION

The air oxidation of As(III) compounds has practical, e.g. storage, and probably biochemical significance. The literature data indicate that the ligands bound to As(III) affect its autoxidation. Thus, alkaline arsenite, "AsO_3^{3-}", was autoxidized at 0.12% per 24 h,[1] while in the presence of sodium sulfite and under proper conditions one molecule of arsenate was produced for every molecule of sulfate formed.[2] Arsenosoalkanes (alkylarsine oxides), $(RAsO)_x$, are oxidized by air, but arsenosoarenes (arylarsine oxides), $(ArAsO)_x$, require stronger oxidizing agents to give arsonic acids.[3] Cacodyl oxide, $Me_2As\text{-}O\text{-}AsMe_2$, in aqueous sulfuric acid is oxidized by air to cacodylic acid,[4] while attempts at the crystallization of $Ph_2As\text{-}O\text{-}AsPh_2$ without the exclusion of air gave diphenylarsinic

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acid (monomeric and dimeric).[5] Basic hydrolysis of Me_2As-SPh gave the cacodylate from the very rapid atmospheric oxidation of the dimethylarsinous acid, Me_2As-OH.[6] Indirect evidence suggests that Ph_2As-OH in methanol is air oxidized back to diphenylarsinic acid during the reduction of this acid with excess ascorbic acid under iodine catalysis.[7]

A study on the air oxidation of aromatic trithioarsenites, $(ArS)_3As$, showed that *para*-substituted phenyl groups with electron-donating groups do not favor autoxidation, while electron-withdrawing groups favor the autoxidation according to Eq. (1):[8]

$$4(ArS)_3As + 3O_2 \rightarrow 2As_2O_3 + 6ArSSAr \tag{1}$$

Likewise, the air oxidation of aliphatic trithioarsenites, $(RS)_3As$, depends on the nature of R. Thus, the esters $(EtS)_3As$, $(n\text{-}PrS)_3As$, and $(n\text{-}BuS)_3As$ are easily oxidized[9,10] [65% oxidation is observed when air is passed through $(n\text{-}BuS)_3As$ for 2 h[10]]. The more polar $As(SCH_2CH_2OH)_3$ is relatively stable to autoxidation.[11] We have found that esters $(RS)_3As$ bearing terminal-COOH groups are autoxidized according to Eq. (1) in a chain-dependent manner; those bearing $—COO^-$ or zwitterionic $—CH(NH_3^+)COO^-$ groups are not autoxidized.[12] From the class of alkyldithioarsonites, $R\text{-}As(SL)_2$ (L = R or Ar), the oily $Et\text{-}As(SEt)_2$, deposited crystalline $Et\text{-}AsO_3H_2$ on contact with air,[13] and the diphenyl allyl- and benzyldithioarsonites, $R\text{-}As(SPh)_2$, formed during the reduction of allyl- and benzylarsonic acid by thiophenol, was decomposed by air to, e.g., As_2O_3, $(PhS)_3As$, $PhCH_2OH$ and PhCH=O, implying a direct binding of dioxygen to As(III).[14] The more polar $Me\text{-}As(SCH_2CH_2OH)_2$ and $Me\text{-}As(Scysteine)_2$ in water are easily autoxidized to $Me\text{-}AsO_3H_2$ and disulfide, RSSR.[15] Thioarsinites are also susceptible to air oxidation. Thus, $Ph_2As\text{-}S\text{-}AsPh_2$ deposited $(Ph_2AsO_2H)_2.2Ph_2As(S)OH$ on attempted recrystallization in air,[16] while Me_2As-(Scysteine) and Me_2As-(Sglutathione) in water were air oxidized to cacodylic acid and disulfides.[15]

In this article, we report exploratory experiments on the air oxidation of the oxygen-bearing **1** and **2** and of sulfur-bearing esters **3–6** in chloroform and in methanol in order to see the effect of the solvent and the nature of the bound to As(III) ligands and to probe on the probable mechanism of the air oxidation of these As(III) compounds.

$(PhAsO)_x$ **1**, $PhAs(SPh)_2$ **3**, $MeAs(SPh)_2$ **5**
$Ph_2As\text{-}O\text{-}AsPh_2$ **2**, Ph_2AsSPh **4**, Me_2AsSPh **6**

RESULTS AND DISCUSSION

Air Oxidation of the Oxygen-Bearing As(III) Compounds 1 and 2

After stirring a chloroform or a methanol solution of **1** in air for 12 days, phenylarsonic acid was not detected by IR, implying that less than 20% oxidation had taken place, according to Eq. (2):

$$2(PhAsO)_x + xO_2 + 2xH_2O \rightarrow 2xPhAsO_3H_2 \tag{2}$$

Cohen and colleagues[17] measured the rate of oxidation of substituted with electron-donating and with electron-withdrawing phenylarsine oxides based on the reaction, Eq. (3):

$$Ar\text{-}AsO_2H^- + RSSR + 2HO^- \rightarrow Ar\text{-}AsO_3H^- + 2RS^- + H_2O \tag{3}$$

Their data are difficult to explain because they do not fall on a straight line when the rates are plotted against Hammett's substituent constant σ.[18] It should be mentioned that the arsonous acid in this system does not add (di)oxygen on the As(III), but acts as a nucleophile, along with the HO^-, on the disulfide.[19]

The oxide **2** was air oxidized, according to Eq. (4), to diphenylarsinic acid faster in chloroform than in methanol (Figure 1). This may be due, in part, to the greater solubility of dioxygen in chloroform ($\sim$20 cm^3/100 mL) than in methanol ($\sim$5 cm^3/100 mL).[20]

$$Ph_2As\text{-}O\text{-}AsPh_2 + O_2 + H_2O \rightarrow 2Ph_2AsO_2H \tag{4}$$

The greater reactivity of **2** compared to **1** for air oxidation in chloroform (this work) and in benzene/pentane[5] is obviously due to the *two* (weak) electron-withdrawing phenyl groups in **2** compared to *one* phenyl group in **1**.

Conceivably, there are two routes for the air oxidation of **2** (Scheme 1). The first, "hydrolysis-oxidation" gives diphenylarsinous acid, which then binds to $^3O_2$ to give the peracid Ph_2AsO_3H, which can oxidize the diphenylarsinous acid, thus producing two molecules of diphenylarsinic acid. The second route is "binding-decomposition." In this, a direct binding of $^3O_2$ to As(III) is assumed, giving a diradical, which rearranges to a zwitterion. The latter, by adding a water molecule, gives a hydroperoxy compound, which collapses into two diphylarsinic acid molecules. This route also rationalizes the air oxidation of $Ph_2As\text{-}S\text{-}AsPh_2$ in MeCN.[16] The low reactivity of **2** dissolved in methanol is difficult to explain. Probably, in methanol, the intramolecularly hydrogen bonded 6-membered intermediate, Scheme 1, is not formed. Our data do not permit a clear selection of a favorable route for the air oxidation of **2**.

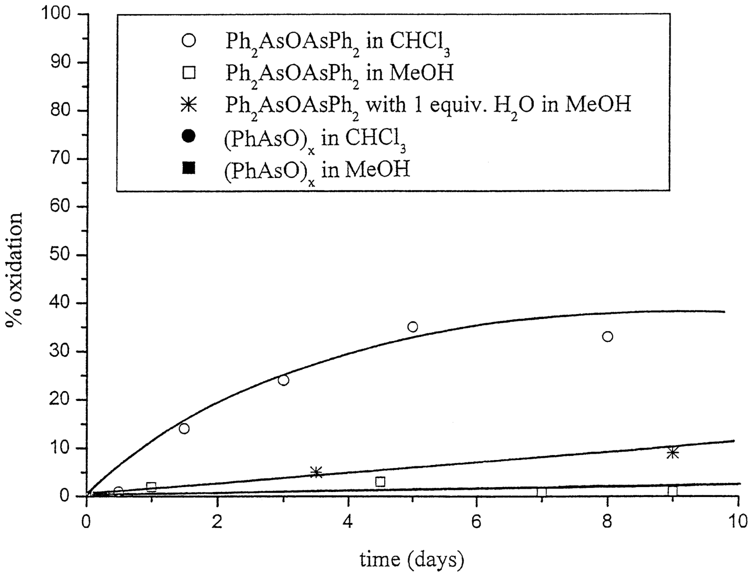
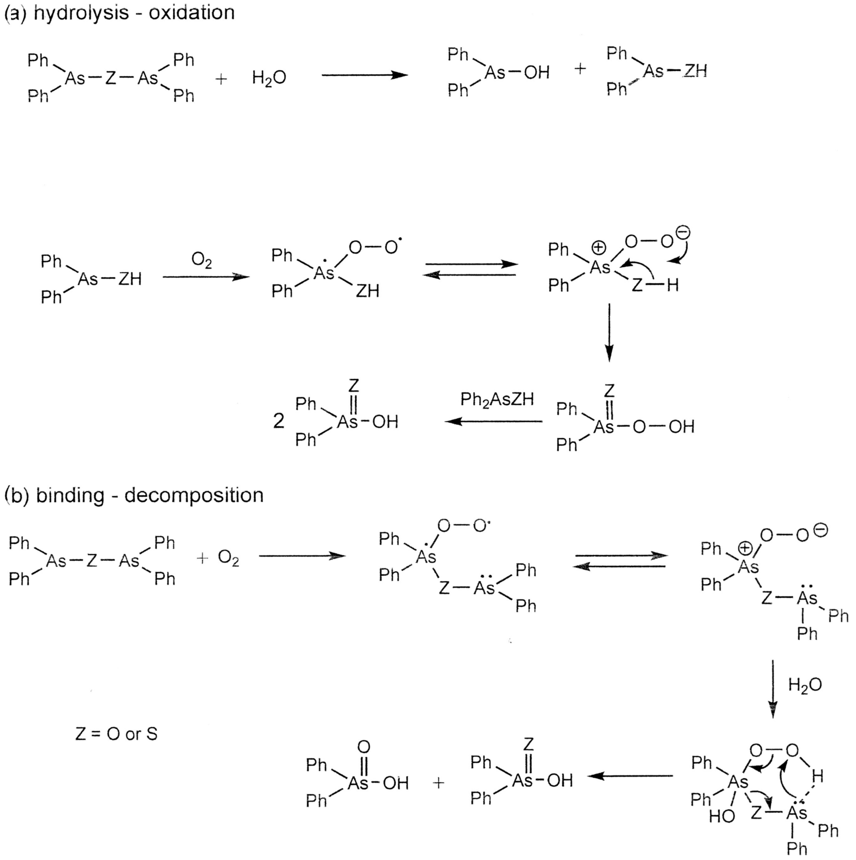


FIGURE 1 Air oxidation of $(PhAsO)_x$, **1** and $Ph_2As\text{-}O\text{-}AsPh_2$, **2** in chloroform and in methanol, and of **2** + H_2O (1:1 mol/mol) in methanol. Phenylarsonic acid, produced from the air oxidation of **1**, was not detected by IR.

While the oxides **1** and **2** in methanol were found to be air oxidized to a very small extent, their hydrated forms (arsonous and arsinous acids) seem to be more easily oxidized by air. Thus, a substituted phenylarsonous acid in water was oxidized to its arsonic acid, and inhibition of the oxidation was observed after acidification or addition of glycine.[21] The protective effect of these reagents is most likely due to a weak hydrogen bond formation with the lone pair of As(III), which can prevent the binding of $^3O_2$ to As(III). The case of air oxidation of diphenylarsinous acid in methanol,[7] mentioned in the introduction, may be due to the fact that upon dioxygen binding, the adduct is converted very easily into a hyperoxy acid, Ph_2AsO_3H, which can oxidize the arsinous acid (Scheme 1), the ascorbic acid, or the hydriodic acid.

Air Oxidation of the Sulfur-Containing As(III) Esters 3–6

Figures 2 and 3 show the air oxidation of the esters **3**–**6** in chloroform and in methanol. Again, the air oxidations were faster in chloroform which, in part, may be attributed to the greater solubility of dioxygen in chloroform.[20] From Figure 2, it can be seen that **4**, having *two* (weak) electron-withdrawing phenyl groups, is air oxidized faster than **3**, which



SCHEME 1

has *one* phenyl group bound to As(III). Conversely, **6**, which has two (weak) electron-donating methyl groups, is air oxidized slower than **5**, which has one methyl group bound to As(III) (Figure 3).

Comparing the pairs **3/5**, and **4/6** (Figures 2 and 3), we see that **3** is air oxidized slightly faster than **5**, while **6** is quite resistant to air oxidation compared not only to **5** but also to **3** and **4**. Thus, it is clear that the nature of the groups bound to As(III) governs its ability to be oxidized by air.

Thiophenol is air oxidized after 12 days to an extent of ~3% in chloroform and <10% in methanol. Therefore, if thiophenol were produced during the oxidation of **3–6**, it could have been detected due to its very slow rate of oxidation to disulfide. The air oxidation of **3** in both chloroform and methanol gave phenylarsonic acid. Phenylarsine oxide, **1**,

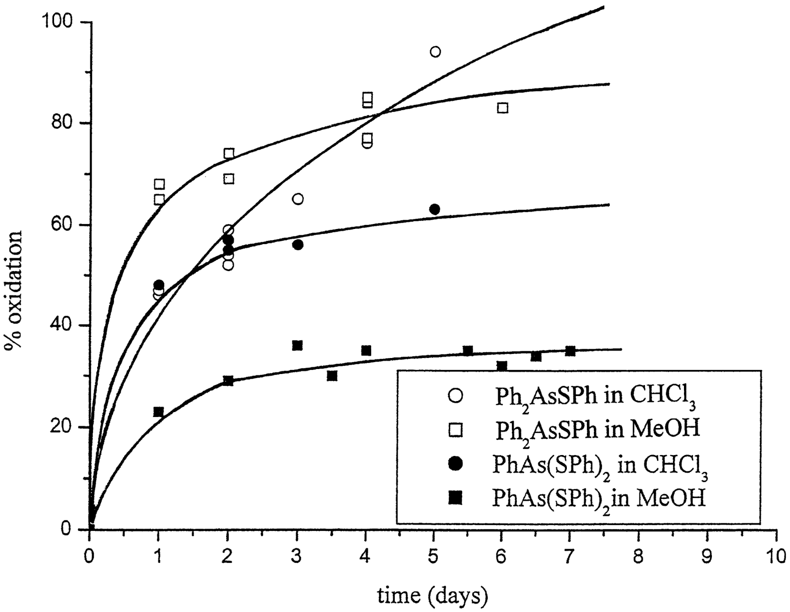


FIGURE 2 Air oxidation of $PhAs(SPh)_2$, **3** and Ph_2AsSPh, **4** in chloroform and in methanol.

was not detected. Thiophenol was not detected, either by smell or by loss of weight, while diphenyl disuslfide was detected by TLC. The air oxidation of **4** in chloroform gave diphenylarsinic acid and diphenyl disulfide, while in methanol, diphenylarsinic acid, disulfide, and small amounts of thiophenol were produced. The presence of diphenyl disulfide did not affect the air oxidation of **5** (Figure 3). Therefore, we studied the air oxidation of equimolar mixtures of **5** and PhSSPh as well as **6** and PhSSPh (simply obtained by the reduction of equivalent amounts of methylarsonic or dimethylarsinic acids and thiophenol in methanol and drying in vacuum). The air oxidation of **5** gave methylarsonic acid while that of **6** gave dimethylarsinic acid.

As in the case of the arsine oxides, there are two routes for the explanation of the data shown in Figures 2 and 3. The first is the "hydrolysis-oxidation," suggested by Cullen and colleagues,[15] which invokes the hydrolysis of the arsenic(III) thioesters to arsonous or arsinous acids and thiol, followed by the oxidation to arsonic or arsinic acids and disulfide. This route probably is not followed during the air oxidation of the esters $(ArS)_3As$[8] and certain $(RS)_3As$,[12] but it must be considered for the air oxidation of **1–6**. It should be noted, however, that this route eventually

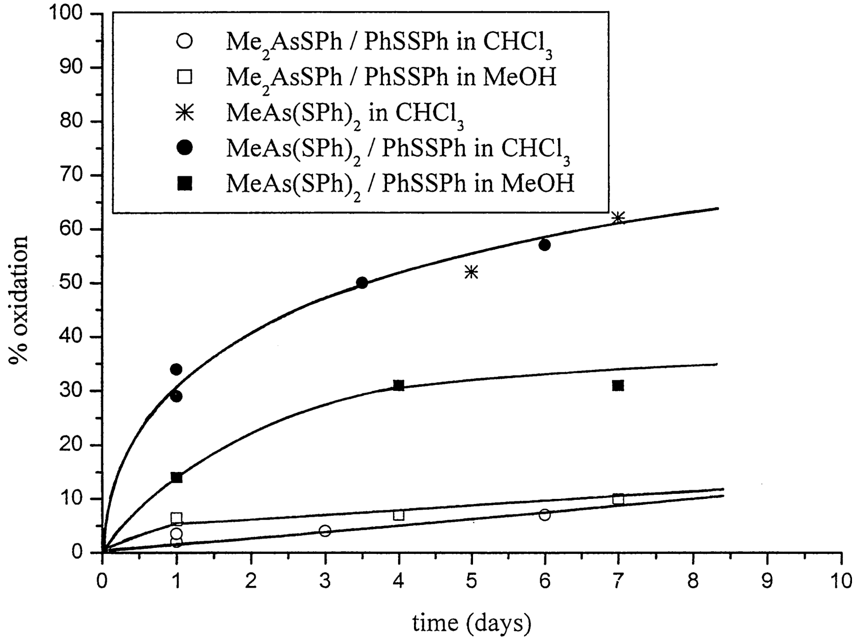


FIGURE 3 Air oxidation of MeAs(SPh)$_2$, **5**, and of equimolar mixtures of **5**/PhSSPh and Me$_2$AsSPh, **6**/PhSSPh in chloroform and in methanol.

requires the binding of dioxygen to arsonous or arsinous acids in order to produce arsonic and arsinic acids. Such a binding will produce diradicals, which will rearrange to the peracids RAsO$_4$H$_2$ and R$_2$AsO$_3$H (see Scheme 1), which can oxidize the thiol to disulfide, which otherwise requires a radical initiator[22] and is fast in nonprotic solvents and takes place faster in alkaline solution.[23] The other route, which can be named "binding-decomposition," assumes the direct binding of dioxygen to As(III) of **3–6** to give a diradical (see Scheme 1) or a zwitterion, As(V)$^+$-O-O$^-$, which can be interconverted via an arsenadioxirane, As(V)(O$_2$).[8] The zwitterion, by addition of one water molecule, can be converted into a hydroperoxy compound, As(V)(OH)(OOH) (see Scheme 1). The diradical from **3** (and **5**) can decompose to the unstable[8] esters of As(V), R-As(O)(SPh)$_2$, which can either be hydrolyzed to R-AsO$_3$H$_2$ and PhSH or by expulsion of PhSSPh to give the oxides (RAsO)$_x$. Since thiophenol, (PhAsO)$_x$ or (MeAsO)$_x$ were not detected, this route may not be followed during the air oxidation of **3** and **5** in chloroform or in methanol. The air oxidation of **4** and **6** in methanol may follow this mechanism because the hydrolysis of the formed Ph$_2$As(O)SPh gives diphenylarsinic acid and thiophenol, both of which were detected along with diphenyl disulfide. Overall, our data do not permit a clear indication on which substrate the dioxygen binds: the arsonous acid, the arsinous acid, or the thioesters **3–6**.

To summarize the air oxidation of **1–6** should involve the binding of $^3O_2$ either to intact **1–6** or their hydrolysis products (arsonous and arsinous acids) producing a diradical. For a diradical to be formed, a transfer of a π^* electron from $^3O_2$ into a contracted,[24] empty, 4d orbital of As(III) is envisioned.[25] It follows, then, that suitable electron-withdrawing groups on As(III) will contract the 4d orbitals to a point that the electron transfer is favorable, while electron-donating groups will have the opposite effect. It seems that a decision on which As(III) compound, i.e., on the intact oxides **1** and **2**, their hydrated forms and esters **3–6**, or their hydrolysis products, dioxygen binds more easily can be resolved only by theoretical calculations.

In spite of the uncertainty on the timing of $^3O_2$ binding on As(III) compounds, the ability of As(III) to bind and activate dioxygen may have implications in chemotherapy[14] or the induction of carcinogenesis[26] because both may involve reactive oxygen species.[27,28] As far as chemotherapy is concerned, this and previous[8,12,14] work from this laboratory indicates that the preparation of As(III) compounds [$(ArS)_3As$/$(RS)_3As$, Ar-As$(SR')_2$/R-As$(SR')_2$, and Ar_2As-SR′/R_2As-SR′] suitable for binding (and activating) $^3O_2$ can be planned.

EXPERIMENTAL

Phenylarsine oxide, **1**, was prepared by the reduction of phenylarsonic acid (Aldrich) with ascorbic acid/iodine.[29] Bis(diphenylarsenic) oxide, **2**, was prepared by the reduction of diphenylarsinic acid[30] with ascorbic acid/iodine,[7] m.p. 91–93°C (lit.[31] 92.5–93.5°C). Diphenyl phenyldithioarsonite, **3**, and diphenyl methyldithioarsonite, **5**, were prepared according to the literature.[32] Methylarsonic acid was prepared by the neutralization of its disodium salt[33] by an equivalent amount of hydrochloric acid and extracting with methanol, m.p. 158–160°C (lit.[34] 160–161°C). Cacodylic acid (dimethylarsinic acid) was from Serva. Equimolar quantities of **5**/PhSSPh and of **6**/PhSSPh were prepared by reducing equivalent quantities of the acids with thiophenol.[32] Silica gel 60 H for thin layer chromatography (TLC) was from Merck.

TLC was run on microslides always using appropriate standards. The spots were made visible by iodine vapors. Melting points were obtained on an Electrothermal model 9100 apparatus. IR spectra were obtained on a Perkin-Elmer model 16PC FT-IR spectrometer.

Preparation of Phenyl Diphenylthioarsinite, 4

To a de-aerated solution of the oxide **2** (142 mg, 0.3 mmol) in methanol (1 mL), thiophenol (65 μl, 0.6 mmol) was added. The product **4** precipitated at once as an oil, which was solidified by cooling at –20°C for 15 min. The solid was broken at r.t., cooled at +4°C for 2 h, centrifuged while cold, washed with methanol (1 mL), cooled at +4°C and centrifuged while cold, to give the product **4** (180 mg, 89%) as a white powder, m.p. 40–42°C (lit.[35] 40°C). IR (KBr): 3062 w, 1576 m, 1476 vs, 1430 s, 1300 w, 1156 w, 1076 s, 1020 s, 996 s, 734 vs, 690 vs.

Air Oxidation of the Oxides 1 and 2

Air Oxidation of 1

Samples of **1** (20.0 mg) dissolved in chloroform or in methanol (3 mL) (40 mM) were stirred in air at r.t., replenishing the solvent from time to time. After a given time, a sample was evaporated giving an oil which was triturated with ether (0.5 ml) in which both **1** and phenylarsonic acid are insoluble. The solid obtained was analysed by IR. Phenylarsonic acid was not detected after 12 days stirring at r.t. Control experiments showed that 20% phenylarsonic acid in **1** (dissolved in methanol, evaporation and drying) can be clearly detected by IR (As=O stretching at 878 cm^{-1}).

Air Oxidation of 2

Samples of **2** (20.0 mg) were dissolved in chloroform or in methanol (3 ml) (14 mM) and stirred at r.t. as in **1**. To the glass obtained, ether (0.5 ml) was added to crystallize the diphenylarsinic acid and to extract the oxide **2**. The ether was syringed off, the solid washed with ether (0.5 ml), dried, weighed and, in the case of chloroform, characterized by m.p. (165–170°C; lit.[30] 174°C) and IR. Results are shown in Figure 1.

Air Oxidation of the Thioesters 3–6

Air Oxidation of 3

Samples of **3** (20–40 mg) were dissolved in chloroform or in methanol (3–6 ml) (18 mM) and stirred in air at r.t. replenishing the solvent from time to time. The smell of thiophenol was not perceptible during the runs. Evaporation and drying in vacuum gave a glass, weighing more than the weighed **3**, implying that thiophenol was not present in the solution. Calculations (based on the phenylarsonic acid isolated in the next step) showed that the weight matched the expected weight from the phenylarsonic acid plus diphenyl disulfide produced. TLC (petroleum ether) showed the presence of PhSSPh. Therefore the gain in weight was due to the formation of phenylarsonic acid. This was verified by extracting the disulfide with boiling ether, leaving a solid which was phenylarsonic acid by m.p. (150–153°C; lit.[34] 158–162°C) and IR. The ether insoluble $(PhAsO)_x$ was not detected by IR. Results are shown in Figure 2.

Air Oxidation of 4

Samples of **4** in chloroform or in methanol (∼20 mM) were air oxidized as in the case of **3**. The smell of thiophenol was not perceptible during the runs. The crude solids obtained after evaporation and drying in vacuum weighed more than the weighed **4**, indicating that diphenylarsinic acid and diphenyl disulfide were the components of the crude solids. However, calculations based on the amounts of the diphenylarsinic acid, isolated in the next step, showed that in methanol, but not in chloroform, thiophenol also was produced. The extraction of the disulfide with boiling ether left diphenylarsinic acid by IR and m.p. (165–169°C; lit.[30] 174°C), from which the percent air oxidation of **4**, shown in Figure 2, was calculated.

Air Oxidation of 5

The experiments were done using either pure **5** or an equimolar mixture of **5** and PhSSPh. The solid obtained was methylarsonic acid by IR and m.p. (155–158°C; lit.[34] 160–161°C). The $(MeAsO)_x$ has an m.p. of 95°C.[36]

Air Oxidation of 6

This air oxidation was done using an equimolar mixture of **6** and PhSSPh. The solid obtained was dimethylarsinic acid (by IR only because of the small amounts of the isolated solid).

Air Oxidation of Thiophenol

A solution of thiophenol (51 μl, 0.5 mmol) in chloroform (3 mL) (0.17 M) was stirred in air for 12 days, replenishing the solvent from time to time. Then a solution of mercuric acetate (80 mg, 0.25 mmol) in methanol (4 mL) was added, and the precipitated mercaptide (86 mg) was centrifuged. The supernatant (16 mg) contained PhSSPh (by TLC), and by extraction with ether gave PhSSPh (2.5 mg) corresponding to ∼3% oxidation of thiophenol. The oxidation in methanol was done similarly, but before the addition of mercuric acetate, the methanol was evaporated and the solid dissolved in chloroform (3 mL). Otherwise most of the mercaptide remains in methanol. A <10% air oxidation of thiophenol in methanol was estimated.

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