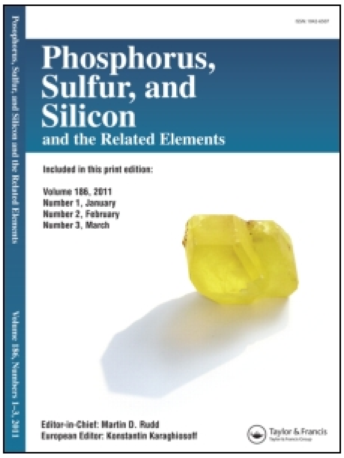

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Theodore D. Sideris[a]; Panayiotis V. Ioannou[a]
[a] Department of Chemistry, University of Patras, Patras, Greece

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Ascorbic Acid/Iodine and Triphenylphosphine/Iodine as Reducing Agents for the As(V)=O Group

Theodore D. Sideris
Panayiotis V. Ioannou
Department of Chemistry, University of Patras, Patras, Greece

The scope of ascorbic acid / iodine and triphenylphosphine / iodine in methanol for the direct reduction of arsenic(V) compounds having the As=O group has been investigated. Ascorbic acid / iodine reduces arsonic acids, diphenylarsinic acid (but not dimethylarsinic acid), and triphenylarsine oxide. The rates of reduction depend on the electronic effects of the ligands bound to arsenic and on the hydrogen-bonding strength of the species, when present. When the As(V) compound has an $-NH_2$ *or an* $-NH_3^+$ *group, the reduction product reacts with a ketonic form of dehydroascorbic acid, giving condensation product(s). Triphenylphosphine / iodine reduced slowly the zwitterionic* o*-aminophenylarsonic acid but reduced faster the hydrochloric acid salt of the same acid. It reduced dimethylarsinic acid as well because the powerful electron-withdrawing* Ph_3P^+ *coordinated to As=O seems to outweigh the electronic and hydrogen bonding effects.*

Keywords Arsinic acids; arsonic acids; ascorbic acid; reductions; triphenylarsine oxide; triphenylphosphine

INTRODUCTION

The reduction of As(V) compounds having the As=O group to As(III) species has analytical, synthetic, and biochemical significance. Thus, arsenic acid can be determined in strongly acidic aqueous media by I^- according to Eqs. (1) and (2):[1]

$$H_3AsO_4 + 2KI + 2HCl \longrightarrow H_3AsO_3 + I_2 + 2KCl + H_2O \qquad (1)$$

$$H_3AsO_3 + 3HCl \rightleftharpoons AsCl_3 + 3H_2O \qquad (2)$$

The system ascorbic acid (AA)/iodide/hydrochloric acid has been used for the reduction of arsenic acid in several kinds of natural waters.[2] Ascorbic acid was used for the "prevention" of the air oxidation of iodide[2]

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Address correspondence to Panayiotis V. Ioannou, University of Patras, Department of Chemistry, Patras, Greece. E-mail: ioannou@chemistry.upatras.gr

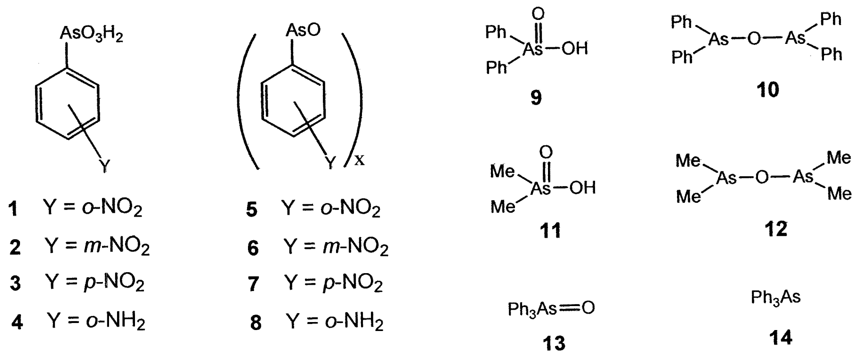
because it reduces iodine to iodide.[3] The I_2 is not only produced by the air oxidation of I^- but also from the reduction of H_3AsO_4 according to Eq. (1). Aiming at the preparation of crystalline dehydro-L-ascorbic acid dimer,[4] AA in methanol has been oxidized by arsenic acid in the presence of a catalytic amount of iodine.[5] In this case the actual reducing agent of arsenic acid is the hydriodic acid, and the iodine produced [Eq. (1)] was reduced by AA. Finally, in a cell, arsenic acid is reduced to arsenous acid by arsenate reductase (E.C. 1.20.4.1).[6] Here the reduction involves thiols and not hydriodic acid.

Arsonic acids, $RAsO_3H_2$, can be reduced to haloarsines, $RAsX_2$, arseno compounds, (RAs)x, or arsines, $RAsH_2$, depending on the reducing agent.[7a] The *direct* reduction of arsonic acids to arsonous acids, $RAs(OH)_2$, or their dehydrated arsenoso compounds (arsine oxides), $(RAsO)_x$, has been achieved in a few cases only (summarized in reference [8]) because the usual reducing system SO_2/I_2/conc. HCl gives the dichloroarsine, $RAsCl_2$, which is then hydrolytically converted into the arsonous acid or arsenoso compound. The use of concentrated hydrochloric acid may be objectionable when an arsonic acid is not stable in it. We have developed a very mild method for the direct reduction of arsonic acids to arsenoso compounds using AA, or triphenylphosphine (TPP), in the presence of a catalytic amount of iodine in methanol,[8] which can be used for hydrophobic or hydrophilic, respectively, arsenoso compounds. C—As bond fission has, so far, been observed only during the reduction of 2-arsonohexanoic acid, which gave As_2O_3 and hexanoic acid.[9]

The reduction of arsinic acids, R_2AsO_2H, can lead to haloarsines, R_2AsX, to bis(dialkyl)diarsines, $R_2As\text{-}AsR_2$, or to arsines, R_2AsH, depending on the reducing agent.[7a] There are no reports in the literature[10a] on the *direct* reduction of arsinic acids to their oxides, $R_2As\text{-}O\text{-}AsR_2$, and the reduction of diphenylarsinic acid by phenylhydrazine gave Ph_3As instead of $Ph_2As\text{-}O\text{-}AsPh_2$.[11] The reduction of arsinic acids, e.g., diphenylarsinic acid,[12] by SO_2/I^-/conc. HCl followed by hydrolysis of the chloroarsines to their oxides also is not common.[10a]

Finally, trialkyl- or triarylarsine oxides, $R_3As{=}O$, have been reduced by SO_2/I^-, $SnCl_2$, or H_3PO_2 to the corresponding arsines, R_3As.[7b]

Wishing to contribute to the mild reduction of arsenic(V) compounds having the As=O group, we report in this article on the use of the AA/iodine and TPP/iodine in methanol for the reduction of aromatic arsonic acids having electron-withdrawing and electron-donating groups, **1–4**, to the oxides **5–8**, of aromatic and aliphatic arsinic acids **9** and **11** to the oxides **10** and **12** and of triphenylarsine oxide, **13**, to triphenylarsine, **14**.



FORMULAE 1–14

RESULTS AND DISCUSSION

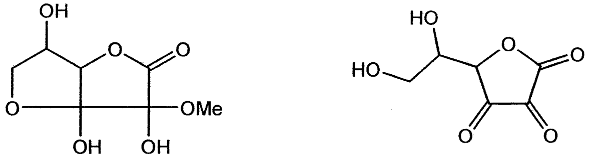
Reduction of Aromatic Arsonic Acids

The reduction of *o*-, *m*-, and *p*-nitrophenylarsonic acids **1–3** by AA/iodine in methanol was smooth. Because we used excess ascorbic acid, the progress of the reduction was checked by TLC by comparing the relative intensities of the spots due to AA and of the dehydroascorbic acid monomer **15**.[4] The lithium hydroxide test[8] did not work well because of the slow precipitation of the lithium salts of these arsonic acids. The rates of the reduction of nitrophenylarsonic acids were $\mathbf{1} \geq \mathbf{2} \gg \mathbf{3}$, and the yields were in the range of 50–90%. The rate of reduction of phenylarsonic acid was faster than the nitrophenylarsonic acids, and the yields of phenylarsine oxide, by the water extraction method, were ~80%.[8]

For the reduction of arsonic acids by HI, we postulated that protonation of the As=O (in these and, in fact, in all compounds containing the As=O group) must *precede* their reduction.[8] Then the $As(V)^+$ atom has a vacant site for entry of the soft I^-. Water elimination, protonation by another HI, and expulsion of I_2 will give the As(III) compound. This hypothesis is in accordance with the rates of reduction of phenyl-, nitrophenyl-, and aminophenylarsonic acids because the easier the protonation the faster the reduction will be. In *water*, the ionization constants of the nitrophenylarsonic acids are[13] $\mathbf{3} \cong \mathbf{2} > \mathbf{1}$ (the much lower ionization constant of the *ortho* acid is attributed to the "ortho effect,"[7c] i.e., intramolecular hydrogen bonding). In methanol, these acids will be less ionized and the protonation of the As=O group will be governed by the position of the electron-withdrawing nitro group on the phenyl group $\mathbf{1} > \mathbf{2} \cong \mathbf{3}$. The rates of reduction that we observed closely follow this order, and therefore, the protonation must be a contributing factor.

The next step is the addition of I^- in the positively charged tetracoordinated $As(V)^+$. The nitro groups at the *ortho*, *meta*, and *para* positions, through their canonical structures, can and do affect the rate of the I^- entry into $-As(OH)_3^+$, so the rates of reduction are **1** $\geq$ **2** $\gg$ **3**.

When an arsonic acid is reduced, the product can be either the arsonous acid, $R—As(OH)_2$, or its dehydrated form: arsenoso compound (arsine oxide), $(RAsO)_x$. The reduction of nitrophenylarsonic acids by SO_2/I^-/conc. HCl gave, after hydrolysis of the dichloroarsine, both the arsonous acids and the oxides.[10b] The AA/iodine reduction of the nitrophenylarsonic acids **1–3** in methanol most likely gave in solution the arsonous acids, $Ar\text{-}As(OH)_2$, but the products isolated were the arsine oxides **5–7** as evidenced by their colors,[14,15] elemental analyses and IR spectra in KBr. The As—O—As asymmetric and symmetric stretching vibrations of arsine oxides, (ArAsO)x, are expected in the region of 750–700 cm^{-1} based on the strong bands of (PhAsO)x found at 742 and 721 cm^{-1}.[8]



15 **16**

FORMULAE 15 and 16

We isolated two oxides **5**, a yellow (50%) and a pale yellow (95%) oxide, free of water and **1** (by elemental analyses and IR spectra: absence of As=O stretching[16] at 910 cm^{-1}). Both decomposed above 230°C[14] (the melting points of oxides have little value as a criterion of purity for they can be mixtures [17] of cyclic, oligomeric, and polymeric $(RAsO)_x$), but they had different IR (KBr) spectra. The yellow had one strong, somewhat broad band at 732 cm^{-1}, while the pale yellow oxide had three sharp bands at 732 (m), 798 (mw), and 636 (s). These bands were also seen in Nujol. The bands at 732 and 798 were also found in **1** being assigned[16] to $\omega(CH)_{arom}$. and to asymmetric As-OH vibrations. At the moment, the different color and IR spectra of the two oxides, **5**, cannot be explained.

The reduction of **2** with SO_2/I^-/conc. HCl followed by alkaline hydrolysis of the dichloroarsine gave the arsonous acid, $Ar—As(OH)_2$, based on the elemental analysis.[14] Neither the exact melting point nor color was reported. A melting point of 147–151°C was stated by Hiratuka.[18] Later, Morgan and colleagues[15] found that the alkaline hydrolysis of the dichloroarsine gave, by autoxidation-reduction, the acid **2** and the yellow 3,3′-diarsonoazoxybenzene, and therefore, they reduced **2** in boiling 5 N H_2SO_4 with SO_2/I^- and obtained the oxide **6** as a white solid after recrystallizations from ethanol and acetone in 72% yield with a melting point of 184.5–187.5°C. The reduction of **2** with AA/iodine in methanol gave the very pale yellow oxide **6** based on the elemental analysis. The IR (KBr) spectra of various preparations of **6** consistently showed a strong, somewhat broad band at 732 cm^{-1} covering the sharp, medium 732 cm^{-1} band of **2**, but their melting points were neither consistent nor sharp: They started darkening from ~70°C, then formed a red granule which, decomposed (swelled) at 107, 140, 168, or 185°C. Also, our oxides **6** were very soluble in MeOH and Me_2CO and moderately soluble in $CHCl_3$. All these data most likely indicate that the oxides **6** we isolated were mixtures of various oligomeric and polymeric entities.

The reduction of **3** with SO_2/I^-/conc. HCl[10b] gave the *yellow* arsonous acid, Ar—$As(OH)_2$, after the alkaline hydrolysis of the intermediate dichloroarsine, with a melting point of 234°C.[18] Doak and colleagues,[14] however, under apparently the same conditions as previously mentioned, obtained the *white* oxide **7**. The reduction of **3** with AA/iodine gave, by elemental analysis, the oxide **7** (45–55%) as an off-white powder, which changed color at 236°C and decomposed at 244°C. Its IR (KBr) spectrum showed a very strong, narrow band at 742 cm^{-1} (which contained the $\omega(CH)_{ar.}$ band[16]) flanked by two strong bands at 782 and 712 cm^{-1}.

The reduction of **4** in its zwitterionic form by stoichiometric amounts of either AA or TPP in the presence of ~10 mol% I_2 was a slow process (~48 h for the consumption of AA or TPP by TLC analyses). Evidently, the protonation[8] of the $-AsO_3H^-$ group to $-As^+(OH)_3$ or $-As^+(OH)_2(OP^+Ph_3)$ was difficult. When the zwitterionic **4** was converted into its hydrochloride, the reductions were fast: 1 h for AA and <3 h for TPP using 5 mol% I_2. Thus, the electron-withdrawing *ortho* $-NH_3^+$ group facilitated the reduction $-AsO_3H_2 \rightarrow -As(OH)_2$ in a manner analogous to *ortho* $-NO_2$ group.

The reduction of the zwitterionic *o*-aminophenylarsonic acid **4** or its hydrochloride by AA/iodine gave a small amount of **15** implying that a small amount of **8** was formed. A less hydrophilic compound running just above **15** was isolated chromatographically. Its IR spectrum showed a γ-lactone (at 1792 cm^{-1}) and an O—As—O band (at 756 cm^{-1}), and the complex ^1H NMR spectrum showed both aromatic (6.5–8.0 ppm) and aliphatic (3.5–5.0 ppm) hydrogens and very small amounts of ethyl acetate and diethyl ether. Most likely, it is a condensation product of *cyclo*-**8** and one of the forms[4,5] of dehydroascorbic acid **16** probably forming a Schiff base. Pecherer[19] reported that dehydroascorbic acid dimer[4] or **15** reacted with $-NH_2/-NH_3^+$ containing compounds like amides and amino acids etc, giving colored products, a behavior resembling that of ninhydrin.

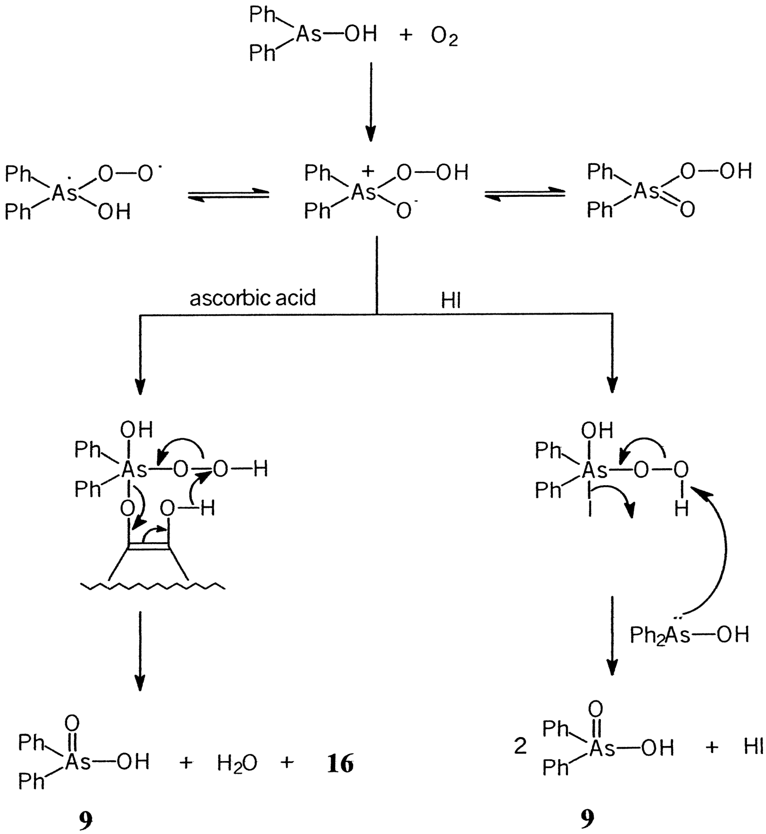
The reaction of the hydrochloride of **4** and TPP/I_2 gave the protonated **8**, which was separated from TPP oxide and excess TPP by extraction in water. After neutralization, **8** precipitated as a gum, which on prolonged cooling, was transformed to an off-white solid. Its melting point was not sharp, resembling the behavior of the *meta*-isomer[14] but not of the *para*-isomer. The latter had a sharp melting point (56–58°C) but the elemental analysis and its empirical formula cited are strange.[20] The IR spectrum of **8** showed a very strong band at 750 cm^{-1} and strong bands at 721, 690, and 629 cm^{-1}.

Summarizing, the rates of reduction of aromatic arsonic acids by AA/iodine and TPP/iodine depend on the nature and the position of the substituent on the aromatic ring. The ease of the protonation of the As=O oxygen and the electronic effects of the aromatic ligand that affect the degree of the positive character of arsenic(V) in $-As^+(OH)_3$ or $-As^+(OH)_2(OP^+Ph_3)$ determine the rate of I^- addition to $As(V)^+$ and therefore its reduction. An arsonic acid having an $-NH_2$ or $-NH_3^+$ group is reduced by both AA/I_2 and TPP/I_2, but with AA, condensation between the $-NH_2/-NH_3^+$ group and dehydroascorbic acid takes place.

Reduction of Arsinic Acids and Triphenylarsine Oxide

The reduction of diphenylarsinic acid **9**/AA/iodine with a 1:1:0.15 molar ratio in nonde-aerated methanol consumed all AA (TLC analysis) but various amounts of **9** were recovered. With a molar ratio of 1:1.5:0.15, all AA had reacted in 16 h, but 18% oxide **10** and 51% acid **9** were isolated. However, with a molar ratio of 1:1.5:0.15 in de-aerated methanol, 55–60% oxide **10** and only ~10% acid **9** were isolated. Finally, with a molar ratio of 1:1.5:0.3 in methanol under reflux for 4 h, ~70% oxide **10** and 8% acid **9** were isolated. These results indicate that diphenylarsinic acid, **9**, is reduced by the mild[8] reducing system AA/iodine much slower than the phenylarsonic acid.[8] Because pure oxide **10** in methanol is not appreciably oxidized by air[32], it seemed that the consumption of the AA by air was *catalyzed* by the oxide. However, control experiments (AA alone, AA + 5% wt/wt **9**, and AA + 5% wt/wt **10**, in methanol at r.t.) showed that **15** was not formed after 48 h of stirring in air. These results leave the precursor of **10**, Ph_2As-OH, as a probable catalyst for the oxidation of AA and regenation of **9** as shown in Scheme 1.

The binding of dioxygen to Ph_2As-OH converts it to a peroxyarsinic acid, Ph_2AsO_3H. Peracids, e.g., peroxyphenylarsonic acid, $PhAsO_4H_2$,



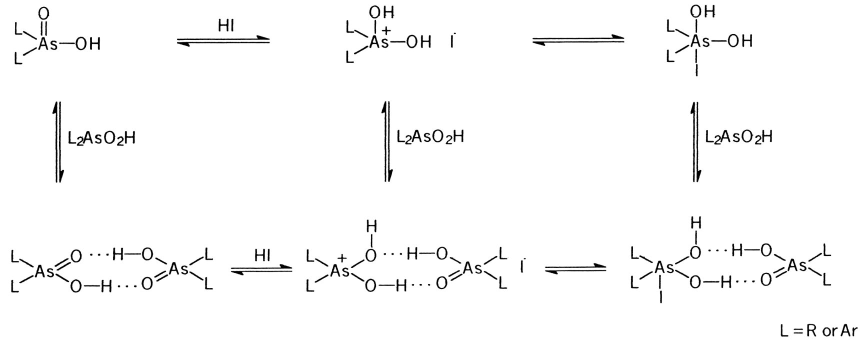
SCHEME 1

have been postulated as intermediates in the arsonic-acid catalyzed epoxidation of olefins by hydrogen peroxide.[21] Then the peracid can react with either AA or HI or both, giving the observed results.

The system **11**/AA/iodine (1:1:0.15 molar ratio) in nonde-aerated methanol did not produce any **15**, and therefore, the oxide **12** was not produced. With a 1:1:0.3 molar ratio, the reduction of cacodylic acid was very slow, consuming ~50% of the AA after 24 h stirring at r.t. (TLC analysis).

The stronger[8] reducing system TPP/iodine reduced both **9** (1:1:0.05 molar ratio) in ~1 h and **11** (1:1:0.05 molar ratio) in 3 h as evidenced by the consumption of TPP (TLC analysis). No attempts were made to isolate the oxide **10** from the lipophilic TPP oxide, while we were unable to separate the oxide **12** from TPP oxide.

The moderate reactivity of diphenylarsinic acid, **9**, and the unreactivity of dimethylarsinic acid (cacodylic acid), **11**, towards AA/iodine can be explained as follows. This reducing system generates HI, which can form an adduct with arsinic acids, $L_2AsO_2H{\cdot}HI$. Such an adduct has been postulated in the extraction of HI by di-*n*-octylarsinic acid and the adduct $Me_2AsO_2H{\cdot}HCl$ has been prepared.[22] In our case, the actual structure of the adduct under a limited amount of HI in methanol (which has a moderate dielectric constant) may be dimeric and not monomeric[22] (Scheme 2).

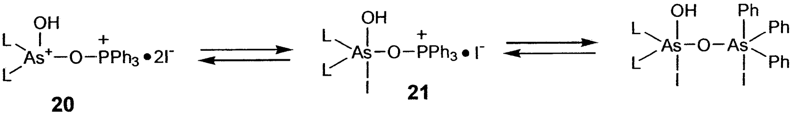


17 **18** **19**

SCHEME 2

Evidence of the hydrogen-bonded species shown in Scheme 2 comes from the observations that arsinic acids are strongly hydrogen bonded **17**,[23] attempts to crystallize the oxide **10** in air and gave, after oxidative hydrolysis, diphenylarsinic acid, **9**, and its dimer **17**,[24] the sulfide Ph_2 As-S-AsPh_2, likewise, gave a hydrogen bonded dimer $(Ph_2AsO_2H)_2{\cdot}2Ph_2As(S)OH$,[25] and attempts at the preparation of the triethylammonium salts of dimethyl- and diphenylarsinic acids in methanol gave after evaporation and drying the free acids and not their salts (this work). Assuming that protonation of the As=O group has taken place (Scheme 2) there are two factors that will determine the outcome of the reduction. The first factor is the addition of I^- to the tetracoordinated $As(V)^+$, which will be favored by the two (weakly) electron-withdrawing phenyl groups, compared to two (weakly) electrondonating methyl groups because they will make the $As(V)^+$ more positive and willing to accept the soft I^-. The second factor is the expulsion of a H_2O molecule from the hydrogen-bonded species **19** to give $L_2As(O)I$ en route to $L_2As(O)I_2$,[8,26] which may be difficult unless the hydrogen bonding breaks down, e.g., by refluxing, as was found.

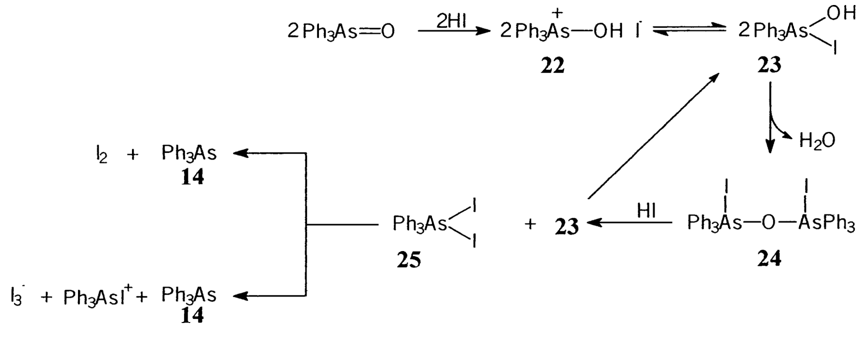
The high reactivity of **9** and the low reactivity of **11** towards the stronger[8] reducing system TPP/iodine can be explained as follows. With this system, "protonation" is achieved by Ph_3P^+-OMe[8] as shown in Eq. (3):



(3)

The Ph_3P^+-group in **20** and **21**, being more electron-withdrawing than the –H, probably disrupts the hydrogen-bonding system analogous to **18** and **19** in Scheme 2 and by outweighing the electron-donating ability of the two methyl groups in cacodylic acid allows the formation of **21**. The expulsion of $Ph_3P{=}O$ gives the $L_2As^+(OH)I{\cdot}I^-$ or $L_2As(OH)I_2$, which is easily converted into oxides **10** and **12**.

Triphenylarsine oxide, **13**, in methanol was reduced by AA/iodine to triphenylarsine, **14**, which precipitated out in 45–50% yields after a 2-hour reaction. No effort was made to optimize the reaction. A probable mechanism for this reduction is shown in Scheme 3. The $Ph_3AsO{\cdot}HI$ adduct may exist as tetra- and pentacoordinated species **22** and **23**.[7d] The intramolecular dehydration of **23** should give **24**, which on further reaction with HI gives **23** and **25**. The latter is a well known[7e] compound and by the expulsion of I_2 or via disproportionation[7e] to Ph_3As and Ph_3AsI^+ and I_3^- gives the product Ph_3As, **14**.



SCHEME 3

To summarize, the direct reduction of arsinic acids by HI, generated by AA and catalytic amount of I_2, involves two key steps: the protonation of the As=O group and entry of the soft Lewis base I^- to the tetra-coordinated $As(V)^+$. The feasibility of both steps depends on the electronic effects of the alkyl or aryl groups bound to the As=O group. Because arsinic acids have the tendency to dimerize in the solid state and probably in solvents with moderate to low dielectric constants, another step should be considered: that of the expulsion of water from a hydrogen-bonded >As(OH)$_2$I. The powerful electron-withdrawing nature of the Ph_3P^+ group seems to outweigh these electronic and hydrogen bonding effects in the reduction of arsinic acids by TPP/iodine in methanol. Triphenylarsine oxide, having three weak electron-withdrawing groups, was easily reduced by AA/iodine.

EXPERIMENTAL

Dimethylarsinic acid (cacodylic acid) was from Serva, while diphenylarsinic acid was prepared in a ~60% yield from triphenylarsine oxide (Aldrich) and sodium hydroxide according to Horner and colleagues,[27] m.p. 173°C [lit.[27] 174°C]. 2-Nitrophenylarsonic and 2-aminophenylarsonic acids were from Aldrich, while 3-nitrophenylarsonic acid (m.p. 177–180°C dec.; lit.[28] 182°C) and 4-nitrophenylarsonic acid (m.p. 300°C dec.; lit.[28] 300°C dec.) were prepared according to Ruddy and colleagues.[28] Ascorbic acid was from Merck. Silica gel 60 H for TLC was from Merck, while silica gel Si60 for column chromatography was from Serva. AR grade solvents and solutions were de-aerated by boiling, flushing with nitrogen, stoppering, and cooling to r.t. TLC was run on microslides. The spots were made visible by iodine vapors and in the case of ascorbic acid and **15** by spraying with 35% sulfuric acid and charring. IR spectra were obtained on a Perkin-Elmer model 16PC FT-IR spectrometer. Elemental analyses were obtained through the Centre of Instrumental Analyses, University of Patras, Patras, Greece.

Reductions with Ascorbic Acid/Iodine

2-Nitrophenylarsonic Acid, 1

To a yellow solution of 2-nitrophenylarsonic acid, **1**, (247 mg, 1 mmol) and ascorbic acid (246 mg, 1.5 mmol) in methanol (4 mL), iodine (13 mg, 0.05 mmol) was added and stirred at r.t. for 90 min. TLC (ethyl acetate) showed the presence of ascorbic acid (R_f 0.38 streaks) and **15** (R_f 0.61). The concentration and addition of water (4 mL) precipitated the product **5** as a yellow solid. Centrifugation and washing with water (3 × 1 mL) and methanol (1 × 2 mL) gave the 2-nitrophenylarsenoxide, **5**, (185 mg, 87%) as a *very pale* yellow powder. M.p. 240–245°C shrinks, 247°C dec. It is insoluble in MeOH, Me_2CO, and $CHCl_3$. Calculated for $C_6H_4NO_3As$ (M_r 213.02): C, 33.83; H, 1.89; N, 6.58%; found: C, 33.62; H, 1.99; N, 6.26%. IR (KBr): 3404 w, broad, 3062 w, 1596 w, 1564 w, 1525 vs, 1454 w, 1338 vs, 1308 m, 1106 m, 856 mw, 796 s, 732 s, 706 m, 634 vs, 590 m.

The reduction of **1** (1 mmol) as previously mentioned gave after evaporating and drying in vacuo an orange foam. The addition of chloroform (15 mL) was followed by the extraction of **15** and AA with water (1 × 10, 3 × 5 mL). An off-white solid was noticed at the interface, which was discarded. The yellow chloroform layer was dried (Na_2SO_4), filtered, evaporated, and dried to give the product, **5** (111 mg, 52%) as a *yellow* powder, insoluble in $CHCl_3$, Me_2CO, and MeOH. M.p.: from 135°C starts darkening, at 225°C forms a dark red granule, and from 230°C melts slowly. Calculated for $C_6H_4NO_3As$ (M_r 213.02): C, 33.83; H, 1.89; N, 6.58%; found: C, 33.67; H, 1.92; N 6.37%. IR (KBr): 3428 w, broad, 1596 w, 1520 vs, 1338 vs, 1308 w, 1104 m, 856 w, 792 m, 734 vs, 650 w, 550 w.

3-Nitrophenylarsonic Acid, 2

Reduced at 1 mmol scale and worked up after 4 h, as in the case of **1**. Concentration of the methanolic solution gave a dark red oil which was extracted with water to give 170 mg, 63%, of a very pale yellow powder. M.p: from 66°C shrinks and darkens, at 82°C forms an orange granule which from 92°C swells and until 114°C decomposes (lit.[15] 184.5–187.5°C for the recrystallized solid from ethanol and acetone **6**). It is very soluble in MeOH, soluble in Me_2CO, moderately soluble in $CHCl_3$, and insoluble in Et_2O, H_2O. Calculated for $C_6H_4NO_3As$ (M_r 213.02): C, 33.83; H, 1.89; N, 6.58%; found: C, 33.63; H, 1.97; N, 6.82%. IR (KBr): 3444 w, broad, 3076 w, 2843 vw, 1600 w, 1522 vs, 1346 vs, 1274 w, 1084 w, 1014 w, 868 w, 810 m, 732 vs, 674 m, 648 m, 566 w.

4-Nitrophenylarsonic Acid, 3

Reduced at 1 mmol scale as in the case of 3-nitrophenylarsonic acid. After 24 h work up gave the oxide **7** as an off white powder (55% yield). M.p. 236°C shrinks and turns red, 244°C dec. (swells). It is insoluble in MeOH, Me_2CO, and $CHCl_3$. Calculated for $C_6H_4NO_3As$ (M_r 213.02): C, 33.83; H, 1.89; N 6.58%; found: C, 33.98; H, 1.93; N 6.15%. IR (KBr): 3444 mw, broad, 1596 w, 1508 vs, 1348 vs, 1312 w, 1280 w, 1104 w, 1072 w, 1012 w, 850 m, 782 s, 742 vs, 712 s, 686 m, 536 w.

Diphenylarsinic Acid, 9

To a de-aerated solution of diphenylarsinic acid, **9** (262 mg, 1 mmol) and ascorbic acid (264 mg, 1.5 mmol) in methanol (5 mL), iodine (38 mg, 15 mol %) was added, and the solution was stirred at r.t. for 24 h. Evaporation gave a yellowish oil, which was dissolved in chloroform (20 mL), washed with water (4 × 5 mL), dried (Na_2SO_4), and evaporated to give a semisolid (290 mg; expected oxide **10**: 237 mg). Extraction with boiling petroleum ether (2 × 5 mL) left impure diphenylarsinic acid, **9**, (28 mg, m.p. 168–170°C; 11% recovery). The extracts were concentrated to ~1.5 mL and cooled at −20°C overnight to give the oxide **10** (139 mg, 59%) as a white solid, m.p. 91–93°C (lit.[29] 92.5– 93.5°C; lit.[12] 91–92°C). IR (KBr): 3454 w, 3052 vw, 1576 vw, 1476 w, 1432 m, 1074 w, 1022 w, 996 w, 736 vs, 694 vs, 550 mw.

In nonde-aerated methanol using 15 mol % iodine, ascorbic acid was completely consumed in 3 days. Yield of **10**: 56%; recovered **9**: 10%.

Triphenylarsine Oxide, 13

In a centrifuge tube, triphenylarsine oxide, **13**, (161 mg, 0.5 mmol) and ascorbic acid (132 mg, 0.75 mmol) were dissolved in de-aerated methanol (2 mL), and iodine (20 mg, 15 mol %) was added. Stirring at r.t. for 2 h gave the solid product (sometimes an oil was obtained, but seeding gave the solid product). TLC (AcOEt) of the supernatant showed that most ascorbic acid had reacted. Centrifugation and washing with water (1 × 1 mL) and methanol (2 × 0.5 mL) gave the product **14** (70 mg, 46%), m.p. 58–61°C (lit.[30] 61°C; lit.[31] 59–60°C), having the same IR (KBr) with an authentic sample of **14**.

Reductions with Triphenylphosphine/Iodine

Hydrochloric Acid Salt of 2-Aminophenylarsonic Acid, 4

2-aminophenylarsonic acid, **4**, (217 mg, 1 mmol) dissolved in methanol (3 mL) was acidified to pH ~2 with concentrated aqueous hydrochloric acid, evaporated, and dried in vacuum over phosphorus pentoxide to give a beige-white solid (272 mg; expected 253 mg). The solid was dissolved in methanol (5 mL), triphenylphosphine (334 mg, 1.2 mmol) and iodine (13 mg, 5 mol %) were added and stirred at r.t. for 8 h. TLC (Et_2O) showed the excess Ph_3P (R_f ~1), $Ph_3P{=}O$ (R_f 0.15), and spots at R_f 0.08 and 0.0. Evaporation gave a light orange gummy oil, which was treated with warm water (2 × 3 mL), cooled to r.t., and filtered (Pasteur pipette plugged with cotton). The insoluble solid was 388 mg (expected 350 mg Ph_3P and $Ph_3P{=}O$). To the clear aqueous filtrate concentrated aqueous ammonia was added with stirring till pH 8. The sticky white gum, which precipitated, was transformed to a hard solid on cooling at +4°C overnight. It was broken with a spatula and centrifuged, and the powder washed with water (1 × 1 mL), centrifuged, and dried over phosphorus pentoxide to give the oxide **8** (110 mg, 60%) as a white powder. It is slightly soluble in $CHCl_3$, moderately soluble in Me_2CO, soluble in MeOH, DMSO, and insoluble in Et_2O. M.p. at 69°C forms a granule and at >90°C swells. Calculated for C_6H_6NOAs (M_r 183.04): C, 39.37; H, 3.31; N 7.65%; found: C, 39.15; H, 3.39; N 7.41%. IR (KBr): 3410 m, 3324 m, 3205 m, 3055 w, 1618 ms, 1586 ms, 1476 ms, 1438 vs, 1308 m, 1158 w, 1116 m, 896 w, 865 w, 750 vs, 722 s, 690 s, 629 ms, 540 w, 506 w.

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