Journal of Organometallic Chemistry, 81 (1974) 49—57
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PREPARATIVE ELECTROCHEMISTRY OF $Ph_3AsOHClO_4$, $(Ph_3AsO)_2HClO_4$, $Ph_3AsOHCl$ AND Ph_3AsOBF_3 BY ANODIC OXIDATION OF TRIPHENYLARSINE

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(Received May 13th, 1974)

Summary

The electrochemical oxidation of triphenylarsine in wet acetonitrile at platinum electrodes is suggested as a procedure for preparing some triphenylarsine oxide derivatives and the anodic behaviour of Ph_3As in presence of suitable substrates (perchlorates, chlorides and tetrafluoborates) is described

Hydroxytriphenylarsonium chloride is formed in a chemical reaction involving triphenylarsine and chlorine radicals produced anodically while in the other cases Ph_3As is directly oxidized at the platinum surface In all processes an hydrolysis reaction due to the wetness of the solvent is also involved.

To account for Ph_3AsOBF_3 formation, elimination of hydrogen fluoride from hydroxytriphenylarsonium tetrafluoborate is suggested. $(Ph_3AsO)_2HClO_4$ is obtained by a partial reduction of $Ph_3AsOHClO_4$ formed in the anodic process involving Ph_3As when perchlorates are used as supporting electrolytes.

Introduction

Triphenylarsine oxide derivatives are usually prepared both by the reaction of the appropriate acid with the arsine oxide or dihydroxide and by partial hydrolysis of the dihalides and subsequent reaction with the appropriate silver salt [1]. Both cases require a preliminary oxidation of triphenylarsine (Ph_3As), either by hydrogen peroxide or potassium permanganate to obtain the oxide (Ph_3AsO), or by halogens to obtain the dihalides (Ph_3AsX_2). In this report we describe a simpler procedure, namely the electrochemical oxidation of Ph_3As in wet acetonitrile in presence of suitable reagents.

The cation $(Ph_3AsO)_2H^+$, containing a very short hydrogen bond, has been recently identified [2] and in a previous paper [3] we have shown its participation in an acid—base equilibrium together with the hydroxytriphenylarsonium cation (Ph_3AsOH^+), the acid dissociation of which takes place in two steps.

It has been reported [4] that the chloride of Ph_3AsOH^+ is a weak electrolyte in acetonitrile solution while the perchlorate, in the same solvent, is an ionic compound, although in the solid state its ionic character is almost lost, as indicated by the observed lowering of the perchlorate ion symmetry.

Ph_3AsOBF_3 has been obtained in unsuccessful attempts to prepare $Ph_3AsOHBF_4$ [4]; a loss of hydrogen fluoride is claimed to account for its formation.

The electrochemical behaviour of the compounds cited is also investigated both to provide an identification tool and to elucidate some aspects of the acid—base equilibria involving triphenylarsine oxide.

Results and discussion

Perchlorate as supporting electrolyte

Figure 1 shows a typical cyclic voltammetric curve exhibited from a solution of Ph_3As in wet (10^{-1} *M* H_2O) acetonitrile. Only a single anodic peak (1) at +1.25 V can be observed while on the reverse scan three cathodic peaks (2, 3, 4), at —0.30 V, —0.95 V and —1.29 V respectively, appeared when only peak 1 is traversed. The ill-defined anodic peaks 5, 6 and 7 may be attributed to the oxidation of the products of peaks 4, 3 and 2 respectively. The height of peak 1 was linearly concentration-dependent

By comparison with solutions of H^+ and H_2 in acetonitrile [5], peaks 2 and 7 were identified as corresponding to the reduction of H^+ and the oxidation of H_2 respectively.

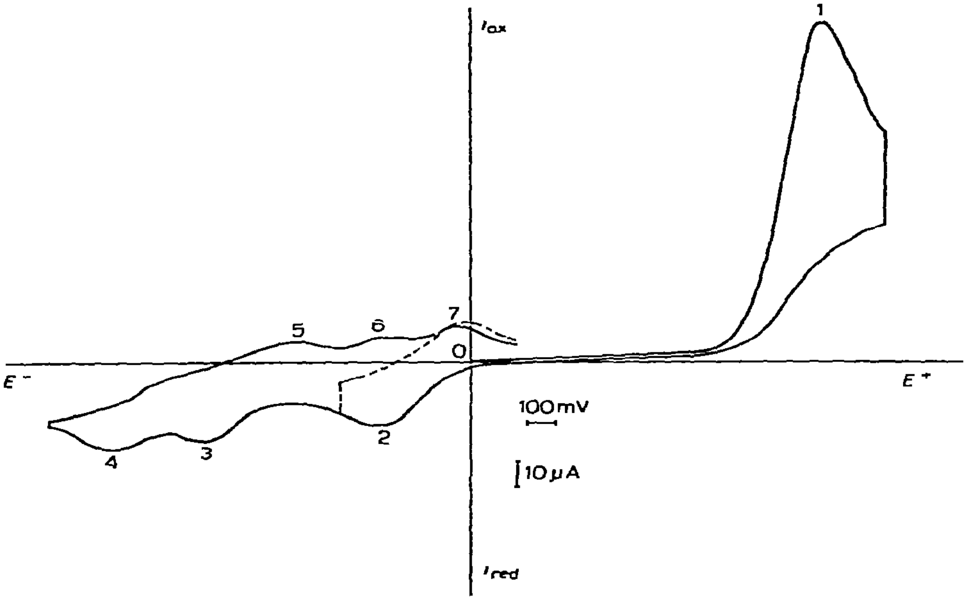

Fig 1 Cyclic voltammetric curves with platinum electrode in a 2 3 × 10^{-3} *M* Ph_3As, 0 1 *M* $NaClO_4$, CH_3CN solution Scan rate 0 2 V s^{-1}

Also in peaks 3 and 4 hydrogen is involved as a product of the reduction processes. This was checked by carrying out cyclic voltammetric tests on an acid solution of Ph_3AsO. Furthermore, peaks 5 and 6 were exhibited when these tests were performed on Ph_3AsO solutions containing hydrogen gas.

Controlled potential coulometric experiments, carried out on solutions of Ph_3As in the concentration range 10^{-3} *M* to 5×10^{-2} *M* at a potential value of +1.3 V, showed that 2 moles of electrons are released from each mole of arsine.

Voltammograms performed by a Pt electrode with periodic renewal of the diffusion layer [6] on the electrolyzed solutions showed three cathodic waves located at about the same potentials as peaks 2, 3 and 4 of Fig. 1. The height of the first cathodic wave, previously attributed to the reduction of H^+, was double that of the second and the third ones.

When some exhaustively electrolyzed solutions were potentiometrically titrated by a standard solution of tetrabutylammonium hydroxide, three inflections were observed indicating that three acids of different strength were produced in the anodic reaction. The amounts of base corresponding to the three equivalence points were in the same ratio (2/1/1) as the heights of the three cathodic waves. Furthermore, the total amount of acid species agreed strictly with the moles of the electrons (2) transferred in the anodic process.

After completion of the electrolyses a product was recovered, as described in the experimental section. It was identified as hydroxytriphenylarsonium perchlorate ($Ph_3AsOHClO_4$) by melting point (163°), elemental analysis and IR spectra [4].

Voltammetric tests carried out in acetonitrile solutions of this product allowed gave two cathodic waves located at potential values corresponding to peaks 3 and 4 of Fig. 1. This finding agrees well with the electrochemical behaviour of the Ph_3AsOH^+ prepared following Harris and Inglis's procedure [4].

On the basis of these results we can formulate reaction 1 for the anodic process This accounts for the first two inflections observed in the potentiometric titration alone.

$$Ph_3As + H_2O \rightarrow Ph_3AsOH^+ + H^+ + 2e^- \qquad (1)$$

The third inflection in the titration curve can be explained if the hydroxytriphenylarsonium cation undergoes two subsequent acid dissociations according to the equilibria 2 and 3. This behaviour was checked in our electrochemical study in which the values of the two acid dissociation constants were also given [3].

$$2Ph_3AsOH^+ \rightleftharpoons Ph_3AsO\text{---}H\text{---}OAsPh_3^+ + H^+ \qquad (2)$$

$$Ph_3AsO\text{---}H\text{---}OAsPh_3^+ \rightleftharpoons 2Ph_3AsO + H^+ \qquad (3)$$

The triphenylarsine oxide derivative containing a very short hydrogen bond involved in these acid—base equilibria evidently originates from the neutralization reaction 4. The Ph_3AsO, obtained when Ph_3AsOH^+ is neutralized, reacts with the excess of this cation present in the titrated solution.

$$Ph_3AsO + Ph_3AsOH^+ \rightarrow (Ph_3AsO)_2H^+ \qquad (4)$$

In a similar way two cathodic waves are observed in the voltammetric experiments carried out on Ph_3AsOH^+ solutions; the hydrogen ions released in the first acid dissociation of the hydroxytriphenylarsonium cation are reduced at less negative potentials than the H^+ released in the second dissociation reaction.

In order to confirm this view some Ph_3As solutions were exhaustively electrolized at +1.3 V (anodic process 1 in Fig. 1) and subsequently electrolyzed at −1.0 V (cathodic process 3 in Fig. 1). While in the anodic process 2 moles of electrons per mole of Ph_3As were involved, as mentioned above (reaction 1), in the cathodic process only 1.5 moles of electrons were spent, corresponding to the reactions shown in eqn. 5.

$$\begin{array}{l} 2H^+ + 2e^- \rightarrow H_2 \text{ (peak 2)} \\ 2Ph_3AsOH^+ + 1e^- \rightarrow (Ph_3AsO)_2H^+ + \tfrac{1}{2}H_2 \text{ (peak 3)} \\ \hline 2Ph_3AsOH^+ + 2H^+ + 3e^- \rightarrow (Ph_3AsO)_2H^+ + 3/2H_2 \end{array} \qquad (5)$$

Furthermore, acid—base titrations carried out on these electrolyzed solutions show that only 0.5 hydrogen ions per mole of initial Ph_3As were present, as would be expected from the neutralization reaction 6.

$$(Ph_3AsO)_2H^+ + OH^- \rightarrow 2Ph_3AsO + H_2O \qquad (6)$$

The product obtained after completion of these two subsequent electrolyses, recovered as described in the experimental section, was identified as $(Ph_3AsO)_2HClO_4$ by melting point [7] (210°), elemental analysis, and IR spectra [2]. Cyclic voltammograms recorded on acetonitrile solutions of this recovered product show the cathodic peak 4 alone. Moreover, controlled-potential coulometric experiments performed at −1.4 V indicated that 1 mole of electrons per mole of $(Ph_3AsO)_2HClO_4$ (mol. wt. 745) was involved in the cathodic reaction and simultaneously evolution of hydrogen gas was observed. After completion of these electrolyses triphenylarsine oxide was the only product recovered in the solutions.

Perchlorate as supporting electrolyte in presence of chloride ions

When cyclic voltammetric tests were carried out on 0.1 *M* TBAP/acetonitrile solutions, in which the concentration of chloride ions was varied from 10^{-3} *M* to 10^{-2} *M*, an anodic peak located at +0.72 V was observed in accord with a previous study [8].

Although the oxidation of triphenylarsine occurs at a more positive potential value (E_p = +1.25 V), an anodic process (peak 1) preceding the oxidation of the chloride ions (peak 2) was observed when Ph_3As was added to these solutions. This peak (see Fig. 2) was located at +0.42 V and its height linearly increased with Ph_3As concentration

The voltammetric picture reported in Fig. 2 was obtained by employing a freshly-cleaned Pt electrode, when the electrode was allowed to stand in the solution all the oxidation peaks shifted toward more anodic potential, probably owing to the poisoning effect of either the chloride ions or of the arsenic compounds on the electrode surface.

Peaks 4 and 6 in Fig. 2 were identified as due to the HCl oxidation and reduction respectively, by comparison with the pure compound. Moreover, peaks 3 and 7 could be attributed to $Ph_3AsOHCl$ oxidation and reduction respectively by carrying out cyclic voltammetric tests on solution of a sample of this compound prepared according to ref. 4. Finally, the anodic peaks 9 and 8 are due to the oxidation of H_2 in presence of chloride ions and in presence of Ph_3AsO together

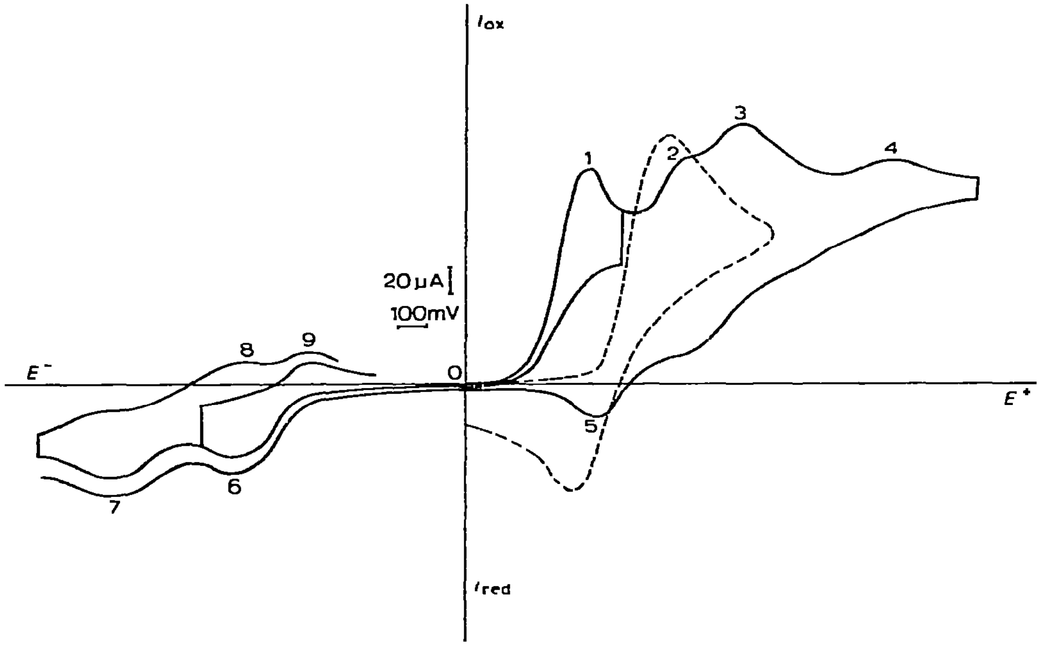

Fig 2 Cyclic voltammetric curves with platinum electrode in (—) 4 0 × 10^{-3} M Ph_3As, 1 2 × 10^{-2} M n-Bu_4NCl, 0 2 M n Bu_4NClO_4, CH_3CN solution (- -) 9 × 10^{-3} M n-Bu_4NCl, 0 2 M n Bu_4NClO_4, CH_3CN solution Scan rate 0 2 V s^{-1}

with Cl^- respectively; a check was also made in this case by voltammetric tests. The cathodic peak 5 is associated with the oxidation of Cl^- ions (peak 2) in a catho-anodic process.

The appearance of peaks 6 and 7 after peak 1 is traversed (heavy solid line in Fig 2) indicates that hydrogen chloride and hydroxytriphenylarsonium chloride are formed in the first oxidation step

Controlled-potential coulometric experiments carried out at +0.45 V showed that two moles of electrons per mole of Ph_3As were involved in this anodic process On the basis of these findings reaction scheme 7 can be suggested.

$$2Cl^- \rightarrow 2Cl^\bullet + 2e^-$$
$$2Cl^\bullet + Ph_3As + H_2O \rightarrow Ph_3AsOHCl + HCl \qquad (7)$$

This view is supported by the results obtained by carrying out preparative electrolyses in Ph_3As/acetonitrile solution in which $LiClO_4$ was employed as supporting electrolyte and LiCl as substratum. (In these experiments the lithium salts were preferred to facilitate recovery of the anodic product). In fact a product, recovered as described in the experimental section, was identified as $Ph_3AsOHCl$ by m.p. (170°) and IR spectra [4]. In addition its polarographic behaviour (two cathodic wave with $E_{1/2}$ values of −1.5 V and −2.70 V respectively) was the same as that exhibited by the compound when chemically prepared [4].

To account for the shift towards less positive potentials of the chloride oxidation in presence of Ph_3As it must be admitted that the chemical reaction following the charge transfer in reaction 7 is faster than the radical dimerization to produce chlorine.

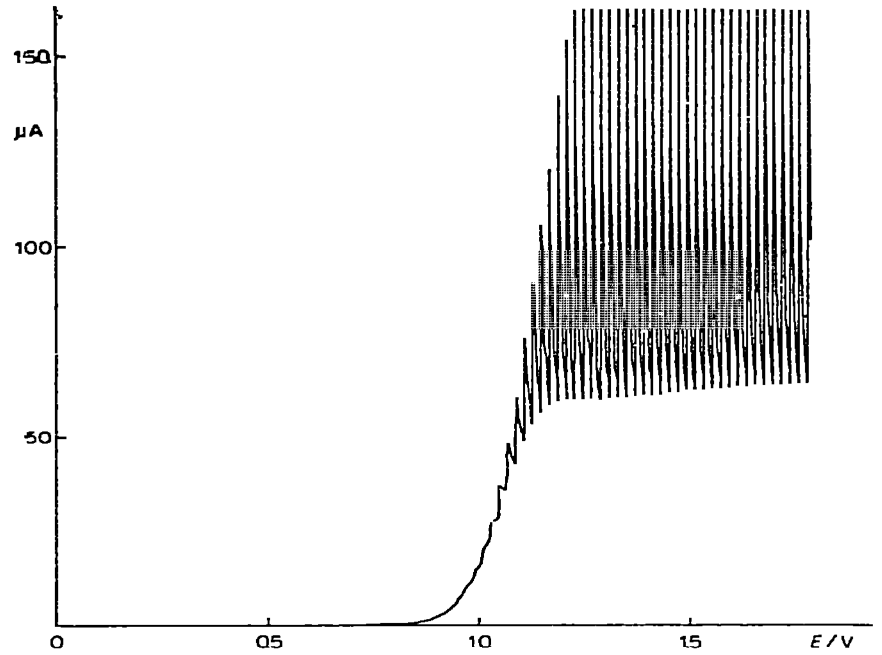

Fig 3 Voltammogram obtained in a 2×10^{-3} M Ph_3As, 0 1 M Et_4NBF_4 CH_3CN solution Platinum working electrode with periodic renewal of the diffusion layer

It can be remarked that in the reduction of hydroxytriphenylarsonium chloride a single wave is observed unlike the behaviour of corresponding perchlorate This can be explained by taking into account the lowering of the ionic character of these salts by replacing the perchlorate ion with the stronger base chloride Consequently the lower proton activity, due to lesser amounts of free Ph_3AsOH^+, prevents the formation of $(Ph_3AsO)_2H^+$

Tetrafluoroborate as supporting electrolyte

Voltammetric tests performed on Ph_3As in wet (10^{-1} M H_2O) acetonitrile solutions with Et_4NBF_4 as supporting electrolyte showed an anodic wave (see Fig 3) located at the same potential value ($E_{1/2}$ = +1 05 V) as when the supporting electrolyte was $NaClO_4$. No information could be gained by cyclic voltammetry because all cathodic peaks associated with the anodic one were ill-defined and poorly-reproducible. However, controlled-potential coulometric experiments at +1.3 V indicated that two moles of electrons per mole of Ph_3As are released. The oxidation product recovered from the exhaustively-electrolyzed solution, as described in the experimental section, was identified as Ph_3AsOBF_3 by elemental analyses, m.p. (230°) and IR spectra [4].

Furthermore, the polarographic picture obtained in an acetonitrile solution of the recovered product (see Fig. 4) agreed exactly with that exhibited by a solution of a pure sample of Ph_3AsOBF_3 prepared according to ref. 4.

To account for these findings reaction mechanism 8 is suggested. Clearly,

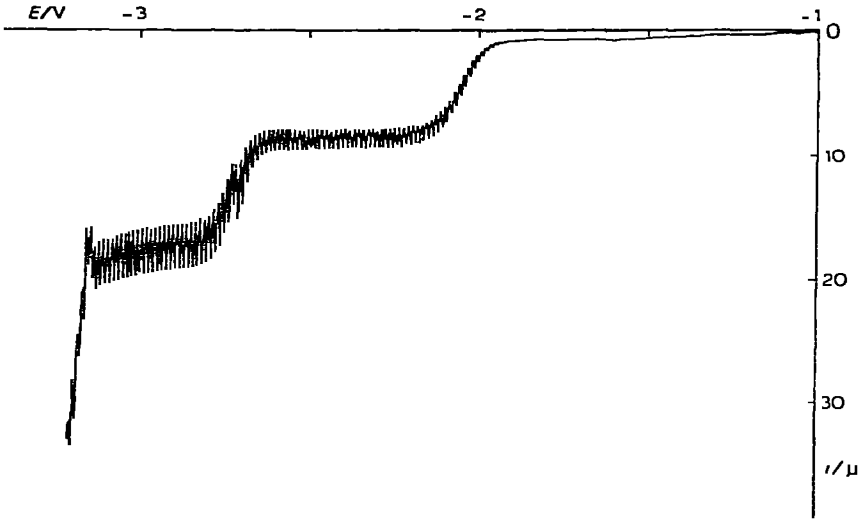

Fig 4 Polarogram obtained in a 6 × 10^{-3} M Ph_3AsOBF_3, 0 1 M Et_4NBF_4, CH_3CN solution DME with mechanical control of the drop time

$$\begin{array}{l} Ph_3As \rightarrow Ph_3As^{\bullet +} + e^- \\ Ph_3As^{\bullet +} + H_2O + 2BF_4^- \rightarrow Ph_3AsOHBF_4 + HBF_4 + e^- \\ Ph_3AsOHBF_4 \rightarrow Ph_3AsOBF_3 + HF \\ \hline Ph_3As + H_2O + 2BF_4^- \rightarrow Ph_3AsOBF_3 + HF + HBF_4 + 2e^- \end{array} \qquad (8)$$

hydrogen fluoride is eliminated from the tetrafluoroborate compound which is presumably formed as an intermediate. The ill-defined and poorly-reproducible peaks obtained in the cyclic voltammetric tests can be explained by the fact that the HF formed in the electrochemical pathway produces a poisoning effect on the platinum surface.

Experimental

Chemicals and reagents

All chemicals were reagent grade (C. Erba and Schuchardt). Reagent grade acetonitrile was purified by distilling repeatedly from phosphorus pentoxide [9] In order to obtain a solvent containing water in a concentration level of about 10^{-1} *M*, small weighed amounts of water were added to the distilled acetonitrile and the mixture stored under nitrogen. The content of water was tested by Karl Fischer titration.

Et_4NBF_4 was prepared by neutralizing HBF_4 with Et_4NOH. All supporting electrolytes ($NaClO_4$, TBAP, Et_4NBF_4, n-Bu_4NCl, $LiClO_4$ and LiCl) were recrystallized and dried in a vacuum oven.

Triphenylarsine was used without further purification because thin layer chromatographic tests and the melting point had proved its purity. Triphenylarsine oxide was crystallized from benzene [10].

Stock solutions of anhydrous perchloric acid in acetonitrile were prepared by oxidizing hydrogen gas dissolved in TBAP/acetonitrile solutions [5].

Apparatus and procedure

All experiments were carried out at 25 ± 0.1° in H-shaped cells with cathodic and anodic compartments separated by sintered glass disks. All potentials are referred to a silver—0.1 *M* silver nitrate electrode in acetonitrile medium. In the voltammetric measurements the working electrodes were either platinum spheres with periodic renewal of the diffusion layer [6] or stationary platinum sphere microelectrodes. Polarograms were performed by a DME with mechanical control of the drop time. Coulometric and preparative electrolyses were carried out by employing platinum foils as working electrodes and a large mercury pool as counters

Further experimental details and all electrochemical and spectrophotometric instrumentation have been described in a previous paper [11]

Acid—base titrations were performed with standard solutions of n-Bu_4NOH in acetonitrile and the end point detection was made potentiometrically by using a general purpose Beckmann glass electrode.

Electrochemical preparations

$Ph_3AsOHClO_4$. 100 ml of 5 × 10^{-2} *M* Ph_3As, 0.1 *M* H_2O, 1 *M* $NaClO_4$ acetonitrile solution were electrolyzed under nitrogen atmosphere at +1.3 V vs. Ag/0.1 *M* Ag^+ acetonitrile electrode in a two-compartment cell. With a platinum working electrode (approximate area 40 cm^2) the electrolysis time was about 3 h. After completion of the electrolysis the solvent was evaporated under vacuum at low temperature and the residual solid was shaken with $CHCl_3$ to separate the insoluble $NaClO_4$. By adding ether to the filtrate white crystals were obtained. They were recrystallized from chloroform—ether. Analytical and physical data were consistent with previous results [4]

$(Ph_3AsO)_2HClO_4$. 100 ml of 5 × 10^{-2} *M* Ph_3As, 0.1 *M* H_2O, 1 *M* $NaClO_4$ acetonitrile solution deaerated with nitrogen were electrolyzed first at +1.30 V and subsequently at −1.00 V vs. Ag/0.1 *M* Ag^+ acetonitrile electrode in a two-compartment cell About 5 h was required to complete these electrolyses (area of Pt electrode about 40 cm^2). At the end of the electrolyses the acetonitrile solution was evaporated under vacuum at low temperature. In order to separate the insoluble $NaClO_4$, the oxidation product was extracted with $CHCl_3$, the resulting solution, treated with ether, gave a white precipitate which was recrystallized from ethanol—ether. All analytical and physical data were consistent with published results [2, 7].

$Ph_3AsOHCl$ 100 ml of 5 × 10^{-2} *M* Ph_3As, 0.1 *M* LiCl, 0.1 *M* H_2O, 0.75 *M* $LiClO_4$ acetonitrile solution were electrolyzed at +0.45 V vs. Ag/0.1 *M* Ag^+ acetonitrile electrode in a two-compartment cell under nitrogen. The electrolysis was completed in about 3 h (electrode surface: about 40 cm^2); the solvent was evaporated under vacuum at low temperature and the product was extracted from the residual solid with chloroform. White crystals were obtained by adding ether to the chloroform solution. Recrystallization was made from chloroform—ether. Analytical and physical data agreed well with those reported previously [4].

Ph_3AsOBF_3. 100 ml of 5×10^{-2} *M* Ph_3As, 0.1 *M* H_2O, 1 *M* Et_4NBF_4 acetonitrile solution were electrolyzed at +1.3 V vs. Ag/0.1 *M* Ag^+ acetonitrile electrode in a two compartment cell under nitrogen atmosphere. (Electrolysis time: about 3 h with a 40 cm^2 working electrode). The exhaustively electrolyzed solution was evaporated under vacuum at low temperature and the residual supporting electrolyte was separated from the oxidation product by shaking with $CHCl_3$.

When ether was added to the chloroform solution, white crystals were obtained which were recrystallized from chloroform—ether. All analytical and physical data were consistent with data given by Harris and Inglis [4].

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