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SHORT COMMUNICATION

A Convenient Preparation and the Electrolytic Conductance of Triphenylarsine Difluoride.

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Triphenylarsine oxide - hydrogen halides, $Ph_3AsO\cdot HX$, (formerly known as triphenylarsine hydroxyhalides) [1] are, in the case of the chloride and bromide, prepared readily by either a hydrolytic reaction or an addition reaction as follows [2]:

$$Ph_3AsX_2 + H_2O \longrightarrow Ph_3AsO\cdot HX + HX \qquad (1)$$

$$Ph_3AsO + HX \longrightarrow Ph_3AsO\cdot HX \qquad (2)$$

$$(X = Cl \text{ or } Br)$$

An attempt to prepare triphenylarsine oxide-hydrogen fluoride via reaction (2) using hydrofluoric acid (40%) gave a white crystalline product, the carbon and hydrogen analysis of which was close to that expected for $Ph_3AsO\cdot HF$, but in the infrared spectrum there were no bands attributable to ν(As–O) or ν(O–H). Analysis for fluorine established that the product was in fact triphenylarsine difluoride (which has a molecular weight only slightly different from that of $Ph_3AsO\cdot HF$). Thus under the conditions used in the reaction the triphenylarsine oxide is fluorinated with loss of oxygen:

$$Ph_3AsO + 2HF \longrightarrow Ph_3AsF_2 + H_2O \qquad (3)$$

This provides a more convenient method of preparing triphenylarsine difluoride than those described previously which involve either fluorination of the hydrolytically unstable triphenylarsine dichloride using silver fluoride [3] or oxidative fluorination of triphenylarsine using sulphur tetrafluoride [4] or perfluoro-N-fluoropiperidine[5].

It has been established that triphenylarsine dichloride and triphenylarsine dibromide may also be prepared by reactions analogous to (3). By treating triphenylarsine oxide with concentrated hydrochloric or hydrobromic acid and isolating the product in a dry atmosphere we have been able to obtain pure samples of Ph_3AsCl_2 and Ph_3AsBr_2 respectively. However for these dihalides, which, unlike the difluoride, are very moisture sensitive, this method offers no advantage over the standard addition reaction:

$$Ph_3As + X_2 \longrightarrow Ph_3AsX_2$$

An X-ray crystal structure analysis of a sample of Ph_3AsF_2 prepared as described has been carried out by Prof. G. Ferguson et al.[6]: this showed that the compound has a molecular trigonal bipyramidal structure with the fluorine atoms in the axial positions. It was of interest therefore to study the electrolytic conductance of the difluoride for comparison with the other dihalides which give conducting solutions in certain solvents [7].

Triphenylarsine difluoride dissolves in acetonitrile and the resulting solutions have a very low, but probably significant, molar conductance ($\Lambda_m = 0.3\ ohm^{-1}\ cm^2\ mol^{-1}$ at concentration 0.01M) Ph_3AsF_2 must therefore be regarded as an extremely weak electrolyte,

$$Ph_3AsF_2 \rightleftharpoons Ph_3AsF^+ + F^- ,$$

in this solvent. Triphenylarsine difluoride thus follows the trend set by the dichloride and dibromide [7], the molar conductance values of which, in the same solvent, are higher but still indicative of weak electrolyte behaviour. For the series, values of molar conductance at 25° and concentration 0.01M are:

	$\Lambda_m/ohm^{-1}\ cm^2\ mol^{-1}$
Ph_3AsF_2	0.3
Ph_3AsCl_2	4.0
Ph_3AsBr_2	25.3

It is clear that these dihalides, which are covalent in the solid state [6, 8], undergo ionisation through the influence of the solvent. The trend observed may be attributed mainly to the trend in arsenic-halogen bond strengths (As–F > As–Cl > As–Br).

EXPERIMENTAL

Triphenylarsine oxide hydrate was prepared by a standard method [9]. The hydrohalic acids used were of Analar grade. Pure anhydrous acetonitrile suitable for conductance studies was prepared by the method described by Smith and Witten [10] (the specific conductance of the purified solvent was ca. 10^{-7} ohm^{-1} cm^{-1} at 25°). A modified dipping electrodes type conductance cell was used. It contained smooth platinum electrodes, and its design was such that the solution did not come into contact with the atmosphere during measurement of conductance. Conductance was measured using a Phillips resistance bridge (Type GM 4249). Hydrolytically unstable dihalides were handled in a nitrogen-filled dry-box.

Reaction between triphenylarsine oxide and hydrofluoric acid

Triphenylarsine oxide hydrate (0. 65g, 1. 91 mmol) and water (30 ml) were heated together to boiling and stirred vigorously. Hydrofluoric acid (20 ml of 40% acid) was then added slowly. A white precipitate formed and the warm mixture was stirred for a further 30 min. The product was isolated by filtration, washed with water, and dried (Yield, 0. 57g; 87%). Recrystallisation from acetone gave white lath-shaped crystals, m. p. 134-136°. Analysis: Found: C, 62. 7; H, 4. 3; F, 11. 3% Calculated for $C_{18}H_{15}AsF_2$: C, 62. 8; H, 4. 4; F, 11. 1%.

Reaction between triphenylarsine oxide and concentrated hydrochloric acid

Triphenylarsine oxide hydrate (0. 53g, 1. 57 mmol) was shaken with concentrated hydrochloric acid (30 ml) for several hours. The solid crystalline oxide did not dissolve but appeared to be replaced by a finely divided powder. This was filtered quickly in the dry-box and dried under vacuum, m. p. (sealed tube), 210-215° (with decomposition). Analysis: Found: C, 57. 5; H, 3. 8; Cl, 18. 3%. Calculated for $C_{18}H_{15}AsCl_2$: C, 57. 3; H, 4. 0; Cl, 18. 8%.

Reaction between triphenylarsine oxide and concentrated hydrobromic acid

Triphenylarsine oxide hydrate (0. 60g, 1. 77 mmol) was shaken with hydrobromic acid (30 ml of 47% acid). The oxide dissolved, and after several hours the solvent was removed by freeze drying. The residue, a colourless viscous liquid, was pumped for 2 hours, and then transferred to the dry-box. Trituration with acetonitrile (2 ml) gave a white crystalline solid. Dry ether (25 ml) was added to the mixture which was filtered, washed with ether and the product dried under vacuum. m. p. (sealed tube) 230-233° (with decomposition) Analysis: Found: C, 46. 6; H, 3. 2; Br, 35. 5%. Calculated for $C_{18}H_{15}AsBr_2$, C, 46. 4; H, 3. 2; Br, 34. 3%.

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