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TRIARYLARSINE HALIDES

AND RELATED COMPOUNDS

A Thesis

presented for the degree of

Doctor of Philosophy

in the Faculty of Science of the

University of St. Andrews

by

Frank Inglis, B.Sc.

September, 1967

United College of St. Salvator
and St. Leonard, St. Andrews.



In 5466

I declare that this thesis is my own composition, that the work of which it is a record has been carried out by myself, and that it has not been submitted in any previous application for a higher degree.

The thesis describes results of research carried out in the Chemistry Department of Glasgow University during the year beginning 1st October, 1964, and in the Chemistry Department of the United College of St. Salvator and St. Leonard, University of St. Andrews, since 1st October, 1965, under the supervision of Dr. G.S.Harris.

I hereby certify that Frank Inglis has spent eleven terms at research work under my supervision, has fulfilled the conditions of Ordinance No.16 (St. Andrews), and is qualified to submit the accompanying thesis in application for the degree of Doctor of Philosophy.

Director of Research

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ABSTRACT

The course of reaction of tri-*p*-tolylarsine [$(\textit{p}\text{-tol})_3\text{As}$] and tri-*p*-chlorophenylarsine [$(\textit{p}\text{-Cl.C}_6\text{H}_4)_3\text{As}$] with the halogens Br_2 , IBr and I_2 in methyl cyanide solution has been determined by conductimetric methods. $(\textit{p}\text{-tol})_3\text{As}$ reacts with these halogens in the same way as triphenylarsine, forming the 1:1 adduct $(\textit{p}\text{-tol})_3\text{AsBr}_2$ and the 1:2 adducts $(\textit{p}\text{-tol})_3\text{AsBr}_n\text{I}_{4-n}$ ($n = 4, 2, 0$). $(\textit{p}\text{-Cl.C}_6\text{H}_4)_3\text{As}$ forms the same stable compounds with bromine, but those with IBr and I_2 appear to take part in extensive equilibria in solution. Even so both 1:1 and 1:2 adducts of both arsines with all of these halogens, and the 1:1 adducts with chlorine, have been isolated as crystalline solids. The conductances of the compounds which are stable in solution have been measured and compared with those of the corresponding triphenylarsine compounds. All the 1:2 adducts are strong electrolytes in methyl cyanide, but the 1:1 adducts with chlorine and bromine are weak electrolytes, whose molar conductances depend on the nature of the aryl group. A qualitative correlation has been drawn between the electronegativity of the aryl group in $\text{Ar}_3\text{AsHal}_2$ compounds and their molar conductances in solution. The same correlation explains the relative stabilities of the 1:2 adducts $\text{Ar}_3\text{AsBr}_n\text{I}_{4-n}$ in solution.

This comparison has been extended to the hydrolysis products of the dichlorides and dibromides of these arsines, the hydroxy-

halides $\text{Ar}_3\text{As}(\text{OH})\text{Hal}$, which have commonly been regarded as structurally analogous to the dihalides. It has been shown that although these are weak electrolytes in methyl cyanide, and therefore probably covalent solids, like the dihalides, their electrolytic conductances are independent of the nature of the aryl groups. With the support of these observations the infrared spectra of the triarylar sine hydroxyhalides have been interpreted in terms of a covalent structure involving very strong hydrogen bonding between the triarylar sine oxide and hydrogen halide, and it has been suggested that they should be regarded as 1:1 acid-base adducts and named triarylar sine oxide hydrohalides. They are thus not analogous to the corresponding dihalides.

Other hydroxy derivatives of triphenylarsine have also been considered as 1:1 adducts of triphenylarsine oxide with acids. These include the new trihalides $\text{Ph}_3\text{As}(\text{OH})\text{Hal}_3$, obtained by addition of halogen to triphenylarsine hydroxyhalides, and the hydroxyperchlorate. It has been concluded from the high electrolytic conductance of the trihalides and the perchlorate that when the acid is sufficiently strong the adduct may be considered to be an ionic hydroxytriphenylarsonium salt, although there is evidence that fairly strong hydrogen bonding to the anion is necessary to stabilise the cation.

It has been shown that triphenylarsine hydroxyiodide, the 1:1 compound of triphenylarsine oxide with hydrogen iodide, cannot be

prepared because reaction occurs between equivalent quantities of hydroxytriphenylarsonium and iodide ions. Addition of HI to triphenylarsine oxide has been found to lead instead to 2:1 adducts $(\text{Ph}_3\text{AsO})_2\text{HI}$ and $(\text{Ph}_3\text{AsO})_2\text{HI}_3$. These adducts have been characterised as ionic compounds containing the bis(triphenylarsine oxide)hydrogen ion $[(\text{Ph}_3\text{AsO})_2\text{H}]^+$, and a series of stable crystalline solids has been prepared all members of which are salts of this cation. Attention has been directed to previous reports of analogous adducts whose structures have not been recognised.

The products of complete hydrolysis of the triarylarsonic dihalides, the oxides Ar_3AsO , have been examined briefly, and some evidence presented to support a suggestion that triarylarsonics do not form hydroxides, as often assumed, but that such compounds are hydrates of the oxides.

The reaction of triphenylbismuth with halogens has also been examined. The only dihalides of triphenylbismuth which are stable at normal temperatures are the dichloride and dibromide, but the di-iodide is stable at -35° . No evidence has been found for the existence of any tetrahalides of triphenylbismuth. These features of the chemistry of triphenylbismuth have been related satisfactorily to the trends in properties of the triphenyl derivatives of other group VB elements.

I N T R O D U C T I O N

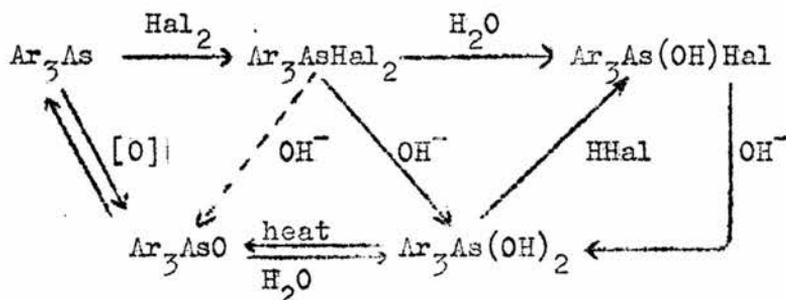
I N T R O D U C T I O N

Organic derivatives of arsenic occupy a distinctive place in the history of organometallic chemistry, which has often been considered to begin with Bunsen's investigation into the nature of 'cacodyl', tetramethyldiarsine, and the intensive search, early this century, for arsenic compounds of therapeutic value led to the synthesis of more organic derivatives of arsenic than of any other element.

Among the most stable derivatives of arsenic(III) are the triarylarisines Ar_3As , of which a characteristic reaction is the addition of halogen to form the series of arsenic(V) halides $\text{Ar}_3\text{AsHal}_2$. These are well known because of their ease of formation from the large number of available arsines. Discussion of compounds of this type and their derivatives forms the subject of this part of the thesis.

Like most compounds of group VB elements with halogens the triarylarisenic dihalides are hydrolytically unstable. They have usually been recognised to hydrolyse in two steps, corresponding to replacement of one and both halogen atoms by the hydroxyl group. Corresponding to the series of arsines and dihalides there are therefore analogous series of hydrolysis

products generally referred to in the literature as the hydroxyhalides, $\text{Ar}_3\text{As}(\text{OH})\text{Hal}$, and dihydroxides, $\text{Ar}_3\text{As}(\text{OH})_2$. The dihydroxides dehydrate on heating to form the series of oxides Ar_3AsO , and the dihalides of some arsines hydrolyse directly to the oxide without forming a dihydroxide. Under appropriate conditions the reactions may be reversed, and the relationships between these types of compounds are summarised in the diagram.



These crystalline derivatives, which with the exception of the majority of dihalides are stable, have been used frequently to characterise arsines, but have not themselves been extensively studied.

The analogous triaryl derivatives of the other group VB elements (M) except nitrogen have been reported, and the alkyl derivatives corresponding to all of these are also well known, though less stable. Furthermore the halides R_3MHal_2 (R = Ar or Alk) may be regarded as members of the series $\text{R}_n\text{MHal}_{5-n}$ (n = 0 to 5) the extremes of which are the pentahalides MHal_5 and the fully substituted organic derivatives R_5M . Although the structures of

the triarylsarsine dihalides have not been completely defined, sufficient work has been done on these related group VB compounds to leave them in little doubt. Since it is in the general framework of these derivatives that the dihalides and their hydrolysis products are of most interest, the pattern of structures and properties among them will be outlined.

Compounds R_5M and $MHal_5$.

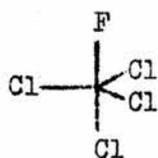
The only authenticated R_5M compounds are the pentaphenyls¹, related derivatives in which four of the co-ordination sites of M are occupied by two biphenylene groups², and some penta-alkenyls³. Pentaphenylphosphorus adopts the simplest structure possible for a derivative of phosphorus(V), forming a molecular lattice of trigonal bipyramidal units⁴, and the isomorphous pentaphenylarsenic must have the same structure⁵. Pentaphenylantimony differs in that its molecules are tetragonal pyramids⁶, but this is atypical, being the only known example of this configuration for a pentaco-ordinate atom outside the transition metal complexes⁷.

On the other hand the pentahalides $MHal_5$ exhibit a considerable variety of phase-dependent structures⁸ which illustrate the more characteristic co-ordination numbers, 4 and 6, of M rather than that of 5, suggested by their stoichiometry. In phases which favour ion formation they adopt ionic structures $[MHal_4]^+[MHal_6]^-$ (e.g. $PCl_5(s)$, PBr_5 in polar solvents) or $[MHal_4]^+Hal^-$ (e.g. $PBr_5(s)$).

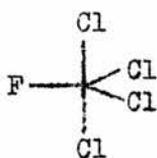
In these cases it is probable that steric factors determine which anion is present. It is mostly in phases which do not favour ion formation that the simple trigonal bipyramidal molecules are found (e.g. $\text{PF}_5(\text{g}), (\text{l}); \text{PCl}_5(\text{g}); \text{AsF}_5(\text{g}), (\text{l}); \text{SbF}_5(\text{g}); \text{SbCl}_5(\text{g})$), although antimony pentachloride has a molecular lattice in the solid state. A few other associated structures are encountered among the halides, such as the octahedral dimer of antimony pentafluoride in the liquid state, but the above are most characteristic.

Isomerism in pentacovalent molecules

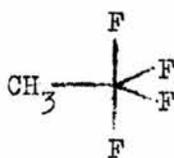
A number of mixed pentahalides are known, particularly of phosphorus, and with them (as with the organo-substituted pentahalides, $\text{R}_n\text{MHal}_{5-n}$) the possibility of geometrical isomerism arises in their covalent molecules because of the non-equivalence of axial and equatorial positions in the trigonal bipyramid. Without exception, however, all such structures so far determined conform to the empirical rule that the axial positions are occupied by the most electronegative ligands⁷. Thus the infrared and raman spectra of $\text{FPCl}_4(\text{g}), (\text{l})$ are consistent with C_{3v} molecular symmetry [I] and not C_{2v} [II]⁹, while electron diffraction shows C_{2v} symmetry for CH_3PF_4 [III]¹⁰.



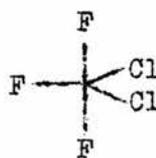
[I]



[II]



[III]



[IV]

It seems also that when the ionisation of $MHal_5$ to $[MHal_4]^+[MHal_6]^-$ takes place the most electronegative halogen atoms are found in the anion. For example PF_3Cl_2 (which as a gas or liquid has the structure $[IV]^{11,12}$) is ionic in the solid state and contains hexafluorophosphate(V) ions, i.e. $[PCl_4]^+[PF_6]^-$ ¹³. The further possibility of optical isomerism arising from the presence of three different substituents in the equatorial plane when axial substituents are also different has not been investigated. It is considered unlikely in the halides because of the facility with which intramolecular halogen exchange occurs¹⁴, and although it might occur in dihalides with three different equatorial organic substituents the slightest degree of ionisation in solution would lead to racemisation.

Compounds $RMHal_4$ and R_2MHal_3 .

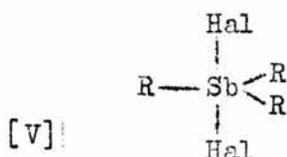
Although many of the intermediate members of the series R_nMHal_{5-n} with $n = 1$ and 2 are known they have not received as much attention as the others. Recently, however, a considerable number of fluorophosphoranes (e.g. RPF_4 ; $R = CH_3, C_2H_5, n-C_4H_9, C_6H_5$), and a few of the analogous arsenic and antimony compounds, have been studied by F^{19} nuclear magnetic resonance spectroscopy in liquid and solution states^{11,15}, and experimental data are in keeping with trigonal bipyramidal structures of the expected symmetry for all of these in which association does not occur.

The structures of gaseous CH_3PF_4 and $(\text{CH}_3)_2\text{PF}_3$ have been unambiguously determined by electron diffraction¹⁰, and that of crystalline Ph_2SbCl_3 by X-ray diffraction¹⁶, with the same result. The majority of structures quoted are therefore covalent penta-co-ordinate molecules, but it must be noted that only that of Ph_2SbCl_3 refers to the crystalline state and none to an ionising solvent. Some at least of them would be expected to ionise in solution, and indeed the behaviour of certain RPHal_4 in solution¹⁷ is in keeping with the presence of ions RPHal_3^+ and RPHal_5^- or Hal^- . Parallel behaviour is observed in R_2PHal_3 compounds¹⁸, but conductance measurements which would determine the extent of this ionisation have not been made, and no structural studies of the solid state have been reported.

Compounds R_3MHal_2 .

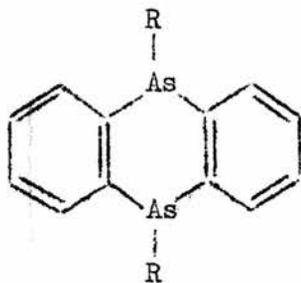
The derivatives R_3MHal_2 have received more attention. In particular conductimetric studies in methyl cyanide of the phenyl derivatives have shown that the phosphorus dihalides are strong electrolytes and the antimony and bismuth dihalides non-electrolytes, suggesting that the solids are respectively ionic and covalent¹⁹. The arsenic derivatives are only weak electrolytes and therefore probably covalent in the solid state²⁰. The chlorides furnish hexaco-ordinate $\text{Ph}_3\text{MHal}_3^-$ anions in solution, the dibromides simple bromide ions (cf. the phosphorus pentahalides).

Earlier vibrational studies²¹ had supported the ionic structure $R_3PHal^+Hal^-$ for the solid trimethylphosphorus dihalides, and infrared spectra of trimethyl-, triethyl-, and triphenylantimony dihalides^{22,23} were consistent with molecules of D_{3h} symmetry [V].

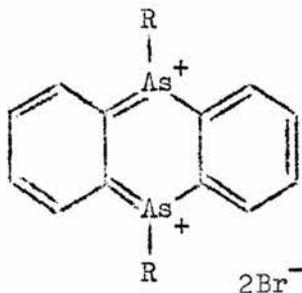


X-ray analysis has established this geometry for $(CH_3)_3SbHal_2$ (Hal = Cl, Br, I)²⁴, $(ClCH:CH)_3SbCl_2$ ²⁵, Ph_3SbCl_2 ²⁶, and Ph_3BiCl_2 ²⁷. Dipole moment measurements in benzene solution led to the same conclusion for the dichlorides of arsenic, antimony and bismuth²⁸.

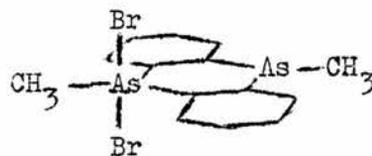
The only triorganoarsenic dihalide whose structure in the solid state has been determined by X-ray diffraction techniques²⁹ is the dibromide of 5,10-dihydro-5,10-dimethyl arsanthrene [VI] ($R = CH_3$). Jones and Mann showed that this dibromide has the



[VI]



[VII]



[VIII]

anomalous structure [VII] in solution, because of the favourable conditions for aromaticity³⁰, but considered it possible from the behaviour of the corresponding di-iodide that in the solid

state one of the arsenic atoms would revert to the trivalent state while the other adopted the configuration of a normal arsenic(V) dibromide [VIII]. This was found to be the case: the configuration about the arsenic(V) atom was the expected trigonal bipyramid, slightly distorted by the constraining effect of the heterocyclic ring, and in particular the Br-As-Br angle was almost 180° and the As-Br bonds considerably longer (2.6\AA) than in comparable derivatives of arsenic(III) such as arsenic tribromide (2.3\AA) or bromodiphenylarsine (2.4\AA). Only the heavy atoms were located in the corresponding di-iodide²⁹, but their positions were in keeping with the same structure and the As-I bond lengths (2.80 , 2.89\AA) were much longer than in other arsenic iodides (arsenic tri-iodide and iododiphenylarsine, 2.5\AA).

It is a characteristic of these pentacovalent compounds that axial M-X bonds are longer than normal M-X single bonds, and in particular than equatorial M-X bonds. The difference appears to be least in those compounds containing most halogen. In phosphorus pentafluoride, for instance, axial and equatorial P-F bonds are respectively 1.577\AA and 1.534\AA ³¹, but in $(\text{CH}_3)_2\text{PF}_3$ they are 1.643\AA and 1.553\AA ¹⁰, compared to the average of $1.53 \pm 0.02\text{\AA}$ for a variety of phosphorus fluorides^{32a}. Axial and equatorial P-C bond lengths in pentaphenylphosphorus are 1.987 and 1.850\AA respectively⁴ compared to an average of $1.84 \pm 0.06\text{\AA}$ for a number of alkyl and aryl derivatives of phosphorus^{32b}.

Wells²⁴ noted the abnormal length of the Sb-Hal bonds in the trimethylantimony dihalides and they have therefore been described as "intermediate between ionic and covalent" and as "resonance" linkages. Jensen²⁸ also concluded that these Sb-Hal bonds were very polar from the high atomic polarisability of the compounds. The Bi-Cl bonds in triphenylbismuth dichloride are likewise longer than expected for a covalent bond ($2.61 \pm 0.01 \text{ \AA}$ (av.) compared with $2.48 \pm 0.02 \text{ \AA}$ for BiCl_3)²⁷.

Compounds R_4MHal .

Quaternary organic derivatives of phosphorus, arsenic, and antimony are all stable crystalline solids, and all experimental evidence is in keeping with their being ionic halides. No tetraalkylbismuth derivatives are known, but unstable tetra-arylbismuthonium halides have been obtained at low temperatures^{33a}.

Bonding in covalent penta- and hexaco-ordinate species.

It seems appropriate to draw attention here to the difficulty of describing the bonding in these compounds. This is the general problem of non-transition metal compounds containing a central atom with an 'expanded octet' which include polyhalide ions and inert gas compounds. They are usually described as having σ bonds formed by overlap of appropriate bonding orbitals of the ligands with directed hybrid orbitals of the central atom

- sp^3d hybrids for pentaco-ordination and sp^3d^2 for hexaco-ordination, non-bonding orbitals being occupied by lone pairs for lower co-ordination numbers. The validity of placing as much importance on higher energy d orbitals as on the s and p orbitals occupied in the central element is open to question, and in at least two of these species, ICl_2^- and ICl_4^- , nuclear quadrupole resonance spectroscopy has shown the bonds to have negligible d and s character³⁴. The electron-pair repulsion theory originated by Sidgwick and Powell³⁵, and extended by Gillespie and Nyholm³⁶, has had considerable success in explaining the geometries of these molecules, but lacks any truly quantitative basis, and requires the introduction of the same hybrid orbitals if a bond is to be described as anything more than a pair of electrons.

A molecular orbital treatment of the bonding in I_3^- and ICl_2^- , first put forward by Pimentel in 1951³⁷, has been extended to all polyhalides with great success by Havinga and Wiebenga³⁸, and to all 'expanded octet' compounds by Rundle³⁹, but has not been widely accepted. When rigorously applied it requires no introduction of hybrid orbitals and takes account of slight distortions which the Gillespie-Nyholm approach explains satisfactorily though qualitatively, but a simplified approach which neglects these allows its essential points to be seen clearly. ICl_2^- , for instance, is described as having a single, linear, three-centre

bond, formed by overlap of an iodine p_{σ} orbital with p_{σ} orbitals of the chlorine atoms. In molecular orbital theory mixing of these three atomic orbitals gives rise to three molecular orbitals - one bonding, one antibonding and one essentially non-bonding. The four electrons available for what is normally regarded as two I-Cl electron-pair bonds would then occupy the bonding and non-bonding molecular orbitals. An important result of this approach is that, since only two of the electrons are involved in the bonding, the I-Cl bond order must be only about half. Determinations of the stretching force constants of bonds in trihalide ions are in keeping with this⁴⁰.

The extension of this theory to more highly co-ordinated atoms is obvious. The square planar ion ICl_4^- has two three-centre bonds which employ two p orbitals of the iodine atom at right angles, and octahedral ions such as Ph_6Sb^- and AsCl_6^- use all three p orbitals of the central atom to form three such bonds mutually at right angles. The equatorial bonds of trigonal bipyramidal pentaco-ordinate structures may be considered as normal single bonds employing sp^2 hybrid orbitals of the central atom, but the axial bonds are in fact a single three-centre bond. This immediately explains the abnormally long axial bonds in the compounds discussed, such as $(\text{CH}_3)_3\text{SbCl}_2$, and their difference from equatorial bonds between the same atoms, as in $(\text{CH}_3)_2\text{PF}_3$.

Because the non-bonding orbital distributes charge chiefly

on the terminal atoms of a three-centre bond the theory predicts that formation of such a bond is favoured by ligands of high electronegativity, and thus the 'preference' of the most electronegative ligands for axial sites in trigonal bipyramidal molecules, and the high polarity of these bonds, are explained. Since the ionisation of MX_5 to MX_4^+ and MX_6^- represents formation of one species containing four electron-pair bonds and another containing three three-centre bonds it is to be expected that the more electronegative ligands will be found in the latter, the hexaco-ordinate anion. The scarcity of pentaco-ordinate molecules (MY_5 , MX_3Y_2 , etc.) containing less electronegative substituents (Y), such as alkyl groups, in the axial positions, and of corresponding MY_6^- ions, can be similarly explained.

The stability of the three-centre bond must depend on the similarity in energy of the orbitals of the terminal atoms employed. If their energies differ markedly a non-bonding orbital cannot result from their combination. Thus a three-centre bond is most stable when symmetric (as demonstrated by the greater stabilities of symmetrical trihalide ions) and it is possible that the reason for all R_4MX compounds being ionic is the instability of the linear R-M-X bond relative to the stability of the symmetric R_4M^+ ion with electron-pair bonds. This would certainly explain why, although all R_5M and the majority of R_3MX_2 are covalent, all R_4MX are, anomalously, ionic.

Adoption of this theory does not explain everything. The difference between axial and equatorial bonds in PF_5 ³¹, for instance, is much less than it predicts. However, as stated earlier the above is a very restricted application of a general molecular orbital treatment, and consequently cannot be expected to account for every variation from its general principles. Nor has the possibility of additional bonding between the halogen p_{π} orbitals and d_{π} orbitals of M, which would shorten M-Hal bonds, been considered. But on the whole this appears to be a very useful approach, particularly suited to the R_3MHal_2 compounds, and certainly worth more attention than it has received.

Products of Hydrolysis of Compounds R_3MHal_2 .

a) Oxides

The oxides R_3MO can be obtained by direct oxidation of R_3M as well as by hydrolysis of R_3MHal_2 . Trialkyls in general are oxidised by atmospheric oxygen, but triaryls require a stronger oxidising agent such as peroxide or permanganate^{33b}. The structures of these derivatives of phosphorus and arsenic are well known; they are Lewis bases and often used as ligands in transition metal complexes, many of which have been analysed by X-ray diffraction techniques. The molecule has the tetrahedral configuration expected for tetraco-ordinate M, and bonding is

adequately described by the use of sp^3 hybrid orbitals of M to form four σ bonds. The M-O distance is shortened by additional bonding arising from overlap of filled p_{π} orbitals on the oxygen with the empty d_{π} orbitals on M. Here it is worth noting the contrast with amine oxides, in which the N-O bond must be a very polar single bond because such π bonding is not possible.



Absence of an Sb-O stretching frequency in the expected region of the infrared spectrum of triphenylstibine oxide has led to the suggestion that the antimony derivatives R_3SbO have a polymeric structure containing Sb-O-Sb bonds⁴¹. Little is known about the nature of the bismuth oxides, but they are likely to be similar.

b) Hydroxyhalides and dihydroxides of triorganostibines and bismuthines

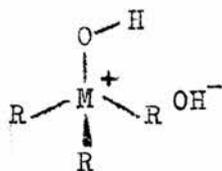
There is comparatively little experimental data on which to base deductions as to the nature of the dihydroxides and hydroxyhalides. There seems, however, to be a distinction between those of phosphorus and arsenic on the one hand and those of antimony and bismuth on the other. The dihydroxides and hydroxyhalides of stibines and bismuthines are insoluble in water, whereas those of phosphines and arsines are soluble. The dihydroxides of phosphorus and arsenic dehydrate readily to the corresponding oxide on heating; those of antimony and bismuth do not^{33c}.

$\text{Ph}_3\text{Sb}(\text{OH})_2$, for instance, is stable up to its melting point

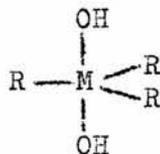
of 212° at atmospheric pressure^{33b}, and though $\text{Ph}_3\text{Bi}(\text{OH})_2$ decomposes at 100° it does not form an oxide^{33c}. Comparison with the analogous dihalides suggests that the antimony and bismuth compounds are covalent, occurring as trigonal bipyramidal molecules, while those of phosphorus and arsenic are possibly not. The zero dipole moment of $\text{Ph}_3\text{Sb}(\text{OH})_2$ ⁴² and the infrared spectrum of $(\text{CH}_3)_3\text{Sb}(\text{OH})_2$ ²² are in keeping with D_{3h} molecular symmetry, as is found in the dihalides. Thus it is likely that the dihydroxides of stibines and bismuthines are covalent molecules and therefore that the intermediate hydroxyhalides are also. Jensen has measured the dipole moment of $\text{Ph}_3\text{Sb}(\text{OH})\text{Cl}$ in dioxan and considers that the hydroxyl and chlorine groups are both bound directly to the antimony⁴², but it is of interest to note that recently considerable doubt has been cast on the existence of these antimony hydroxyhalides, particularly those of trialkyl stibines²², as a result of the failure of several attempts⁴³ to repeat early preparations.

c) Dihydroxides of triorganophosphines and arsines.

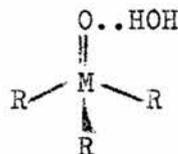
The structures of the phosphorus and arsenic compounds have been much more a matter for speculation. Mann has discussed the three probable formulations ([IX],[X],[XI], overleaf) of the dihydroxides, and suggests that the one adopted may depend on R, as reflected in the very different stabilities of the various $\text{R}_3\text{M}(\text{OH})_2$ ⁴⁴.



[IX]

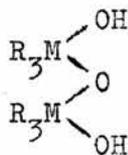


[X]

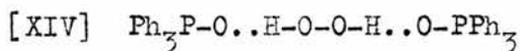
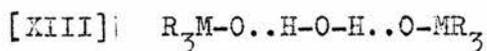


[XI]

Some dihydroxides are reported to decompose immediately to the oxide R_3MO , others to an intermediate 'sesqui' stage, generally formulated $(\text{R}_3\text{MOH})_2\text{O}$ [XII]. However, several workers have recognised that certain 'dihydroxides' are in fact monohydrates of the oxides [XI]. In particular Jensen⁴² deduced that the dihydroxides of triphenylphosphine and triphenylarsine should be formulated $\text{Ph}_3\text{MO} \cdot \text{H}_2\text{O}$ from measurement of their dipole moments in benzene, and more recently indisputable evidence from infrared spectroscopy⁴⁵ and X-ray analysis⁴⁶ has confirmed this for the arsenic compound in the solid state. Infrared spectroscopy and H_2O ¹⁸ exchange experiments likewise confirm the existence of $\text{Ph}_3\text{PO} \cdot \text{H}_2\text{O}$ rather than $\text{Ph}_3\text{P}(\text{OH})_2$ in the solid state and in aqueous solution⁴⁷. Sidgwick⁴⁸ suggested the same formulation for amine oxide hydrates, but Mann⁴⁴ opposed the hydrate type structures on the ground that the 'sesqui' compound [XII] would then have to be reformulated as [XIII]. But there seems to be no particular objection to this, and indeed the exactly



[XII]



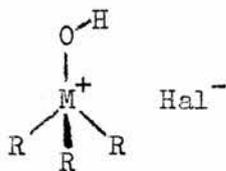
analogous structure [XIV] has been suggested for a 2:1 adduct of triphenylphosphine oxide with hydrogen peroxide on the evidence of its infrared spectrum⁴⁹.

No comparable evidence has been presented for the existence of a true dihydroxide. The work of Meisenheimer⁵⁰, who showed that optically active phosphine oxides $RR'R''PO$ do not racemise in the presence of base, as they would on formation of $RR'R''P(OH)_2$ [X], strongly suggests that such a structure does not occur. Conversely the failure to date of all attempts to resolve arsine oxides $RR'R''AsO$ could be taken as an indication that arsine hydroxides do occur, but there is no reason to expect this difference and Mann has suggested⁴⁴ that manipulative difficulties may be responsible. The one arsine for which Mann proposes a structure of type [X] is 5,10-dihydro-5,10-ditolyl-arsanthrene⁵¹, and in the light of more recent work the 'tetrahydroxide' of this compound is equally well explained as a hydrate of the dioxide. The same work of Meisenheimer⁵⁰ is used by Mann⁴⁴ to argue for the existence of the ionic form [IX], but only in that this preserves the tetrahedral configuration of the central atom, and if the oxide hydrate structure [XI] is accepted this answers the purpose equally well. No experimental facts are available which are not compatible with the formulation of dihydroxides as oxide hydrates, but though it is likely that all so-called dihydroxides are oxide hydrates in the solid state

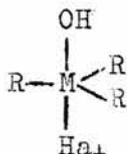
the possibility of their adopting another structure in polar solvents, and particularly water, cannot be dismissed without considerably more experimental evidence.

d) Hydroxyhalides of triorganophosphines and arsines.

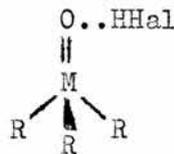
Deductions as to the nature of the hydroxyhalides have been based on very little experimental evidence, mostly referring to aryl derivatives, but three structures are possible as in the case of the dihydroxides. The alternative form of [XV], $R_3M^+Hal^-OH^-$ is unlikely in view of the acidity of solutions of hydroxyhalides^{33d}, and Steinkopf and Schwon, having concluded from thermal cleavage studies that the hydroxyl group rather than the bromine atom of arsine hydroxybromides should be associated with the arsenic atom, formulated them $[R_3As(OH)]Br$ ⁵².



[XV]



[XVI]



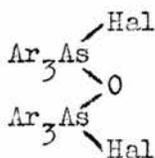
[XVII]

The hydroxyhalides are alternatively available from the addition of halogen acid to the corresponding oxides, and may therefore be regarded as acid-base adducts, whatever their exact structure. Hadzi has examined the infrared spectra of the crystalline 1:1 adducts of triphenylphosphine oxide with HCl and HBr, as part of a general study of hydrogen bonded systems, and

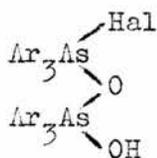
is of the opinion that proton transfer to the oxygen base does not occur, though he expresses some doubt in the case of the hydrobromide⁵³. The adducts must therefore be formulated $\text{Ph}_3\text{PO} \cdot \text{HHal}$ [XVII] rather than $\text{Ph}_3\text{POH}^+\text{Hal}^-$ [XV]. The covalent structure [XVI] he regards as unlikely because of the absence of an identifiable P-Hal stretching frequency in the infrared spectrum.

Extension of these conclusions to the analogous arsenic compounds would be unwise. Comparison with the corresponding dihalides suggests that the arsenic derivatives are more likely to be covalent than the phosphorus derivatives, but the greater basicity of Ph_3AsO when compared with Ph_3PO ⁵³ suggests that formation of Ph_3AsOH^+ is more likely than Ph_3POH^+ . The acidity of solutions of arsine hydroxyhalides has been taken as evidence for the presence of $\text{Ar}_3\text{As}(\text{OH})^+$ ions^{33d}, and certainly they react as ionic halides in solution, which has led Mann to state that they are 'true salts' and indeed to use them as evidence for an ionic formulation of the derived dihydroxides⁴⁴. But no measurements have been made to determine the degree of ionisation, which may be only slight, as in the triarylar sine dihalides.

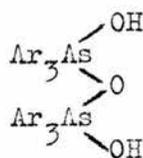
Lyon and Mann have isolated crystalline compounds from $\text{Ar}_3\text{AsO}/\text{HHal}$ systems which can obviously be related to the hydroxyhalides by elimination of water [XVIII] or HHal [XIX] between two molecules⁵⁴.



[XVIII]



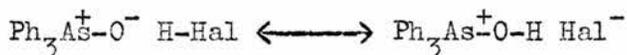
[XIX]



[XX]

Mann refers to them as derivatives of [XX] and uses their isolation as evidence that [XX] is the correct formulation of compounds $(\text{Ar}_3\text{As})_2\text{O}_3\text{H}_2$, but as pointed out in the previous section there is no direct evidence for structure [XX], and doubts as to its existence must cast doubts also on structures [XVIII] and [XIX], and hence on the structure [XVI] for the hydroxyhalides. It is of relevance to any discussion of these compounds that, in spite of the very large number of triarylarisines, and corresponding hydroxyhalides, known, derivatives of types [XVIII] and [XIX] have been reported only for tri-*o*-tolylarsine.

In one of his valuable papers on the structure of pentavalent derivatives of group VB elements⁴² Jensen records the very high dipole moment of 9.2D for triphenylarsine hydroxychloride, and explains it by means of a resonance hybrid formulation [XXI].



[XXI]

He considers that this value is not sufficiently high for an ionic structure, and his evidence seems to fall in line with Hadzi's observations on the phosphorus compounds, but has been generally neglected in published discussions on the hydroxyhalides.

Finally it must be observed that this discussion of hydroxyhalides is in fact restricted to chlorides and bromides. No hydroxyfluoride has been reported, which is not surprising in view of the affinity of fluoride for hydrogen, but neither have many hydroxyiodides. This is difficult to explain since many di-iodides are known and the odd hydroxyiodides which have been reported, such as those of phenyldimethylarsine⁵⁵ and phenyldipseudocumylarsine⁵⁶, were obtained by the same methods which produce the chlorides and bromides. Lyon and Mann have reported isolation of $\text{Ph}_3\text{As}(\text{OH})\text{I}$ from the reaction of Ph_3AsO and HI ($\text{KI} + \text{HOAc}$)⁵⁴, but do not give sufficient evidence in support of their claim. Clearly further investigation of these compounds is required.

R E S U L T S A N D

D I S C U S S I O N

P A R T I

TRIARYLARSINE/HALOGEN SYSTEMS

TRIARYLARSINE/HALOGEN SYSTEMS

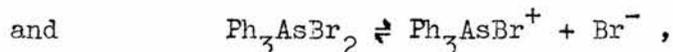
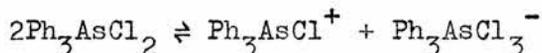
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TRIARYLARSINE/HALOGEN SYSTEMS

Introductory Note: Triphenylarsine/Halogen Systems.

Many dihalides, and some tetrahalides, of triorganoarsines are known, and a systematic study of compounds of this type is being carried out by Harris and co-workers. In particular, Beveridge and Harris have recently measured the electrolytic conductances of the triphenylarsine derivatives, and made a detailed conductimetric study of the course of reaction of halogens with triphenylarsine, in methyl cyanide solution²⁰.

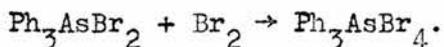
These authors have found that the dichloride and dibromide of triphenylarsine are weak electrolytes, ionising according to the equations



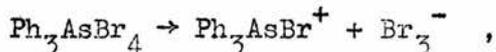
and have deduced from this that the compounds are probably covalent in the solid state. The different modes of ionisation of these dihalides can be related to the stability of anions of the type $\text{Ph}_3\text{AsHal}_3^-$: when Hal = Br the greater size of the bromine atom probably causes steric overcrowding, and its lower electronegativity may also be a contributory factor to the instability of $\text{Ph}_3\text{AsBr}_3^-$. In this connection it is significant that the

existence of the hexaco-ordinate arsenate(V) ions AsF_6^- and AsCl_6^- has been established, but AsBr_6^- has not been reported⁸. SbBr_6^- presumably owes its existence to the greater size of its central atom.

A number of tetrahalides of triphenylarsine, $\text{Ph}_3\text{AsBr}_n\text{I}_{4-n}$, have been obtained by the addition of halogen to one of the dihalides²⁰, e.g.

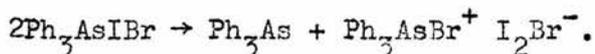


It has been shown that these are all strong 1:1 electrolytes in methyl cyanide solution, giving halotriphenylarsonium and trihalide ions, e.g.



and are therefore probably ionic solids also, containing the same ions. The reaction is essentially between a halide ion and halogen, the cation's importance being that it is large enough to form a stable lattice with the resultant trihalide ions.

Another two dihalides, Ph_3AsI_2 and Ph_3AsIBr , have been isolated as solids, but cannot be compared with the dibromide and dichloride because they are unstable in solution, disproportionating to the corresponding tetrahalide, e.g.



It was thought of interest to examine the reactions of halogens with other triarylarsonines, and the products of these

reactions, in the same way, in order to determine whether the course of reaction, and the stability of the adducts formed, was dependent on the nature of the aryl group. Groups were chosen to represent those slightly less, and slightly more electro-negative than the phenyl group. Tri-*p*-tolylarsine [$(\underline{p}\text{-tol})_3\text{As}$] and tri-*p*-chlorophenylarsine [$(\underline{p}\text{-Cl.C}_6\text{H}_4)_3\text{As}$] were selected because they appeared to form an evenly graded series with triphenylarsine: the pK_a 's of the carboxylic acids $\underline{p}\text{-tolCO.OH}$, PhCO.OH and $\underline{p}\text{-Cl.C}_6\text{H}_4\text{CO.OH}$ (4.35, 4.17, 4.03 respectively)⁵⁷ suggest that the electron-repelling effect of the \underline{p} -tolyl group is approximately as much more than that of the phenyl group as that of the \underline{p} -chlorophenyl group is less.

It was expected that the effect of small changes in the electronegativity of the aryl substituent would be most noticeable in the electrolytic conductance of those derivatives which were weak electrolytes. Attention was therefore paid to the molar conductances of the dihalide derivatives in particular.

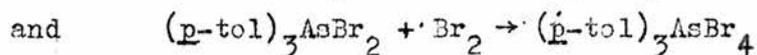
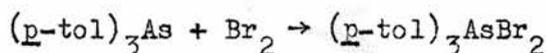
Results and Discussion.

A. Conductimetric Titration Studies of Tri-p-tolylarsine/Halogen Systems.

Conductance-composition graphs for the systems $(p\text{-tol})_3\text{As}/\text{Hal}_2$ ($\text{Hal}_2 = \text{Br}_2, \text{IBr}, \text{I}_2$) are reproduced in figure 1.

(a) $(p\text{-tol})_3\text{As}/\text{Br}_2$.

Discontinuities at the 1:1 and 2:1 $\text{Br}_2:(p\text{-tol})_3\text{As}$ mole ratios indicated formation of the adducts $(p\text{-tol})_3\text{AsBr}_2$ and $(p\text{-tol})_3\text{AsBr}_4$. The two consecutive reactions



therefore occur. The solution remained colourless up to the 1:1 mole ratio, and thereafter had the bright yellow colour of the tribromide ion. By analogy with the system $\text{Ph}_3\text{As}/\text{Br}_2$ ²⁰ isolation of a colourless dibromide and a yellow tetrabromide from appropriate mixtures of the reactants was expected. The only important difference from the corresponding triphenylarsine system was the higher rate of increase of conductivity up to the 1:1 mole ratio, attributable to formation of a more highly conducting dibromide. The high conductance at the 2:1 mole ratio ($\Lambda_m = 93.7 \text{ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$, $c_m = 0.004 \text{mole/l}$) indicates that the tetrabromide is a strong 1:1

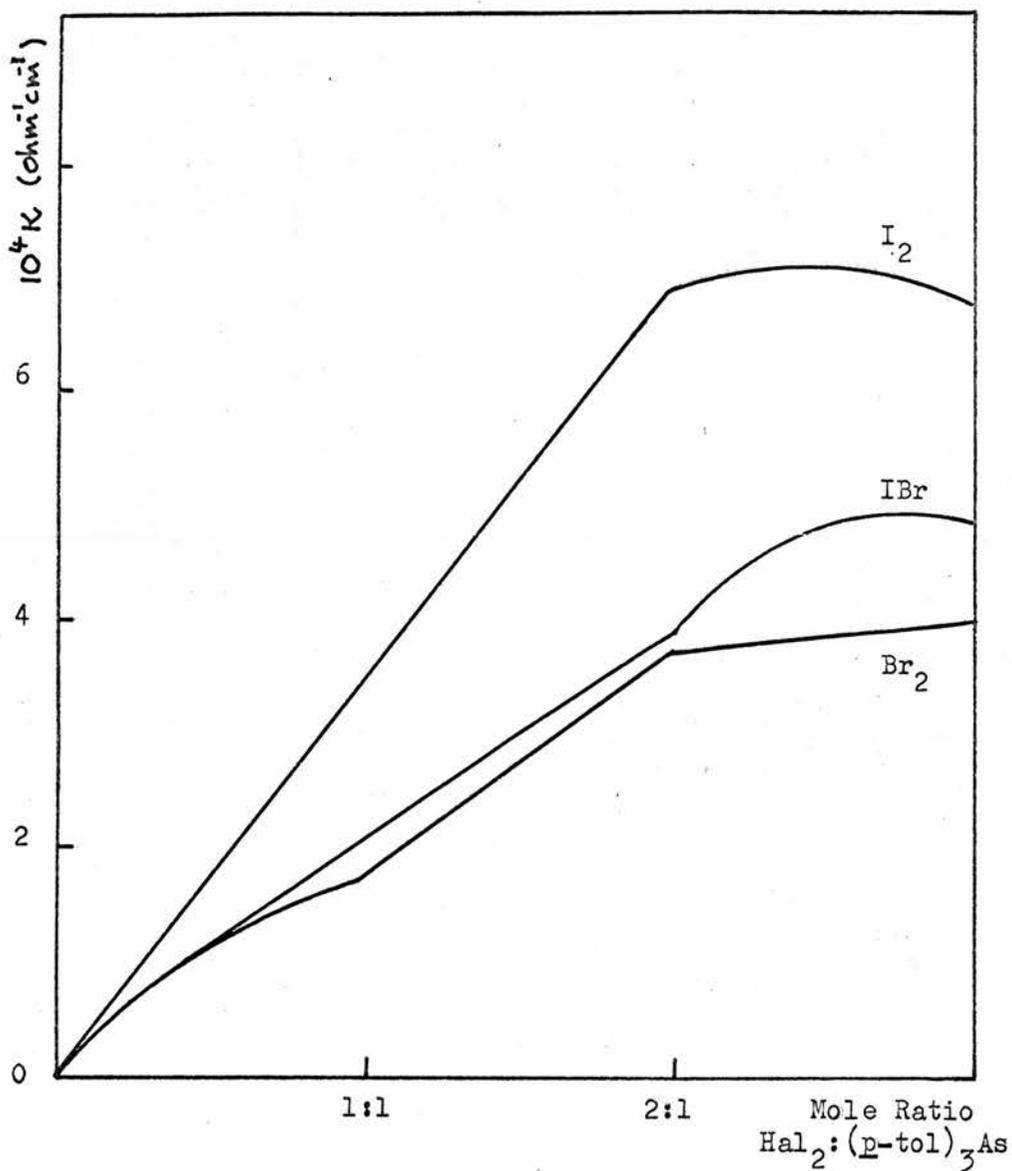
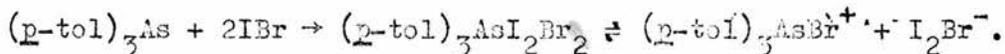


Fig.1 Conductimetric Titrations of Tri-p-tolylarsine with Halogens in Methyl Cyanide

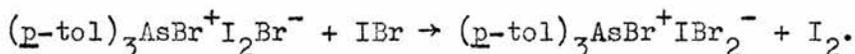
electrolyte. (Strong 1:1 electrolytes have Λ_m ca.100 in methyl cyanide.)

(b) (p-tol)₃As/IBr.

The solution showed the characteristic colour of the trihalide ion from the first addition of halogen, and the conductance rose uniformly up to the 2:1 IBr:(p-tol)₃As mole ratio, indicating that the strong electrolyte (p-tol)₃AsI₂Br₂ was the only adduct formed in solution up to that point. The reaction occurring is therefore, by analogy with the Ph₃As/IBr system,



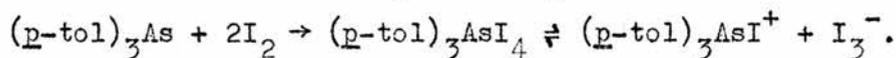
After the 2:1 IBr:(p-tol)₃As mole ratio the curve rose slightly, then flattened out and fell again before the 3:1 mole ratio. This is typical of the addition of halogen when reaction does not occur, but by analogy with the behaviour of the Ph₃As/IBr system conversion of the I₂Br⁻ ion to the IBr₂⁻ ion should take place between the 2:1 and 3:1 mole ratios, so that the unreacted halogen is in fact iodine²⁰.



UV spectra of the solution at the 2:1 and 3:1 mole ratios confirmed that this reaction was taking place, showing the characteristic absorptions of the I₂Br⁻ ion (λ_{max} 277m μ , 351m μ) at the former and of the IBr₂⁻ ion (λ_{max} 256m μ) at the latter point.

(c) (p-tol)₃As/I₂.

As in the titration with IBr the strong colour of trihalide ion, this time I₃⁻, appeared at the first addition of halogen, and conductance rose uniformly up to the 2:1 mole ratio. Thereafter the graph flattened out and the conductance fell as the solution was diluted with the relatively poorly conducting iodine solution. Thus (p-tol)₃AsI₄ is the only adduct present in methyl cyanide solutions of (p-tol)₃As and I₂.

(d) Adducts isolated

All the adducts whose existence was shown by conductimetric titration were isolated as crystalline solids by addition of ether to mixtures of the reactants in the appropriate ratio in methyl cyanide. Although existence of (p-tol)₃AsIBr was not indicated in the conductimetric titration the solid compound was obtained by careful addition of IBr to a saturated solution of tri-p-tolylarsine in methyl cyanide: the dihalide precipitated immediately. Similarly, the solid di-iodide was obtained by slow addition of iodine to tri-p-tolylarsine in petroleum ether. A dichloride was also prepared by passage of chlorine into an ether solution of the arsine. The properties of these adducts are summarised in Table 1 overleaf.

Thus all the dihalides reported for triphenylarsine²⁰ exist

for tri-*p*-tolylarsine also. Except for the iodobromide they have been reported before^{58a}. Similarly in the tetrahalide series $(p\text{-tol})_3\text{AsI}_n\text{Br}_{4-n}$ members with $n = 4, 2, 0$ were isolated, and there is no reason to doubt that the others ($n = 3, 1$) exist too. The tetra-iodide has been reported previously^{58a}.

Table 1 Crystalline Adducts of $(p\text{-tol})_3\text{As}$ with Halogens.

Compound	Colour	m.p. (°C)	Λ_m from titration (ohm ⁻¹ cm ² mole ⁻¹)	c_m (mole/l)
$(p\text{-tol})_3\text{AsCl}_2$	white	240-247	-	-
$(p\text{-tol})_3\text{AsBr}_2$	white	250	37.83	.0048
$(p\text{-tol})_3\text{AsBrI}$	yellow orange	145-150d	41.12*	.0048
$(p\text{-tol})_3\text{AsI}_2$	red orange	171.5-173	53.92*	.0068
$(p\text{-tol})_3\text{AsBr}_4$	orange	123-124	93.65	.0041
$(p\text{-tol})_3\text{AsBr}_2\text{I}_2$	dark red	132-136	97.45	.0040
$(p\text{-tol})_3\text{AsI}_4$	chocolate	153	127.9	.0054

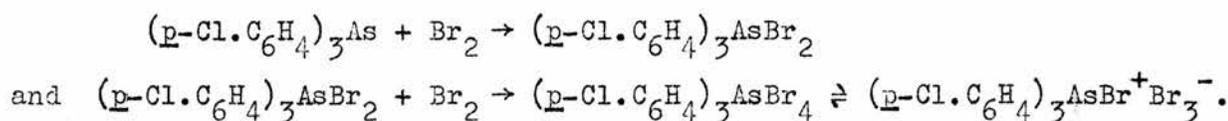
* Calculated on basis of solid state structure: not a true Λ_m because of disproportionation to tetrahalide in solution.

B. Conductimetric Titration Studies of Tri-p-chlorophenylarsine/
Halogen Systems.

Conductance-composition graphs for the systems $(p\text{-Cl.C}_6\text{H}_4)_3\text{As}/\text{Hal}_2$ ($\text{Hal}_2 = \text{Br}_2, \text{IBr}, \text{I}_2$) are reproduced in figure 2.

(a) $(p\text{-Cl.C}_6\text{H}_4)_3\text{As}/\text{Br}_2$.

This graph follows the expected pattern up to the 2:1 $\text{Br}_2:(p\text{-Cl.C}_6\text{H}_4)_3\text{As}$ mole ratio. Conductance rose slowly to a low value at the 1:1 mole ratio, during which time the solution was colourless. From the 1:1 to the 2:1 mole ratio the solution acquired an increasingly intense yellow colour and the conductance rose rapidly. After that the conductance rose only very slowly with addition of the poorly conducting bromine solution. The adducts $(p\text{-Cl.C}_6\text{H}_4)_3\text{AsBr}_2$ and $(p\text{-Cl.C}_6\text{H}_4)_3\text{AsBr}_4$ were thus indicated, arising from the reactions



(b) $(p\text{-Cl.C}_6\text{H}_4)_3\text{As}/\text{IBr}$.

As expected, the conductance of the solution rose rapidly as IBr was added up to the 2:1 $\text{IBr}:(p\text{-Cl.C}_6\text{H}_4)_3\text{As}$ mole ratio, without any discontinuity to indicate formation of a 1:1 adduct, and the solution was strongly coloured from the first addition. Thereafter, however, unlike previous $\text{Ar}_3\text{As}/\text{IBr}$ systems studied, the conductance

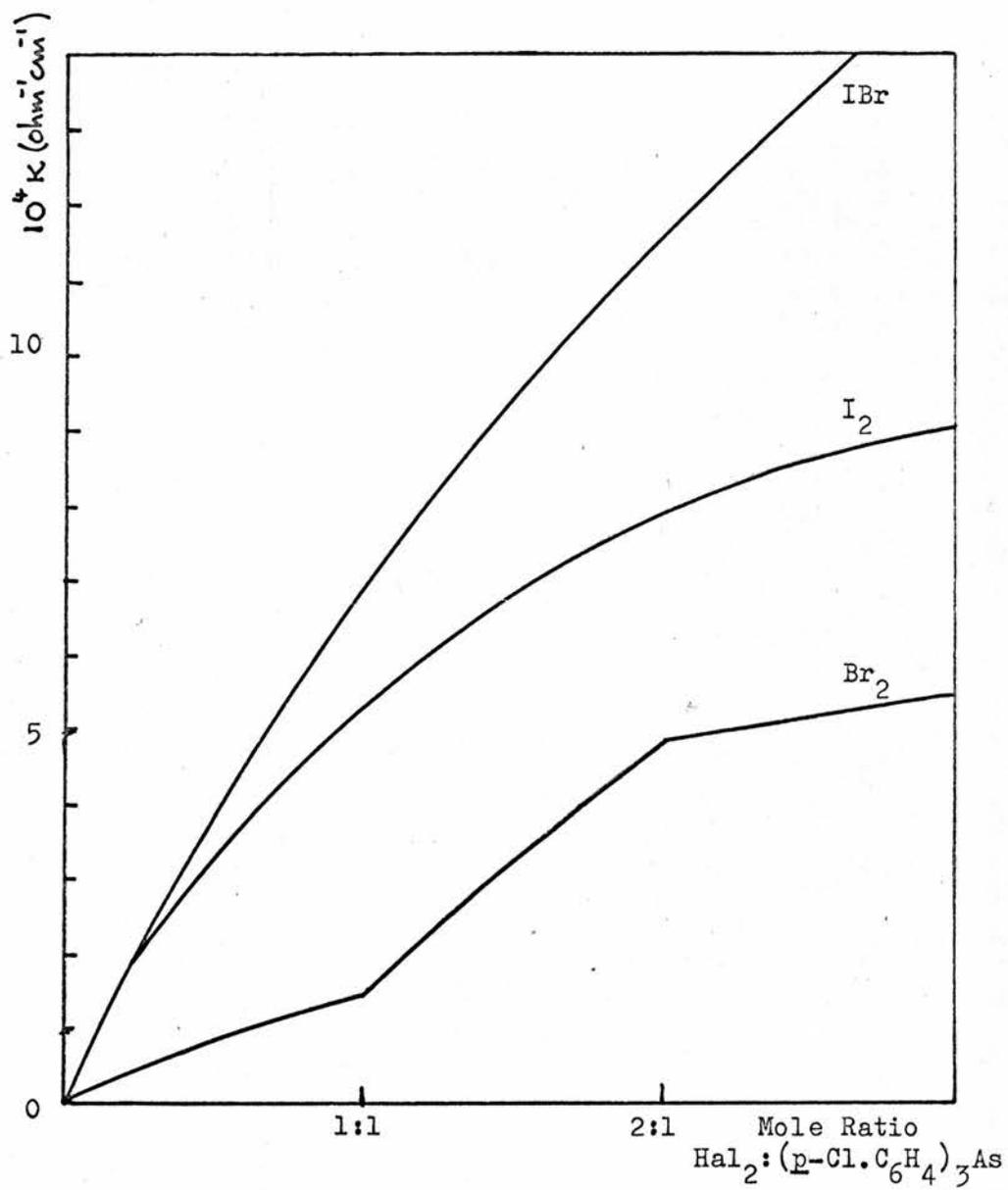


Fig.2 Conductimetric Titrations of Tri-*p*-chlorophenylarsine with Halogens in Methyl Cyanide

continued to rise steadily, without any inflection in the conductance-composition graph at the 2:1 mole ratio, so that there was no indication of the existence of the expected $(p\text{-Cl.C}_6\text{H}_4)_3\text{AsI}_2\text{Br}_2$. Indeed, no definite break was observed as long as the titration was carried on, well beyond the 2:1 mole ratio, the conductance tailing off indefinitely.

(c) $(p\text{-Cl.C}_6\text{H}_4)_3\text{As/I}_2$.

This curve showed features similar to those of the IBr curve. The exact shape and height of the curve, and the position of its maximum, varied with the concentration of the solutions used, but no definite discontinuity was observed.

(d) Adducts isolated.

The bromides whose existence was shown by conductimetric titration were isolated easily. The dichloride was also obtained as expected, and in spite of the negative evidence of the conductimetric titrations the tetrahalides $(p\text{-Cl.C}_6\text{H}_4)_3\text{AsI}_2\text{Br}_2$ and $(p\text{-Cl.C}_6\text{H}_4)_3\text{AsI}_4$ were isolated as crystalline solids from mixtures of the halogen and arsine in the ratio 2:1. The corresponding dihalides were also obtained in the same way as the *p*-tolyl compounds. The properties of these crystalline adducts are summarised in Table 2 overleaf: none of them appears to have been reported before, probably because the parent arsine is one less readily synthesised.

Table 2 Crystalline Adducts of $(p\text{-Cl.C}_6\text{H}_4)_3\text{As}$ with Halogens.

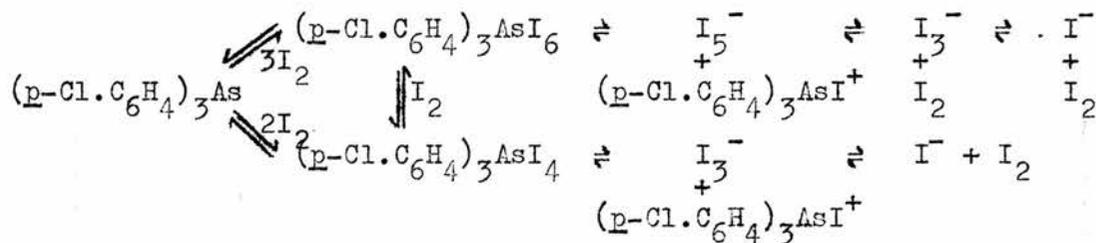
Compound	Colour	m.p. ($^{\circ}\text{C}$)	Δ_m from titration ($\text{ohm}^{-1}\text{cm}^2\text{mole}^{-1}$)	c_m (mole/l)
$(p\text{-Cl.C}_6\text{H}_4)_3\text{AsCl}_2$	white	169-170	-	-
$(p\text{-Cl.C}_6\text{H}_4)_3\text{AsBr}_2$	white	215d.	16.91	.0085
$(p\text{-Cl.C}_6\text{H}_4)_3\text{AsIBr}$	yellow orange	148-150	54.81*	.0083
$(p\text{-Cl.C}_6\text{H}_4)_3\text{AsI}_2$	red orange	148-150	62.43*	.0086
$(p\text{-Cl.C}_6\text{H}_4)_3\text{AsBr}_4$	orange	126-134	72.11	.0069
$(p\text{-Cl.C}_6\text{H}_4)_3\text{AsBr}_2\text{I}_2$	dark red	127-130	121.8*	.0068
$(p\text{-Cl.C}_6\text{H}_4)_3\text{I}_4$	chocolate	160-162	116.0*	.0069

* Calculated on basis of solid state structure; not a true Δ_m because of equilibria in solution.

C. Interpretation of Results.

(a) Reaction of $(p\text{-Cl.C}_6\text{H}_4)_3\text{As}$ with IBr and I_2 .

A clue as to the reaction of IBr and I_2 with $(p\text{-Cl.C}_6\text{H}_4)_3\text{As}$ came from an attempt to prepare the tetra-iodide from the arsine, using a large excess of iodine. The product was a black crystalline solid, which had an appreciable vapour pressure of iodine. Analysis showed it to have the composition $(p\text{-Cl.C}_6\text{H}_4)_3\text{AsI}_6$, which is clearly the penta-iodide $(p\text{-Cl.C}_6\text{H}_4)_3\text{AsI}^+\text{I}_5^-$. Formation of higher polyiodides in the system $(p\text{-Cl.C}_6\text{H}_4)_3\text{As}/\text{I}_2$ would account for the form of the conductance-composition graph: the featureless nature of the curve, without breaks at definite mole ratios, is typical of those obtained for systems in which there is extensive dissociation of the reaction products, or systems in which there are overlapping equilibria, e.g.



Another equilibrium which probably contributes to the absence of a sharp break is halogen exchange at the arsenic atom. This has been shown to occur in related dihalides $(\text{CH}_3)_3\text{SbHal}_2$ ⁵⁹, and it seems likely that the electron-withdrawing effect of the *p*-chlorophenyl groups will weaken the As-Hal bond and so promote

such exchange in this case. A similar equilibrium is likely to occur with IBr, as is formation of higher polyhalide ions, and would be aggravated by the greater possible number of species involving two halogens (e.g., the four trihalide ions I_3^- , I_2Br^- , IBr_2^- , and Br_3^- in place of only I_3^-).

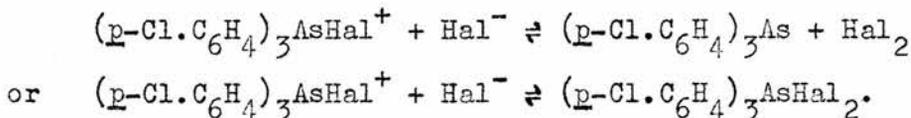
(b) Influence of the aryl group on properties of triarylar sine halides.

It has thus been shown that the number of solid adducts formed by triarylar sines with halogens is not greatly dependent on the nature of the aryl group, but that their behaviour in solution is. This can be understood on consideration of the interaction between the aryl groups and arsenic.

The p-tolyl group is less, and the p-chlorophenyl group more, electronegative than the phenyl group because the effect of the electronegativity of the substituent methyl group or chlorine atom is transferred through the π -bonding system of the benzene ring to the other ring substituent, in this case the central arsenic atom. This leads to an increase of electron density on the arsenic atom in tri-p-tolylarsine and a decrease in tri-p-chlorophenylarsine, compared to triphenylarsine. It may alternatively be said that the arsenic atom is less electronegative in $(p\text{-tol})_3\text{As}$ than in Ph_3As , and more in $(p\text{-Cl.C}_6\text{H}_4)_3\text{As}$. This might be expected to affect the strength of the axial Hal-As-Hal bonds in the dihalides, which are stabilised by increasing difference in electronegativity between central and terminal atoms.

(Introduction, p.12) No such effect is apparent in any difference between corresponding solid dihalides, but this may be one of the factors affecting their electrolytic conductance, as observed qualitatively during the titrations. The arsine which should form the most stable Hal-As-Hal bond, (p-Cl.C₆H₄)₃As, forms a dibromide with less tendency to ionise than that of the arsine least likely to form a stable Hal-As-Hal bond, (p-tol)₃As. Studies of the thermal decomposition of these dihalides might show an interesting difference.

Another factor in determining the degree of ionisation of the dihalides, and also the stability of tetrahalides, is the stability of the resultant halotriarylarsonium ion. Thus the tendency of p-tolyl groups to increase electron density on the arsenic will stabilise the (p-tol)₃AsHal⁺ ion and promote ionisation of (p-tol)₃AsHal₂, while the tendency of p-chlorophenyl groups to reduce electron density on the arsenic will render the (p-ClC₆H₄)₃AsHal⁺ ion less stable (than Ph₃AsHal⁺ and (p-tol)₃AsHal⁺) and therefore make (p-Cl.C₆H₄)₃AsHal₂ a weaker electrolyte. In the case of the tetrahalides of tri-p-chlorophenylarsine it seems likely that the lower stability of the cation (p-Cl.C₆H₄)₃AsHal⁺ contributes to the extensive equilibrium observed during titration by favouring an exchange process such as



Formation of higher polyhalides, such as the established $(\text{p-Cl.C}_6\text{H}_4)_3\text{AsI}_6$, must be related to the nature of the aryl group, since it has not been observed for Ph_3As or $(\text{p-tol})_3\text{As}$. The most likely explanation seems to be that the higher electronegativity of the arsenic atom in $(\text{p-Cl.C}_6\text{H}_4)_3\text{As}$ promotes association between cation and anion in all ionised halides, and in favourable conditions can lead to further association of halogen with the anion, e.g.

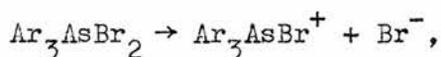


D. Conductance Measurements.

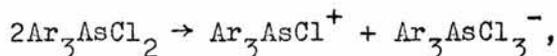
Accurate measurement of the conductances of some of the halides of tri-p-tolylarsine, triphenylarsine and tri-p-chlorophenylarsine was obviously desirable to set the above observations on a more quantitative footing. The involvement of the iodine-containing dihalides in equilibria in methyl cyanide solution suggested that comparison of their conductances would be of doubtful value, and the comparison was therefore restricted to the dichlorides and dibromides. The conductances of these compounds were measured over a range of concentrations and a plot of molar conductance (Λ_m) against square root of molar concentration ($\sqrt{c_m}$) constructed for each. These curves are reproduced in figures 3 and 4, and the measured conductances are recorded in Tables 3 and 4 on pages 41 to 44.

It is immediately obvious that the dibromides show exactly the expected variation in conductance. At $c_m = 0.01 \text{ mole/l}$, for instance, the concentration chosen for comparison, molar conductances are 54.0, 33.5, and $11.5 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$ respectively for $(\text{p-tol})_3\text{AsBr}_2$, Ph_3AsBr_2 and $(\text{p-Cl.C}_6\text{H}_4)_3\text{AsBr}_2$, so that not only is $(\text{p-tol})_3\text{AsBr}_2$ a stronger electrolyte than Ph_3AsBr_2 and $(\text{p-Cl.C}_6\text{H}_4)_3\text{AsBr}_2$ a weaker, but the difference between p-tolyl and phenyl compounds is the same as between phenyl and p-chlorophenyl.

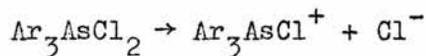
The dichlorides on the other hand do not form a consistent set. There is no significant difference between the conductances of $(p\text{-tol})_3\text{AsCl}_2$ and Ph_3AsCl_2 in the range of concentrations studied, although that of $(p\text{-Cl.C}_6\text{H}_4)_3\text{AsCl}_2$ is considerably less. This can be related to the different modes of ionisation of dichlorides and dibromides of triarylsarsines²⁰. Ionisation of the dibromides involves only charge separation,



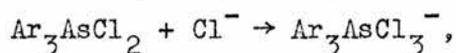
and therefore depends on the nature of the aryl groups as discussed above. Ionisation of the dichlorides, however,



involves removal from, and addition to, the same species Ar_3AsCl_2 of a chloride ion. It may be considered to take place in the two steps



and



and it is possible that however much a change in the electronegativity of the aryl group favours one of these steps it hinders the other to the same degree, so that there is no nett difference in the tendency of the dichloride to ionise. However, the lower conductance of $(p\text{-Cl.C}_6\text{H}_4)_3\text{AsCl}_2$ shows that some other, unrecognised, factor is involved.

It can therefore be concluded that the nature of the aryl group in triarylsarsine-halogen adducts has considerable influence on the stability of the adducts, as witnessed by their electrolytic

behaviour in solution, but only the dibromide appears to be a reliable guide to the direction and magnitude of that influence, when it is measured in this way.

Downs and Schmutzler have recently published some results which appear to form an interesting complement to those recorded here⁶⁰. They have examined the vibrational spectra of the series of fluorophosphoranes $(\text{CH}_3)_n\text{PF}_{5-n}$ ($n = 0$ to 3) in the vapour state, and conclude from calculated bond orders of the axial P-F bonds that these are markedly weakened as n increases, i.e. as the three axial fluorine atoms of the trigonal bipyramidal PF_5 molecule are successively replaced by the much less electronegative methyl groups. These compounds therefore form a series analogous to $(p\text{-Cl.C}_6\text{H}_4)_3\text{AsBr}_2$, Ph_3AsBr_2 , and $(p\text{-tol})_3\text{AsBr}_2$, although the overall change in the electronegativity of the arsenic atom must be considerably greater in the former series. Unfortunately the Br-As-Br stretching frequencies are too low (v. Appendix) to allow use of the same spectroscopic technique (which gives much more direct information on bonding) in investigation of the Ar_3AsBr_2 series, but measurement of the electrolytic conductances of the series of fluorophosphoranes would be of interest.

Table 3 The Conductance of Triarylarsonic Dichlorides in Methyl Cyanide at 25°C.

$(p\text{-tol})_3\text{AsCl}_2$		Ph_3AsCl_2		$(p\text{-Cl.C}_6\text{H}_4)_3\text{AsCl}_2$	
$10^2 c_m$ (mole/l)	Λ_m (ohm ⁻¹ cm ² mole ⁻¹)	$10^2 c_m$ (mole/l)	Λ_m (ohm ⁻¹ cm ² mole ⁻¹)	$10^2 c_m$ (mole/l)	Λ_m (ohm ⁻¹ cm ² mole ⁻¹)
.207	20.01	.160	23.18	.254	4.57
.500	15.94	.339	18.01	.473	3.85
.741	14.24	.523	15.35	.695	2.96
.969	12.96	.712	13.62	.952	2.62
1.23	11.95	.918	12.36	1.21	2.36
1.49	11.35	1.07	11.64	1.49	2.17
1.76	10.70	1.27	10.99	1.80	2.04
2.04	10.17	1.49	10.21	2.12	1.88
2.33	9.76	1.71	9.63	2.45	1.82
limit of solubility		1.93	9.25	2.77	1.73
		2.14	8.85	3.13	1.64
		2.43	8.43		

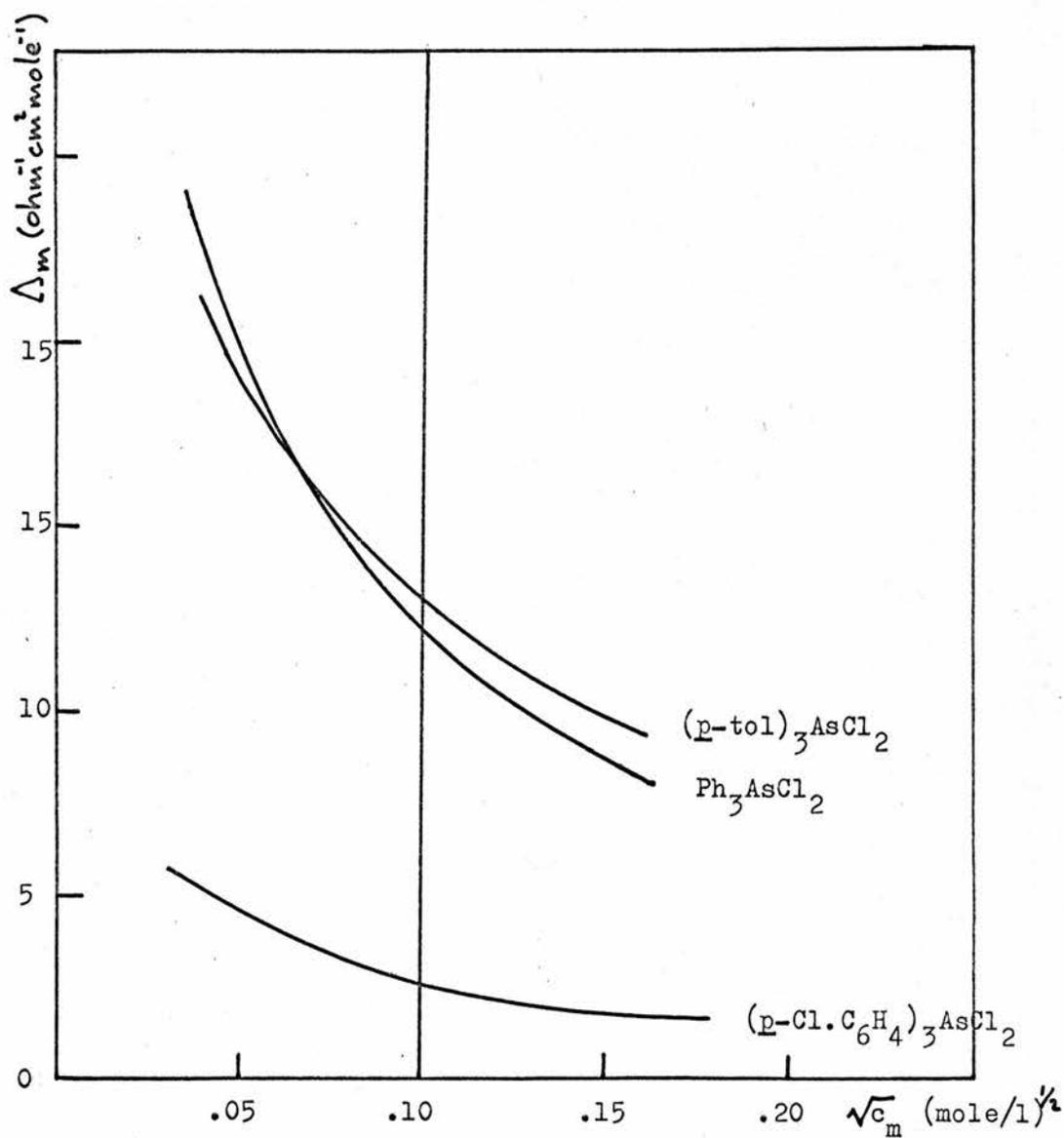


Fig.3 The Electrolytic Conductances of Triarylarsonic Dichlorides in Methyl Cyanide at 25°C

Table 4 The Conductance of Triarylarsonic Dibromides in Methyl Cyanide at 25°C.

$(p\text{-tol})_3\text{AsBr}_2$		Ph_3AsBr_2		$(p\text{-Cl}\cdot\text{C}_6\text{H}_4)_3\text{AsBr}_2$	
$10^2 c_m$ (mole/l)	Λ_m (ohm ⁻¹ cm ² mole ⁻¹)	$10^2 c_m$ (mole/l)	Λ_m (ohm ⁻¹ cm ² mole ⁻¹)	$10^2 c_m$ (mole/l)	Λ_m (ohm ⁻¹ cm ² mole ⁻¹)
.274	80.52	.190	62.77	.107	31.26
.455	69.49	.399	47.87	.247	20.80
.694	60.98	.583	41.73	.387	17.44
limit of solubility		.809	36.38	.526	15.18
		1.04	33.09	.672	13.65
		1.21	30.80	.816	12.75
		1.46	28.69	.962	11.65
		1.73	26.73	1.12	10.86
		2.02	24.92	1.28	10.25
		2.32	23.72	1.45	9.69
		2.68	21.07	1.67	9.08
		2.99	20.09	1.90	8.50

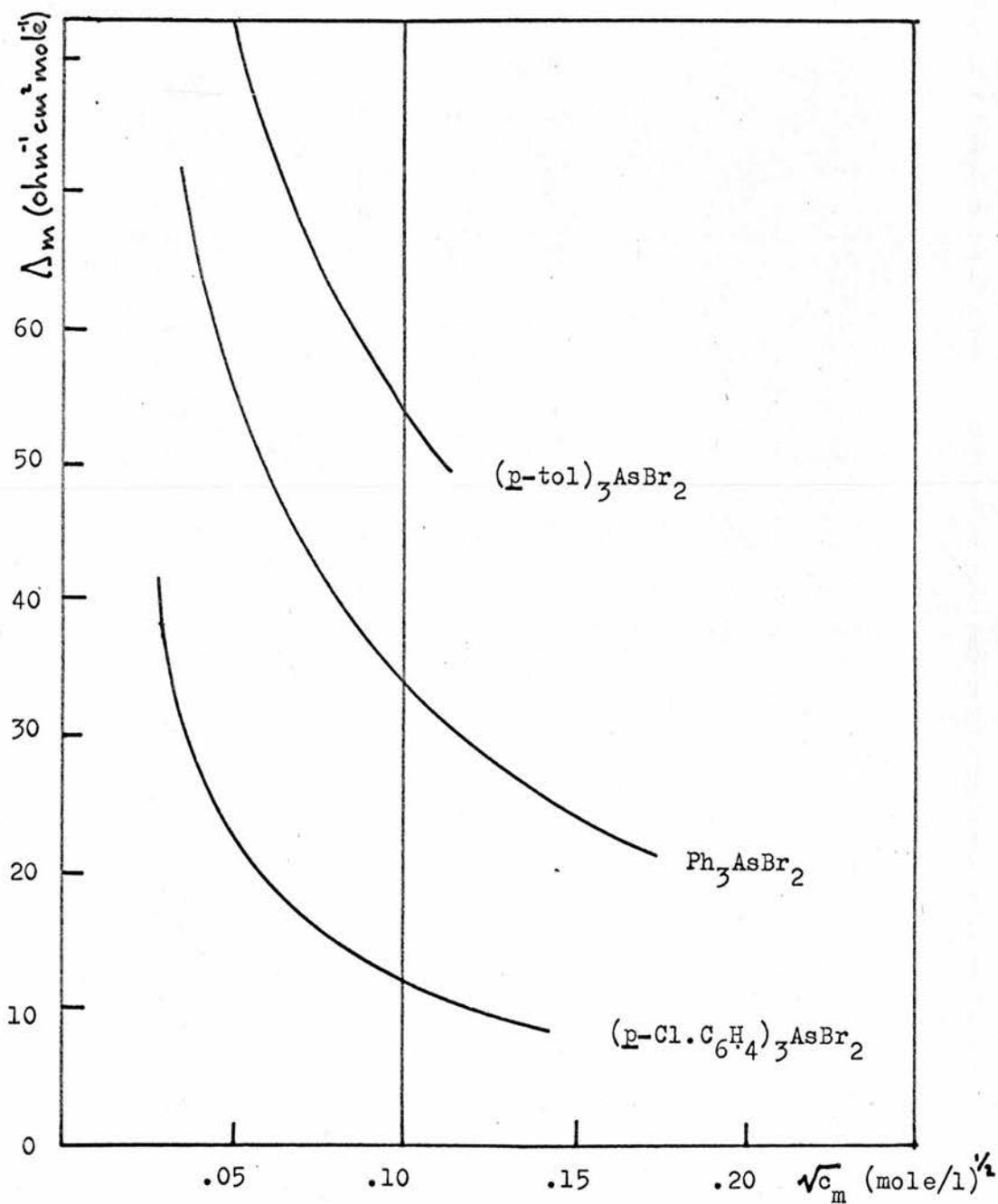


Fig.4 The Electrolytic Conductances of Triarylarsonic Dibromides in Methyl Cyanide at 25°C

P A R T II

PRODUCTS OF HYDROLYSIS OF TRIARYLARSENIC DIHALIDES, AND SOME

RELATED COMPOUNDS

B. (h) Interpretation of the Infrared Spectra of Triaryarsine Hydroxyhalides with reference to the proposed structure

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PRODUCTS OF HYDROLYSIS OF TRIARYLARSENIC DIHALIDES

The 'dihydroxides' and hydroxyhalides of triarylarisines have long been recognised as close analogues of the dihalides, but little experimental work has been done which could confirm or refute this reasonable assumption. It was therefore thought of value to extend recent studies on triphenylarsenic dihalides²⁰ to the series of hydrolysis products $\text{Ph}_3\text{As}(\text{OH})\text{Hal}$, $\text{Ph}_3\text{As}(\text{OH})_2$ and Ph_3AsO , and since the corresponding *p*-tolyl (*p*-tol) and *p*-chloro-phenyl (*p*-Cl.C₆H₄) compounds were available these were also studied in this context.

A. Triarylarisine Oxides and Dihydroxides.

(a) Infrared spectra and solid state structures.

As noted in the introduction (p.16), it has been shown that triphenylarsine dihydroxide, as obtained from hydrolysis of the dihalides $\text{Ph}_3\text{AsHal}_2$, is correctly formulated $\text{Ph}_3\text{AsO}\cdot\text{H}_2\text{O}$ in the solid state and in benzene solution at least. Hydrolysis of tri-*p*-tolylarsenic dibromide, $(\text{p-tol})_3\text{AsBr}_2$, with aqueous alkali yielded a colourless crystalline solid identical with the compound described in the literature^{58b} as tri-*p*-tolylarsenic dihydroxide, but the infrared spectrum of this product showed that it too was

a hydrate of the oxide, $(p\text{-tol})_3\text{AsO}\cdot\text{H}_2\text{O}$. The distinctive $\nu(\text{As-O})^{41}$ appeared as a very strong absorption at 890cm^{-1} and the absorptions characteristic of lattice water^{61a} were observed at 3440, 3280 and 1645cm^{-1} . There were no absorptions which could be attributed to $\nu(\text{O-H})$ of As-OH groups.

Additional evidence was the occurrence in the spectra of both these 'dihydroxides' of fairly strong and extremely broad absorption bands near 600cm^{-1} (e.g. in the spectrum of $\text{Ph}_3\text{AsO}\cdot\text{H}_2\text{O}$ over the range 750 to 500cm^{-1} , with maxima at 670cm^{-1} and 560cm^{-1}). These can probably be assigned to the librational modes of the water molecule^{61a}, since they disappear on dehydration along with the absorptions due to the stretching and bending modes.

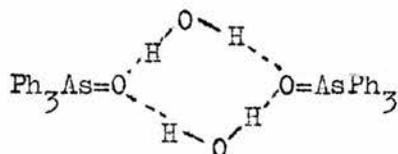
Alkaline hydrolysis of tri-*p*-chlorophenylarsenic dibromide on the other hand produced a white solid identifiable as the anhydrous oxide $(p\text{-Cl}\cdot\text{C}_6\text{H}_4)_3\text{AsO}$ from its infrared spectrum, which showed no hydroxyl stretching frequencies at all, but an As-O stretching frequency of 893cm^{-1} (mean of doublet).

(b) Interconversion of oxides and 'dihydroxides'.

The anhydrous oxides vary in their affinity for water. Aqueous alkaline hydrolysis of halides of triphenylarsine and tri-*p*-tolylarsine yielded only the hydrated oxides, from which the anhydrous compounds were obtained by the action of heat. At 100° prolonged heating was necessary to remove the last traces of

water from these oxides, and they picked up moisture slowly from the atmosphere at ambient temperature. In contrast, tri-p-chlorophenylarsine oxide, obtained directly from aqueous alkali solution, did not become hydrated, even under the action of boiling water.

X-ray analysis of triphenylarsine oxide monohydrate has shown that in the crystals the oxide molecules are linked in pairs by hydrogen bonds through water molecules⁴⁶, and it seemed



reasonable to relate the ease of hydration of an oxide to the nature of the aryl substituent: an electron-withdrawing group such as p-chlorophenyl would render the oxide a poorer Lewis base (by increasing π -bonding between the oxygen and arsenic atoms) and therefore less likely to form hydrogen bonds. However, a survey of which triarylarisines have been reported to form oxide hydrates or dihydroxides did not support this idea. For instance, the hydrolysis products of halides of triphenylarsine and tri-p-tolylarsine are reported to be the 'dihydroxides', while that of the corresponding halides of the intermediate diphenyl-p-tolylarsine is the oxide^{58b,c}. But much of the literature data on organoarsenic chemistry is old and possibly inaccurate, and a new investigation might find such a relationship.

(c) Infrared spectra and structures in solution.

The infrared spectra of triphenylarsine oxide and its monohydrate were recorded in chloroform solution also. That of the anhydrous oxide was the same as in the solid state except for slight splitting of $\nu(\text{As-O})$ ($899/885\text{cm}^{-1}$), and the appearance of a strong and rather broad absorption at 2960cm^{-1} (figure 5). In the absence of any hydroxyl groups the latter was interpreted as $\nu(\text{C-H})$ of chloroform, lowered from 3030cm^{-1} by formation of a strong complex with the oxide. In support of this, splitting of $\nu(\text{As-O})$ is characteristically found in transition metal complexes in which an arsine oxide is co-ordinated through the oxygen⁶². The infrared spectrum of Ph_3AsO in chloroform has been reported by Bernstein and co-workers⁴¹, who assigned $\nu(\text{As-O})$ by the use of 0^{18} . They too report an absorption at 2965cm^{-1} without assignment. They also report a weak absorption at ca. 3300cm^{-1} , and attribute it to traces of water, which they found very difficult to remove completely. This is in agreement with the present work.

In methyl cyanide solution the extra absorption did not appear, but unfortunately this solvent was not found useful in the regions of most interest for infrared studies.

The spectrum of triphenylarsine oxide monohydrate also showed the absorption at 2960cm^{-1} , and $\nu(\text{As-O})$ at $899/885\text{cm}^{-1}$, but in addition weak, broad absorptions at 3320 and 3180cm^{-1} , attributable to hydrogen bonded water (figure 5). Chloroform

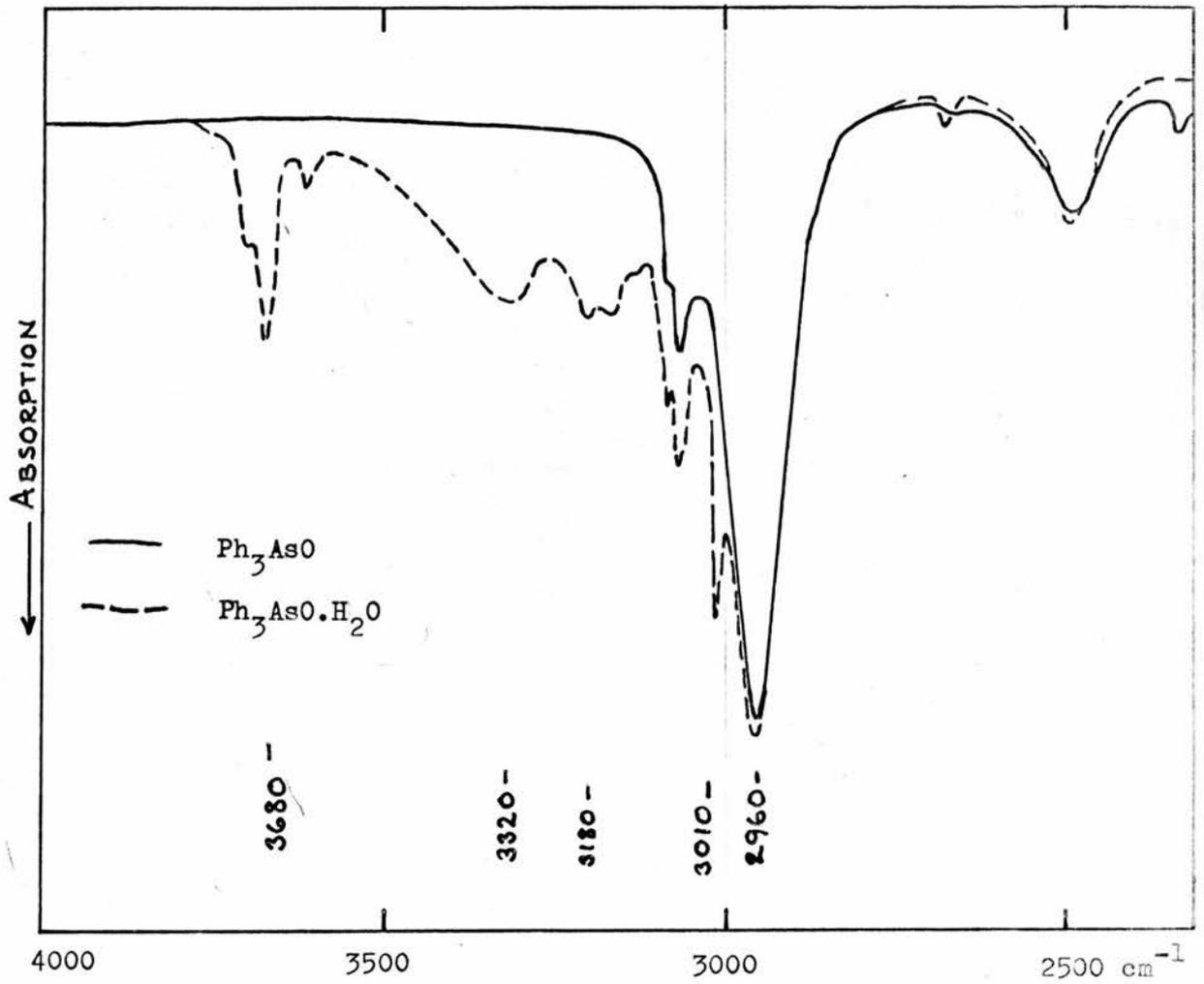


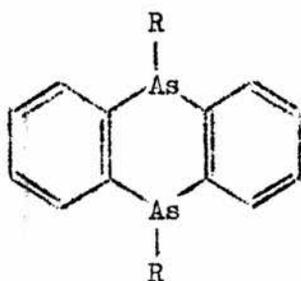
Fig.5 Infrared Spectrum of Triphenylarsine Oxide and Triphenylarsine Oxide Monohydrate in Chloroform solution

absorptions at 3680 and 3010cm^{-1} also appeared in this spectrum. There was thus no evidence for the existence of either $\text{Ph}_3\text{As}(\text{OH})_2$ or $\text{Ph}_3\text{AsOH}^+\text{OH}^-$ in chloroform solution (or in methyl cyanide, so far as could be observed), and this evidence is in accordance with the proposal that neither of these species exists for any arsine.

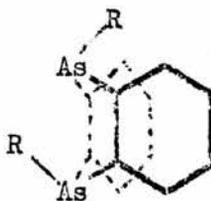
(d) Re-interpretation of some earlier structural evidence.

It seems relevant to point out at this stage that the findings which Mann has quoted⁴⁴ as evidence for a true dihydroxide of an arsine can now be re-interpreted adequately using an oxide hydrate structure.

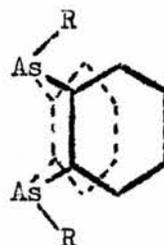
The triorganoarsine 5,10-dihydro-5,10-di-*p*-tolylarsanthrene (i) ($\text{R} = \text{p-CH}_3\cdot\text{C}_6\text{H}_4$) occurs in two isomeric forms, (ii) and (iii), because the pyramidal geometry of arsenic(III) causes folding of the ring system along the As-As axis⁵¹.



(i)



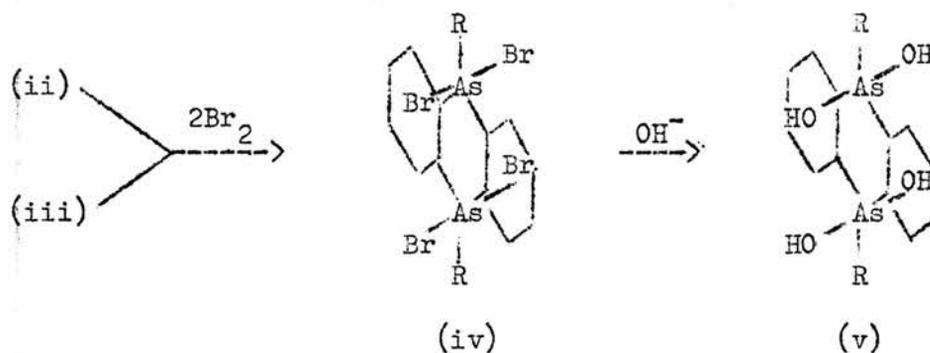
(ii)



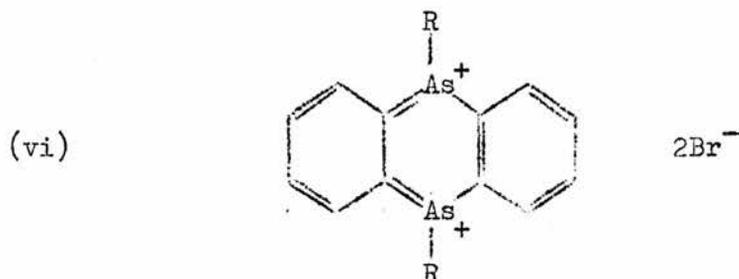
(iii)

The 'tetrahydroxide' of this diarsine was considered to have a necessarily planar ring system because the isomers give the same 'tetrahydroxide', which therefore seems to have lost the fold which

gives rise to the isomerism⁵¹. This in turn would require a C-As-C angle of 120° and implies the normal trigonal bipyramidal configuration for pentavalent arsenic (v). The 'tetrahydroxide' was obtained by hydrolysis of a tetrabromide, also considered planar (iv).

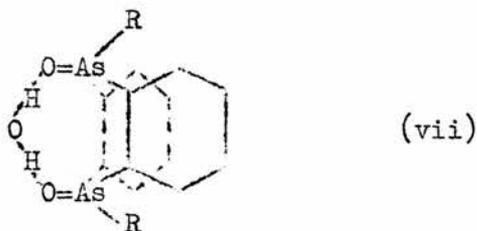


However, the dibromide in solution undoubtedly has the anomalous form (vi), with a planar cation^{30,51}, and addition of a further molar equivalent of bromine to this to form a tetrabromide would be expected to produce tribromide ion, rather than the covalent tetrabromide (iv) assumed. Thus formation of the tetrabromide, or indeed the dibromide, destroys the isomerism of the parent arsanthrene even before hydrolysis is carried out, by giving rise to a molecule which in solution has a cation with a planar ring



system. Such a reaction scheme if correct invalidates Mann's argument⁴⁴.

Hydrolysis of the tetrabromide must involve hydroxide attack at both arsenic atoms, which have a formal positive charge. This might be expected to yield two isomeric oxides (the oxides of (ii) and (iii)) in equal quantities, and these would probably crystallise as their hydrates from aqueous solution. In this case the 'identical tetrahydroxides' would be a mixture of two dioxide dihydrates. It is likely, however, that hydrogen bonding through a water molecule could stabilise the cis isomer and so lead to preferential formation of a monohydrate of the cis isomer (vii). This would be almost indistinguishable from a tetrahydroxide by analysis.



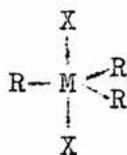
There is therefore no indisputable evidence for the existence of dihydroxides of triarylar sines, and it is considered likely that all so-called dihydroxides will be found to be oxide hydrates, at least in the solid state and in non-aqueous solvents.

B. Triarylsarsine Hydroxyhalides

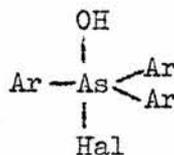
Although, as demonstrated in the preceding section, the 'dihydroxides' are not at all analogous to the dihalides of triarylsarsines, the hydroxyhalides, which are more closely related to these dihalides in formula, might be expected to parallel them in structure and properties, and this comparison was a useful approach to the determination of the structure of these compounds.

(a) Introduction.

Since established structures of compounds of the type R_3MX_2 ($M = As, Sb, Bi$) are all trigonal bipyramidal with D_{3h} symmetry (viii)⁷, the likely structure for the $Ar_3As(OH)Hal$ compounds would then seem to be (ix).

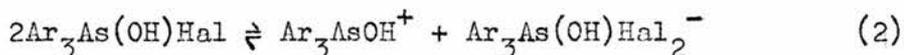
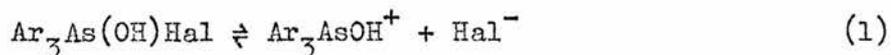


(viii)

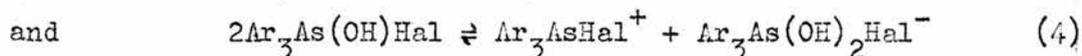
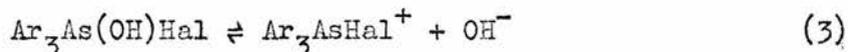


(ix)

Again by analogy with the dihalides they would be expected to be covalent in the solid state and weak electrolytes in a polar solvent, ionising according to one of the equations



Such chemical evidence as already exists, such as the acidity of solutions of triarylar sine hydroxyhalides^{33d}, does not favour the alternative ionisation schemes



Furthermore, just as addition of halogens to tertiary arsine dihalides generates a series of ionic tetrahalides $\text{R}_3\text{AsHal}^+\text{Hal}_3^-$ ²⁰, so it should be possible to add halogen to the hydroxyhalides and obtain hydroxytrihalides $\text{Ar}_3\text{AsOH}^+\text{Hal}_3^-$, provided the ionisation characteristics of $\text{Ar}_3\text{As}(\text{OH})\text{Hal}$ did not forbid this.

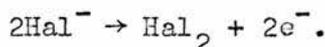
(b) Electrolytic behaviour of $\text{Ph}_3\text{As}(\text{OH})\text{Cl}$ and $\text{Ph}_3\text{As}(\text{OH})\text{Br}$.

The conductances of $\text{Ph}_3\text{As}(\text{OH})\text{Cl}$ and $\text{Ph}_3\text{As}(\text{OH})\text{Br}$ in methyl cyanide at 25° were measured over a range of concentrations (Table 5, overleaf) and were found by intrapotation to be 5.7 and 20.0 $\text{ohm}^{-1}\text{cm}^2\text{mole}^{-1}$ respectively at $c_m = 0.01\text{mole/l}$. Since strong 1:1 electrolytes have molar conductances of ca. $100\text{ohm}^{-1}\text{cm}^2\text{mole}^{-1}$ at this concentration both compounds are weak electrolytes, the chloride extremely so. This was to be expected for covalent solids, and the alternative possibility of the compounds' being ionic solids containing tetraco-ordinate arsonium ions and halide or hydroxide ions (which would be strong electrolytes in solution) could be dismissed.

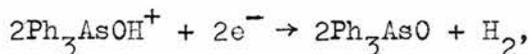
Table 5 The Conductance of Triphenylarsine Hydroxyhalides in Methyl Cyanide at 25°C.

$\text{Ph}_3\text{As}(\text{OH})\text{Cl}$		$\text{Ph}_3\text{As}(\text{OH})\text{Br}$	
$10^2 c_m$ (mole/l)	Λ_m (ohm ⁻¹ cm ² mole ⁻¹)	$10^2 c_m$ (mole/l)	Λ_m (ohm ⁻¹ cm ² mole ⁻¹)
.246	9.76	.192	41.5
.435	7.70	.416	29.3
.630	6.71	.651	24.1
.823	6.07	.912	20.7
1.03	5.69	1.18	18.5
1.26	5.44	1.45	16.8
1.51	5.13	1.73	15.6
1.76	4.89	2.02	14.6
2.02	4.69	2.35	13.6
2.30	4.57	2.65	12.9
2.60	4.42	2.97	12.2
2.88	4.34	3.30	11.7

During electrolysis of a methyl cyanide solution of $\text{Ph}_3\text{As}(\text{OH})\text{Br}$ free bromine (yellow colour) was observed to form at the anode and a gas was liberated at the cathode. On ignition, a sample of this gas, mixed with a little air, first burned with a blue flame, then exploded, and was thus identified as hydrogen. Slow liberation of hydrogen was observed during electrolysis of $\text{Ph}_3\text{As}(\text{OH})\text{Cl}$ also, although chlorine was not detected at the anode, doubtless due to its very low concentration. Methyl cyanide solutions of $\text{Ph}_3\text{As}(\text{OH})\text{Hal}$ therefore contain halide ions and not hydroxide, as expected from their chemical behaviour. The overall process occurring at the anode is



The process occurring at the cathode must then be

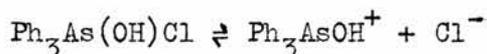


and this was confirmed by observation in the infrared spectrum of the catholyte after electrolysis of the characteristic $\nu(\text{As}-\text{O})$ of Ph_3AsO at 890cm^{-1} , absent from the infrared spectrum of the anolyte. These observations support ionisation schemes (1) and (2) equally well, since $\text{Ar}_3\text{As}(\text{OH})\text{Hal}_2^-$ would behave simply as $[\text{Ar}_3\text{As}(\text{OH})\text{Hal} + \text{Hal}^-]$ (cf. $\text{Ph}_3\text{AsCl}_3^-$ 20).

Attempts were then made to determine the transport numbers of the ions produced in methyl cyanide solution, but it was found difficult to obtain reproducible results, probably because of the low conductance of the compounds, which led to only small changes in concentration at the electrodes and consequent difficulty in accurate analysis. Several determinations on solutions of

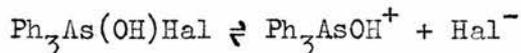
$\text{Ph}_3\text{As}(\text{OH})\text{Cl}$ gave an average value for the transport number of the cation of 0.46 for ionisation (1), and 0.23 for ionisation (2). Since transport numbers of about 0.5 are expected for large ions of the same charge, this result favours ionisation (1) rather than (2). The same conclusion was reached for the bromide.

As an additional check on the possible formation of $[\text{Ph}_3\text{As}(\text{OH})\text{Cl}_2]^-$, which was expected by analogy with the ionisation of Ph_3AsCl_2 ²⁰, a conductimetric titration of $\text{Ph}_3\text{As}(\text{OH})\text{Cl}$ with tetramethylammonium chloride was carried out. The resultant conductance-composition curve was without any discontinuity which would indicate formation of the 1:1 complex $[(\text{CH}_3)_4\text{N}]^+[\text{Ph}_3\text{As}(\text{OH})\text{Cl}_2]^-$, and did not differ appreciably from that obtained when the same tetramethylammonium chloride solution was added to pure solvent. There was thus no indication of the formation of the anion $\text{Ph}_3\text{As}(\text{OH})\text{Cl}_2^-$, and this result along with that of the transport experiments suggested that the simple ionisation scheme



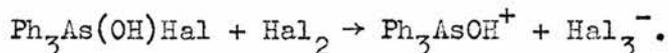
was correct.

Thus the hydroxyhalides of triphenylarsine appear to be covalent solids like the corresponding dihalides, and even weaker electrolytes in solution, differing from them only in that both chloride and bromide ionise to give the simple halide ion in solution.



(c) Reaction of $\text{Ph}_3\text{As}(\text{OH})\text{Hal}$ with halogens.

Previous work on the reactions of the dihalides Ph_3MHal_2 with halogen has shown that conductimetric titration is a valuable technique for following the course of reaction^{19,20}. Conductimetric titrations of $\text{Ph}_3\text{As}(\text{OH})\text{Hal}$ (Hal = Cl, Br) with ICl, Br_2 , IBr, and I_2 were therefore carried out in methyl cyanide. All the conductance-composition graphs were remarkably alike (figure 6), showing a rapid rise in conductance up to the 1:1 $\text{Hal}_2:\text{Ph}_3\text{As}(\text{OH})\text{Hal}$ mole ratio, followed by a slow, steady drop. In every case the solution acquired the strong colour of a trihalide ion from the first addition of halogen. Molar conductances at the 1:1 mole ratios were greater than $100\text{ohm}^{-1}\text{cm}^2\text{mole}^{-1}$ ($c_m = \text{ca. } 0.001 \text{ mole/l}$), and these results were therefore interpreted as showing formation of the strong 1:1 electrolyte $\text{Ph}_3\text{As}(\text{OH})\text{Hal}_3$:



The unusual sharpness of the discontinuity at the 1:1 mole ratio was attributed to the absence of the equilibrium involving halogen exchange at the cation, which is possible in other systems containing halotriphenylarsonium ions. Only the graph indicating formation of $\text{Ph}_3\text{As}(\text{OH})\text{ClBr}_2$ showed any curvature at the 1:1 mole ratio, and this is probably due to the dissociation equilibrium of ClBr_2^- , one of the least stable trihalide ions.

Thus the existence in solution in methyl cyanide of hydroxy-triphenylarsonium salts containing the anions ICl_2^- , ClBr_2^- , IBrCl^- ,

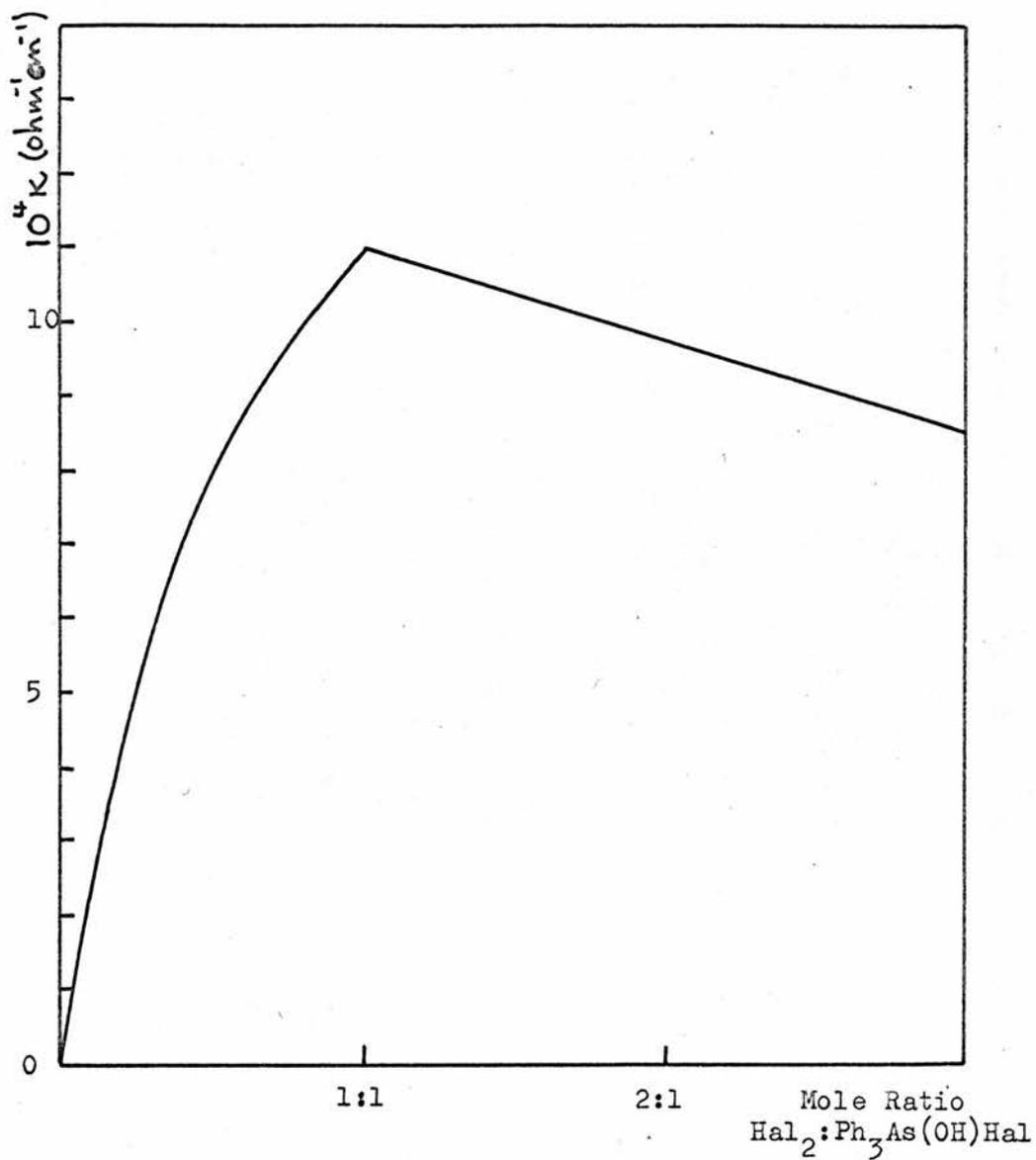


Fig.6 Typical Conductimetric Titration of a Triphenylarsine Hydroxyhalide with Halogen in Methyl Cyanide

I_2Cl^- , Br_3^- , IBr_2^- and I_2Br^- was demonstrated. The tribromide and dichloroiodate(I) were isolated as crystalline solids, but no attempt was made to isolate the others.

In their electrolytic properties and in their reaction with halogens the hydroxyhalides therefore parallel the behaviour of the dihalides, with the exception that the hydroxychloride ionises differently from the dichloride. However examination of the infrared spectra led to different conclusions, and as will be shown in the following section these indicate a structural difference between the two types of compound.

(d) Hydrogen bonding in the triphenylarsine hydroxyhalides.

The infrared spectra of solid triphenylarsine hydroxychloride and hydroxybromide were similar, and differed from those of the hydroxytriphenylarsonium trihalides isolated (to be discussed later). Their most prominent feature was very strong absorption in the region $2750 - 2000\text{cm}^{-1}$ (figure 7a), which could be attributed only to an O-H stretching mode under the influence of very strong hydrogen bonding. $\nu(\text{O-H})$ is reported in this region for the related amine oxide hydrohalides⁶³ and arsenic acids⁶⁴. The hydroxychloride also had a strong, rather broad absorption at 1593cm^{-1} , close to the reported stretching frequency of the H-Cl bonds in the hydrogen dichloride ion HCl_2^- (1565cm^{-1})⁶⁵. Similar

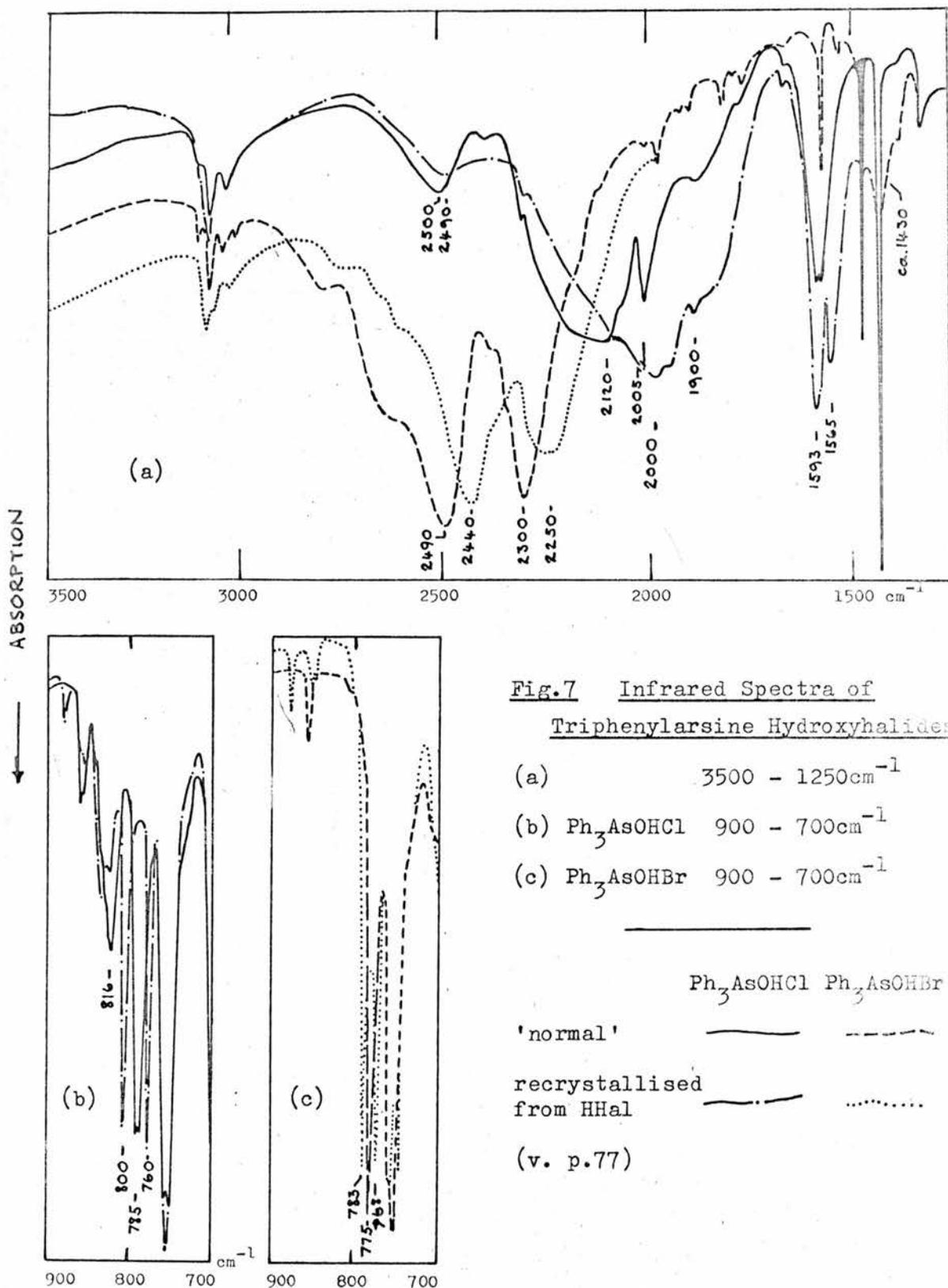


Fig.7 Infrared Spectra of
Triphenylarsine Hydroxyhalides

- (a) 3500 - 1250 cm^{-1}
 (b) Ph₃AsOHCl 900 - 700 cm^{-1}
 (c) Ph₃AsOHBr 900 - 700 cm^{-1}

interpretation of the 1593cm^{-1} absorption as an H-Cl stretch would support extremely strong hydrogen bonding between the oxygen and chlorine atoms, and suggest a structure in which the hydrogen atom is shared more or less equally between them. Assignment of a band in the infrared spectrum of zinc hydroxyfluoride to the stretching of an H-F bond has similarly been suggested⁶⁶, and an absorption in the spectrum of the HClNO_3^- ion is attributed to H-Cl stretching⁶⁷.

In the spectrum of the hydroxybromide on the other hand there is no absorption corresponding to the H-Br stretching frequency of HBr_2^- , 1690cm^{-1} ⁶⁸, but there is a broad peak at ca. 1430cm^{-1} , not present in the hydroxychloride or triphenylarsine itself, whose intensity and exact position are obscured by the strong phenyl ring absorption at 1435cm^{-1} (figure 7a). This may indicate a relatively weaker H-Br bond corresponding to the higher O-H frequency which implies a stronger O-H bond than in the hydroxychloride.

(e) Proposed structure of $\text{Ph}_3\text{As}(\text{OH})\text{Hal}$ in the solid state.

These observations did not support the expected structure (ix) (p.53), in which intramolecular hydrogen bonding is impossible. Intermolecular hydrogen bonding of such strength is less likely, and would be at least partially disrupted in solution. Infrared spectra recorded of solutions in chloroform

the two hydroxyhalides it seems reasonable to suggest that the hydroxybromide also has the structure proposed by Jensen for the hydroxychloride. All presently available evidence therefore suggests that the hydroxyhalides are most correctly represented



and called triphenylarsine oxide hydrohalides.

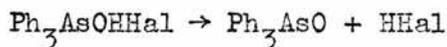
(f) Hydroxyhalides of (p-tol)₃As and (p-Cl.C₆H₄)₃As.

The infrared spectra of the hydroxyhalides of tri-p-tolylarsine and tri-p-chlorophenylarsine differ from those of the corresponding arsines in exactly the same way as do those of the phenyl compounds, and in the 2750 - 2000cm⁻¹ range are almost identical to those of the corresponding triphenylarsine hydroxyhalides, suggesting that they have the same structure. The conductances of these compounds were found not to differ significantly from those of their phenyl counterparts over the range of concentrations studied (Table 5, p.55). This observation means that the nature of the aryl group has no effect on the conductance of triarylararsine hydroxyhalides, in contrast to the dihalides, and supports Jensen's structure in preference to the conventional one, since if the molecule were trigonal bipyramidal its conductance behaviour in methyl cyanide would be expected to resemble that of the dihalides. In the proposed structure, however, the halogen is isolated from the arsenic atom and the

influence of the aryl groups attached to it, and the degree of ionisation in solution would depend principally on the nature of the halogen atom.

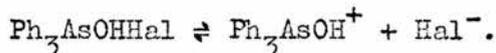
(g) The structure of $\text{Ph}_3\text{As}(\text{OH})\text{Hal}$ in solution.

The infrared spectra of the triphenylarsine hydroxyhalides were obtained in chloroform solution also. They differed from the spectra of the solids principally in the appearance of a strong absorption in each case at 2980cm^{-1} . This was interpreted as the C-H stretching frequency of complexed chloroform, following the interpretation of the spectrum of triphenylarsine oxide (p.48). The hydroxyl absorptions shifted only slightly higher, as was to be expected, and it was concluded that the hydroxyhalides retain their strongly hydrogen bonded structure in solution, not undergoing the possible dissociation to the oxide



to any observable extent. Absence of any detectable $\nu(\text{As-O})$ at 890cm^{-1} confirmed this, and so far as could be observed the spectra in methyl cyanide were the same.

Since conductance measurements in methyl cyanide had shown the presence in solution of a low concentration of Ph_3AsOH^+ and Hal^- ions there must be an equilibrium



No absorption obviously attributable to the Ph_3AsOH^+ ion was

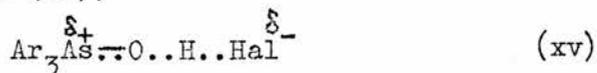
observed, but this was not surprising in view of the very small degree of ionisation of the compounds, particularly the chloride. Conversely this rendered it even less likely that the solid state spectrum was that of an ionic structure.

The possibility that the absorption at 2980cm^{-1} was the O-H stretching frequency of the ion Ph_3AsOH^+ was originally considered, but was dismissed on several grounds. (i) It did not appear when the solvent was methyl cyanide, in which a higher concentration of ions was to be expected; (ii) it was a very strong absorption in relation to the concentration of $\text{Ph}_3\text{AsOHHal}$, and therefore much more in relation to the concentration of Ph_3AsOH^+ ; (iii) a very similar absorption was present in the infrared spectrum of a solution of Ph_3AsO in dry chloroform, which cannot contain Ph_3AsOH^+ ions. Although infrared spectra must be interpreted with caution in regions of strong solvent absorption it is thus considered that the peaks at 2980cm^{-1} in the spectra of the hydroxyhalides can be attributed to solvent rather than solute.

(h) Interpretation of the Infrared Spectra of TriaryarsineHydroxyhalides with reference to the proposed structure.

The hydrogen atom in Ph_3AsOHCl was loosely described as shared equally by the oxygen and chlorine atoms. A more exact description of the bonding between the oxygen, hydrogen and halogen atoms is desirable, particularly since triaryarsine hydroxyhalides have been described as true salts, and preliminary results of an X-ray analysis of Ph_3AsOHCl do not appear to eliminate the possibility of discrete ions in the solid state⁴⁶. The possibility of an ionic solid was dismissed earlier because of the low conductance of the hydroxyhalides, but evidence directly referable to the solid state is obviously necessary. A closer examination of the infrared spectra should provide this.

The two extreme possibilities for the structure of all triaryarsine hydroxyhalides correspond to Jensen's canonical forms (xiii) and (xiv) (p.63) of Ph_3AsOHCl . Absence of the $\nu(\text{As-O})$ of Ar_3AsO at ca. 890cm^{-1} permits dismissal of any structure close to (xiv). In structure (xiii) hydrogen bonding between cation and anion is almost inevitable, and it is suggested that this is in fact so strong that it must be regarded as a bond of fractional order. A more correct representation of the structure would then be (xv),



where .. represents a bond of order less than one, and all bonds

are covalent, though polar. This structure may be regarded as the result of competition for a proton between the bases Ar_3AsO and Hal^- , and analogous to hydrogen bonded species such as HF_2^- and HCl_2^- , differing only in that the hydrogen bond links different groups.

(i) Assignment of frequencies.

$\nu(\text{O-H})$.

The absorption assigned to $\nu(\text{O-H})$ is complex, consisting of two principal (and very intense) bands with subsidiary shoulders (figure 7a, p.61); a direct relationship between frequency and bond order cannot therefore be drawn. It corresponds closely to the $\nu(\text{O-H})$ absorption described by Hadzi and Kobilarov in the infrared spectrum of various liquid adducts of carboxylic acids and oxygen bases⁶⁹. These authors have discussed the origin of this complex absorption at considerable length, but find no one theory entirely satisfactory. However, they stress the absence of the characteristic carboxylate ion absorptions and therefore do not claim an ionic structure.

The other absorptions found (by comparison with the spectra of the parent arsines) to be characteristic of the hydroxyhalides are collected in Table 6 below.

Table 6: Characteristic Frequencies (cm^{-1}) in the Infrared Spectra of Triaryarsine Hydroxyhalides $\text{Ar}_3\text{AsOHHal}$ ($2000 - 625\text{cm}^{-1}$)

Hal	Cl			Br			assignment
Ar	Ph	p-tol	pClC ₆ H ₄	Ph	p-tol	pClC ₆ H ₄	
				*	731	722	$\gamma(\text{O-H})$
	785	778	788	775	773	774	$\nu(\text{As-O})$
	816	820	*				$\gamma(\text{O-H})$
	1230/41	ca.1200	1203	1199	ca.1200	1213	$\delta(\text{O-H})$
	1593	1563	1565	ca.1430	ca.1400	ca.1400	$\nu(\text{H-Hal})?$

* Region obscured by aromatic ring vibrations.

$\nu(\text{As-O})$.

A strong, sharp absorption at ca. 780cm^{-1} was assigned to $\nu(\text{As-O})$. Gordy's rule⁷⁰ predicts⁷¹ the range of frequencies $960-775\text{cm}^{-1}$ for As-O bonds of order two to one, and suggests a bond order very close to one in this case. This may be compared with 940cm^{-1} for $(\text{C}_6\text{F}_5)_3\text{AsO}$ ⁷², 890cm^{-1} for Ph_3AsO (present work), and 778cm^{-1} for $\nu_{\text{as}}(\text{AsOAs})$ of $(\text{AsO}_2\text{Cl})_x$ ⁷³. The difference of $5-14\text{cm}^{-1}$ between the frequencies for corresponding chloride and bromide must be attributed to the influence of the halogen atom, and is not compatible with the presence of the free ion Ph_3AsOH^+ . The

low As-O bond order on the other hand is compatible with presence of Ph_3AsOH^+ , but again comparison with the non-ionic adducts of Hadzi and Kobilarov is useful. They report that in these acid-base adducts $\nu(\text{X-O})$ of the base depends on the strength of the acid, quoting, for instance, values of 1073, 1017, and 1015cm^{-1} for $\nu(\text{S-O})$ of dimethylsulphoxide in solution in carbon tetrachloride, dichloroacetic acid and trichloroacetic acid respectively. The change in $\nu(\text{As-O})$ of Ar_3AsO on formation of the HCl or HBr adduct is comparable to the above change in $\nu(\text{S-O})$ of $(\text{CH}_3)_2\text{SO}$, since HCl and HBr are stronger acids than $\text{Cl}_3\text{C.COOH}$, and thus the assertion that the dimethylsulphoxide adducts are not ionic⁶⁹ lends support to the claim that neither are the Ar_3AsO adducts ionic.

$\delta(\text{O-H})$ and $\gamma(\text{O-H})$.

Two absorptions observed to be characteristic of the hydroxyhalides, one at ca. 1200cm^{-1} and the other in the $700 - 800\text{cm}^{-1}$ region, could be reasonably assigned to the in-plane [$\delta(\text{O-H})$] and out-of-plane [$\gamma(\text{O-H})$] bending frequencies of the hydroxyl group. Support for this comes from Cook's extensive studies of protonated bases, mostly carbonyl compounds. He has found in these great variation in the (complex) $\nu(\text{O-H})$ absorption, but recognised a very characteristic $\delta(\text{O-H})$ at ca. 1260cm^{-1} , independent of the anion, while $\gamma(\text{O-H})$ appeared in the $700 - 900\text{cm}^{-1}$ region and was

very dependent on the anion present⁷⁴. This dependence of $\gamma(\text{O-H})$ on the anion of the acid, also observed in the hydroxyhalides (Table 6), likewise indicates a strong interaction between the different parts of the molecule.

Cook frequently reports splitting of $\delta(\text{O-H})$ due to correlation field coupling, the second component appearing at ca. 1340cm^{-1} . No such splitting was observed here, however, although $\delta(\text{O-H})$ of Ph_3AsOHCl shows a very small splitting, incompletely resolved.

$\nu(\text{H-Hal})?$

The absorption at 1593cm^{-1} in the spectrum of Ph_3AsOHCl has been tentatively regarded as due to the stretching of a weak H-Cl bond, and a possible equivalent in the spectrum of the bromide was detected at ca. 1430cm^{-1} . Corresponding absorptions in the spectra of the other triaryllarsine hydroxyhalides are recorded in Table 6. It is interesting that Cook describes a similar absorption in the spectra of many of his adducts of bases with HCl, and in some of the HBr adducts. He suggests that it is the first overtone of $\gamma(\text{O-H})$ intensified by interaction with another vibrational mode, probably $\nu(\text{O-H})$. The feature is most prominent in the chlorides, which fits either interpretation, in that Cl^- is a stronger base than Br^- and would give rise to a stronger H-Hal bond, while it also results in a lower $\nu(\text{O-H})$ and greater chance of interaction. Without a more detailed spectroscopic study a distinction cannot be made between these possible origins of the band.

(ii) Spectra of deuterated compounds.

Deuteration of Ph_3AsOHCl and Ph_3AsOHBr was attempted by exchange in D_2O . In each case the product was a mixture of $\text{Ph}_3\text{AsOHHal}$ and $\text{Ph}_3\text{AsODHal}$, but several new absorptions could be picked out in its infrared spectrum.

$\nu(\text{O-H})$ was lowered by a factor of only about 1.2 in each case, and the shape of the $\nu(\text{O-D})$ absorption was not the same as that of the $\nu(\text{O-H})$ absorption. The same change has been observed in the spectra of carboxylic acid-base adducts on deuteration⁶⁹. The other characteristic frequencies of the chloride at 1593 and 1230cm^{-1} moved to 1160 and 900cm^{-1} respectively, while that at 816cm^{-1} was reduced in relative intensity, though the spectrum was not recorded far enough to observe $\gamma(\text{O-D})$. The 1199cm^{-1} absorption of Ph_3AsOHBr moved to 874cm^{-1} on deuteration, but any change in the other frequencies could not be observed because of stronger phenyl ring absorptions. In each case where a shift was observed, other than $\nu(\text{O-H})$, the ratio of frequencies was 1.37.

These observations support the assignments made, and in particular the shift of the 1593cm^{-1} absorption seems more suited to a fundamental $\nu(\text{H-Cl})$ than to an overtone of $\gamma(\text{O-H})$.

(iii) Conclusion

These spectra all support the view that triarylar sine hydroxychlorides are most accurately described as covalent acid-base

adducts. The nature of the hydroxybromides is less certain: they are intermediate between the chlorides and ionic compounds, but seem to be sufficiently similar to the former to be regarded as covalent also.

It must be recognised that if this structure is correct and the halogen atom is not independent of the rest of the molecule the assignments are only approximate, and should properly be made to vibrations of the chain $As-O-H-Hal$ as a whole rather than to individual bonds or angles. Cook makes the same point in discussing the spectra of his adducts, but since the approximations made are usually sufficiently accurate the above arguments are not invalidated.

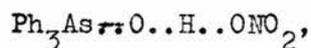
C. Related Hydroxy Derivatives of Triarylarines.

Several compounds related to the hydroxyhalides are known for many arsines, particularly a picrate and nitrate. Some sulphates and chromates have also been reported⁵⁸, and trihalides have been obtained in the present work. These derivatives are made either by the action of acid on the oxide Ar_3AsO , or from a hydroxyhalide by substitution of or addition to the anion. They have not been studied systematically, but it is clear that those formed from acids of similar strength to HCl and HBr are most likely to be covalent adducts like the hydroxyhalides, and not hydroxytriarylarsonium salts.

(a) Triphenylarsine hydroxynitrate.

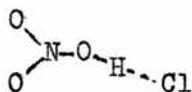
Triphenylarsine hydroxynitrate alone was prepared as representative of this group of compounds, and it is interesting to compare its infrared spectrum with that of the hydroxychloride. It showed no definite absorption attributable to a hydroxyl group, although very weak general absorption in the range $3000 - 2000\text{cm}^{-1}$ was observed. The highest frequency absorption other than $\nu(C-H)$ was a broad band at 1650cm^{-1} , which is probably best described as an NO_2 asymmetric stretch⁷⁵, and the only absorption which could be found in the region in which $\nu(As-O)$ was expected was a rather broad one of medium intensity at 830cm^{-1} . The other absorptions

of the NO_3 group are difficult to assign, but absorption over most of the region $1700 - 625\text{cm}^{-1}$ was rather high, and the spectrum as a whole resembled that of certain adducts characterised by Hadzi as containing strong, almost symmetrical hydrogen bonds, in particular that of triphenylarsine oxide with trichloroacetic acid⁵³. Hence the hydroxynitrate appears to be more correctly a triphenylarsine oxide-nitric acid adduct,

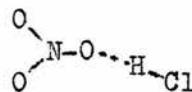


with the central proton less closely associated with the oxide than in the HCl adduct.

In view of this the published infrared spectrum of the intermediate species, the ClHNO_3^- anion, is of considerable interest. The above conclusions suggest that at least in the solid state the affinity of the nitrate ion for a proton is greater than that of the chloride ion, and that therefore the complex anion should have the structure (xvi). The infrared spectrum has been



(xvi)



(xvii)

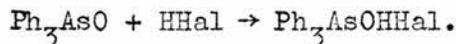
interpreted by Salthouse and Waddington⁶⁷ as favouring (xvii), but in view of its close resemblance to that of Ph_3AsOHCl it is suggested that their interpretation is wrong, and that the comparisons used to assign frequencies were inadequate.

Absorptions at 2250 and 1700 cm^{-1} assigned to the H-Cl stretch and O-H-Cl in-plane bend respectively seem more suited to O-H stretching and H-Cl stretching (or O-H-Cl asymmetric and symmetric stretching) (cf. Ph_3AsOHCl frequencies ca. 2100 and 1593 cm^{-1}). Description of frequencies as far apart as 1700 and 870 cm^{-1} as in-plane and out-of-plane O-H-Cl bending frequencies is unlikely when the O-H-Cl unit is linear, and the latter is a reasonable frequency for $\gamma(\text{O-H})$. Assignment of a frequency as low as 393 cm^{-1} to $\nu(\text{O-H})$ or its first overtone is not in keeping with the strength of bonding implied by the high bending frequencies. Although alternative assignments for these frequencies (which are sensitive to deuteration) cannot be made safely without closer examination of the whole spectrum, the evidence presented by Salthouse and Waddington seems compatible with the present findings only if these reassignments are accepted.

The observed loss of HCl from the ClHNO_3^- ion on heating does not necessarily reflect the structure in the crystalline solid at room temperature or favour structure (xvii), since heating of (xvi) would also be expected to give HCl. On the other hand the molar conductance of $\text{Ph}_3\text{AsOHONO}_2$ in methyl cyanide indicates that it is a stronger electrolyte than Ph_3AsOHBr . ($\Lambda_m = 27.1$ for nitrate, 20.0 for bromide, $c_m = 0.01\text{mole/l}$). Using the same reasoning as before this would support structure (xvii) in solution, but the extrapolation from solution to solid state is unsound, and insufficient data is available for this point to be discussed.

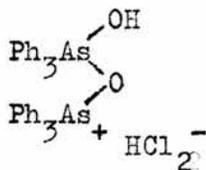
(b) Modified forms of the triphenylarsine hydroxyhalides.

Addition of HHal to triarylar sine oxides has long been known as a route to the hydroxyhalides^{58d}, e.g.

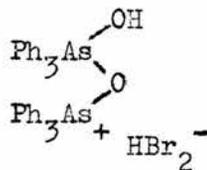


Ph_3AsOHCl and Ph_3AsOHBr were obtained by this method on several occasions, but in one instance the interesting observation was made that the product from reaction of Ph_3AsO with HCl , although having the correct analysis and melting point for Ph_3AsOHCl , had a different infrared spectrum. The same product was obtained on slow crystallisation of normal Ph_3AsOHCl from dilute aqueous HCl . On heating (at 100° to remove traces of solvent) it reverted to normal Ph_3AsOHCl , which explains why it necessarily has the same melting point (171°) as normal Ph_3AsOHCl . This conversion was noted to occur also on recrystallisation from methyl cyanide/ether, at room temperature. The only observable differences of this product from normal Ph_3AsOHCl were the following in the infrared spectrum of the solid (figure 7, p.61): (i) the strong hydroxyl absorption occurred at a slightly lower frequency (fig.7a); (ii) the strong absorption at 1593cm^{-1} , attributed to $\nu(\text{H-Cl})$ in normal Ph_3AsOHCl , was accompanied by another at 1565cm^{-1} (fig.7a); (iii) the sharp peak at 785cm^{-1} in normal Ph_3AsOHCl was replaced by two at 760 and 800cm^{-1} (fig.7b). None of these differences was observed when the spectrum was recorded in solution: in that case the spectrum was indistinguishable from that of normal Ph_3AsOHCl .

Points (ii) and (iii) appeared to indicate the presence of two types of H-Cl and As-O bonds, and the structure (xviii) was considered. This is analogous to tri-*o*-tolylarsine hydroxy-oxybromide, reported by Lyon and Mann⁵⁴, except that one of the



(xviii)



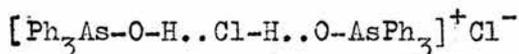
(xix)

bonds must be ionic.

Recrystallisation of Ph_3AsOHBr from dilute aqueous HBr likewise produced a compound having the same analysis and melting point, but differing in its infrared spectrum, in that $\nu(\text{O-H})$ was lower and there were two peaks at ca. 780cm^{-1} in place of the single one at 775cm^{-1} in the spectrum of the normal hydroxybromide (fig.7c). No difference was observed in the 1400cm^{-1} region, but $\delta(\text{O-H})$ of the bromide shifted slightly lower and a weak peak at 1340cm^{-1} became intensified.

These compounds appeared to be completely analogous from their infrared spectra, but the bromide did not seem to fit the structure (xix), since the characteristic frequencies of the HBr_2^- ion⁶³ could not be observed. Also in the case of the chloride although the 1565cm^{-1} absorption was correct for HCl_2^- the 1180cm^{-1} absorption⁶⁵ could not be observed. Furthermore, while one of the absorptions at ca. 780cm^{-1} could be satisfactorily compared

with the As-OH stretching frequency of $\text{Ph}_3\text{AsOHHal}$ the other did not compare well with the As-O-As asymmetric stretching frequency of $(\text{Ph}_2\text{As})_2\text{O}$, synthesised for comparison, which occurred as a broad band about 750cm^{-1} . The close similarity between these compounds suggests that they are but slightly modified forms of the structure $\text{Ph}_3\text{AsOHHal}$. They may simply represent a different crystalline form in which coupling of certain vibrational modes is possible and results in splitting of some of the absorptions of the normal $\text{Ph}_3\text{AsOHHal}$. In this connection the appearance of a stronger absorption at 1340cm^{-1} in the spectrum of the modified hydroxybromide is reminiscent of the correlation field splitting reported by Cook (v. p.71 and ref.74), which is dependent on crystal site as well as molecular symmetry. These modified hydroxyhalides might also be structural isomers; for example, the hydrogen bonded structure



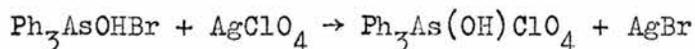
is a possibility: its similarity to Ph_3AsOHCl would account for the similarity of the spectra, while its asymmetry would account for the duplication of some absorptions.

The first interpretation seems the more probable, but only X-ray analysis of the two structures is likely to be able to determine the exact nature of the difference between them.

(c) Hydroxytriphenylarsonium salts

The hydroxy derivatives of triphenylarsine so far studied appeared to be covalent acid-base adducts. That is, for example, $\text{Ph}_3\text{As}(\text{OH})\text{Cl}$ is really $\text{Ph}_3\text{As}-\text{O}\cdots\text{H}\cdots\text{Cl}$. The stronger the acid, however, the less symmetric the hydrogen bond (H moves nearer O), and it seemed likely that a sufficiently strong acid (HX) would give rise to an ionic hydroxytriphenylarsonium salt, $\text{Ph}_3\text{AsOH}^+\text{X}^-$.

Synthesis of triphenylarsine hydroxyperchlorate from the reaction



was therefore attempted in the hope that the perchlorate, if it formed at all, would be an ionic solid containing hydroxytriphenylarsonium ions. When solutions of Ph_3AsOHBr and silver perchlorate were mixed an immediate precipitate of silver bromide was obtained, and the perchlorate extracted from the resultant solution analysed correctly, after recrystallisation, for $\text{Ph}_3\text{As}(\text{OH})\text{ClO}_4$.

The infrared spectra of solid and solution state were the same, and the high conductance in methyl cyanide solution ($\Lambda_m > 100 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$, $c_m = 0.01 \text{ mole/l}$) identified the compound as a strong 1:1 electrolyte. The hydroxyl absorption consisted of a single broad but sharp band at ca. 3000 cm^{-1} , quite different from that of the hydroxyhalides (figure 8). This may therefore be assigned to the O-H stretching vibration of the Ph_3AsOH^+ ion. Such a low frequency for $\nu(\text{O-H})$ indicates that hydrogen bonding

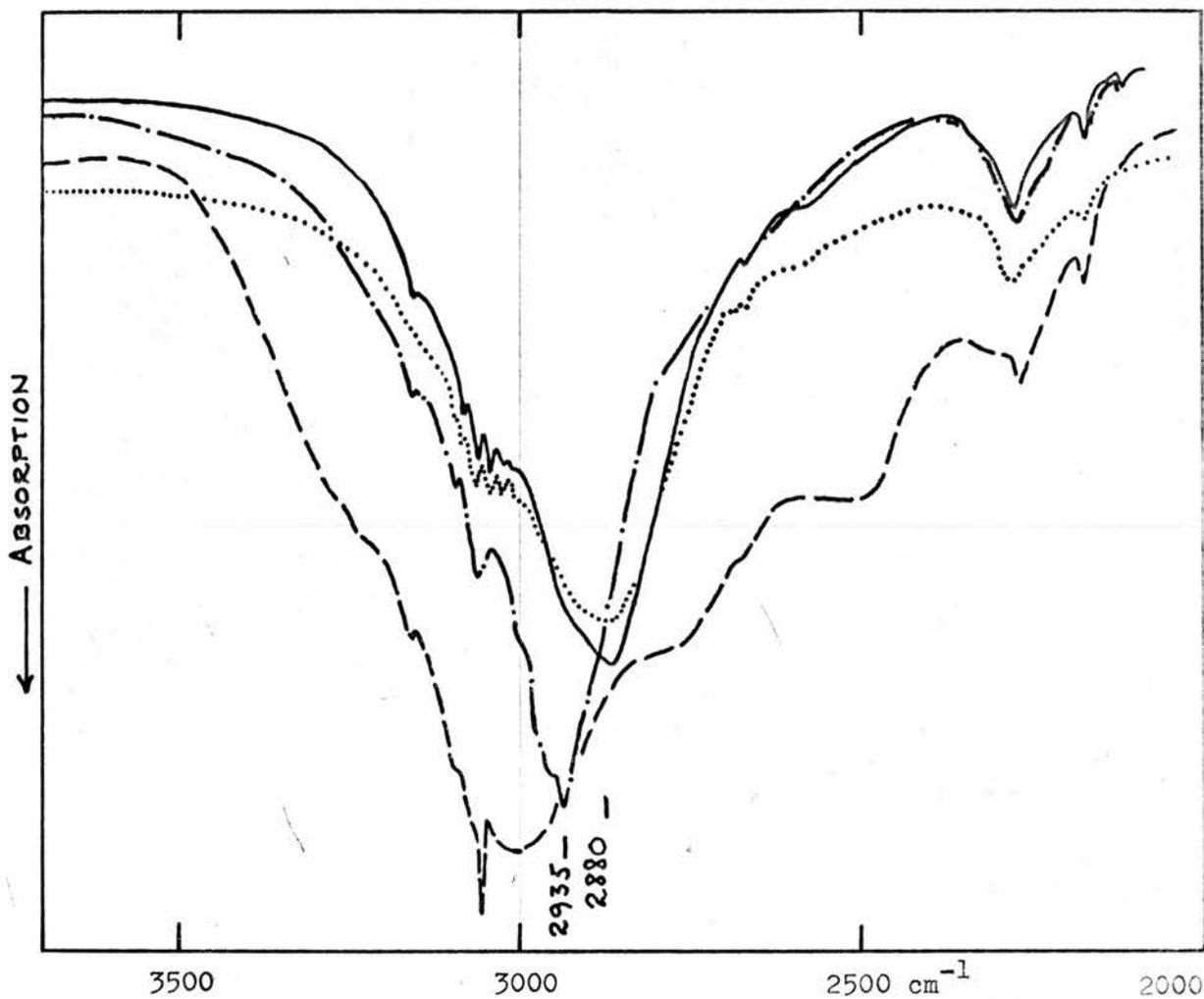
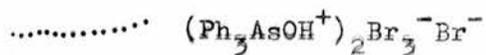
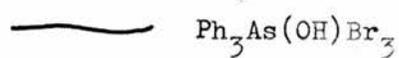
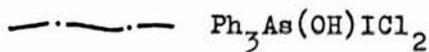
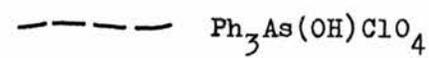


Fig.8 The characteristic Hydroxyl stretching frequency in the Infrared Spectrum of Hydroxytriphenylarsonium Salts (Hexachlorobutadiene mull)



is still strong, but in view of the compound's electrolytic behaviour it may be regarded as occurring between cation and anion - i.e. the proton is to be associated with the As-O rather than the perchlorate ion. Hydrogen bonding to one oxygen of the perchlorate ion was confirmed by observation of two absorptions at ca. 1100cm^{-1} in the infrared spectrum, instead of the single ν_3 of the free ion, and of a third absorption at 928cm^{-1} , the frequency of the infrared inactive ν_1 of the free ion: these features of the spectrum indicate lowering of the symmetry of ClO_4^- from T_d to C_{3v} ^{61b}.

The hydroxytrihalides whose existence as strong electrolytes in methyl cyanide solution was demonstrated are presumably similar to the perchlorate. The rather labile tribromide (prepared by addition of bromine to Ph_3AsOHBr), was found to have an infrared spectrum like that of the perchlorate in the 3000cm^{-1} region (fig.8), showing that it has the expected structure $\text{Ph}_3\text{AsOH}^+\text{Br}_3^-$, analogous to $\text{Ph}_3\text{AsBr}^+\text{Br}_3^-$. The product obtained on addition of ICl to Ph_3AsOHCl likewise appears to have the structure $\text{Ph}_3\text{AsOH}^+\text{ICl}_2^-$, with some hydrogen bonding between the ions. (fig.8)

The persistence of strong hydrogen bonding in all compounds of this type prepared suggested that hydrogen bonding might be necessary to stabilise the cation. Preparation of hydroxytriphenyl-arsonium tetraphenylborate, in which such bonding is impossible between cation and anion, was therefore attempted, without success,

and to date there are no compounds $\text{Ph}_3\text{AsOH}^+\text{X}^-$ known in which the anion could not take part in hydrogen bonding with the cation.

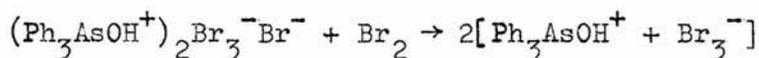
As noted before the triphenylarsine hydroxyhalides in forming trihalides are behaving as normal ionic halides. They also act as halide ion donors to suitable acceptor molecules, and the compounds $[\text{Ph}_3\text{AsOH}^+]_2[\text{HgHal}_4]^{2-}$ (Hal = Cl, Br) have recently been reported⁴⁵. They have an infrared spectrum similar to that described above for the trihalides and perchlorate, and are therefore also hydroxy-triphenylarsonium salts.

(d) A mixed anion compound.

An interesting hydroxytriphenylarsonium salt was isolated during attempts to prepare $\text{Ph}_3\text{As}(\text{OH})\text{Br}_3$. Trihalides of this type were commonly prepared by addition of ether to a methyl cyanide solution containing halide and halogen in the correct proportion: precipitation of the crystalline trihalide usually occurred. But attempts to prepare $\text{Ph}_3\text{As}(\text{OH})\text{Br}_3$ in this way invariably produced orange crystals, m.p. 150° , whose bromine content corresponded exactly to the formula $\text{Ph}_3\text{As}(\text{OH})\text{Br}_2$.

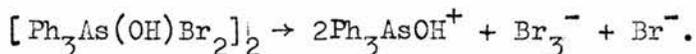
The infrared spectrum of this compound contained a peak at 3000cm^{-1} which suggested the presence of Ph_3AsOH^+ ions, and its UV spectrum showed the presence of tribromide ions. These data can best be explained by the formulation $(\text{Ph}_3\text{AsOH}^+)_2\text{Br}_3^-\text{Br}^-$, containing both bromide and tribromide ions. In support of this

the extinction coefficient of the tribromide ion calculated on the basis of this formula was in good agreement with published values, and when a conductimetric titration of the compound with bromine was carried out a break occurred at the 1:1 mole ratio, indicating that the reaction

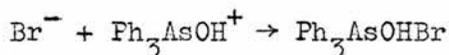


was taking place (figure 9). Freeze drying of a solution in methyl cyanide of equal amounts of Ph_3AsOHBr and $\text{Ph}_3\text{As}(\text{OH})\text{Br}_3$ produced a homogeneous orange solid identical to the above, lacking in particular the characteristic hydroxyl absorption bands of Ph_3AsOHBr in its infrared spectrum.

In solution a compound of this type would normally be expected to furnish four ions, thus:



However interaction of Br^- with Ph_3AsOH^+ will occur to a large extent in this case to produce covalent Ph_3AsOHBr , since this latter is a weak electrolyte in methyl cyanide.



Thus one mole of the mixed anion compound gives rise to two ions and not four as the formula of the solid suggests. In keeping with this the molar conductance in solution is that expected for a strong 1:1 electrolyte, and only slightly greater than that of $\text{Ph}_3\text{As}(\text{OH})\text{Br}_3$. The infrared spectrum of $(\text{Ph}_3\text{AsOH}^+)_2\text{Br}_3^-\text{Br}^-$ in solution in chloroform is the same as the combined spectra of Ph_3AsOHBr and $\text{Ph}_3\text{As}(\text{OH})\text{Br}_3$ in the same solvent. (figure 10).

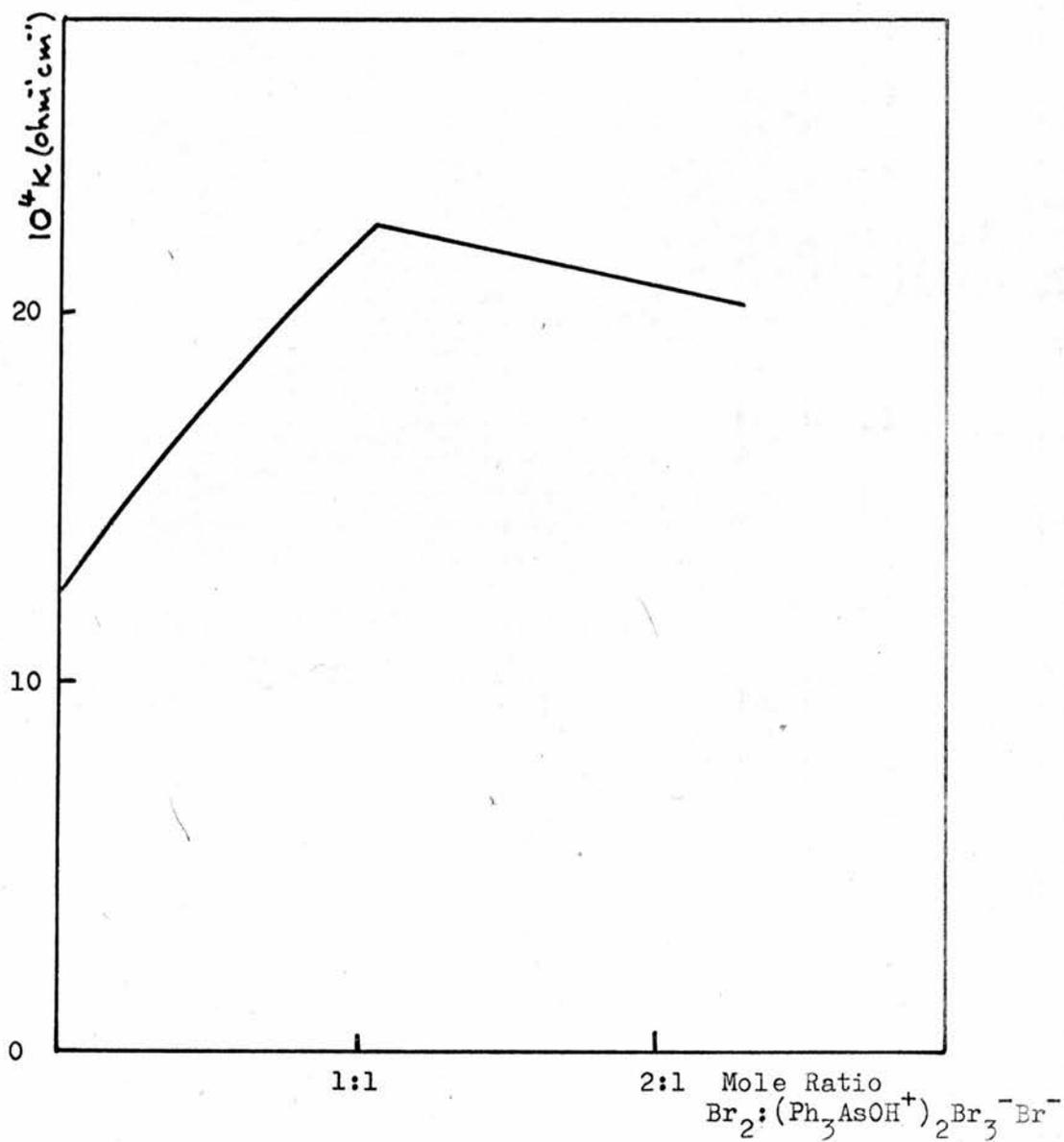


Fig.9 Conductimetric Titration of $(\text{Ph}_3\text{AsOH}^+)_2\text{Br}_3^-\text{Br}^-$ with Bromine in Methyl Cyanide

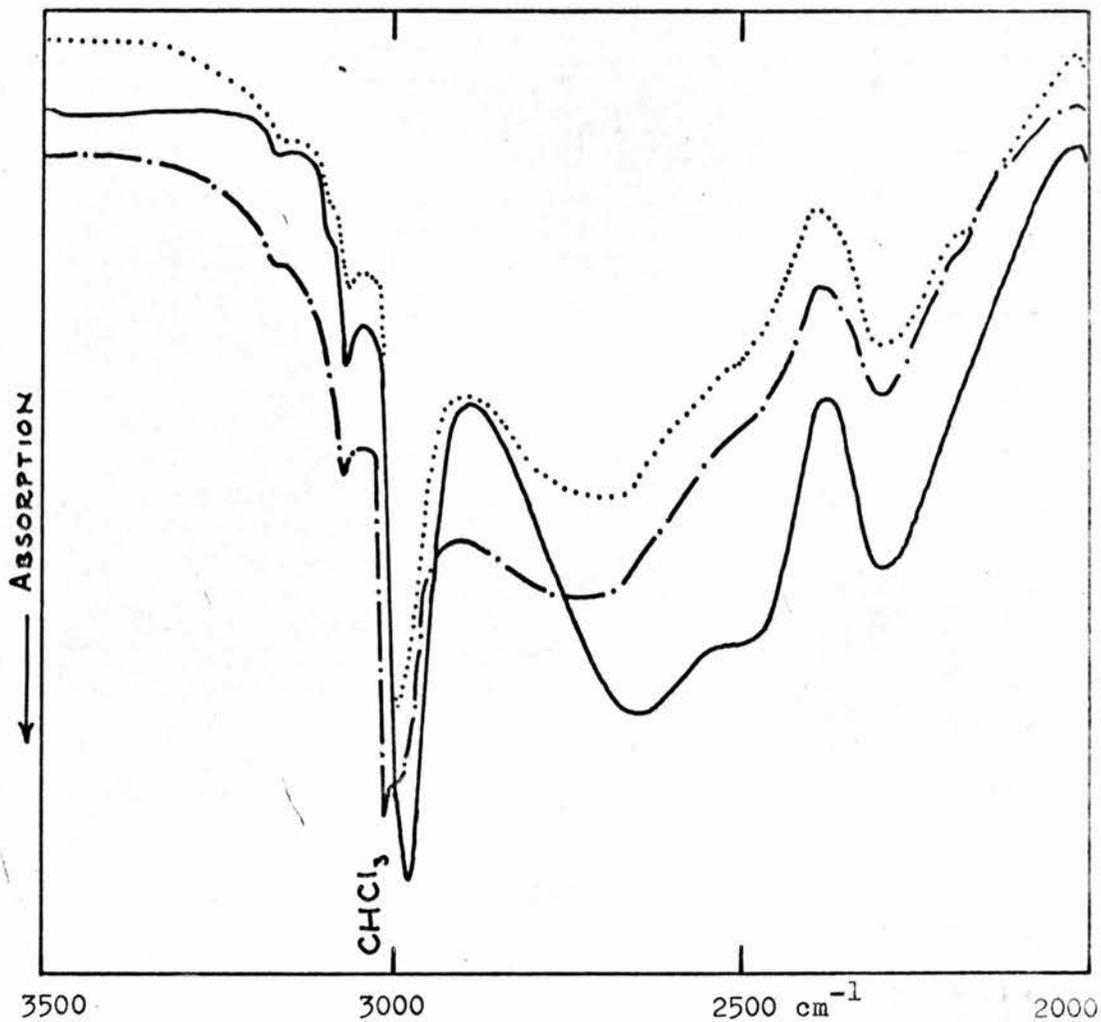


Fig.10 Infrared Spectra in Chloroform Solution of

- (a) Ph_3AsOHBr —
- (b) $\text{Ph}_3\text{As(OH)Br}_3$ ·····
- (c) $(\text{Ph}_3\text{AsOH}^+)_2\text{Br}_3^- \text{Br}^-$ - · - · -

The tribromide $\text{Ph}_3\text{As}(\text{OH})\text{Br}_3$ itself was obtained only by freeze drying a solution containing equimolar quantities of Ph_3AsOHBr and Br_2 , and was a soft orange solid (m.p. ca. 60°) smelling strongly of bromine, which lost bromine on standing if not kept in a tightly sealed container. On being washed with ether it was converted to the mixed anion compound. Thus it seems that crystallisation of $(\text{Ph}_3\text{AsOH}^+)_2\text{Br}_3^-\text{Br}^-$ rather than $\text{Ph}_3\text{AsOH}^+\text{Br}_3^-$ must be a question of lattice stability. In solution the mixed anion compound does not exist as such, and if ether is added to the methyl cyanide solution of equal amounts of Ph_3AsOHBr and $\text{Ph}_3\text{As}(\text{OH})\text{Br}_3$ it is Ph_3AsOHBr which precipitates first. The mixed anion compound appears later, when a sufficient excess of bromine is present, but $\text{Ph}_3\text{As}(\text{OH})\text{Br}_3$ cannot be isolated at all in this way.

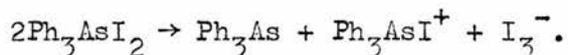
The corresponding p-tolyl compound was obtained from the reaction of tri-p-tolylarsine with excess bromine in wet methyl cyanide. A compound believed to have a similar constitution has since been isolated from the reaction of Ph_3AsCl_2 and ICl in moist methyl cyanide: its analysis is consistent with the formulation $(\text{Ph}_3\text{AsOH}^+)_2\text{ICl}_2^-\text{Cl}^-$ ⁷².

(e) Triphenylarsine hydroxyiodide.

As mentioned in the introduction, there are no well authenticated reports of the existence of triarylsarsine hydroxy-

iodides, but since a few have been reported once in the literature (v. p.21), and no good reason could be seen for their non-existence, several attempts were made to synthesise triphenylarsine hydroxy-iodide for comparison with the chloride and bromide.

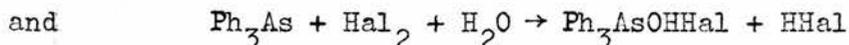
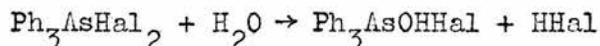
Whereas atmospheric moisture hydrolyses the dichloride and dibromide of triphenylarsine to the corresponding hydroxyhalide it was found possible to prepare the di-iodide in undried solvent and handle it in the open without effect on its composition. Reaction of triphenylarsenic di-iodide in solution is complicated by its disproportionation



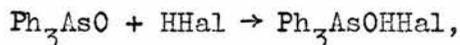
It was not surprising, therefore, that treatment of the di-iodide with hot water produced a red (tri-iodide) solid which appeared from its poor infrared spectrum and melting point to be a mixture, but neither was there any evidence for the presence of a hydroxy compound in this product. When a stronger base was used (e.g. dilute ammonium hydroxide) complete hydrolysis to the oxide occurred.

When water was added to the red (tri-iodide containing) solution of Ph_3AsI_2 in ordinary acetone the colour disappeared. Although this seemed to indicate a definite reaction freeze drying of the colourless solution yielded only a mixture of products similar to that obtained by the action of hot water on the di-iodide. These were thought to include Ph_3As , Ph_3AsI_2 and Ph_3AsI_4 .

Thus the reactions



which yield the hydroxychloride and bromide do not lead to a hydroxyiodide. The other common route to hydroxyhalides,



was therefore examined, but reaction of Ph_3AsO with HI again led to a mixture of products, which did not include the desired one. The elucidation of the course of this reaction is the subject of the following section, and during the work described there it was found that immediate reaction occurs between equivalent quantities of hydroxytriphenylarsonium ions and iodide ions. It is therefore obvious that triphenylarsine hydroxyiodide cannot exist in solution, since by extrapolation from the chloride and bromide considerable ionisation would be inevitable. These observations throw extreme doubt on all reports of the preparation of tertiary arsine hydroxyiodides.

D. General Conclusions.

It has been shown that the hydroxyhalides of triphenylarsine do not have the structure based on pentaco-ordinate arsenic which has often been assumed. They are more correctly regarded as adducts of molecular hydrogen halide with the base triphenylarsine oxide, and these, and other hydroxy derivatives of triphenylarsine, may be considered as structures resulting from the competition of triphenylarsine/oxide and another, anionic, base for a proton. The position of the proton in the central bond of the molecule depends on the basicity of the anion, compared with triphenylarsine oxide. Thus with a strong acid such as perchloric the proton is associated almost entirely with the Ph_3AsO molecule, $\text{Ph}_3\text{AsOH}^+\text{ClO}_4^-$, while with a weaker, such as nitric, the proton is equally shared by Ph_3AsO and anion, $\text{Ph}_3\text{AsOHONO}_2$. When the acid is very weak, e.g. acetic, the proton remains associated with it and no compound formation with Ph_3AsO occurs.

These ideas can be used to rationalise the non-existence of the hydroxyhalides $\text{Ph}_3\text{As}(\text{OH})\text{F}$ and $\text{Ph}_3\text{As}(\text{OH})\text{I}$. The affinity of fluoride for hydrogen is sufficiently great to remove a proton completely from Ph_3AsOH^+ , while that of iodide is so low that it cannot stabilise Ph_3AsOH^+ by hydrogen bond formation and further reaction takes place. They thus represent the extremes of the structure $\text{Ph}_3\text{AsOHHal}$ in which the proton is associated entirely with one part of the molecule.

P A R T III

SOME ADDUCTS OF TRIPHENYLARSINE OXIDE WITH PROTONIC ACIDS

SOME ADDUCTS OF TRIPHENYLARSINE OXIDE WITH PROTONIC ACIDS.

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SOME ADDUCTS OF TRIPHENYLARSINE OXIDE WITH PROTONIC ACIDS.

The compounds described in the previous part of this thesis may all be regarded as 1:1 adducts of the base Ph_3AsO with protonic acids, although in some cases the free acid (e.g. HBr_3) is not known. This part of the thesis deals with the preparation and properties of a series of 2:1 adducts of Ph_3AsO with the same acids.

A. Reaction of Triphenylarsine Oxide with Acids.

(a) Reaction of Ph_3AsO with HI

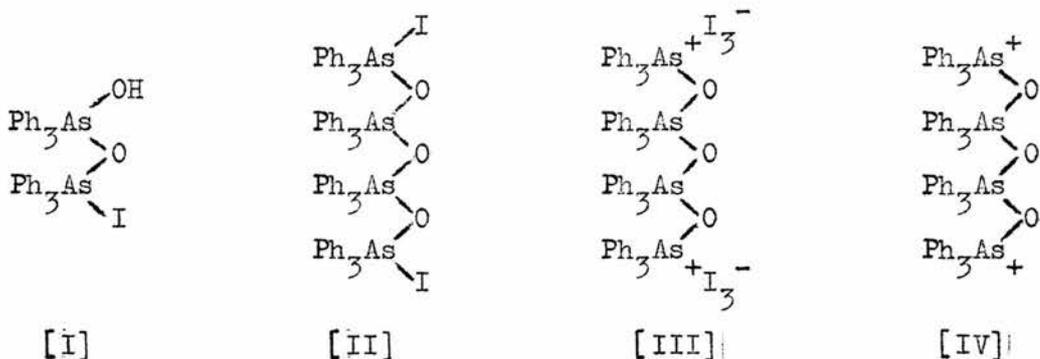
During the study of triphenylarsine hydroxyhalides attempts were made to prepare the hydroxyiodide by the action of hydriodic acid on triphenylarsine oxide. Addition of dilute aqueous HI to a solution of $\text{Ph}_3\text{AsO}\cdot\text{H}_2\text{O}$ in boiling water resulted in immediate precipitation of a mass of yellow-brown crystals. These dissolved in polar solvents to give a red solution from which addition of ether initiated consecutive crystallisation of two compounds, the first forming pale yellow plates, m.p. $153 - 155^\circ$, [Y],

the other chocolate brown needles, m.p. 116 - 118°, [Z]. The original product appeared to have been [Y] discoloured by [Z].

[Y] and [Z] had identical infrared spectra in the range 4000 - 625cm⁻¹, the most conspicuous feature of which was absence of the very characteristic absorptions of the hydroxyl group which were present in the spectra of the other triarylsarsine hydroxyhalides. There was in fact no absorption above 1700cm⁻¹ attributable to a hydroxyl group. The colour of [Z] suggested that it was a tri-iodide, and the identical spectra (figure 11) were in keeping with the reasonable assumption that [Y] and [Z] were the iodide and tri-iodide respectively of the same cation. The UV spectrum in methyl cyanide solution of [Z] confirmed the presence of tri-iodide (λ_{\max} 293, 366m μ). Surprisingly, [Y] also gave a red solution containing I₃⁻, but by recording the UV absorption of a dilute solution of [Y] at regular intervals and extrapolating to zero time it was shown that a fresh solution of [Y] contained no I₃⁻. The concentration of tri-iodide ion rose to a steady maximum within 5 minutes, and in stronger solutions the colour change over this period was visible. All attempts to isolate a solid tri-iodide from a solution of [Y] failed, [Y] being recovered invariably. A solution of [Y] is therefore one extreme of the equilibrium of a reversible reaction, [Y] itself being the other.

[Y] contained 16.31% iodine, and assuming that no Ph-As

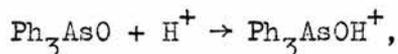
bonds had been broken in the reaction, this required an I:As ratio of 1:2. A simple adduct $2\text{Ph}_3\text{AsO}\cdot\text{HI}$ seemed unlikely because of the lack of evidence for the presence of a hydroxyl group: it was thought that formation of such an adduct must involve protonation of the oxygen atom and result in the appearance of an O-H stretching frequency in the infrared spectrum of the product. The possible structure [I] for a 2:1 adduct, for instance, is analogous to tri-o-tolylarsine hydroxy-oxyiodide reported by Lyon and Mann⁵⁴. The only other reasonable structure, an



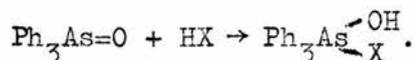
extension of [I], then appeared to be [II], which would have almost the same percentage composition as [I]. Although such a structure is unknown among compounds of pentavalent arsenic analogous cyclic structures have been found in compounds of trivalent arsenic with amines⁷⁶. Further support for [II] came from the fact that [Z], containing 36.72% iodine, fitted the structure [III], i.e. [II] with tri-iodide ions in place of the iodine atoms of [Y], and could be isolated from an equimolar mixture of [Y] and I_2 .

Data collected on [Y] and [Z] fitted these formulations fairly well, but not completely. The general high level of absorption in the infrared spectrum from 1700 to 625cm^{-1} could be ascribed to the large number of phenyl groups in the unit cell of the crystal, and a rather broad peak at 770cm^{-1} to the large number of As-O bonds. C, H and I elemental analyses were correct for these formulations.

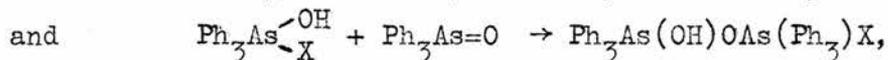
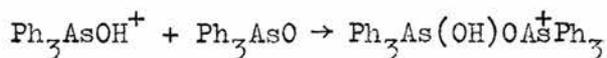
But the molecules [II] and [III] do not contain a hydroxyl group, and this was not easily accounted for. An acid might be expected to form an ionic product by protonation of the base Ph_3AsO ,



or a covalent product by addition across the As-O double bond:



But subsequent condensations of the type



which would be necessary to produce the suggested condensed species, would not be expected to involve the hydroxyl group at all. Thus while the formation of [I], for instance, is readily understandable, formation of [II] is not. Nor could any readily acceptable mechanism be found for the formation of I_3^- from [II], which would necessitate the intermediate formation of iodine.

The high conductance of both [Y] and [Z] suggested that they were ionic, and they were therefore formulated $[A]^{2+}[I^-]_2$ and $[A]^{2+}[I_3^-]_2$ respectively, where $[A]^{2+}$ was the cation tentatively assigned the structure [IV].

(b) Reaction of Ph_3AsO with HCl and HBr .

HCl and HBr are known to add to triphenylarsine oxide to form the hydroxyhalides $Ph_3AsOHHal$ (v. previous section and ref.58d), but in view of the anomalous results obtained with HI the reaction of Ph_3AsO with HBr and HCl was examined afresh.

Addition of excess aqueous HBr to a solution of $Ph_3AsO \cdot H_2O$ in boiling water produced a slight yellow colouration but no immediate precipitate. On cooling a little yellow oil separated which eventually crystallised as orange needles. The decanted solution on further standing deposited colourless crystals. These substances had the same infrared spectrum as [Y] and [Z] except for three extra absorptions in that of the colourless crystals at 3470, 3380 and 1600 cm^{-1} , attributable to lattice water^{61a}. Recrystallisation from methyl cyanide/ether produced an unhydrated form of the colourless compound, which was also obtained when the aqueous reaction mixture was extracted with chloroform. By analogy with the reaction between Ph_3AsO and HI the products of this reaction could be written as $[A]^{2+}[Br^-]_2$, $[A]^{2+}[Br_3^-]_2$, and $[A]^{2+}[Br^-]_2 \cdot xH_2O$. The UV spectrum of the

orange solid in methyl cyanide solution confirmed the presence of Br_3^- (λ_{max} 271m μ), and analysis of all three products was in fair agreement with the proposed formulae.

Formation of these substances rather than the recognised Ph_3AsOHBr was puzzling, and no set conditions were found which would guarantee formation of one rather than the other. In a number of reactions the new substances were most often obtained, but several times the product was Ph_3AsOHBr , or Ph_3AsOHBr was recovered from attempts to recrystallise the other bromide. The proportion of HBr to Ph_3AsO was not observed to be the governing factor.

The product of reaction of $\text{Ph}_3\text{AsO}\cdot\text{H}_2\text{O}$ with HCl under the same conditions was not $[\text{A}]^{2+}[\text{Cl}^-]_2$, but either Ph_3AsOHCl or its modification described previously (p.77).

(c) Reaction of Ph_3AsO with other acids.

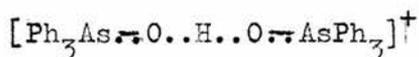
All the above compounds reacted with excess silver perchlorate in ethanol to give a precipitate of silver halide, and addition of ether to the filtrate yielded white needles, m.p. 205 - 206 $^\circ$. The infrared spectrum of this perchlorate was identical with that of [Y] again, apart from the absorptions at 1090 and 630 cm^{-1} characteristic of the perchlorate ion. Its identification as $[\text{A}]^{2+}[\text{ClO}_4^-]_2$ was supported by analysis, and gave further weight

to the theory that all these compounds had a common cation, without further confirming its identity. The same perchlorate was also obtained from the reaction of Ph_3AsO with perchloric acid in water.

Several unidentified substances previously obtained from aqueous systems containing Ph_3AsO and an acid could be explained by similar formulae. All had the same infrared spectrum apart from the absorptions characteristic of the anion present, and in each case analysis agreed with the formula $[\text{A}]^{2+}[\text{X}^-]_2$.

(d) Identification of products.

At this stage, in view of the novel proposed structure and the uncertainty as to the exact nature of the cation an X-ray analysis of one of this series of compounds was carried out by the Glasgow Crystallography Group. The compound examined was one isolated from an aqueous system containing $\text{Ph}_3\text{AsO} \cdot \text{H}_2\text{O}$, HBr and HgBr_2 , analysis of which fitted the formula $[\text{A}]^{2+}[\text{HgBr}_3^-]_2$. The crystal structure analysis showed that the correct formulation of this compound was $[(\text{Ph}_3\text{AsO})_2\text{H}^+]_2[\text{Hg}_2\text{Br}_6]^{2-}$ 77. The cation consisted of two Ph_3AsO molecules held together by a very short, and probably symmetrical, hydrogen bond through a proton:



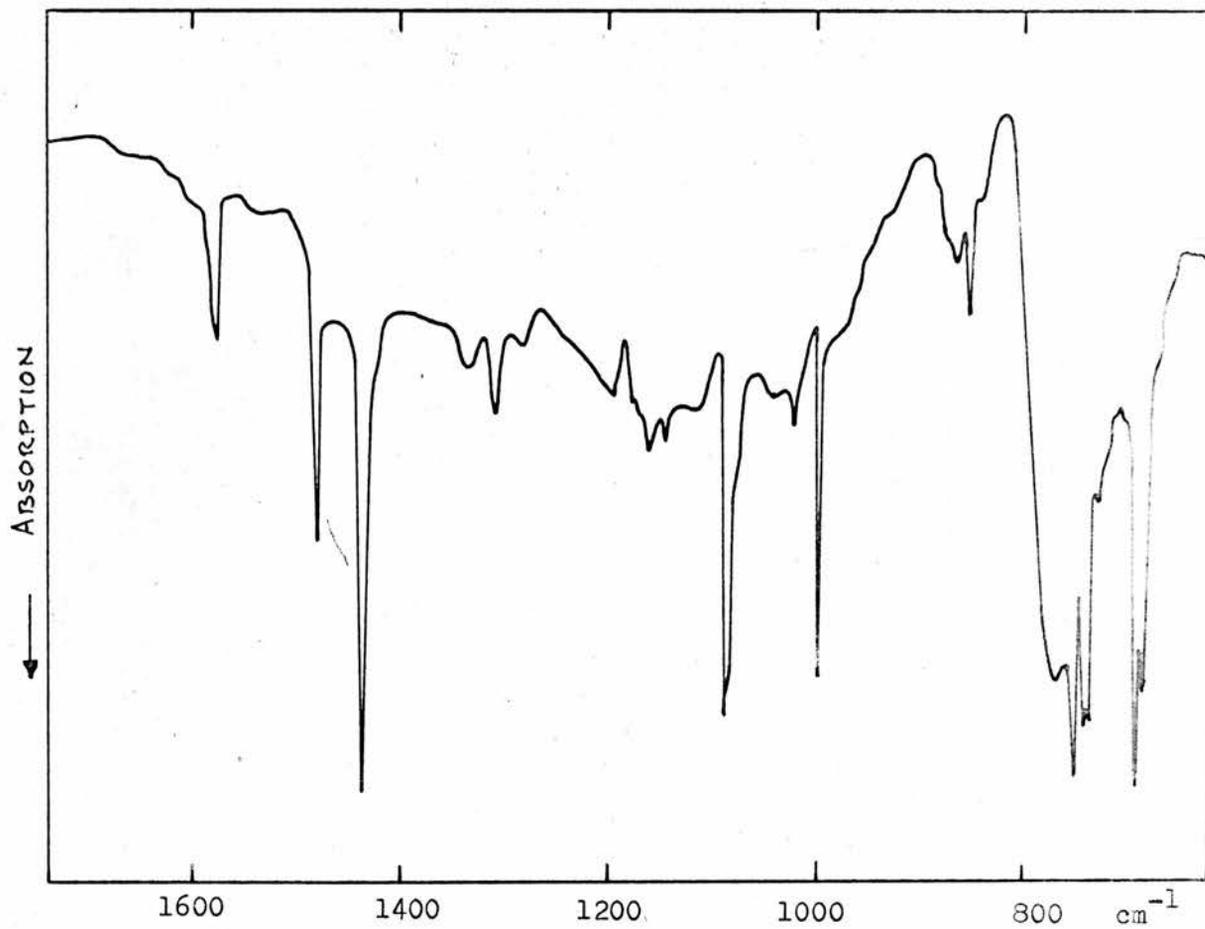
It thus seemed likely that all compounds with the infrared spectrum described above contained the same cation, $[(\text{Ph}_3\text{AsO})_2\text{H}]^{\dagger}$,

and that all those formulated $[\Lambda]^{2+}[X^-]_2$ should be reformulated $[(\text{Ph}_3\text{AsO})_2\text{H}]^+\text{X}^-$. Analysis figures were recalculated on this basis and were found in every case to be marginally closer to the experimental values than before.

This identification of the cation was supported, on re-examination, by the prominent features of the infrared spectrum of these compounds (figure 11), which corresponded closely to those described by Hadzi as typical of strong, symmetrical hydrogen bonds. These were: absence of an observable O-H stretching frequency above 1700cm^{-1} , and strong general absorption, interrupted by transmission windows, over the range 1700 to 625cm^{-1} ⁵³. A rather broad absorption of medium intensity which occurred in the infrared spectrum of all these compounds between 850 and 890cm^{-1} seemed likely to be the As-O stretching frequency, lowered from the 890cm^{-1} of the oxide by co-ordination through the oxygen atom. In keeping with this the crystallographic data⁷⁷ show an As-O bond length slightly greater than that in $\text{Ph}_3\text{AsO}\cdot\text{H}_2\text{O}$.

Several ions of like structure have been reported. In particular Hadzi assigned the structure $[\text{C}_6\text{H}_7\text{N}\cdots\text{O}\cdots\text{H}\cdots\text{O}\cdots\text{NC}_6\text{H}_7]^+\text{Br}^-$ to the hemihydrobromide of α -picoline-N-oxide $[(\text{C}_6\text{H}_7\text{NO})_2\cdot\text{HBr}]$ on very similar spectral evidence⁵³, and X-ray analysis has confirmed this⁷⁸. The hemihydrohalides of triphenylphosphine oxide, $(\text{Ph}_3\text{PO})_2\cdot\text{HBr}$, probably have the same structure. Other ions known to contain symmetrical hydrogen bonds are mostly anions.

Fig.11 The characteristic Infrared Spectrum of the
Bis(triphenylarsine oxide)hydrogen Cation
 $[(\text{Ph}_3\text{AsO})_2\text{H}]^+$

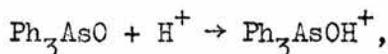


The first of this complex type recognised was the hydrogen bis(phenylacetate) ion⁷⁹; the related anions HHal_2^- are now well documented. In all such ions where the hydrogen bond is between oxygen atoms a strong, broad absorption appears in the infrared spectrum at ca. 800cm^{-1} , and this has been tentatively assigned to the 'OHO' stretch⁸⁰. In all the bis(triphenylarsine oxide)-hydrogen compounds a broad peak occurs at ca. 770cm^{-1} .

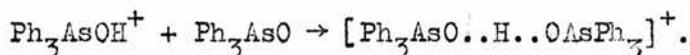
The structure of the anion of the particular compound on which the structural determination was carried out is also an interesting one, although of no direct concern here. The $[\text{Hg}_2\text{Br}_6]^{2-}$ ion is a novel halogenomercurate(II) complex with the same configuration as the well-known AlCl_3 dimer: each mercury atom is tetrahedrally co-ordinated by bromine atoms, two of which form bridges between the mercury atoms. Tetrahedral co-ordination of mercury is fairly common, but no ion of this type appears to have been recognised before. It may be compared, however, with part of the structure of tetramethylammonium tribromomercurate(II). The relative positions of the HgBr_3 units in the crystal of this compound led White to the conclusion that the anionic part of the molecule is intermediate between discrete HgBr_3^- ions and an infinite chain $[(\text{HgBr}_3)_n]^{n-}$ ⁸¹. The anion $[\text{Hg}_2\text{Br}_6]^{2-}$ can be considered as an isolated section of that chain with $n = 2$.

(e) The general reaction of Ph_3AsO with acids.

Recognition of the nature of the common cation of the compounds described led to a rationalisation of the general reaction of Ph_3AsO with acids. [Y] is indeed a 2:1 adduct of Ph_3AsO and HI, as originally suggested by analysis. The first step in its formation may be regarded as the predicted protonation



but the second step must involve attack of Ph_3AsO at the hydrogen atom rather than the arsenic:



The same reaction will occur with any acid, but the product isolated will depend on whether the second Ph_3AsO molecule or the anion has the greater affinity for the proton. Thus chloride can apparently displace one Ph_3AsO to produce Ph_3AsOHCl , since the compound $[(\text{Ph}_3\text{AsO})_2\text{H}]^+\text{Cl}^-$ has not been isolated, and likewise addition of nitric acid to Ph_3AsO has always been observed to lead to $\text{Ph}_3\text{AsOHONO}_2$ and never $[(\text{Ph}_3\text{AsO})_2\text{H}]^+\text{NO}_3^-$. With several other anions (e.g. ClO_4^-) either Ph_3AsOHX or $[(\text{Ph}_3\text{AsO})\text{H}]^+\text{X}^-$ could be obtained from the reaction of Ph_3AsO with HX . The second was always the easier to isolate, particularly if conditions at all favoured an ionic product. (v. Experimental section for conditions)

Apart from this limitation it seems that the reaction of Ph_3AsO with acid is general in forming the cation $[(\text{Ph}_3\text{AsO})_2\text{H}]^+$, and that the solid product isolated depends on what anions are

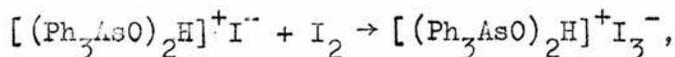
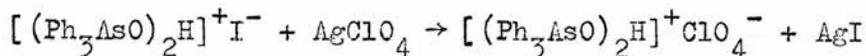
present in solution. When the only anion is that of the acid the product is necessarily a salt of that acid, but in the presence of suitable other species complex anions can be formed, such as the $[\text{Hg}_2\text{Br}_6]^{2-}$ ion obtained when Ph_3AsO reacted with HBr in the presence of HgBr_2 .

Although the basic reaction is thus a simple one it remains necessary to explain the production of trihalide ion in the case of the reactions with EI and HBr . This is doubtless the same problem as the presence of tri-iodide ion in solutions of $[(\text{Ph}_3\text{AsO})_2\text{H}]^+\text{I}^-$, and the two observations will be discussed together later.

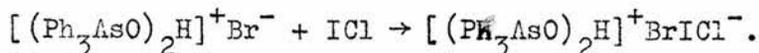
B. Bis(triphenylarsine oxide)hydrogen Salts.

(a) Properties.

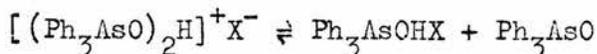
All but one of these compounds encountered have been found to be stable and to behave as ordinary salts in solution. The iodide is exceptional in being 'unstable' in solution, as described previously, but even so it can be recovered unchanged and undergoes reactions in solution as an iodide, e.g.



so that its said instability is in fact an equilibrium reaction. This will be discussed later. The reaction of the halides with silver perchlorate to give the perchlorate and silver halide has already been mentioned, and they were also found to add on halogens to give trihalides, e.g. the above equations, and:



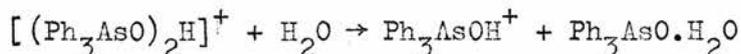
It was thought likely that the dissociation



would occur in solution, but the infrared spectra of the tribromide, tri-iodide and perchlorate in dry chloroform solution showed little change from the solid state. The strong absorption due to the symmetrical hydrogen bond was still present, and none attributable to the hydroxyl group of the corresponding Ph_3AsOHX or to $\nu(\text{As}-\text{O})$ of Ph_3AsO was observed. A strong, sharp peak which appeared at

ca. 3000cm^{-1} was assigned to chloroform, as in the spectra of the oxides and hydroxyhalides. Very weak absorption similar to the hydroxyl absorptions of $\text{Ph}_3\text{AsOEHCl}$ in position and shape was observed, but since it appeared in the spectrum of the perchlorate it could not be associated with the molecule $\text{Ph}_3\text{As}(\text{OH})\text{X}$ (v. p.80: $\text{Ph}_3\text{As}(\text{OH})\text{ClO}_4$ is transparent in this region). It is possible that this absorption also is due to the complexed chloroform. In contrast to hydroxytriphenylarsonium perchlorate the spectrum of the perchlorate group in bis(triphenylarsine oxide)hydrogen perchlorate consisted of only two absorptions, one very strong at 1100cm^{-1} , the other of medium intensity, at 625cm^{-1} , i.e. those characteristic of the free ion. When wet chloroform was used, however, hydroxyl absorptions similar to those of hydroxytriphenylarsonium perchlorate and tribromide appeared, and the spectrum of the perchlorate group showed a reduction in symmetry from T_d to C_{3v} , though the broad absorption of the O-H-O bond was still present with reduced intensity.

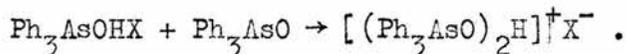
It thus seems that the bis(triphenylarsine oxide)hydrogen ion is stable in solution provided no water is present, though a slight degree of dissociation may exist in some solvents.



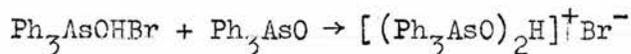
The conductances of all these compounds were in keeping with the above observations, showing that they are strong 1:1 electrolytes in methyl cyanide ($\Lambda_m > 100\text{ohm}^{-1}\text{cm}^2\text{mole}^{-1}$, $c_m = 0.01\text{ mole/l}$).

(b) Other methods of synthesis.

The idea that the $[(\text{Ph}_3\text{AsO})_2\text{H}]^{\dagger}$ ion took part in the above equilibrium suggested another synthetic route to its salts:



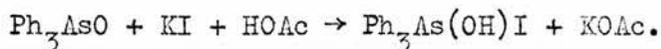
In accordance with this it was found that addition of ether to methyl cyanide solutions of equivalent quantities of any hydroxy derivative of triphenylarsine (other than the chloride or nitrate) and triphenylarsine oxide precipitated the expected product, e.g.



A conductimetric titration of Ph_3AsO with Ph_3AsOHBr was carried out to check this. Whereas gradual addition of Ph_3AsOHBr to methyl cyanide produced a slow and slight rise in conductance, its addition to the same volume of a methyl cyanide solution of the oxide resulted in a rapid rise to a much higher conductance. Formation of a strong electrolyte was thus indicated, but no break occurred at the 1:1 mole ratio in the conductance-composition graph, which was a smooth curve rising to a maximum at about the 1.5:1 mole ratio (figure 12). However the form of this graph was typical of the formation of a strong electrolyte in an equilibrium reaction, and is considered to be evidence both of formation of the expected bromide from Ph_3AsO and Ph_3AsOHBr and of its dissociation into these components in methyl cyanide.

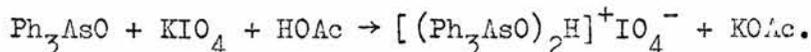
Attempts to add Ph_3AsO and Ph_3AsOHCl yielded only the same products as were obtained by the action of hydrochloric acid on the oxide.

Lyon and Mann have reported⁵⁴ the formation of triphenylarsine hydroxyiodide from Ph_3As and AlCl_3 , on treatment with potassium iodide and acetic acid in aqueous solution, but clearly imply that the reaction in which the hydroxyiodide is formed is



This is essentially the same as addition of aqueous hydriodic acid to Ph_3AsO , but nonetheless the attempt was made to repeat the latter part of their preparation. Addition of acetic acid to a boiling aqueous solution of $\text{Ph}_3\text{AsO} \cdot \text{H}_2\text{O}$ and a large excess of KI resulted in immediate precipitation of $[(\text{Ph}_3\text{AsO})_2\text{H}]^+\text{I}^-$. More of the same product crystallised as the solution cooled, giving a total yield of 95%. A trace of $[(\text{Ph}_3\text{AsO})_2\text{H}]^+\text{I}_3^-$ was easily separated, but there was no $\text{Ph}_3\text{As}(\text{OH})\text{I}$. In view of these results Lyon and Mann's identification of their product as triphenylarsine hydroxyiodide was to be doubted, but an easy preparation of $[(\text{Ph}_3\text{AsO})_2\text{H}]^+\text{I}^-$, uncontaminated by the tri-iodide, had been found.

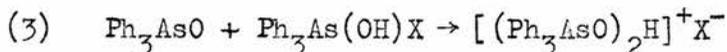
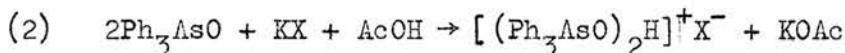
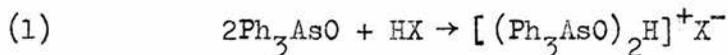
Replacement of the potassium iodide by another potassium salt led to formation of other bis(triphenylarsine oxide)hydrogen salts with equal ease, e.g.



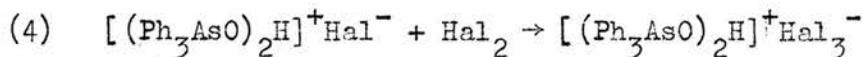
This is therefore a route to these salts when the corresponding acids are not readily available, and it should be possible to synthesise such a salt containing any anion, by addition of acetic

acid to an aqueous solution of Ph_3AsO and another salt of that anion, or such other compounds as can generate the anion, provided only that all components of the system are stable under such conditions.

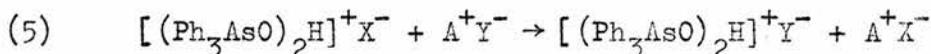
Thus three general methods are available for the preparation of this type of compound:



In addition trihalides are readily prepared by addition of halogen to the halides:



and some salts may be prepared by a double decomposition reaction:



Compounds obtained by this latter route included the perchlorate, as described before, and the tetraphenylborate, which was the product of attempts to prepare hydroxytriphenylarsonium tetraphenylborate by mixing equivalent amounts of triphenylarsine hydroxychloride and sodium tetraphenylborate in water.

Table 7 lists the bis(triphenylarsine oxide)hydrogen salts prepared and the method by which each was obtained.

Table 7: Bis(triphenylarsine oxide)hydrogen Salts.

Anion	Colour	m.p. (°C)	Method of Preparation*				
			1	2	3	4	5
Br^-	white	170-171	*		*		
I^-	pale yellow	154-155	*	*			
ICl_2^-	bright yellow	147-149			*	*	
BrICl^-	pale orange	99-100				*	
I_2Cl^-	dark red	97-98				*	
Br_3^-	orange	89-91	*		*	*	
IBr_2^-	orange	115-116				*	
I_2Br^-	dark red	110-111				*	
I_3^-	chocolate	116-118	*			*	
ClO_4^-	white	205-206	*		*		*
IO_4^-	white	172-173		*			
$\text{Hg}_2\text{Br}_6^{2-}$	white	146-147	*				
PtCl_6^{2-}	pale orange	184-186	*				
Ph_4B^-	white	**					*

* Refers to equation on p.108.

** Identified from its infrared spectrum, but not otherwise characterised.

C. Some Related Compounds.

One compound in this series of particular interest was the hexachloroplatinate(IV), $[(\text{Ph}_3\text{AsO})_2\text{H}^+]_2\text{PtCl}_6^{2-}$. This was obtained by the action of hydrochloric acid on a mixture of triphenylarsine hydroxychloride and platinum tetrachloride in water, in an attempt to prepare a complex reported by Michaelis in 1902, for which he found the unusual stoichiometry $[\text{Ph}_3\text{As}(\text{OH})\text{Cl}]_3\text{PtCl}_4^{56}$. The above hexachloroplatinate fitted Michaelis' description well in every respect except analysis, and the correct formulation was immediately obvious from its infrared spectrum. In view of the unusual stoichiometry proposed by Michaelis and the similarity of his system to others which give rise to bis(triphenylarsine oxide)hydrogen salts it is probable that for once his analysis was at fault.

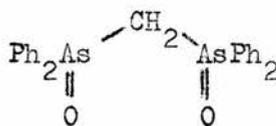
Analogous 4:1 complexes between trialkylphosphine oxides and chloroplatinic acid, or other complex acids such as ferrocyanic, chloroauric and iodobismuthic, were reported by Pickard and Kenyon in 1906, without their structures being fully understood⁸². Similar complexes of chloroplatinic acid with amides are known, and in 1903, in a review of what he believed to be a type of ammonium salt, Werner mentioned several, of general formula $(\text{amide})_4 \cdot \text{H}_2\text{PtCl}_6$, along with a great many other amido-acid and amide-acid-halogen complexes obviously analogous to

those of triphenylarsine oxide reported here⁸³. Although their nature was not recognised at that time it is now certain that, since amides protonate at the oxygen atom and not the nitrogen⁸⁴, these cannot be ammonium salts, but must be formulated as salts with complex hydrogen bonded cations, e.g. $[(\text{amide})_2\text{H}]^+\text{Br}^-$ and $[(\text{amide})_2\text{H}]^+\text{I}_2\text{Cl}^-$. The crystal structure of the benzamide-hydrogen tri-iodide complex $[(\text{benzamide})_2\text{H}]^+\text{I}_3^-$ has been determined, but without recognition of the position of the proton⁸⁵.

More recently the infrared spectra of a few of these amide complexes have been reported, and they are in general similar to those of the triphenylarsine oxide ones^{74,86}. Cook, in his studies of 1:1 base-acid complexes, has encountered several 2:1 complexes, particularly with acids like HAsF_6 , which he recognises from their infrared spectra to contain cations with symmetrical hydrogen bonds⁷⁴. The bases used are amides and other carbonyl compounds, and the spectra are in general like those of the triphenylarsine oxide complexes.

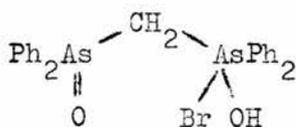
An interesting variant of the bis(triphenylarsine oxide)-hydrogen ion occurs in some salts obtained by Cookson and Mann, by addition of acids to methylenebis(diphenylarsine oxide) $[\text{V}]$ ⁸⁷.

$[\text{V}]$:

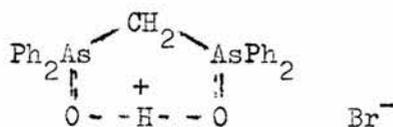


This dioxide adds only one molar equivalent of acid, to form a mono-hydroxyhalide or nitrate. A di-hydroxychloride was isolated, but was very readily converted to the mono derivative. This was attributed by Cookson and Mann to inductive deactivation of the second arsenic atom by formation of a partial positive charge at the first. The weight of evidence in favour of this phenomenon is such that it must be accepted⁸⁸, but in the light of the present discoveries about Ph_3AsO it seemed likely that the favourable relationship of the two oxide groups for formation of a hydrogen bond would be a contributing factor.

To test this point a sample of the diarsine was oxidised with hydrogen peroxide and treated with HBr. The product conformed to the published description of the monohydroxybromide (written as [VI] by Cookson and Mann), but its infrared spectrum was very similar to that of bis(triphenylarsine oxide)hydrogen bromide, showing no hydroxyl absorptions like that of Ph_3AsOHBr , but intense absorption over most of the range $1600 - 625\text{cm}^{-1}$. This appears to be sufficient evidence that the compound adopts the structure [VII]. The chloride and nitrate were also



[VI]



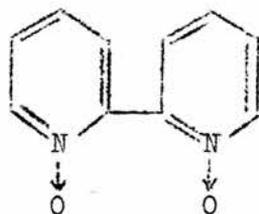
[VII]

prepared and found to have the same structure as the bromide, on the evidence of their infrared spectra. Formation of the

chloride and nitrate of this cation must reflect the stabilising effect of the chelate ligand [V] on the complex cation, since the corresponding triphenylarsine oxide complexes do not exist. It was noted in particular that the part of the infrared spectrum due to the NO_3 unit in the nitrate was characteristic of the free NO_3^- ion and nothing like that of the same unit in triphenylarsine hydroxynitrate, which shows very strong hydrogen bonding.

The di-hydroxychloride of this diarsine [V] may contain the above complex cation and the HCl_2^- anion rather than two AsOHCl units, and so not be exceptional. A sample was prepared, but its infrared spectrum was difficult to interpret because of strong absorption due to water of crystallisation.

Recently analogous 1:1 complexes of 2,2'-dipyridyl-1,1'-dioxide [VIII] with several acids have been reported and recognised from their infrared spectra⁸⁹.



[VIII]

This dioxide does not form 1:2 adducts with acids either.

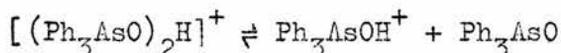
D. Interpretation of the Reaction between Triphenylarsine Oxide
and Hydriodic Acid.

As expected, a common explanation was found for the production of $[(\text{Ph}_3\text{AsO})_2\text{H}]^+\text{I}_3^-$ in the reaction of Ph_3AsO with HI and the presence of tri-iodide ion in solutions of $[(\text{Ph}_3\text{AsO})_2\text{H}]^+\text{I}^-$.

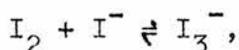
In order to eliminate the possibility that atmospheric oxidation was producing the iodine in the reaction of Ph_3AsO with HI freshly regenerated HI was distilled under a stream of nitrogen into a boiling aqueous solution of $\text{Ph}_3\text{AsO}\cdot\text{H}_2\text{O}$ previously flushed out with nitrogen. A large excess of HI was used, but as soon as the first drop of HI entered the oxide solution the red colour of tri-iodide appeared. Thus the triphenylarsine oxide itself, or the immediate product of its reaction with HI, must be responsible for the oxidation of iodide to iodine. Since the most likely product of the reaction is the ion Ph_3AsOH^+ , the possibility of its being the oxidising agent was investigated.

It was found that addition of any hydroxy derivative of triphenylarsine to any ionic iodide, in any suitable solvent, produced tri-iodide immediately. Only very slight oxidation was brought about by $\text{Ph}_3\text{AsO}\cdot\text{H}_2\text{O}$ under the same conditions, but in the presence of acid it too appeared to produce complete oxidation. It thus seemed likely that the presence of hydroxytriphenylarsonium

ions in the aqueous solution was responsible for the production of I_3^- . This was also the most likely reason for the presence of tri-iodide in solutions of bis(triphenylarsine oxide)hydrogen iodide. The probability of the equilibrium



in solution has been discussed (p.103), and however far to the left it may lie, the smallest concentration of Ph_3AsOH^+ will serve to oxidise some iodide to iodine, which will take part in the further equilibrium

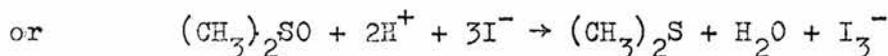
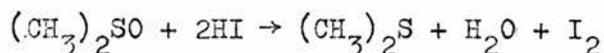


and reaction will continue as long as iodide is present. There was slight evidence for the first equilibrium in the infrared spectra of $[(Ph_3AsO)_2H]^+$ salts in chloroform, and much stronger evidence that it is catalysed by water.

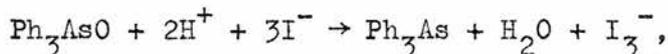
Attempts were made to establish the exact stoichiometry of the reaction between Ph_3AsOH^+ and I^- by several means, without success. Measurement of the ultraviolet absorption at 293m μ (a characteristic wavelength of the I_3^- ion) of methyl cyanide solutions containing different proportions of iodide ($Ph_4As^+I^-$) and hydroxytriphenylarsonium ions ($Ph_3AsOH^+ClO_4^-$) showed that tri-iodide concentration was maximum when the $I^-:Ph_3AsOH^+$ ratio was slightly greater than 1:1, but conductimetric titrations of the two components of the system showed no clear discontinuity, particularly at that point. That $[(Ph_3AsO)_2H]^+I^-$ can be

recovered unchanged from its solutions indicates that the reaction between cation and anion proceeds by a series of equilibria, and such equilibria lead to smooth conductance-composition curves in conductimetric titrations.

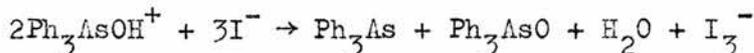
In the absence of more direct evidence concerning the reaction comparison with a closely analogous system is useful. HI is known to reduce dimethylsulphoxide to dimethylsulphide^{90,91}, according to the equation



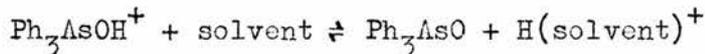
The same reaction involving triphenylarsine oxide can be postulated:



which is equivalent to



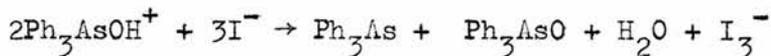
since the rapid equilibrium



can be expected. Reduction of Ph_3AsO to Ph_3As by HI is likely, since a recognised synthetic route to triarylsarsines is treatment of the corresponding oxide with iodine and SO_2 in aqueous HCl solution⁹².

Extension of this reaction to the equilibrium of $[(\text{Ph}_3\text{AsO})_2\text{H}]^+\text{I}^-$ is simple. Three moles of the salt are necessary to provide the three iodide ions, and the requisite number of Ph_3AsOH^+ ions is

obtained from dissociation of the cation. Thus



becomes $2[(\text{Ph}_3\text{AsO})_2\text{H}]^+ + 3\text{I}^- \rightarrow \text{Ph}_3\text{As} + 3\text{Ph}_3\text{AsO} + \text{H}_2\text{O} + \text{I}_3^-$

or $3[(\text{Ph}_3\text{AsO})_2\text{H}]^+\text{I}^- \rightleftharpoons \text{Ph}_3\text{As} + 3\text{Ph}_3\text{AsO} + \text{H}_2\text{O} + [(\text{Ph}_3\text{AsO})_2]^+\text{I}_3^-$.

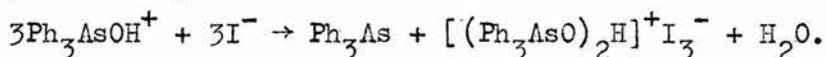
The infrared spectrum of a solution of the iodide in chloroform was in keeping with this. The characteristic broad band due to the cation was still present, with considerably reduced intensity, and $\nu(\text{As-O})$ of Ph_3AsO appeared at 890cm^{-1} , with an intensity in keeping with the concentration required by the equilibrium. No absorption characteristic of the water could be observed, but in view of its low concentration this did not seem serious.

If the above equilibrium is correct it should be reversed by addition to the system of triphenylarsine or water. Addition of either of these to a solution of the iodide in methyl cyanide was found to cause the disappearance of the red colour of the tri-iodide ion, leaving the solution colourless. There is thus some evidence for all the postulated products of the equilibrium, and though the mechanism by which it proceeds has not been determined, the overall stoichiometry appears to be correct.

Reduction of dimethylsulphoxide by HI has been studied kinetically in dimethylsulphoxide/water by Krueger⁹⁰ and in acetic acid/water by Landini and co-workers⁹¹, and mechanisms have been suggested. It would be unwise to speculate on their extension to the reaction of triphenylarsine oxide, but it is worth while

pointing out that the latter authors invoke a pentaco-ordinate (presumably trigonal bipyramidal) intermediate even more suited to the chemistry of arsenic than to that of sulphur.

It is also clear from the above discussion that a compound $\text{Ph}_3\text{AsOH}^+\text{I}^-$ cannot exist in solution, and therefore that it is unlikely that triphenylarsine hydroxyiodide can exist at all. Any reaction which might be expected to produce Ph_3AsOHI will in fact yield $[(\text{Ph}_3\text{AsO})_2\text{H}]^+\text{I}_3^-$ by the further step



It can readily be seen that this reaction explains the results of attempts to prepare $\text{Ph}_3\text{As}(\text{OH})\text{I}$ described earlier (p.88) and strongly suggests that all reports of the isolation of triarylar sine hydroxyiodides are erroneous.

P A R T I V

THE REACTION OF TRIPHENYLBISMUTH WITH HALOGENS

THE REACTION OF TRIPHENYLBISMUTH WITH HALOGENS

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THE REACTION OF TRIPHENYLBISMUTH WITH HALOGENSIntroduction

The purpose of the research described in this section was to extend to triphenylbismuth the work carried out by Beveridge and Harris on the reactions of halogens with the triphenyl derivatives of other group VB elements^{19,20}, and so complete the series. The same approach was adopted: the reactions of triphenylbismuth with Br_2 , IBr and I_2 were investigated by the technique of conductimetric titration.

Since the mode of reaction of halogens with triorgano derivatives of group VB elements is well established the chief interest in this work was to see how the bismuth derivatives fitted the general trends within the group, and these will therefore be outlined briefly.

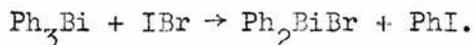
Reaction of Ph_3M ($\text{M} = \text{P}, \text{As}, \text{Sb}$) with one molar equivalent of halogen usually forms a dihalide. All the dichlorides and dibromides Ph_3MHal_2 have been isolated as crystalline solids. The phosphorus compounds are strong electrolytes and ionic solids, the arsenic compounds weak and the antimony compounds non-electrolytes

and probably covalent solids^{19,20}. The corresponding bismuth dihalides are known^{93a} and were expected to be covalent in the solid state and non-electrolytes in solution. The di-iodides are also known in the solid state, but only that of phosphorus is stable in solution. Triphenylbismuth di-iodide has been reported stable in solution only at -80° ⁹⁴. Existence of a mixed dihalide Ph_3PIBr is indicated in solution, but it has not been isolated in the solid state. The corresponding arsenic and antimony compounds are known as solids, but like the di-iodides are unstable in solution^{19,20}. No mixed dihalides of triphenylbismuth have been reported⁹⁵.

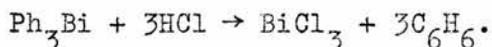
Addition of two molar equivalents of halogen to Ph_3M ($\text{M} = \text{P}, \text{As}, \text{Sb}$) produces tetrahalides. These are all strong electrolytes, and probably ionic solids containing trihalide ions, $\text{Ph}_3\text{MHal}^+\text{Hal}_3^-$. No tetrachlorides have been reported, but all the tetrahalides $\text{Ph}_3\text{MBr}_n\text{I}_{4-n}$ ($\text{M} = \text{P}, \text{As}; n = 0 \text{ to } 4$) have been identified in solution and isolated as crystalline solids^{19,20}. No solid tetrahalides of triphenylstibine have been reported and only Ph_3SbI_4 and $\text{Ph}_3\text{SbBrI}_3$, i.e. those containing the stable tri-iodide ion, have been detected in solution¹⁹. No tetrahalides of triphenylbismuth have been reported at all.

Two particular aspects of bismuth chemistry might be expected to influence the number and type of halides formed by

triphenylbismuth. Firstly, the bismuth-carbon bond is relatively weak, so that organo-bismuth compounds in general are less stable than their phosphorus, arsenic and antimony counterparts. Phenyl groups are very easily removed from triphenylbismuth, and under conditions which produce adducts Ph_3MX_2 of the arsine and stibine triphenylbismuth cleaves to give the compounds Ph_2BiX and PhBiX_2 ⁹⁵. This has been the result of attempts to prepare the mixed dihalides⁹⁶, e.g.



With sufficiently reactive halides removal of phenyl groups is complete⁹⁷, e.g.



It was therefore to be expected that some reactions of Ph_3Bi would be complicated by phenyl migrations.

Secondly, bismuth(V) compounds are relatively few, and stable organic derivatives are confined to the type Ar_3BiX_2 , and a few Ar_3BiO compounds, where X represents Cl, Br, $\text{CH}_3\text{CO.O-}$, $\text{C}_6\text{H}_5\text{CO.O-}$, and several other similar groups⁹⁵. There are no corresponding alkyl derivatives, and it has been suggested that the phenyl groups may play an essential part in their structure, and that the bismuth atoms are not pentavalent at all⁹⁸. The recent determination of the structure of triphenylbismuth dichloride²⁷, a trigonal bipyramidal molecule of D_{3h} symmetry as expected, seems to refute this suggestion, but nonetheless there appears to be a

fundamental difference between certain bismuth(V) organic derivatives and those of other group VB elements. Not only is pentaphenylbismuth less stable than the other Ph_5M compounds, but it is purple whereas they are colourless or pale yellow¹. Such a distinction would seem to reflect a basic difference in structure, and the same purple colour is observed in the (unstable) product of attempts to prepare triphenylbismuthonium tetraphenylcyclopentadienylide, although the corresponding phosphorus, arsenic and antimony compounds are stable and colourless or yellow⁹⁹.

The relative scarcity of bismuth(V) compounds is usually attributed to the 'inertness' of the atom's $6s^2$ electron pair, and its consequent reluctance to form hybrid orbitals requiring promotion of one s electron to a d orbital. It is interesting that the C-Bi-C angles in triphenylbismuth are close to 90° , suggesting that only p orbitals of bismuth are used in the bonding¹⁰⁰. However, a description of the bonding in pentacovalent group VB derivatives which requires the use of neither s nor d orbitals has been adopted in the present work (v. p.9), and therefore an alternative explanation for the scarcity of bismuth(V) compounds must be found. Since bismuth is the least electronegative of the group VB elements it should form more stable three-centre bonds than the other elements, rather than less stable. It may be that the 6d orbitals are of too high energy to participate in

effective π -bonding to strengthen a three-centre bond, as the empty d orbitals of other group VB elements probably can. Certainly triphenylbismuth shows no donor character, where triphenylstibine, and the corresponding arsine and phosphine, do, particularly when stabilisation by $d_{\pi}-d_{\pi}$ or $p_{\pi}-d_{\pi}$ bonding is possible^{93b}.

While it is possible to predict the structures of bismuth(V) compounds by analogy with other group VB compounds, their actual determination is of more than usual interest because of their relative scarcity. Thus the X-ray analysis of the structure of Ph_3BiCl_2 is a valuable guide to the accuracy of predictions, but the structure of Ph_5Bi would be a useful clue to the difference between bismuth(V) and other group VB elements in the pentavalent state.

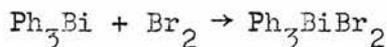
Results and Discussion

A. Conductimetric Titration Studies of Triphenylbismuth/Halogen Systems.

Conductance-composition graphs for the systems $\text{Ph}_3\text{Bi}/\text{Hal}_2$ ($\text{Hal}_2 = \text{Br}_2, \text{IBr}, \text{I}_2$) in methyl cyanide solution, which will be referred to in the following discussion, are reproduced in figure 13. Titrations were carried out in nitrobenzene also, but results were independent of solvent and do not require separate discussion.

(a) Reaction of Ph_3Bi with Br_2 .

Addition of bromine to a solution of triphenylbismuth in methyl cyanide or nitrobenzene had negligible effect on the (near zero) conductance of the solution, which also remained colourless, until the 1:1 $\text{Br}_2:\text{Ph}_3\text{Bi}$ mole ratio was passed. The graph then corresponded exactly to that obtained on addition of bromine solution to the solvent alone, and the solution acquired the yellow colour of bromine. Formation of a colourless non-electrolyte Ph_3BiBr_2 ($\Lambda_m = 0.140\text{ohm}^{-1}\text{cm}^2\text{mole}^{-1}$, $c_m = 0.011\text{ mole/l}$ at the 1:1 mole ratio) by the reaction



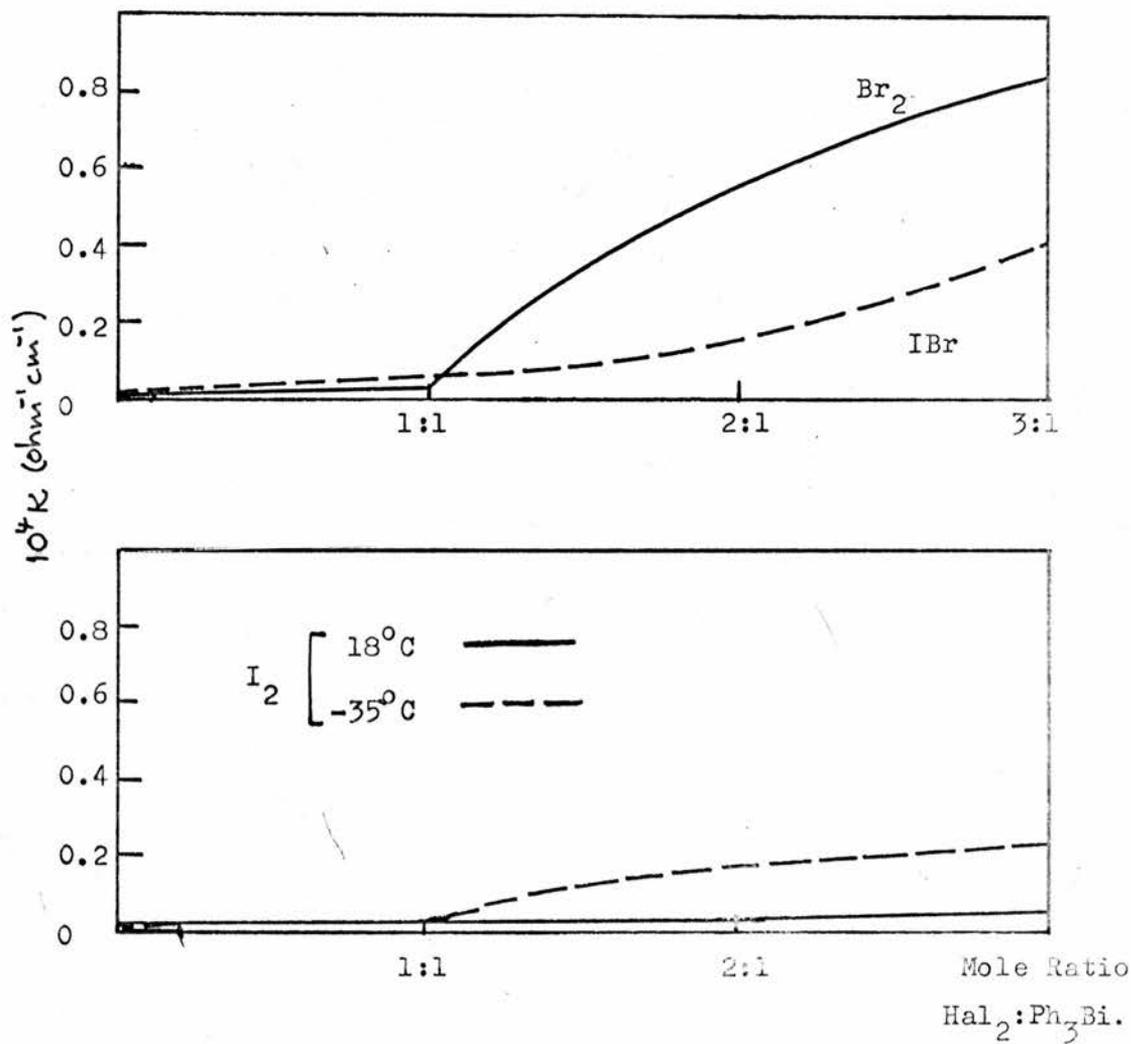
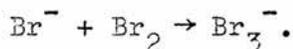


Fig.13 Conductimetric Titrations of Triphenylbismuth with Halogens in Methyl Cyanide

was thus confirmed, but the low conductance at the 2:1 mole ratio ($\Lambda_m = 4.35 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$, $c_m = 0.010 \text{ mole/l}$) indicated that no tetrabromide was formed. The two observations are in keeping, since formation of a tetrabromide requires the presence of bromide ions for the further reaction

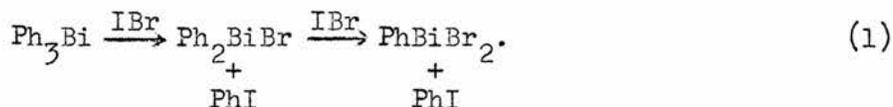


Ph_3BiBr_2 continues the trend in group VB: Ph_3PBr_2 is a fairly strong electrolyte, Ph_3AsBr_2 a weak electrolyte, and Ph_3SbBr_2 virtually non-ionic in methyl cyanide solution. Non-formation of a tetrabromide Ph_3BiBr_4 is also in keeping with the trend, since Ph_3PBr_4 and Ph_3AsBr_4 are known, but Ph_3SbBr_4 is not^{19,20}.

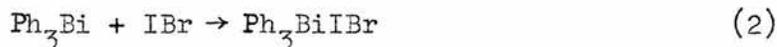
(b) Reaction of Ph_3Bi with IBr .

The conductance of the triphenylbismuth solution rose only very slightly from its near zero value as IBr solution was added, until the 2:1 $\text{IBr}:\text{Ph}_3\text{Bi}$ mole ratio was reached. It then rose slightly more rapidly, but no more than on addition of IBr to pure solvent. The inflection at the 2:1 mole ratio indicated that a reaction between two moles of IBr and one of triphenylbismuth was taking place, but the low conductance at that point ($\Lambda_m = 1.48 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$, $c_m = 0.010 \text{ mole/l}$) was not in keeping with formation of the tetrahalide $\text{Ph}_3\text{BiI}_2\text{Br}_2$. When the titration was repeated in nitrobenzene solution a slight inflection was observed at the 1:1 mole ratio also. This suggested that

reaction occurred in two stages and was therefore probably that observed on mixing ether solutions of the two reactants⁹⁶:



All products of this reaction are covalent, in keeping with the low conductance throughout, until free IBr is present after the 2:1 mole ratio. The alternative possibility that the reaction

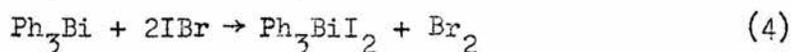
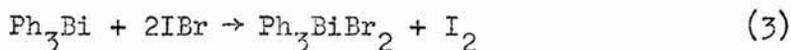


was occurring was unlikely in view of the instability of the known adducts Ph_3AsIBr and Ph_3SbIBr in solution^{19,20} and the fact that Ph_3BiIBr is unknown as a solid⁹⁵, but proof was obtained as follows.

Freeze drying of 1:1 and 2:1 mixtures of IBr and Ph_3Bi in methyl cyanide yielded respectively a pale yellow solid and a bright yellow solid. The former was identified as Ph_2BiBr by bromine analysis and from the identity of its melting point and infrared spectrum with those of an authentic sample. The bromine content of the bright yellow solid was only slightly more (33.10%) than that of PhBiBr_2 (35.83%) and its infrared spectrum was identical with that of an authentic sample. Thin layer chromatography of these solids (using benzene, on SiO_2) along with previously prepared samples of Ph_2BiBr and PhBiBr_2 supported these identifications and showed a trace of Ph_3Bi present in the Ph_2BiBr . The impurity present with the PhBiBr_2 which raised the bromine content of the solid sample without affecting its

infrared spectrum, was probably BiBr_3 . Qualitative tests for iodine on the two solids isolated were negative.

To confirm that the reaction was taking place in solution, and that the solid products were not formed during the freeze drying, the reaction was studied cryoscopically in nitrobenzene. This technique distinguishes reaction scheme (1) from all other possibilities (e.g. (2), and (3) and (4) below) since it is the only one which for each mole of Ph_3Bi used produces two moles at the 1:1 mole ratio and three at the 2:1 mole ratio.



Results are presented in Table 8.

Table 8: Reaction of Ph_3Bi with IBr in nitrobenzene.

Moles Ph_3Bi present	Moles IBr added	$-\Delta T_f$ (Cent.degs)	Total moles present	
			Calc.from $-\Delta T_f$	Calc.from(1)
0.000313	0.000			
	0.000310	0.229	0.000620	0.000623
	0.000621	0.299	0.000912	0.000933
	0.000931	0.339	0.001151	

The reaction of Ph_3Bi with IBr in methyl cyanide and nitrobenzene solutions was thus confirmed to be according to equation (1). It was thought possible that Ph_3BiIBr might be stable in solution at low temperature, and the titration was therefore repeated in methyl cyanide at -35° ; but the resultant graph was identical with that obtained at room temperature.

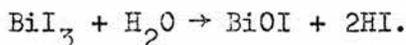
There is therefore no evidence for the presence of any $\text{Ph}_3\text{Bi-IBr}$ adduct in methyl cyanide or nitrobenzene solution. Non-existence of the tetrahalide continues the trend of the group: $\text{Ph}_3\text{PI}_2\text{Br}_2$ and $\text{Ph}_3\text{AsI}_2\text{Br}_2$ are known, $\text{Ph}_3\text{SbI}_2\text{Br}_2$ is not^{19,20}.

(c) Reaction of Ph_3Bi with I_2 .

Although the titration of Ph_3Bi with I_2 in methyl cyanide was carried beyond the 3.5:1 $\text{I}_2:\text{Ph}_3\text{Bi}$ mole ratio the conductance-composition graph remained a straight line, and at no point did the conductance rise significantly above that of the Ph_3Bi solution. From the beginning the solution acquired a bright yellow colour; about the 2:1 mole ratio it acquired a greenish tinge, and shortly before the 3:1 mole ratio was reached a black solid precipitated, leaving the supernatant solution dark green. On further addition of iodine the green colour was replaced by that of free iodine. There was thus no indication of the formation of a $\text{Ph}_3\text{Bi-I}_2$ adduct, but the extremely low conductance (less than that expected for an iodine solution, which has a definite

but low conductance) showed that the iodine was being used to form a covalent compound for about three molar equivalents. The same result was obtained in nitrobenzene solution, but the graph showed a slight inflection at the 2:1 mole ratio.

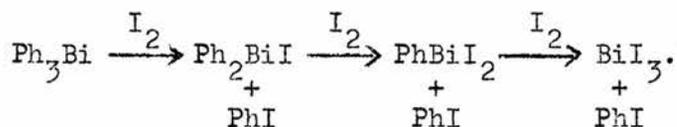
The infrared spectrum of the black precipitate showed absence of phenyl groups, and it was then identified as bismuth tri-iodide by treating a sample with boiling water and obtaining the distinctive bronze solid bismuth oxyiodide:



Clearly triphenylbismuth had undergone the overall reaction



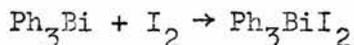
By analogy with the reaction of IBr with Ph_3Bi this would be expected to proceed by stepwise replacement of phenyl groups by iodine:



This is in agreement with the known reaction between Ph_3Bi and I_2 in ether solution, where the products at room temperature are iodobenzene, Ph_2BiI , PhBiI_2 and BiI_3 , in varying proportions depending on the proportion of iodine used⁹⁴. Ph_2BiI and PhBiI_2 are covalent compounds giving bright yellow solutions, and so the low conductance and colour of the solution up to the 3:1 mole ratio are accounted for. The green colour observed when BiI_3 precipitated may reasonably be associated with a radical of

bismuth, since phenyl migration is taking place. A green colour has been attributed to the radical Ph_2Bi in liquid ammonia¹⁰¹, and a transient green colour is observed when BiI_3 is dissolved in acetone.

When ethereal solutions of Ph_3Bi and I_2 are mixed at -80° the adduct Ph_3BiI_2 is formed, although it decomposes when the temperature rises⁹⁴. It was therefore thought worth while to repeat the titration in methyl cyanide at -35° , to see if a stable adduct is formed under these conditions. The conductance-composition graph in this case showed a slight discontinuity between the 1:1 and the 2:1 mole ratios, although conductance remained low throughout the titration. More significantly, the solution remained colourless until the 1:1 mole ratio was passed, then acquired the colour of an iodine solution. No precipitation occurred, even after addition of three molar equivalents of iodine, and on these grounds the reaction



is thought to occur. This is parallel to the behaviour of the $\text{Ph}_3\text{Bi}/\text{Br}_2$ system at room temperature, and like the dibromide Ph_3BiBr_2 , the di-iodide is a non-electrolyte ($\Lambda_m = 0.020\text{ohm}^{-1}\text{cm}^2\text{mole}^{-1}$, $c_m = 0.0097\text{mole/l}$, at -35°C). Again there was no evidence for formation of the tetra-iodide Ph_3BiI_4 . The solution was unchanged as long as it was kept at -35° , but almost as soon as

it was removed from the cooling bath black BiI_3 precipitated. Ph_3BiI_2 in methyl cyanide solution is therefore only just stable at -35° . The products of its decomposition are the same as those of the reaction between Ph_3Bi and I_2 at room temperature.

Again, these findings are in keeping with the trend in group VB insofar as they show that no tetrahalides of triphenylbismuth exist, even in solution, compared to the two of Ph_3Sb , stable only in solution, and the many of Ph_3As and Ph_3P .

(d) Adducts isolated.

The only stable adduct whose existence in solution was shown by conductimetric titration, Ph_3BiBr_2 , was obtained easily by addition of bromine to a solution of triphenylbismuth in ether. Addition of excess bromine did not lead to co-precipitation of a tetrabromide, as it does with triphenylphosphine or arsine. The dichloride, Ph_3BiCl_2 , was also prepared, by addition of chlorine to a solution of triphenylbismuth in ether, from which the dihalide precipitates. These halides were observed to be stable even in contact with water, unlike their phosphorus and arsenic counterparts, which are hydrolysed by atmospheric moisture. They were affected by light, however: samples stored in glass tubes darkened slightly on surfaces exposed to light.

Triphenylbismuth dichloride was found to be a non-electrolyte like the dibromide, and there was therefore little point in

measuring accurately the conductance of their solutions in methyl cyanide. A few representative values were obtained, and these are recorded in Table 9 along with other properties of the dihalides. They are so low that no significance can be put on their variation with concentration.

Table 9: Crystalline adducts of triphenylbismuth with halogens.

Compound	Colour	m.p. (°C)	Λ_m (ohm ⁻¹ cm ² mole ⁻¹)	c_m (mole/l)
Ph_3BiCl_2	white	144-148	0.06	0.012
			0.04	0.025
			0.05	0.050
Ph_3BiBr_2	very pale yellow	121-125	0.09	0.013
			0.15	0.025
			0.15	0.038

B. A Note on Triphenylbismuth as a Lewis Acid

Non-existence of tetrahalides of triphenylbismuth, and possibly the covalent nature of the dihalides in solution, can be related to the instability of halotriphenylbismuthonium ions. This is connected with the poor donor power of Ph_3Bi , also indicative of a reluctance to acquire positive charge. It was therefore thought of some interest to attempt to form a halotriphenylbismuthate ion $\text{Ph}_3\text{BiHal}^-$, in which Ph_3Bi functions as a Lewis acid, by addition of halide ion to Ph_3Bi . Bismuth is known to act as an electron acceptor when bonded to halogen^{93b}, but such behaviour has not been reported for Ph_3Bi .

Conductimetric titrations of triphenylbismuth with ionic halides containing the cations $[(\text{n-C}_4\text{H}_9)_4\text{N}]^+$, $[(\text{C}_2\text{H}_5)_4\text{N}]^+$, Ph_3AsBr^+ and Ph_4As^+ were carried out. Only in the case of Ph_3AsBr_2 did a reaction occur, but the product of this was not $\text{Ph}_3\text{AsBr}^+\text{Ph}_3\text{BiBr}^-$ as hoped, but a mixture of several arsenic and bismuth organo halides, presumably resulting from loss of phenyl groups from bismuth. In every other case, including $\text{Ph}_4\text{As}^+\text{Br}^-$, which was least likely to interfere with any reaction by accepting a phenyl group from bismuth, no reaction occurred, and the conductance-composition graph was identical to that obtained for addition of the halide to the solvent.

It thus seems that triphenylbismuth does not act as a Lewis acid, in spite of its relative weakness as a Lewis base.

APPENDIX

INFRARED SPECTRA

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INFRARED SPECTRA

Infrared spectroscopy was used extensively throughout this work for identification and characterisation of products. Points of particular interest in the spectra of the different classes of compounds dealt with have been discussed in earlier sections; the following is a brief note on the more general features of these spectra.

(a) The Region 4000 - 625cm⁻¹.

The infrared spectra of triphenylarsine and its halides in the rock salt region are those of monosubstituted benzenes, and all absorptions in them can be assigned by comparison with Whiffen's thorough treatment of the halobenzenes¹⁰². Only two absorptions can be related to vibrational modes involving significant movement of the arsenic atom; these are Whiffen's X-sensitive q and r modes in the 1220 - 1060cm⁻¹ and 810 - 650cm⁻¹ ranges respectively, occurring at ca.1075cm⁻¹ and ca.670cm⁻¹ in triphenylarsine and its halogen adducts. They have not been found of any diagnostic value in the present work, however, and the most obvious difference between the different classes of these compounds is only in the relative intensities of the principal absorptions.

The same observation was made on the corresponding p-tolyl and p-chlorophenyl compounds. Although no study of the vibrational spectrum of disubstituted benzene rings comparable to Whiffen's of that of monosubstituted benzenes has been made, it was therefore considered that all absorptions in the spectra of these arsines and their halogen adducts in the rock salt region could likewise be assigned as benzene ring vibrations (except of course for those characteristic of the methyl group of the p-tolyl compounds).

This being the case, it seems unnecessary to record the observed frequencies. Representative spectra of the types of compound dealt with here have been published^{45,103-106}, and the only additional information worth recording is the observation that the spectra of Ph_3AsCl_2 and Ph_3AsBr_2 reported by Jensen and Nielsen¹⁰⁵ correspond exactly to those recorded in the present work for the hydrolysis products Ph_3AsOHCl and Ph_3AsOHBr , which have been discussed in detail (pp.67 et seq.)

(b) The Region 625 - 200 cm^{-1} .

In the region 625 - 200 cm^{-1} , however, absorptions due to characteristic vibrational modes involving As-C and As-Hal bonds might be expected, and would be of more interest in the present work. From a simple theoretical viewpoint the molecule Ar_3As may be regarded when considering the As-C bonds as either a trigonal pyramidal AsC_3 unit or as a benzene ring with a single

substituent $X = \text{Ph}_2\text{As}$. The former would give rise to nine vibrational modes, including two As-C stretching modes, one triply degenerate; the latter would lead to six X-sensitive vibrational modes of the benzene ring, three of which would involve considerable As-C stretching. The theory to combine these two approaches is available¹⁰⁷, but Brown and his co-workers have pointed out that the principal absorptions of the phenyl derivatives of elements of groups IV, V, VI and VII can all be assigned simply as those of a monosubstituted benzene¹⁰⁶. Thus for triphenylarsine they observed Whiffen's X-sensitive t mode (which along with q and r involves appreciable As-C stretching) at $305/311\text{cm}^{-1}$ and the y mode (involving Ph-As out-of-plane deformation) at 470cm^{-1} , while the remaining X-sensitive vibrations, x and u, observed for elements lighter than arsenic, were below 200cm^{-1} .

Harrah, Ryan and Tamborski¹⁰⁴ make the same assignment of the 470cm^{-1} absorption of Ph_3As , while Jensen and Nielsen assign it to the As-C asymmetric stretch, without making any reference to the low frequency X-sensitive vibrations of the phenyl ring. The latter authors, however, were able to record spectra down to only 400cm^{-1} , and therefore lack of knowledge of lower frequency absorptions must affect adversely the reliability of their assignment (cf. also their assignment of an absorption at 595cm^{-1} in the spectrum of platinum complexes of triethylarsine to an As-C asymmetric stretch)¹⁰⁵.

In the present work observations are in agreement with assignment of absorptions as benzene ring frequencies. The only strong absorptions in the far infrared spectrum of triphenylarsine were at 475 and 328cm^{-1} , and corresponding ones were observed in all spectra recorded of triphenylarsine derivatives (Table 10).

Table 10: Infrared Spectra of Triphenylarsine and some derivatives, $625 - 200\text{cm}^{-1}$.

Compound	Characteristic Frequencies (cm^{-1})					
Ph_3As	475m		328m			
Ph_3AsCl_2	465m	420vw	367/40m			240s, br
Ph_3AsBr_2	465s	385vw	360/40m		241w	
Ph_3AsOHCl	550vw	459s	352s	310/290m	260/48w	238vw
Ph_3AsOHBr	550vw	466/50m	350s	310/290w	250vw	230vw

If the 475cm^{-1} absorption were properly described as an As-C asymmetric stretching frequency the symmetric stretch should be observed at a somewhat lower frequency in Ph_3As but not in the dihalides, in which it becomes infrared inactive because the AsC_3 unit is planar. No such absorption was observed, and indeed there are more absorptions in the spectra of the dihalides than in that of the arsine. This may be due simply to splitting of the lower

frequency vibration, but in any case is opposite to that expected for assignment of the 475cm^{-1} absorption as an As-C asymmetric stretch, whereas the same criterion has been used successfully to determine whether or not the R_3M unit in compounds $R_3\text{SnX}$ ¹⁰³ and $R_3\text{SbX}_2$ ^{22,109} is planar or pyramidal.

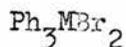
In the absence of comparably detailed work on .

1,4-disubstituted benzenes the spectra of p-tolyl and p-chlorophenyl compounds could not be interpreted so well. A strong absorption probably corresponding to the γ mode of the phenyl ring was observed in each at $510 - 490\text{cm}^{-1}$. The only other absorptions were a number of much weaker ones between 400 and 200cm^{-1} and a single strong, broad absorption in the spectrum of (p-tol)₃AsCl₂ at 245cm^{-1} . Since the only observed absorption comparable to this occurred at 240cm^{-1} in the spectrum of Ph₃AsCl₂ it is assigned to the Cl-As-Cl asymmetric stretch. It is extremely low for an As-Cl stretching frequency (cf. AsCl₃: ν_1 , 412cm^{-1} ; ν_3 , 307cm^{-1} ^{61c}. AsCl₄⁺: ν_1 , 409cm^{-1} ; ν_3 , 492cm^{-1} ¹¹⁰) and is therefore in keeping with the expected (v. p.11) low bond order (cf. also AsCl₆⁻: ν_4 , 220cm^{-1} ¹¹⁰). A similarly low P-F stretching frequency has been observed in the analogous (CH₃)₃PF₂ (asymmetric and symmetric stretching frequencies 670 and 500.5cm^{-1} respectively compared to 945 and 640cm^{-1} for the corresponding vibrational modes of PF₅⁶⁰).

The Sb-Cl stretch in (CH₃)₃SbCl₂ has been assigned²² at 277cm^{-1} , which seems rather high compared with the As-Cl stretch,

but it is difficult to be certain of the effect on this vibrational frequency of changing the phenyl group to a methyl. The only other similar assignments which appear to have been made are those by Jensen and Nielsen of the Sb-Br ($294, 233\text{cm}^{-1}$) and Bi-Br ($242, 219\text{cm}^{-1}$) stretching frequencies in Ph_3MBr_2 ¹⁰⁵. Since these do not compare well with the present assignment of $\nu(\text{As-Cl})$ to 245cm^{-1} and the observation of no corresponding $\nu(\text{As-Br})$, which implies that even that is below 200cm^{-1} , it should be noted that these assignments are based on very little evidence. In the present work no great difference has been observed in the frequencies of phenyl ring vibrations between the arsine itself and its dihalides, whereas Jensen and Nielsen assume a weakening of the M-Ph bonds on formation of a dihalide. Table 11, overleaf, lists the relevant spectral frequencies and suggests, by comparison with the later work of Brown et al.¹⁰⁶, and in keeping with the above observation, alternative assignments which would give values to the Sb-Br and Bi-Br stretching frequencies of ca.180 and ca.160 cm^{-1} respectively. This would be in accordance with an As-Br stretching frequency of ca.200 cm^{-1} and the As-Cl stretching frequency of 240-245 cm^{-1} . Such assignments, however, are of little more value than the original ones, and are made only to show that the little data available is consistent.

Table 11: Assignment of M-Br stretching frequencies in Compounds



COMPOUND	Frequencies reported in reference 105. (cm ⁻¹)				
Ph ₃ SbBr ₂	162/70/86/96s, br			238s	294s
Ph ₃ Bi		192/7w		216/24/36s	
Ph ₃ BiBr ₂	148/55/63/68s, br		219s		242s
Assignments					
ref.105	ν(M-Ph)	ν(M-Br)	ν(M-Ph)	ν(M-Br)	ν(M-Br)
ref.106			X-sens. t		X-sens. y 272/67 in Ph ₃ Sb
(suggested revision)	ν _{as} (M-Br)	X-sens. t	X-sens. t		X-sens. y

EXPERIMENTAL

EXPERIMENTAL

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EXPERIMENTALI. General Techniques.(1) Handling of materials.

Because of the hydrolytic instability of the chlorides and bromides of triarylarisines it was necessary to handle them in a glovebox. This was flushed with dry nitrogen before use and kept dry by trays of phosphorus pentoxide. The nitrogen was commercial oxygen free nitrogen dried by passage through a column of molecular sieve (AEI-Birlec, Ltd. adsorber type AB12.5). Certain manipulations, chiefly removal of solvents, were carried out in a simple vacuum line, thus avoiding exposure of the sensitive halides to both atmospheric moisture and elevated temperatures. Compounds so handled were stored in sample tubes sealed by a greased ground glass joint and kept in a desiccator over phosphorus pentoxide.

All the oxygen containing compounds described could be handled without special precautions, except for a few polyhalides which tended to lose halogen unless kept in tightly sealed containers.

(2) Conductance measurements.

All conductance measurements were made with a pair of smooth platinum dipping electrodes set in glass. The solution was contained in a tube into which the electrodes were fitted by a ground glass joint, so that atmospheric moisture could be excluded. For a typical measurement the cell was charged with ca. 17.5ml (by weight) of dry solvent and brought to 25° in a thermostatted bath. Successive additions of the solid (ca. 0.02 mmole lots) were made from small sample tubes filled in the drybox, and when solution was complete the resistance was measured repeatedly until constant. Calculation gave a series of up to twelve values of Λ_m over a concentration range of 0.002 - 0.03 molar, and from these a graph of Λ_m against $\sqrt{c_m}$ was plotted. The concentration 0.01M was chosen as standard for comparison, as a compromise between low concentrations at which Λ_m is very dependent on small changes in concentration, and high values of c_m at which it is more nearly constant, but which could not be reached by several less soluble compounds (v. Tables 3 and 4, and figures 3 and 4, pp. 41-44). The exact value of Λ_m at that concentration was obtained from the graph. Only in the case of tri-p-tolylarsenic dibromide was extrapolation necessary. Samples were exposed to the atmosphere only long enough to transfer them from sample tube to solvent. In practice this was found to give satisfactorily reproducible results, and the material could be recovered unhydrolysed from the solution afterwards.

The same precautions were taken in measuring the conductance of even hydrolytically stable compounds, except that samples were not weighed out in the drybox, because the conductance of methyl cyanide is increased by absorption of atmospheric moisture.

The instrument used to measure the resistance between the electrodes was a Phillips PR9500 resistance bridge operating on 1000c/s current. The cell constant was initially determined at one degree intervals from 15° to 25°, using KCl solution 0.01N at 18°, and was not found to vary within the accuracy of measurement. It was checked from time to time and found to be constant at 0.550cm⁻¹.

(3) Conductimetric titrations.

Conductimetric titration is a useful technique for investigation of the course of certain types of reaction, giving information not only on the stoichiometry of the products but also on their electrolytic nature. The value of this can be seen in the results and discussion section of this thesis (v. figs 1, 2, 6, 9 and associated text) and in references 19 and 20.

Methyl cyanide is a convenient solvent because its high dielectric constant (36.7 at 25°C) results in high conductances of electrolytes and consequent easy distinction between non-electrolytes and strong and weak electrolytes. Strong 1:1 electrolytes have Λ_m ca. 100ohm⁻¹cm²mole⁻¹ and weak electrolytes

$\Lambda_m = \text{ca. } 10 - 20 \text{ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$ in methyl cyanide. Nitrobenzene was also used occasionally, but since compounds have much lower conductances in this solvent than in methyl cyanide it was not so useful. However, nitrobenzene had the advantage that cryoscopic measurements could be made in the same solvent, as a further aid to elucidation of reactions, whereas methyl cyanide was found unsuitable for this purpose.

Titrations were carried out in an apparatus designed to exclude atmospheric moisture and to keep halogen solutions from contact with tap grease: a description of the apparatus and its operation has been published¹¹¹. Certain titrations of triphenylbismuth with halogens were carried out at -35° , using a modification of the above apparatus, also described previously¹⁹, which could fit into a dewar flask containing an acetone/ CO_2 bath maintained at -35° .

Addition of a solution of a strong electrolyte to methyl cyanide produces a smoothly curving conductance-composition graph rather than a straight line because the regular increase in conductance due to the increasing number of ions in solution is offset by dilution of the solution by added methyl cyanide, which tends to reduce conductance. In some cases where it was felt that this curvature might be masking a slight inflection in the graph indicative of compound formation addition of solid samples, as in conductance measurements, was resorted to, thus avoiding dilution.

The dipping electrodes and resistance bridge used in the apparatus were the same ones as were used for conductance measurements.

(4) Infrared spectra.

Infrared spectra in the range $4000 - 625\text{cm}^{-1}$ were recorded on a Perkin-Elmer model 237 grating spectrophotometer. Calibration was by the single polystyrene peak at 1603cm^{-1} . Crystalline samples were mounted as mulls in Nujol, hexachlorobutadiene, or KelF no.3 fluorocarbon oil, and held between sodium chloride plates. Solutions were made up in dry chloroform (or, occasionally, methyl cyanide) and contained in cells with silver chloride windows and a nominal path length of 0.2mm. Concentrations used were in the range 30 - 50mg/ml.

A few spectra were recorded down to 200cm^{-1} , using a Perkin-Elmer model 621 grating spectrophotometer equipped with caesium fluoride optics. Nujol mulls were held between caesium iodide plates, protected when necessary by polythene sheet.

(5) Ultraviolet spectra.

UV spectra were recorded on a Unicam SP300 UV/visible recording spectrophotometer. Solutions were made up in graduated flasks from weighed samples and contained in stoppered silica cells of 1cm or 0.5cm path length.

(6) Analyses.

Microanalyses for carbon and hydrogen were carried out by A. Bernhardt in Germany.

Analyses for halogen were made by Volhard's method, in which halide is precipitated from solution by addition of a known excess of silver nitrate and the excess back titrated with ammonium thiocyanate. Samples were hydrolysed to give halide solutions as follows. About 0.1g of material was transferred to a weighed flask (in the drybox if necessary) and 20ml 2N caustic soda was added. This was usually done in a closed system to prevent possible escape of hydrogen halide, although in fact hydrolysis was never observed to be so vigorous as to require this. The solution was allowed to stand some time and then boiled to ensure complete hydrolysis; any residue was reduced to a fine powder. The solution was acidified with concentrated sulphuric acid and saturated with sulphur dioxide to reduce any hypohalite ion, then boiled again to remove excess SO_2 and reduce its volume. It was then cooled, neutralised with concentrated ammonium hydroxide, and acidified with 20ml freshly boiled 6N nitric acid. 20ml standard 0.1N silver nitrate solution was added and the resultant precipitate of silver halide allowed to coagulate in the dark. The hydrolysate was then filtered off into a graduated flask and made up to 100ml with distilled water. Separate 20ml portions were titrated with standard 0.1N ammonium

thiocyanate solution, using ferric indicator.

Silver nitrate solution was made up by weight, using fresh AnalaR AgNO_3 , or standardised against a solution made up by weight from analytical grade potassium bromide dried several hours at 100° . The ammonium thiocyanate solution was standardised against the silver nitrate.

In the few cases where the compound contained both bromine and iodine its total halogen content was determined as above, and iodine alone by a modification of Jannasch's method¹¹². A 20ml portion of the hydrolysate was acidified with glacial acetic acid and treated with 4ml 20 volume peroxide. This brought about selective oxidation of iodide to iodine, which was steam distilled in an all glass apparatus into ammoniacal hydrazine solution. The resultant iodide was determined by Volhard's method as above.

The above procedure was found satisfactory for derivatives of tri-p-chlorophenylarsine, and there was no evidence of interference from the chlorine substituent of the aromatic rings.

II. Source and Purification of Materials.

A. Solvents

(1) Methyl Cyanide

Two methods were used to purify methyl cyanide. In the first, that of Smith and Witten¹¹³, the commercial product (Hopkins and Williams) was allowed to stand one week over potassium hydroxide pellets to remove acid impurities, then filtered and stored over calcium chloride for a further week to remove ammonia and water. It was then refluxed and distilled repeatedly over phosphorus pentoxide until dry, when the P_2O_5 did not cake and turn yellow, but formed a fine suspension in the liquid.

During the latter part of the research a more convenient method was found to be that of Forcier and Olver¹¹⁴. The crude solvent was first refluxed over sodium hydride (1g/l) to remove acrylonitrile, acid impurities and water, then distilled, refluxed over phosphorus pentoxide (2g/l) to remove basic impurities, and distilled again. A final reflux over calcium hydride (2g/l) followed by distillation removed any last traces of water.

In both cases a final distillation on the vacuum line was necessary to remove traces of drying agent. No adverse effects

were noticed when this step was omitted in the first method, but in the second the solvent had considerable reducing power. The chief disadvantage of the first method was the loss of a considerable part of the solvent by polymerisation, possibly because acrylonitrile was not removed. The second method gave equally good methyl cyanide provided freeze distillation was not omitted, and was much quicker and more efficient.

The specific conductance of methyl cyanide purified by these methods varied from batch to batch but was always ca. 10^{-7} ohm⁻¹cm⁻¹. The boiling range was 31 - 32°C.

(2) Nitrobenzene.

For use in conductimetric and cryoscopic work AnalaR nitrobenzene was distilled twice, once at atmospheric pressure, when the fraction boiling at 207 - 208°C was collected, and the other at reduced pressure (65 - 68°C, ca. 2mm). The specific conductance of this nitrobenzene was less than 10^{-7} ohm⁻¹cm⁻¹ at 25°C - too low to measure accurately.

(3) Ether.

Diethyl ether was dried by refluxing it over sodium wire, after preliminary drying over calcium chloride. It was then stored over fresh sodium wire and redistilled before use.

(4) Chloroform.

Chloroform for preparative purposes was commercial grade solvent dried over calcium chloride, filtered and distilled. When intended for spectroscopic use it was freed from ethanol by washing with a large volume of water, dried by passage through a column of alumina, and stored over silica gel.

B. Reagents.

(1) Chlorine

Chlorine, obtained from a cylinder, was dried by passage through concentrated sulphuric acid and a drying tower packed with phosphorus pentoxide, and diluted with dry nitrogen for synthetic use.

(2) Iodine chloride.

Commercial iodine chloride (B.D.H.) was resublimed before use.

(3) Bromine.

AnalaR bromine was stored over calcium bromide. For use in syntheses it was filtered to remove the calcium bromide and distilled on the vacuum line into small ampoules, through a trap at 0°. Solutions were made up by breaking an ampoule, containing a known weight of bromine, under a known weight of solvent.

(4) Iodine bromide.

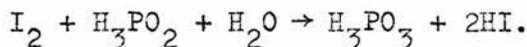
Iodine bromide was resublimed commercial material (B.D.H.) or was made in solution by mixing equivalent quantities of iodine and bromine solutions.

(5) Iodine.

AnalaR grade iodine was resublimed, ground to a fine powder, and stored in a dessicator over phosphorus pentoxide.

(6) Hydrohalic acids.

Ordinary aqueous HCl was used. HBr was AnalaR grade (47%, diluted as necessary). HI was also AnalaR, but since this was always found to be contaminated with iodine it was regenerated before use by the method advocated by Brauer¹¹⁵. The concentrated aqueous solution of HI was brought near to its boiling point and hypophosphorous acid added dropwise until the solution became colourless:



The azeotropic acid was then distilled off through a Vigreux column at 125-127°, under a stream of nitrogen.

(7) General.

Reagents used in the preparation of arsine derivatives described in this thesis, other than those detailed above, (e.g. AgClO₄)

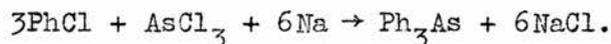
were AnalaR grade and not further purified, unless otherwise stated in the description of the preparation below.

Reagents used in the preparation of starting materials (arsines, etc.), such as arsenic trichloride and bromobenzene, were ordinary commercial materials, purified if necessary by a single distillation or crystallisation.

C. Starting materials

(1) Triphenylarsine.

Triphenylarsine was available which had been prepared by a standard Wurtz type reaction between chlorobenzene and arsenic trichloride¹¹⁶:



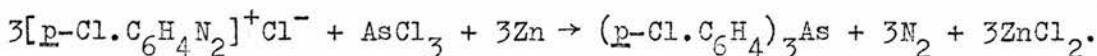
For preparative use it was recrystallised from 95% ethanol: m.p.61°.

(2) Tri-p-tolylarsine.

Tri-p-tolylarsine was synthesised by a standard Wurtz type reaction also, between p-bromotoluene and arsenic trichloride. The method has been described in detail^{58e}. The solvent used was ether, and a first crop of pure white flakes (m.p.146°) separated from the filtered reaction mixture as it cooled. Later crops were purified by recrystallisation from ether.

(3) Tri-p-chlorophenylarsine.

Tri-p-chlorophenylarsine was prepared by decomposing p-chlorophenyldiazonium chloride (as its zinc double salt) with zinc dust in acetone suspension, in the presence of arsenic trichloride:



This preparation is described in detail later (Preparations: Part I) because the method used is not so well known as the Wurtz reaction by which the other triarylsarsines were obtained, and because it is considered useful to record some of the experimental details, not elaborated on in the original description by Hanby and Waters¹¹⁷.

(4) Triphenylarsine Oxide.

Triphenylarsine oxide, as the monohydrate, was available in the laboratory. It had been synthesised by the standard method of peroxide oxidation of triphenylarsine¹¹⁶. The immediate product of the reaction was crystallised from water to yield the hydrate, m.p. 188 - 189°, and no attempt was made to isolate the anhydrous oxide (v. p.46).

(5) Triphenylbismuth.

Triphenylbismuth was prepared by a Grignard reaction from bromobenzene and bismuth tribromide¹¹⁸, and recrystallised from methyl cyanide: m.p. 77 - 78°.

III Preparations.

General Remarks.

Many of the compounds made during the course of this research were prepared in several ways. The method described below is the one which was found to be most convenient or to give the highest yield or purest product. Although many of the preparations are very similar the differences between them are considered sufficient to warrant separate descriptions for most compounds.

Crystallisation of solids in general was effected by adding ether to a solution of the compound in a polar solvent, usually methyl cyanide, but occasionally chloroform, ethanol, or acetone. Melting points of many of the crystalline compounds, mostly triarylsarsine halides, were diffuse, due to decomposition at elevated temperature, but reproducible within a few degrees and therefore characteristic of the compounds without indicating their purity. Purity was ensured by halogen analysis, and in the case of the moisture-sensitive halides by checking that no hydroxyl stretching frequency appeared in the infrared spectrum.

Yields were usually almost quantitative if care was taken to extract successive crops of crystals from the reaction mixture, but normally the initial crop only (generally ca.70%) was taken, particularly in the case of hydrolytically unstable compounds, to avoid repeated handling.

PART I(1) Tri-p-chlorophenylarsine.(a) p-chlorophenyldiazonium tetrachlorozincate(II).

Well-ground p-chloroaniline (125g, 0.98mole) was added with vigorous stirring to a mixture of conc. HCl (350ml) and water (150ml) contained in a 2l beaker surrounded with ice, producing a thick suspension of the hydrochloride. When this had cooled to 0° a solution of sodium nitrite in water (70g, 1.01mole in 90ml), also at 0°, was added slowly (ca. 1hr), care being taken to keep the temperature below 5°. To the resultant clear, brown solution of p-chlorophenyldiazonium chloride was added a solution of zinc chloride (90g, 0.66mole) in HCl (40ml 2M), stirring being maintained. The voluminous cream precipitate was filtered off at the water pump. A small amount of impurity in the form of orange lumps was removed by inspection before the zinc double salt was washed with acetone (170ml AnalaR) and pressed dry. Yield: 203g, 0.42mole, 85% based on amine.

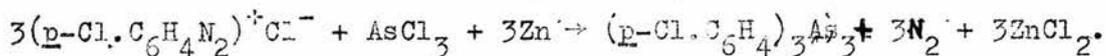
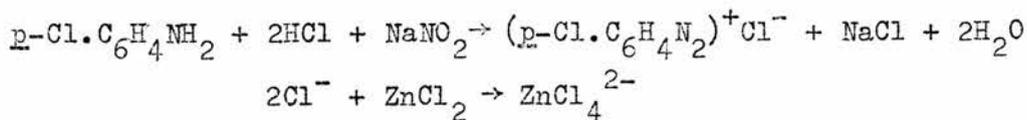
The orange lumps were presumably lumps of unreacted amine coupling with the diazonium ion to produce a coloured azo compound. It was for this reason that the amine was thoroughly ground before use - to ensure as complete reaction as possible. If the amine used was too coarse much of the product was lost in this side reaction when it was washed with acetone. Thorough drying

(on filter paper) was also necessary at this stage to avoid loss of material in the next step by formation of phenol and tars.

(b) Tri-p-chlorophenylarsine. 200g of the dry diazonium salt (0.41mole) was placed in a 2l beaker with acetone (500ml AnalaR) and arsenic trichloride (50g, 0.28mole), and cooled to -10° , with continuous vigorous stirring. Powdered zinc (62.5g AnalaR, 0.96mole) was added in small amounts over a period of ca. 1hr, during which time the temperature of the solution was kept well below 0° . Each addition resulted in vigorous effervescence until nearly all the zinc had been used. When addition of zinc was complete the solution was allowed to warm up. After two hours stirring was stopped and the reaction mixture left overnight. Acetone was removed on a rotary film evaporator, leaving a brown paste, which coagulated slowly when stirred with 75ml 2M HCl. The solid mass was allowed to stand for several hours before being filtered off, dried, and crystallised from petroleum ether (b.p.40/60 $^{\circ}$).

Recrystallisation from ethanol gave white needles of tri-p-chlorophenylarsine, m.p. 75° . Yield, 35.44g, 0.087mole, ca. 31% based on arsenic. (Found: C, 52.26; H, 3.13. Calc. for $C_{18}H_{12}AsCl_3$: C, 52.79; H, 2.95%).

The equations for the above reactions are:



(2) Tri-p-tolylarsenic dichloride

Dry chlorine gas was bubbled through a solution of tri-p-tolylarsine (1.742g, 5mmole) in chloroform, until a strong green colour showed the presence of excess. The solvent was distilled off on the vacuum line. The resultant white solid was dissolved in a minimum of dry chloroform and ether added until crystallisation began. After the solution had stood for one day at 0° 1.424g of white crystals, m.p. 240-247°, were filtered off. (Lit. m.p. 228-230° ^{58a}) (Found: C, 60.18; H, 5.13; Cl, 16.75. Calc. for $C_{21}H_{21}AsCl_2$: C, 60.16; H, 5.05; Cl, 16.91%).

(3) Tri-p-tolylarsenic dibromide

Bromine (0.4480g, 2.8mmole) was added from an ampoule to a solution of tri-p-tolylarsine (0.9767g, 2.8mmole) in chloroform. After filtration ether was added until precipitation of the white product appeared to be complete, whereupon the crystals (1.1195g) were filtered off: m.p. 250°(d), Lit. value 245° ^{58a}. (Found: C, 49.74; H, 4.28; Br, 30.84. Calc. for $C_{21}H_{21}AsBr_2$: C, 49.63; H, 4.17; Br, 31.45%).

(4) Tri-p-tolylarsenic bromide iodide

A solution of iodine bromide (0.5547g, 2.6mmole) in the minimum of methyl cyanide was added dropwise to a stirred

suspension of finely ground tri-p-tolylarsine in a saturated solution of the arsine in methyl cyanide (total: 0.9344g, 2.7mmole). Bright orange solid precipitated with every drop of bromine solution added, and soon all the arsine had dissolved. Small amounts of a dark red solid precipitated at each addition also, but immediately redissolved. The dark red supernatant liquid was decanted and the remaining homogeneous orange crystalline solid (0.9542g) washed with ether and dried: m.p. 145-150°(d). (Found: C, 46.43; H, 4.10; Br, 14.32; I, 22.75. $C_{21}H_{21}AsBrI$ requires: C, 45.44; H, 3.81; Br, 14.39; I, 22.86%).

(5) Tri-p-tolylarsenic di-iodide

(i) Solutions of tri-p-tolylarsine and iodine (equivalent quantities) in chloroform and ether respectively were mixed, and some dark crystals of the tetra-iodide formed. During prolonged storage of the solution at 0° these were replaced by red-orange needles, m.p. 171.5-173°. (Lit. value 172°^{58a}). (Found: C, 42.16; H, 3.67; I, 41.34. Calc. for $C_{21}H_{21}AsI_2$: C, 41.88; H, 3.52; I, 42.15%).

(ii) Dropwise addition of iodine in petroleum ether (b.p. 40-60°) to a slurry of tri-p-tolylarsine in the same solvent initially precipitated a yellow solid. When a few dark crystals of the tetra-iodide appeared in the bottom of the flask the suspension of di-iodide was decanted and the yellow powder filtered

off. The melting point of this sample was only 168-170°, and normal recrystallisation was not possible because the di-iodide disproportionates in solution to the tetra-iodide, but analysis for iodine was satisfactory (found: I, 42.93%).

(6) Tri-p-tolylarsenic tetrabromide

Attempts to precipitate (p-tol)₃AsBr₄ from 2:1 mixtures of bromine and tri-p-tolylarsine led to mixtures of the dibromide and tetrabromide. But freeze drying of a methyl cyanide solution containing the arsine and a slight excess of bromine (0.5983g, 0.9mmole:0.3260g, 2.02mmole) gave a uniformly orange solid (0.6846g). This was redissolved in the minimum of methyl cyanide and ether was added until crystallisation began. After standing some time at 0° the orange needles were filtered off, washed with ether and dried: m.p. 123-124°. (Found: C, 37.59; H, 3.30; Br, 47.63. C₂₁H₂₁AsBr₄ requires: C, 37.76; H, 3.17; Br, 47.85%).

(7) Tri-p-tolylarsenic dibromide di-iodide

(i) A solution of iodine bromide (1.0603g, 5.12mmole) in methyl cyanide was added dropwise to a stirred slurry of tri-p-tolylarsine (0.8928g, 2.56mmole) in the same solvent. Initially orange (p-tol)₃AsBrI precipitated and the arsine dissolved, but as more IBr was added the precipitate also dissolved. A large excess of ether was added to the filtered solution, which

was then stored two hours at 0° . Dark red crystals were separated by decantation, washed with ether, and dried: m.p. $132-136^{\circ}$. (Found: C, 32.74; H, 3.61; Br, 21.66; I, 34.40. $C_{21}H_{21}AsBr_2I_2$ requires: C, 33.10; H, 2.78; Br, 20.97; I, 33.31%). The initial yield was 0.5982g: a further 0.4343g of the same material was obtained as a red powder on freeze drying the remaining solution.

(ii) Addition of ether to a chloroform solution of iodine (0.2377g, 0.94mmole) and tri-p-tolylarsenic dibromide (0.4760g, 0.94mmole) precipitated red needles which were filtered off and washed with ether: m.p. 132° . (Yield 0.5757g)

(8) Tri-p-tolylarsenic tetra-iodide

To a solution of tri-p-tolylarsine (1.74g, 5mmole) in chloroform (60ml) was added a solution of iodine (2.54g, 10mmole) in 150ml ether. Bronze-coloured plates began to form, and after the solution had stood some hours at 0° these were filtered off and washed with ether (4.03g: m.p. 153° as Lit. ^{58a}) (Found: C, 29.72; H, 2.43; I, 58.69. Calc. for $C_{21}H_{21}AsI_4$: C, 29.45; H, 2.47; I, 59.29%).

(9) Tri-p-chlorophenylarsenic dichloride

Tri-p-chlorophenylarsine (3.1218g) was weighed into a flask with a little methyl cyanide, insufficient to effect complete

solution, which was then flushed out with dry nitrogen. A stream of dry chlorine was passed through the solution and the excess arsine dissolved. Rapid crystallisation suddenly took place, but passage of chlorine was maintained until the contents of the flask were green. Excess chlorine and some solvent were blown off with dry nitrogen. The white crystals remaining were filtered off and dried on filter paper in the drybox: m.p. 169-170°. (Found: C, 45.70; H, 2.98; Cl, 14.60. $C_{18}H_{12}AsCl_5$ requires: C, 45.00; H, 2.52; hydrolysable Cl, 14.76%).

When this preparation was attempted in chloroform solution a white powder (m.p. 200-210°) was obtained which appeared to contain chloroform of crystallisation. There was an extra absorption in its infrared spectrum at 762cm^{-1} , which is a C-Cl stretching frequency of chloroform (ν_5 ; 757cm^{-1} 119). Carbon and hydrogen analyses were correct for a dichloride containing half a mole of solvent of crystallisation (Found: C, 41.95; H, 2.42. $C_{18}H_{12}AsCl_5 \cdot 0.5CHCl_3$ requires: C, 41.14; H, 2.33%), but though chlorine analysis gave hydrolysable chlorine content too high for the dichloride (19.37%) it did not agree with any simple formulation. However the degree to which the above chloroformate would hydrolyse is unpredictable, and therefore chlorine analysis by the method used is an unreliable guide in this case. When crystallisation of this compound was effected from chloroform/ether at 0° it formed long white needles, which

collapsed to a powder on warming to room temperature. These crystals are likely to be an etherate, or possibly a higher chloroformate, stable only at low temperature.

(10) Tri-p-chlorophenylarsenic dibromide

A solution of bromine (0.4411g, 2.76mmole) in chloroform was added to tri-p-chlorophenylarsine (1.1309g, 2.76mmole) in the same solvent and the solution was filtered. No precipitate appeared on addition of a large excess of ether, even on prolonged storage at 0°, but when the solution was cooled to -80° for several hours white needles (1.0456g) separated: m.p. 215°(d). (Found: C, 37.54; H, 1.97; Br, 27.88. $C_{18}H_{12}AsBr_2Cl_3$ requires: C, 37.97; H, 2.12; Br, 28.07%).

(11) Tri-p-chlorophenylarsenic bromide iodide

Tri-p-chlorophenylarsine (0.2047g, 0.5mmole) was dissolved in a solution of iodine bromide (0.1034g, 0.5mmole) in methyl cyanide (3.5ml). After storage for a week at 0° the solution deposited yellow-orange needles, m.p. 148-150° (0.2037g). (Found: C, 36.06; H, 2.29; Br, 12.03; I, 20.60. $C_{18}H_{12}AsBrCl_3I$ requires: C, 35.08; H, 1.96; Br, 12.96; I, 20.59%).

(12) Tri-p-chlorophenylarsenic di-iodide

Addition of a dilute solution of iodine in petroleum ether

(b.p. 40-60°) to a saturated solution of tri-p-chlorophenylarsine in the same solvent resulted in precipitation of a small amount of orange powder, soon followed by the dark tetra-iodide. The orange powder was separated by decantation and dried on filter paper: m.p. 148-50°. (Found: C, 31.83; H, 1.05; I, 39.14.

$C_{18}H_{12}AsCl_3I_2$ requires: C, 32.59; H, 1.82; I, 38.26%).

The yield of this compound was very low because tetra-iodide was precipitated preferentially unless the arsine:iodine ratio was very high, and also apparently because this di-iodide is appreciably soluble in petroleum ether. Like the corresponding p-tolyl compound it could not be recrystallised because of its disproportionation to tetra-iodide in solution.

(13) Tri-p-chlorophenylarsenic tetrabromide.

A solution of bromine (1.3952g, 8.7mmole) in methyl cyanide (10ml) was added dropwise to a slurry of tri-p-chlorophenylarsine (1.4223g, 3.5mmole) in methyl cyanide. The slurry thinned as the arsine dissolved, then thickened again as the white dibromide precipitated. Finally the solution turned yellow and all the white solid dissolved to give an orange solution. On addition of about two volumes of ether fine orange needles began to form. When crystallisation appeared complete they were filtered off: m.p. in the range 126-134°. (Found: C, 30.09; H, 2.37; Br, 43.29.

$C_{18}H_{12}AsBr_4Cl_3$ requires: C, 29.65; H, 1.66; Br, 43.83%).

(14) Tri-p-chlorophenylarsenic dibromide di-iodide

Tri-p-chlorophenylarsenic dibromide (0.4501g, 0.79mmole) and iodine (0.2010g, 0.79mmole) were dissolved in the minimum quantities of methyl cyanide and the solutions were mixed. No immediate precipitate appeared when 10 volumes of ether were added, but after several days storage at 0° a small quantity of dark red prisms (0.1160g) could be filtered off: m.p. 148°. (Found: C, 26.20; H, 1.39; Br, 18.60; I, 31.75. $C_{18}H_{12}AsBr_2Cl_3I_2$ requires: C, 26.26; H, 1.47; Br, 19.41; I, 30.83%).

(15) Tri-p-chlorophenylarsenic tetra-iodide

Iodine (0.5082g, 2mmole) dissolved in methyl cyanide (20ml) was added dropwise to a slurry of tri-p-chlorophenylarsine (0.4097g, 1mmole) in the same solvent (5ml) with vigorous stirring. Almost immediately dark crystals of the tetra-iodide began to separate. When addition was complete all the arsine had dissolved and the solution was very dark. The fine dark chocolate-coloured crystals were filtered off (0.5449g). Addition of ether to the filtrate did not yield a second crop: the product appears to be appreciably soluble in ether, unlike the tetra-iodide derivatives of other arsines. m.p. 160-162°. (Found: C, 24.50; H, 1.63; I, 54.86. $C_{18}H_{12}AsCl_3I_4$ requires: C, 23.57; H, 1.52; I, 55.34%).

(16) Tri-p-chlorophenylarsenic hexa-iodide

A large excess of iodine dissolved in chloroform was added to a chloroform solution of the mixed residues of several attempted preparations of tri-p-chlorophenylarsenic di-iodide, a mixture of the arsine itself and the tetra-iodide, with the intention of converting them wholly to the tetra-iodide. The solution was then filtered and four volumes of ether were added. An insoluble residue was identified as tri-p-chlorophenylarsenic tetra-iodide. When the filtrate had stood for 48 hours at 0° a small quantity of glossy greenish black crystals were filtered off. The high iodine content of these crystals suggested that they contained not the expected tri-iodide ions, but penta-iodide ions.

(Found: I, 67.7. $C_{18}H_{12}AsCl_3I_4$ requires: I, 55.34. $C_{18}H_{12}AsCl_3I_6$ requires: I, 65.0%). The fact that the analysis is high rather than low for this formulation supports it. When the solid was kept in a sample tube with a polythene stopper absorption of iodine by the plastic was observed. This does not occur with the tetra-iodide.

(17) Triphenylarsenic Dihalides.

The samples of triphenylarsenic dichloride and dibromide on which the conductance measurements were made were donated by M.F.Ali. They were analytically pure and had been prepared by a published method²⁰.

PART II(1) Triarylsarsine hydroxyhalides.

The six hydroxyhalides $\text{Ar}_3\text{AsOHHal}$ (Ar = Ph, (p-tol), (p-Cl.C₆H₄); Hal = Cl, Br) were prepared by the standard method of aqueous hydrolysis of the corresponding dihalide $\text{Ar}_3\text{AsHal}_2$. The procedure adopted was as follows.

The triarylsarsine (ca. 3g) was weighed into a 100ml flask and methyl cyanide (ca. 40ml, usually insufficient to effect complete solution) added. No precautions were taken to exclude moisture. Chlorine was then bubbled through the solution or a concentrated solution of bromine in methyl cyanide added dropwise, until a permanent colour showed the presence of halogen in excess of the 1:1 ratio. Continuous stirring or swirling of the solution was maintained to keep excess arsine in suspension, but solution was complete soon after addition of halogen began, and the white dihalide usually began to precipitate before the 1:1 mole ratio was reached. When crystallisation appeared to be complete and the solid had settled the supernatant liquid was decanted and the residue (partially hydrolysed dihalide) dissolved in the minimum quantity of boiling acetone. Water (ca. 1ml) was added to the solution and boiling continued for a few minutes to ensure complete hydrolysis. The solution was then filtered hot and allowed to cool before ether (1 to 2 vol.) was added. White

crystals of the hydroxyhalide precipitated immediately or when the filtrate was cooled to 0° . They were recrystallised from acetone/ether and dried under vacuum. (Found, for triphenylarsine hydroxychloride, m.p. $170-171^{\circ}$: Cl, 9.91. Calc. for $C_{18}H_{16}AsClO$: Cl, 9.87%. Found, for triphenylarsine hydroxybromide, m.p. $166-167^{\circ}$: Br, 19.9. Calc. for $C_{18}H_{16}AsBrO$: Br, 19.8%. Found, for tri-*p*-tolylarsine hydroxychloride, m.p. $179-181^{\circ}$: Cl, 9.26. Calc. for $C_{21}H_{22}AsClO$: Cl, 8.85%. Found, for tri-*p*-tolylarsine hydroxybromide, m.p. $207-209^{\circ}$: Br, 17.7. Calc. for $C_{21}H_{22}AsBrO$: Br, 18.0%. Found, for tri-*p*-chlorophenylarsine hydroxychloride, m.p. $176-178^{\circ}$: C, 46.62; H, 2.82; Cl, 7.54. $C_{18}H_{13}AsCl_4O$ requires: C, 46.79; H, 2.83; hydrolysable Cl, 7.67%. Found, for tri-*p*-chlorophenylarsine hydroxybromide, m.p. $201-210^{\circ}$: C, 41.93; H, 2.50; Br, 16.57. $C_{18}H_{13}AsBrCl_3O$ requires: C, 42.69; H, 2.59; Br, 15.78%).

(2) Triarylsarsine oxides

The oxides of tri-*p*-tolylarsine and tri-*p*-chlorophenylarsine were obtained by alkaline hydrolysis of the dibromides. The partially hydrolysed dibromide was prepared as described in (1) above, but instead of being dissolved in aqueous acetone the solid material left when the methyl cyanide was decanted was stirred into 2M sodium hydroxide solution, which was then brought to the boil. When the solution cooled the oxide was deposited, tri-*p*-tolylarsine oxide as white needles of the

monohydrate, m.p. 96° (Found: C, 65.35; H, 6.55. Calc. for $C_{21}H_{23}AsO_2$ ($C_{21}H_{21}AsO \cdot H_2O$): C, 65.97; H, 6.06%), tri-p-chlorophenylarsine oxide as an amorphous powder, m.p. 100° . (Found: C, 50.04; H, 3.18. $C_{18}H_{12}AsCl_3O$ requires: C, 50.80; H, 2.84%). For $Ph_3AsO \cdot H_2O$ v. p. 154.

The anhydrous oxides of triphenylarsine and tri-p-tolylarsine were obtained by heating the hydrate for several hours at 100° . Identity was confirmed from the infrared spectra without analysis.

(3) Triphenylarsine hydroxynitrate

A solution of triphenylarsine oxide monohydrate in concentrated nitric acid was boiled down until only a yellow oil remained. When cooled and triturated with ether this oil solidified and was recrystallised from methyl cyanide/ether to give white crystals, m.p. $99-100^{\circ}$. (Found: C, 55.65; H, 4.07; N, 3.76. Calc. for $C_{18}H_{16}AsNO_4$: C, 56.50; H, 4.10; N, 3.64%).

This reaction is described in the literature as a preparative method for triphenylarsine dinitrate^{58b}, but no such product was obtained in this work.

(4) Hydroxytriphenylarsonium perchlorate

To triphenylarsine hydroxybromide (0.349g, 0.87mmole) in ethanol (10ml), silver perchlorate (0.180g, 0.87mmole) in the same solvent was added. Silver bromide precipitated immediately

and was filtered off. The filtrate was evaporated nearly to dryness under vacuum and the viscous residue taken up in chloroform, and on adding ether white crystals were obtained. These, recrystallised from chloroform/ether and dried under vacuum, had m.p. 163-165°. (Found: C, 51.32; H, 3.83. $C_{18}H_{16}AsClO_4$ requires: C, 51.15; H, 3.58%).

(5) Hydroxytriphenylarsonium dichloriodate(I)

Iodine chloride (0.447g, 2.75mmole) in methyl cyanide (3ml) was added dropwise to a stirred solution of triphenylarsine hydroxychloride (0.985g, 2.75mmole) in methyl cyanide (8ml) which immediately became bright yellow. Addition of up to 50ml ether did not precipitate a solid, even on cooling to 0°. The solution was freeze dried to a yellow oil, which on trituration with ether gave a bright yellow solid, m.p. 76-78°. (Found: C, 41.71; H, 2.92. $C_{18}H_{16}AsCl_2IO$ requires: C, 41.49; H, 3.10%).

(6) Hydroxytriphenylarsonium tribromide.

Excess of water (0.5ml, ca. 28mmole) was added to methyl cyanide (40ml) containing triphenylarsine (0.122g, 0.4mmole) and bromine (0.128g, 0.8mmole) and the solution kept for 1 hour. 20ml of the resultant solution when freeze dried produced a low-melting dark orange solid, m.p. ca. 65° (Found: Br, 43.3. $C_{18}H_{16}AsBr_3O$ requires: Br, 42.6%), which could be kept unchanged

for several weeks in a sealed tube, but lost bromine readily in the open and on treatment with ether, the latter producing orange crystals $\text{Ph}_3\text{AsOHBr}_2$ (v. (7), below).

(7) Hydroxytriphenylarsonium tribromide bromide.

To the second 20ml portion of the solution prepared in (6) above ether (40ml) was added, and after several hours at 0° orange crystals formed, m.p. $106-108^\circ$ (Found: C, 45.45; H, 3.65; Br, 32.59. $\text{C}_{36}\text{H}_{32}\text{As}_2\text{Br}_4\text{O}_2$ requires: C, 44.76; H, 3.34; Br, 33.03%). This was identical to the material obtained when the above tribromide was washed with ether.

Note: on the attempted preparation of Hydroxytriphenylarsonium Tetrphenylborate.

Several attempts were made to prepare this compound by mixing equivalent quantities of a triphenylarsine hydroxyhalide and sodium tetrphenylborate. In every case a white solid precipitated, but was shown by its infrared spectrum to be bis(triphenylarsine oxide)hydrogen tetrphenylborate and not a hydroxytriphenylarsonium salt.

PART III(1) Bis(triphenylarsine oxide)hydrogen bromide.

Triphenylarsine oxide hydrate (0.9911g) was suspended in 20 ml of near boiling water, stirred vigorously, and 5ml of aqueous HBr (4.7%) added. The oxide dissolved and a yellow colour developed in the solution. On continued heating droplets of an orange oil collected on the bottom of the beaker. The aqueous solution was decanted, allowed to cool, and extracted with 2 x 20ml of chloroform. Addition of ether to the dried extract precipitated a first crop of 0.4448g of white crystals, m.p. 170-171° (Found: C, 59.35; H, 4.29; $C_{36}H_{31}As_2BrO_2$ requires: C, 59.61; H, 4.31%). A correct bromine analysis for this formula was never obtained (e.g. found: Br, 14.17, 13.72, 12.68: required: Br, 11.02%), but the identity of the product was unmistakable from its infrared spectrum, and the correct carbon and hydrogen analyses and constant melting point for different samples suggest that it was pure.

If the above decanted aqueous solution was reduced in volume and left to evaporate slowly a hydrated form of the bromide was obtained as white crystals, m.p. 170-172°, which did not lose water even at that temperature. Bromine analyses on this compound were also always high, but carbon and hydrogen analyses were in agreement with this identification, which was based on the infrared

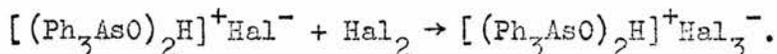
spectrum (Found: C, 57.22; H, 4.56. $C_{36}H_{31}As_2BrO_2 \cdot xH_2O$
 requires: C, 58.16; H, 4.47, (x = 1): C, 56.59; H, 4.63, (x = 2)).

(2) Bis(triphenylarsine oxide)hydrogen iodide.

To a stirred solution of triphenylarsine oxide monohydrate (3.40g, 10mmole) in boiling water (250 ml) 33g of potassium iodide dissolved in water (50ml) was added, followed by 10 ml glacial acetic acid. Addition of the iodide produced a slight yellow colour, and addition of the acid produced an immediate pale yellow crystalline precipitate. The solution was brought back to the boil and filtered. Very pale yellow needles began to separate immediately from the filtrate, and after drying had m.p. 154-155°. A further quantity of the same material was obtained by recrystallising the filtered original precipitate from boiling water. The total yield was 3.57g, ca. 95%. (Found: C, 56.04; H, 4.40; I, 16.31. $C_{36}H_{31}As_2O_2I$ requires: C, 55.98; H, 4.05; I, 16.43%). Another small crop from the mother liquor was contaminated by a few dark crystals of the tri-iodide.

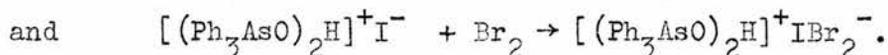
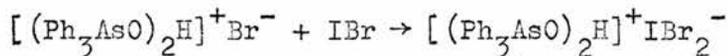
(3) Bis(triphenylarsine oxide)hydrogen trihalides.

All trihalides were most conveniently prepared in the same way, by the reaction



No restrictions were found on this reaction; bis(triphenylarsine-

oxide)hydrogen iodide could be used in spite of its equilibrium with tri-iodide in solution, and if there were alternative routes to a trihalide both apparently worked equally well, e.g.



In general equivalent quantities of the two reactants were dissolved in a minimum of methyl cyanide and ether added until the solution became turbid. After storage at 0° for a few hours crystals of the trihalide were filtered off. The first crop was ca.60-70% of the theoretical yield and analytically pure. Almost quantitative yields could be obtained by repeated extractions of the solution. Melting points and analytical results for all the trihalides prepared are listed below.

Trihalide ion	m.p. ($^\circ\text{C}$)	Found		Required for $\text{C}_{36}\text{H}_{31}\text{As}_2\text{O}_2\text{Hal}_3$	
		%C	%H	%C	%H
ICl_2^-	147-149	50.51	3.60	51.27	3.71
BrICl^-	99-100	49.34	3.99	48.71	3.52
I_2Cl^-	97-93	45.72	3.52	46.26	3.34
Br_3^-	39-91	48.11	3.50	48.85	3.53
IBr_2^-	115-116	46.63	3.43	46.33	3.35
I_2Br^-	110-111	43.24	2.99	44.16	3.19
I_3^-	116-118	41.98	3.08	42.14	3.04

(4) Bis(triphenylarsine oxide)hydrogen perchlorate.

Equivalent quantities of triphenylarsine hydroxychloride (0.36g, 1mmole) and silver perchlorate (0.21g, 1mmole) were separately dissolved in a minimum of ethanol and the solutions were mixed. The immediate precipitate of silver chloride was filtered off and ether added to the filtrate until crystals began to appear. After the solution had stood for an hour at 0° the white crystals (0.32g) were filtered off and dried; m.p. 205-206° (Found: C, 58.10; H, 4.20. $C_{36}H_{31}As_2ClO_6$ requires: C, 58.05; H, 4.19%), infrared spectrum shows: ClO_4^- , ν_3 1100 cm^{-1} ; ν_4 630 cm^{-1} .

This procedure was originally carried out in an attempt to prepare hydroxytriphenylarsonium perchlorate, but in fact it led invariably to a high yield of the above compound, presumably because conditions favour an ionic product. Conditions which do yield $Ph_3As(OH)ClO_4$ are described on p.169.

(5) Bis(triphenylarsine oxide)hydrogen periodate.

Addition of 5ml glacial acetic acid to a vigorously stirred solution of triphenylarsine oxide monohydrate (0.34g) and potassium periodate (3g) in boiling water (50ml) initiated rapid crystallisation of glittering white plates. When filtered off and dried these had m.p. 172-173° and required no further purification (Found: C, 51.67; H, 3.80. $C_{36}H_{31}As_2IO_6$ requires: C, 51.70; H, 3.74%); infrared spectrum: IO_4^- , ν_3 852 cm^{-1} (vs).

(6) Bis(triphenylarsine oxide)hydrogen di- μ -bromo-tetrabromo-dimercurate(II).

A solution of triphenylarsine oxide monohydrate (0.50g) in 4.7% aqueous HBr (20ml) was added to a solution of mercury(II) bromide (0.28g) in boiling water. The solution became turbid and on cooling deposited a colourless oil, which solidified on overnight storage at 0°. The (greyish) solid was dissolved in boiling ethanol and the solution filtered and allowed to cool. Addition of ether brought about slow crystallisation of white needles, (0.26g) m.p. 146-147. (Found: C, 39.9; H, 2.9; $C_{72}H_{62}As_4Br_6Hg_2O_4$ requires: C, 39.82; H, 2.88%).

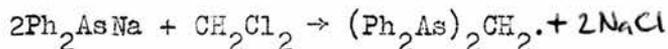
(7) Bis(triphenylarsine oxide)hydrogen hexachloroplatinate(IV).

To a solution of triphenylarsine oxide monohydrate (0.53g) in boiling water (150ml) was added an aqueous solution of chloroplatinic acid (0.38g $H_2PtCl_6 \cdot 4H_2O$). A slight initial precipitate redissolved, but when the solution cooled an orange powder separated and was filtered off and washed with water and ether, m.p. 184-186°(d.) (Found: C, 51.23; H, 3.37; Cl, 11.75. $C_{72}H_{62}As_4Cl_6O_4Pt$ requires: C, 50.91; H, 3.68; Cl, 12.52%).

(8) Methylenebis(diphenylarsine oxide).

Cookson and Mann obtained this diarsine dioxide from the monoxide³⁷. Since that compound was not available the dioxide was prepared by direct oxidation of the diarsine. The diarsine

itself was first synthesised by the reaction between methylene chloride and sodiodiphenylarsine in liquid ammonia:



Triphenylarsine (6.12g, 0.02mole) was added in small lots to a vigorously stirred solution of sodium (1g > 0.04mole) in liquid ammonia (200ml), and the solution became dark red. A solution of methylene chloride (2g > 0.02 mole) was then added and the red colour disappeared. After a short interval water (50ml) was added cautiously and the ammonia was allowed to evaporate off. From the remaining aqueous slurry the solid material was filtered off, washed with methanol, and crystallised from ethanol to give white needles of $(\text{Ph}_2\text{As})_2\text{CH}_2$, m.p. 96-97°. Lit. value 96-97°³⁷). This method has been used to synthesise other diarsines and the corresponding phosphines¹²⁰, but does not appear to have been used to obtain this one.

The diarsine (.472g) was oxidised to the dioxide by refluxing it gently in ethanol (15ml) with aqueous hydrogen peroxide (5ml 20vol.). When the solvent was removed by freeze drying the solid residue fitted the description of the dioxide as a deliquescent glass³⁷, and addition of acids to an aqueous solution of this substance yielded products as described by Cookson and Mann³⁷ (v. p. 111).

PART IV(1) Triphenylbismuth dichloride.

Chlorine was bubbled through a solution of triphenylbismuth in ether until sudden crystallisation took place. The greenish ether was decanted and the crystals were washed with ether and dried on filter paper, m.p. 125-128°. Recrystallisation from ethanol yielded beautiful white needles, m.p. 144-148°. (Found: C, 42.26; H, 3.04; Cl, 13.81. Calc. for $C_{18}H_{15}BiCl_2$: C, 42.30; H, 2.96; Cl, 13.87%).

(2) Triphenylbismuth dibromide.

Dropwise addition of a solution of bromine in ether to a solution of triphenylbismuth in the same solvent precipitated a pale yellow powder. Recrystallisation from ethanol yielded tiny, very pale yellow needles, m.p. 121-125°. (Found: C, 35.99; H, 2.48; Br, 26.50. Calc. for $C_{18}H_{15}BiBr_2$: C, 36.02; H, 2.52; Br, 26.63%).

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