616. *The Constitution of Complex Metallic Salts. Part XIV. The Action of Trialkyl-phosphines and -arsines on the Tetrahalides of Tin and Uranium.*

By JOHN A. C. ALLISON and FREDERICK G. MANN.

Trialkyl-phosphines and -arsines combine with stannic chloride and bromide to give covalent compounds of type $[(R_3P)_2SnCl_4]$ and $[(R_3P)_2SnBr_4]$: the corresponding tetra-iodo-analogues could not be isolated as stable compounds. The structure of " bridged " derivatives of composition $[(R_3P)_2SnCl_4,HgCl_2]$ and $[(R_3P)_2PdCl_2,SnCl_4]$ which have been isolated is discussed.

Trialkylphosphines combine with uranium tetrachloride and tetrabromide to give similar covalent derivatives $[(R_3P)_2UCl_4]$ and $[(R_3P)_2UBr_4]$, but no indication of the formation of analogous trialkylarsine derivatives was obtained. The salt, tris-2 : 2'-dipyridyluranium hexathiocyanate, $[dpy_3U](SCN)_6$, is described.

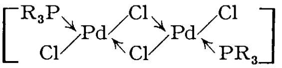
THE structure and properties of the covalent compounds which the tertiary aliphatic phosphines and arsines form with the halides (and other salts) of several heavy metals have already been investigated (cf. Mann *et al.*, *J.*, 1935, 1549; 1936, 873, 1503; 1937, 1828; 1938, 702, 1949, 2086; 1939, 1622; 1940, 1209, 1230, 1235). The main types into which these compounds fall can be briefly summarised. Of the univalent metals, cuprous and argentous bromide and iodide combine with the phosphines and arsines to give four-fold molecules of type (I), the highly symmetrical structure of which has been fully elucidated by *X*-ray analysis. Aurous halides, however, give simple linear molecules of type (II).

$[(R_3P)CuI]_4$ (I.)

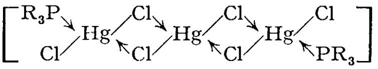
$[R_3P\rightarrow AuCl]$ (II.)

$[(R_3P)_2PdCl_2]$ (III*a*.)

$[(R_3P)_2HgCl_2]$ (III*b*.)



(IV.)



(V.)

$[(R_3P)_3(CdBr_2)_2]$ (VI.)

$[R_3P\rightarrow AuBr_3]$. (VII.)

Of the bivalent metals, palladous halides give simple compounds of type (III*a*), in which the molecule is planar, and the phosphine (or arsine) molecules are almost certainly in the *trans*-positions to one another. Cadmium and mercuric halides give derivatives similar in type (III*b*), but since the central metallic atom has the tetrahedral configuration, no question of geometric isomerism arises.

When, however, these palladium compounds of type (III*a*) are treated with a second equivalent of palladous halide, the " bridged " compounds of formula $[(R_3P)_2(PdCl_2)_2]$ and of type (IV) are readily obtained: these compounds exist in only one crystalline form, which has the structure shown in (IV), *i.e.*, the planar molecule has a centre of symmetry with the phosphine (or arsine) units therefore in the *trans*-positions to one another. Cadmium and mercuric halides give similar " bridged " compounds $[(R_3P)_2(HgCl_2)_2]$ of type (IV) which also have a centre of symmetry; since, however, the metals have the tetrahedral configuration, it follows that if the central bridged $HgCl_2Hg$ ring is in the plane of the paper, one phosphine (or arsine) unit must be above, and the other below, this plane. Cadmium and mercury differ from palladium, however, in that they allow this process of bridging to be continued by the insertion of further metallic halide units, and crystalline compounds of type $[(R_3P)_2(HgBr_2)_3]$ (V) and of type $[(R_3P)_2(HgBr_2)_4]$ are known. The tetrahedral configuration now entails the disappearance of the centre of symmetry in the tri-mercuric compound (V) and its reappearance in the tetra-mercuric derivative. Cadmium and mercury differ also from palladium in forming well-defined derivatives of type $[(R_3P)_3(HgI_2)_2]$ (VI), the structure of which is unknown.

Of the tervalent metals, auric halides form highly crystalline derivatives of type (VII). A large number of these compounds containing mixed halogen groups have been prepared (Mann and Purdie, *J.*, 1940, 1235), and the auric atom has been shown to have the tetrahedral configuration (Perutz and Weiss, *J.*, 1946, 438).

The great majority of these compounds, by virtue of their covalent character, have sharp m. p.s and are soluble in various organic solvents, in which their molecular weights can be determined, and from which they can frequently be recrystallised. The comparative stability of the phosphine and arsine derivatives varies considerably with the type of compound: for example, the phosphine members of type (II) and (III*a*) can often be distilled unchanged in a vacuum, whereas the arsine analogues decompose under these conditions; on the other hand, the arsine derivatives of type (I) are notably more stable than the phosphine members.

In view of these properties, it was of interest to extend this work to metals which give well-defined 4-covalent tetrahalides : our main work has been performed on the stannic halides, and then extended to the uranium tetrahalides. It was of particular interest to determine whether the latter metal would give covalent phosphine or arsine derivatives which might be soluble in organic solvents and even volatile without decomposition.

We found that the trialkylphosphines in alcoholic solution readily combined with stannic chloride to give the crystalline *tetrachlorobis(trialkylphosphine)tin* (VIII) and with stannic bromide to give the analogous *bromo*-compound (IX). The corresponding tetraiodo-compounds

$[(R_3P)_2SnCl_4]$	$[(R_3P)_2SnBr_4]$	$(R_3PH)_2[SnCl_6]$	$(R_3PH)_2[SnBr_6]$	$[(R_3As)_2SnCl_4]$
(VIII.)	(IX.)	(X.)	(XI.)	(XII.)

were too unstable for satisfactory isolation. If, however, the trialkylphosphines were added to stannic chloride dissolved in hydrochloric acid, the crystalline salt, *bis(trialkylphosphonium) chlorostannate* (X), was obtained, and the analogous *bromostannate* (XI) was similarly prepared. The formation of covalent compounds of type (VIII) was not limited to phosphines, for the similar use of trialkylarsines furnished the crystalline *tetrachlorobis(trialkylarsine)tin* (XII).

The compounds prepared are shown in the following table, in which Pr represents the *n*-propyl group.

Type.	Compound.	M. p.	Type.	Compound.	M. p.	Type.	Compound.	M. p.
(VIII)	$[(Et_3P)_2SnCl_4]$	145—150°	(X)	$(Et_3PH)_2[SnCl_6]$	232—234°	(XII)	$[(Et_3As)_2SnCl_4]$	155—159°
	$[(Pr_3P)_2SnCl_4]$	157—159		$(Pr_3PH)_2[SnCl_6]$	203—205		$[(Et_3As)_2SnBr_4]$	126—132
(IX)	$[(Et_3P)_2SnBr_4]$	170—171	(XI)	$(Et_3PH)_2[SnBr_6]$	186—188			
	$[(Pr_3P)_2SnBr_4]$	103—106		$(Pr_3PH)_2[SnBr_6]$	156—160			

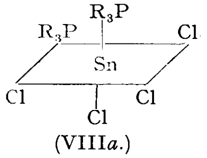
The iodo-compounds corresponding to (VIII) and (IX) underwent such rapid decomposition when they were removed from the mother-liquor that they were not further investigated.

The above chloro- and bromo-compounds present a number of points of interest which will be discussed under separate headings.

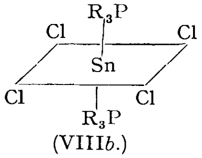
Stability.—In the above series of compounds, the chloro-derivatives were uniformly more stable than the corresponding bromo-derivatives. Even so, the covalently bound phosphine molecules in compounds of type (VIII) could be detached from the tin atoms to form the phosphonium ions in compounds of type (X), whilst in the bromo-derivatives (IX) and (XI) the conversion could be induced in either direction. For example, if hydrogen chloride was passed into a cold alcoholic suspension of the compound $[(Pr_3P)_2SnCl_4]$, a clear solution was soon obtained, and addition of ether then precipitated the salt $(Pr_3PH)_2[SnCl_6]$: the reverse process however was not achieved. Similarly the compound $[(Pr_3P)_2SnBr_4]$, when warmed with hydrobromic acid containing a small proportion of alcohol, was converted into the salt $(Pr_3PH)_2[SnBr_6]$, but the latter in turn when boiled in alcoholic solution readily lost hydrogen bromide and deposited the original covalent compound $[(Pr_3P)_2SnBr_4]$.

All these stannic compounds underwent decomposition in boiling aqueous alcohol.

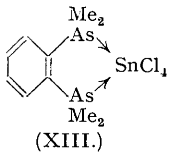
Configuration.—It will be obvious that covalent compounds of type (VIII), (IX), and (XII) could all theoretically exist as two distinct geometric isomerides : for example, a compound of



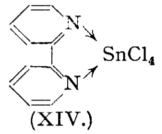
(VIII*a*.)



(VIII*b*.)



(XIII.)

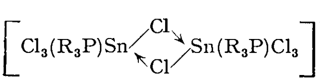


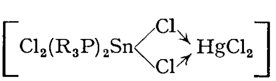
(XIV.)

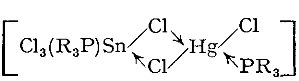
type (VIII) could exist in the *cis*(or 1 : 2)-bisphosphine form (VIII*a*) and in the *trans*(or 1 : 6)-bisphosphine form (VIII*b*). All the compounds of the above three types that we have prepared have, however, been well-defined crystalline compounds which were apparently homogeneous, and no indication of the existence of geometric isomerism could be obtained. It would appear therefore that one isomeride has a considerably greater stability than the other, and it is probable that the more stable form is the form with the greater symmetry, *i.e.*, the *trans*-form (VIII*b*). Evidence on this point (which is at present lacking) could be obtained either by an *X*-ray investigation of the solid compounds or by a measurement of their dipole moments; the latter is difficult owing to their low solubility in cold non-polar solvents.

It is clear, however, that *cis*-compounds of the general type (VIII*a*) can exist if the nature of the co-ordinating molecule necessitates this configuration. Chatt and Mann (*J.*, **1939**, 1622) have found that *o*-phenylenebis(dimethylarsine), $C_6H_4(AsMe_2)_2$, has a very strongly chelating action on metals, and we find that it readily combines with stannic chloride to give *tetrachloro-*[o*-phenylenebis(dimethylarsine)*]*tin* (XIII). Similarly, 2 : 2′-dipyridyl combines with stannic chloride to give *tetrachloro-*(2 : 2′*-dipyridyl*)*tin* (XIV), and the *tetrabromo-* and *tetra-iodo*-analogues of (XIV) have also been prepared. In all these derivatives, the co-ordinating group must necessarily occupy the *cis*(or 1 : 2)-positions about the central tin atom.

Bridged Compounds.—It has been shown by Mann and Purdie (*J.*, **1936**, 873) that alkylphosphine compounds of type $[(R_3P)_2PdCl_2]$ when heated in a vacuum distil unchanged, whereas the analogous arsine compounds $[(R_3As)_2PdCl_2]$ when similarly treated lose half their arsine content with the formation of the bridged derivatives $[(R_3As)_2(PdCl_2)_2]$. The bridged derivatives in both series can be readily obtained, however, by boiling the unbridged compounds in alcoholic solution with ammonium palladochloride. We have investigated the application of both these methods to the preparation of a bridged tin compound of type (XV), in which two 6-covalent octahedra are bridged through two chlorine atoms, but without success. The compound $[(Pr_3P)_2SnCl_4]$ when heated either at atmospheric pressure or in a vacuum melts and at higher temperatures decomposes, but no indication of volatilisation of the unchanged compound, or of the formation of a bridged derivative of type (XV) could be obtained. Alternatively, the compound $[(Pr_3P)_2SnCl_4]$ was heated with one equivalent of stannic chloride under a variety of conditions, but the required bridged derivative could not be prepared.

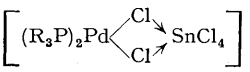

(XV.)

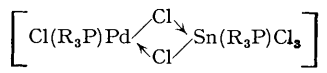

(XVI*a*.)

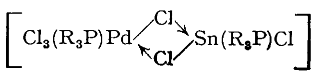

(XVI*b*.)

When, however, the compound $[(Pr_3P)_2SnCl_4]$ was boiled with one equivalent of mercuric chloride in alcoholic solution, the crystalline *tetrachlorobis(tripropylphosphine)-μ-dichlorotin-mercury*, m. p. 206—207°, was readily obtained. This was a stable compound which could be recrystallised unchanged from alcohol. The *triethyl* analogue was similarly prepared. It is impossible to say whether these compounds have the structure (XVI*a*), in which the tin is still co-ordinated to both phosphine molecules, or the structure (XVI*b*), in which both metallic atoms share the phosphine molecules. It must be remembered that when a compound of type $[(R_3P)_2PdCl_2]$ reacts with ammonium palladochloride to give the bridged compound $[(R_3P)_2(PdCl_2)_2]$, one phosphine molecule certainly migrates to the second palladium atom, since the latter compound has the bridged *trans*-symmetric structure (IV), and the isomeric $[(R_3P)_2PdCl_2PdCl_2]$ compounds have never been prepared: the same applies to the corresponding mercury compounds. Furthermore, the labile nature of phosphine molecules when co-ordinated to tin is shown by the fact that the compound $[(Pr_3P)_2SnBr_4]$ when boiled with mercuric bromide gave the bridged compound $[(Pr_3P)_2(HgBr_2)_2]$; *i.e.*, all the phosphine has been transferred to the mercury. Similarly, the compounds $[(Pr_3P)_2SnCl_4]$ and $[(Pr_3P)_2SnBr_4]$ when heated in alcoholic solution with potassium palladobromide both gave *dibromobis(tripropylphosphine)palladium*, $[(Pr_3P)_2PdBr_2]$, all the phosphine having again been transferred to the second metal. In view of these facts it is more probable that our new bridged tin–mercury compounds have the structure (XVI*b*) than (XVI*a*). In either case they represent rare examples of a 6-co-ordination octahedral complex being bridged to a 4-co-ordination tetrahedral complex. It should be noted that the formation of these bridged complexes provides no evidence for the configuration of the parent compounds $[(R_3P)_2SnCl_4]$, since theoretically either the *cis-* or the *trans*-form of the latter could give rise to the bridging structure.

Although the formation of a tin–palladium bridged compound by the above methods failed, we found that when equimolecular quantities of dichlorobis(tri-*n*-propylphosphine)palladium and stannic chloride were boiled together in carbon tetrachloride solution, combination readily occurred to give *tetrachlorobis(tripropylphosphine)-μ-dichloropalladium-tin* as pale yellow crystals considerably less soluble than the parent compounds. Here again it is impossible to say whether simple union has occurred to give the compound (XVII*a*), or whether the phosphine molecules have been distributed between the two metals to give the compound (XVII*b*). [The third possibility, namely, that in addition two of the chlorine atoms have been transferred from the tin to the palladium atoms to give a palladic–stannous compound (XVII*c*) can be dismissed, because a palladic compound of this type would almost certainly be more deeply coloured].


(XVII*a*.)


(XVII*b*.)


(XVII*c*.)

The new compound is therefore an example of a 6-co-ordination octahedral complex bridged to a 4-co-ordination planar complex.

Uranium tetrachloride and tetrabromide differ from their stannic analogues in one important respect, namely, that although they form similar covalent complex compounds with aliphatic tertiary phosphines, they do not apparently combine with tertiary arsines. We find that uranium tetrachloride combines with triethyl- and tri-*n*-propyl-phosphines to give the corresponding *tetrachlorobis(trialkylphosphine)uranium* compounds $[(R_3P)_2UCl_4]$ as pale yellow needles, and uranium tetrabromide gives the analogous *tetrabromo*-compounds $[(R_3P)_2UBr_4]$ as darker yellow crystals. The m. p.s of these compounds fall on passing from the ethyl to the propyl analogues, and also on passing from the tetrachloro-compounds to their tetrabromo-analogues :

$[(Et_3P)_2UCl_4]$, m. p. 253—256°
$[(Pr_3P)_2UCl_4]$, ,, 208—210°

$[(Et_3P)_2UBr_4]$, m. p. 230—232°
$[(Pr_3P)_2UBr_4]$, ,, 182—185°

These four crystalline uranium compounds appear to be stable indefinitely at room temperature. They can be recrystallised rapidly from methyl, ethyl, and *n*-propyl alcohols, but longer boiling with these solvents, or even prolonged contact with the cold solvents, causes decomposition with evolution of free phosphine. All attempts to volatilise these compounds by heating in a vacuum, or to induce them by these means to lose half their phosphine content and so form a bridged compound, have failed.

Attempts to make the tetraiodo-derivatives, $[(R_3P)_2UI_4]$, also failed, as in the case of the analogous stannic compounds.

We have obtained no decisive indication of complex formation between uranium tetrachloride or tetrabromide and triethyl-, tri-*n*-propyl-, and tri-*n*-butyl-arsine. Furthermore, *o*-phenylenebis(dimethylarsine), in spite of its vigorous chelating properties, and ethylenebis(diphenylarsine) appeared also to be inert towards these uranium tetrahalides.

In view of these results, we have investigated briefly the action of 2 : 2′-dipyridyl on uranium tetrachloride, but no definite stable product has been isolated. When, however, the alcoholic mother-liquor containing these two compounds was treated with potassium thiocyanate, a small yield of the yellow crystalline *tris-2 : 2′-dipyridyluranium hexathiocyanate*, $[dpy_3U](SCN)_6$, was obtained, presumably owing to atmospheric oxidation.

EXPERIMENTAL.

The triethylphosphine used in the following experiments was freshly prepared by thermal decomposition of the complex derivative $[Et_3P,AgI]_4$ (cf. Mann and Purdie, *J.*, 1938, 708).

Phosphine Derivatives of Stannic Halides.—Tetrachlorobis(triethylphosphine)tin (VIII; R = Et). A solution of stannic chloride (0·5 g.) in alcohol (10 c.c.) was added with cooling and stirring to one of triethylphosphine (0·5 g., 2·2 mols.) also in alcohol (10 c.c.). The white crystals of the above *compound* which rapidly separated were collected, washed with a small quantity of alcohol and dried; m. p. 145—150° (decomp.) (Found : C, 29·2; H, 6·5. $C_{12}H_{30}Cl_4P_2Sn$ requires C, 29·0; H, 6·1%). This compound is almost insoluble in ether and petrol. It is moderately soluble in cold benzene, chloroform, ethyl carbonate, and carbon tetrachloride, but on boiling these solutions a smell of phosphine develops and the solution becomes turbid, finally depositing an insoluble white precipitate. In methyl and ethyl alcohol and in acetone it is slightly soluble in the cold and readily soluble in the hot solvent : hot concentrated solutions rapidly became turbid as above, and recrystallisation was not attempted.

Bis(triethylphosphonium) chlorostannate (X; R = Et). When triethylphosphine (0·5 g., 2·2 mols.) was added to stannic chloride (0·5 g.) dissolved in concentrated hydrochloric acid (1 c.c.) diluted with water (1 c.c.), the colourless, slightly hygroscopic crystals of the above *salt* rapidly separated. After one recrystallisation from alcohol they had m. p. 232—234° (decomp.) (Found : C, 25·7; H, 6·1. $C_{12}H_{32}Cl_6P_2Sn$ requires C, 25·3; H, 5·7%). The solubility of this salt in organic solvents is similar to that of the previous compound, except that it is readily soluble in cold methyl alcohol and acetone: it can be recrystallised without decomposition from ethyl or *n*-propyl alcohol.

When triethylphosphine (0·5 g.) was added to a solution of stannic chloride (2 g.) in alcohol (10 c.c.) at room temperature, the above salt crystallised, indicating that partial hydrolysis of the stannic chloride had occurred in these circumstances.

*Tetrachlorobis(tri-*n*-propylphosphine)tin* (VIII; R = Pr). Prepared by the addition of stannic chloride (0·5 g.) to the phosphine (0·7 g., 2·2 mols.), each dissolved in chilled alcohol (20 c.c.), this *compound* separated as colourless crystals, m. p. 157—159° (Found : C, 36·9; H, 7·3. $C_{18}H_{42}Cl_4P_2Sn$ requires C, 37·2; H, 7·3%). It is more stable than its ethyl homologue and its solubility in certain solvents is markedly different: for example, it is very soluble in cold chloroform to give a solution which is stable when hot; it recrystallises readily from benzene, ethyl carbonate, and acetone, but is sparingly soluble in hot petrol and carbon tetrachloride to give a faintly turbid solution, and is almost insoluble in boiling methyl and ethyl alcohol, and ether.

When hydrogen chloride was passed into an alcoholic suspension of this compound, a clear solution was readily obtained, and subsequent dilution with ether precipitated the following compound.

*Bis(tri-*n*-propylphosphonium) chlorostannate* (X; R = Pr). Tri-*n*-propylphosphine (0·7 g.) was added to a solution of stannic chloride (0·5 g., 1 mol.) in concentrated hydrochloric acid (1 c.c.) diluted with water (1 c.c.). After ½ hour's shaking, the precipitate of the above *salt* was collected and twice recrystallised from alcohol; the slightly hygroscopic, colourless crystals had m. p. 203—205° (slight efferv.) (Found: C, 32·9; H, 6·7. $C_{18}H_{44}Cl_6P_2Sn$ requires C, 33·05; H, 6·8%). It is readily soluble in cold concentrated hydrochloric acid and in methyl alcohol, but can be recrystallised from ethyl, propyl, and butyl alcohols: it is insoluble in the other common organic solvents and in water.

Tetrabromobis(triethylphosphine)tin (IX; R = Et). When the phosphine (0·6 g., 2·5 mols.) was added to a solution of stannic bromide (1 g.) in chilled alcohol (20 c.c.), this *compound* separated as cream-coloured crystals, m. p. 170—171° (decomp.) (Found: C, 20·75; H, 4·5. $C_{12}H_{30}Br_4P_2Sn$ requires C, 21·4; H, 4·5%). It is readily soluble in cold methyl alcohol, but can be recrystallised from ethyl alcohol, benzene, or ethyl carbonate: these recrystallisations have to be performed rapidly and with care, however, otherwise the compound may separate as an oil which subsequently solidifies, or it may undergo partial dissocation, liberating free phosphine.

When this compound was warmed with concentrated hydrobromic acid containing ethyl alcohol, it was readily converted into the following compound.

Bis(triethylphosphonium) bromostannate (XI; R = Et). Triethylphosphine (0·6 g., 2·5 mol.) was added to a solution of stannic bromide (1 g.) in hydrobromic acid (4 c.c.) of constant b. p. The pale yellow crystals of the above *salt*, when collected, washed with ether, and dried, had m. p. 186—188° (Found: C, 17·5; H, 4·0. $C_{12}H_{32}Br_6P_2Sn$ requires C, 17·2; H, 3·9%). The salt could be recrystallised from hydrobromic acid or from alcohol, but analysis indicated that this process caused progressive conversion into the previous compound.

*Tetrabromobis(tri-*n*-propylphosphine)tin* (IX; R = Pr). This compound was prepared by interaction of the phosphine (0·8 g., 2·2 mols.) and stannic bromide (1 g.), each dissolved in alcohol (40 c.c.). It was very slightly soluble in boiling methyl and ethyl alcohol, ether, carbon tetrachloride, and petrol but soluble in hot benzene, chloroform, and ethyl carbonate, but these solvents all gave cloudy solutions which deposited a yellow oil or viscous syrup on cooling. The *compound* was ultimately recrystallised from hot benzene containing a small proportion of the free phosphine and obtained as cream-coloured crystals, m. p. 103—106° (decomp.) (Found: C, 28·2; H, 5·4. $C_{18}H_{42}Br_4P_2Sn$ requires C, 28·5; H, 5·6%).

*Bis(tri-*n*-propylphosphonium) bromostannate* (XI; R = Pr). This *compound*, prepared as the ethyl analogue, formed pale yellow, slightly hygroscopic crystals, m. p. 156—160° (decomp.), and was recrystallised from alcohol before analysis (Found: C, 23·6; H, 4·6. $C_{18}H_{44}Br_6P_2Sn$ requires C, 23·5; H, 4·8%). Each of the above two compounds could be converted into the other by the methods described for the corresponding ethyl analogues. Both the above chlorostannates (X) are very soluble in cold pyridine: on boiling the solution a white precipitate separates after one minute and the smell of phosphine becomes apparent. The tetrachlorobisphosphinetin compounds (VIII) are moderately soluble in cold pyridine, but are similarly decomposed immediately on boiling. All the bromo-compounds (IX) and (XI) are also decomposed by pyridine but although phosphine is liberated no precipitate separates.

It is noteworthy that tri-*n*-propylphosphine gave no similar compounds with lead tetrachloride, the latter instead undergoing rapid reduction to lead dichloride.

*Dichlorobis(tri-*n*-propylphosphine)-μ-dichlorodimercury.* This compound, prepared for direct comparison with the following compound, was readily obtained by the addition of the phosphine (0·5 g.) to a solution of mercuric chloride (0·8 g., 1 mol.) in alcohol (10 c.c.), the mixture being then boiled and cooled. The colourless *dimercury* compound which separated was readily recrystallised from alcohol and had m. p. 136—137° (Found: C, 25·1; H, 4·8. $C_{18}H_{42}Cl_4P_2Hg_2$ requires C, 25·0; H, 4·9%).

*Tetrachlorobis(tri-*n*-propylphosphine)-μ-dichlorotin-mercury* (XVI, *a–b*). When tetrachlorobis(tri-*n*-propylphosphine)tin (VIII; R = Pr) (1·41 g.) was added to a solution of mercuric chloride (0·66 g., 1 mol.) in alcohol (10 c.c.), and the mixture boiled, a clear solution was obtained, which however when stirred deposited colourless crystals of the *tin-mercury* compound whilst still boiling. This compound could be recrystallised from methyl, ethyl and propyl alcohols, but separated very slowly from the cold solution; it had m. p. 206—207° (Found: C, 25·3; H, 4·8. $C_{18}H_{42}Cl_6P_2HgSn$ requires C, 25·4; H, 5·0%). This compound has a carbon and hydrogen content almost identical with that of the previous compound: its identity was confirmed by (*a*) qualitative tests for mercury and tin, and the facts that (*b*) a mixture with the previous compound had m. p. 195—205°, (*c*) the rates of crystallisation of the two compounds from alcohol were markedly different.

Dichlorobis(triethylphosphine)-μ-dichlorodimercury. This compound, prepared in the usual way, recrystallised readily from alcohol and had m. p. 163—164° (Found: C, 18·4; H, 4·0. $C_{12}H_{30}Cl_4P_2Hg_2$ requires C, 18·5; H, 3·9%).

Tetrachlorobis(triethylphosphine)-μ-dichlorotin-mercury (XVI, *a–b*). Prepared as the propyl analogue and recrystallised by adding petrol to its alcoholic solution, this *compound* had m. p. 210—211° (decomp.) depressed to 198° by admixture with the previous compound (Found: C, 19·3; H, 3·9. $C_{12}H_{30}Cl_6P_2HgSn$ requires C, 18·8; H, 3·9%). Its identity was further confirmed by tests for the presence of the two metals.

*Dibromobis(tri-*n*-propylphosphine)palladium.* This *compound*, prepared by the addition of the phosphine (0·6 g., 2·2 mols.) to a solution of potassium palladobromide (0·8 g.) in aqueous alcohol (20 c.c.) and subsequently recrystallised from methyl alcohol, formed orange-yellow needles, m. p. 87—88° (Found: C, 36·5; H, 7·3. $C_{18}H_{42}Br_2P_2Pd$ requires C, 36·8; H, 7·2%).

When a mixture of tetrachlorobis(tri-*n*-propylphosphine)tin (0·6 g.), potassium palladobromide (0·5 g., 1 mol.), and alcohol (100 c.c.) was boiled under reflux until a clear solution was obtained, and then cooled and evaporated in a desiccator, yellow crystals separated, leaving ultimately a white residue. The yellow crystals, picked out by hand, had m. p. 86·5—87·5°, alone and mixed with the previous compound. The reaction is therefore of the type :

$$[(Pr_3P)_2SnCl_4] + K_2PdBr_4 = [(Pr_3P)_2PdBr_2] + K_2[SnCl_4Br_2]$$

The same palladium compound was obtained when the tetrabromo-tin compound was employed in place of the tetrachloro-compound.

*Tetrachlorobis(tri-*n*-propylphosphine)-µ-dichloropalladium-tin* (XVII, *a–b*). Filtered solutions of dichlorobis(tripropylphosphine)palladium (0·99 g.) and stannic chloride (0·5 g., 1 mol.), each in carbon tetrachloride (10 c.c.), were mixed and boiled under reflux for 4 hours. A red oil separated after 1 hour and became slowly converted into minute pale yellow crystals of the above *compound*, m. p. 172—173° (slight preliminary softening) (Found : C, 28·65; H, 5·6. $C_{18}H_{42}Cl_6P_2PdSn$ requires C, 28·5; H, 5·6%). It is readily soluble in methyl and ethyl alcohols, chloroform, and acetone, and moderately soluble in ethyl carbonate and dioxan : contact with these solvents makes the compound sticky, however, and some dissociation probably occurs.

No stable compound could be obtained by the union of tetrabromobis(tri-*n*-propylphosphine)tin and mercuric bromide or of tetrachlorobis(tri-*n*-propylphosphine)tin and cadmium chloride.

Arsine Derivatives of Stannic Halides.—Tetrachlorobis(triethylarsine)tin. This *compound*, prepared as its phosphine analogue, separated as colourless crystals, m. p. 155—159° (decomp.) (Found : C, 24·4; H, 5·2. $C_{12}H_{30}Cl_4As_2Sn$ requires C, 24·7; H, 5·2%). In solution in the lower alcohols it underwent partial dissociation, and recrystallisation was not attempted.

Tetrabromobis(triethylarsine)tin. This *compound* formed cream-coloured crystals, m. p. 126—132° (decomp.) (Found : C, 19·0; H, 4·2. $C_{12}H_{30}Br_4As_2Sn$ requires C, 18·9; H, 4·0%).

*Tetrachloro-[*o*-phenylenebis(dimethylarsine)]tin* (XIII). When a solution of stannic chloride (1 g.) in alcohol (20 c.c.) was added to one of the diarsine (1 g., 1·1 mols.) in alcohol (10 c.c.), this *compound* separated as white crystals, m. p. 214—224° (with preliminary softening and decomp.) (Found : C, 22·2; H, 3·1. $C_{10}H_{16}Cl_4As_2Sn$ requires C 22·0; H, 3·0%). It is readily soluble in cold alcohol (apparently with partial dissociation), and insoluble in non-polar solvents. The use of an excess of the diarsine did not cause further co-ordination with the metal.

2 : 2'-*Dipyridyl Derivatives of Tin.—Tetrachloro-*2 : 2'-*dipyridyltin* (XIV). A solution of dipyridyl (0·6 g.) in alcohol (20 c.c.) was added to one of stannic chloride (1 g., 1 mol.) also in alcohol (20 c.c.). When the mixture was set aside for 2 hours with occasional stirring, the initial sticky white precipitate of the above *compound* was converted into white crystals, m. p. >400° (Found : C, 28·9; H, 2·0; N, 6·8. $C_{10}H_8N_2Cl_4Sn$ requires C, 28·8; H, 1·9; N, 6·7%). It is insoluble in most organic liquids, but can be recrystallised from glycol monomethyl ether : the crystals become pink on prolonged exposure to the solvent, but remain white if rapidly filtered off and dried.

The *tetrabromo*-analogue, similarly prepared, formed pale brown needles, m. p. >400°, which were too insoluble for purification (Found : C, 21·0; H, 1·6; N, 5·0. $C_{10}H_8N_2Br_4Sn$ requires C, 20·2; H, 1·4; N, 4·7%).

The *tetraiodo*-analogue, similarly prepared, formed a brick-red powder or dark red crystals, m. p. >400° (Found : C, 15·5; H, 1·5; N, 3·6. $C_{10}H_8N_2I_4Sn$ requires C, 15·4; H, 1·0; N, 3·6%). It is insoluble in all the usual organic liquids.

Phosphine Derivatives of Uranium Tetrahalides.—Tetrachlorobis(triethylphosphine)uranium. Triethylphosphine (1·2 g., 2·5 mols.) was added to a solution of uranium tetrachloride (1·5 g.) in cold alcohol (20 c.c.), and the mixture was boiled for 10 minutes and cooled. The yellowish-green precipitate, when collected and twice recrystallised from alcohol, gave the above *compound* as pale yellow hygroscopic needles, m. p. 253—256° (decomp. to brown liquid) (Found : C, 23·0; H, 5·1. $C_{12}H_{30}Cl_4P_2U$ requires C, 23·4; H, 4·9%). The compound is soluble in methyl, ethyl, and propyl alcohols, but the solution undergoes slow decomposition with liberation of phosphine. The compound is insoluble in benzene, ethyl carbonate, ether, chloroform, carbon tetrachloride, and petrol.

*Tetrachlorobis(tri-*n*-propylphosphine)uranium.* This *compound*, when similarly prepared and recrystallised, formed pale yellow hygroscopic needles, m. p. 208—210° (decomp. to green liquid) (Found : C, 31·0; H, 6·0. $C_{18}H_{42}Cl_4P_2U$ requires C, 30·9; H, 6·0%). Its solubility in various solvents was closely similar to that of the previous compound.

Tetrabromobis(triethylphosphine)uranium. This *compound* was similarly prepared, and was purified first by recrystallisation from alcohol and then by precipitation from its solution in *n*-propyl alcohol by the addition of petrol. It formed hygroscopic yellow needles, m. p. 230—232° (decomp. to brown liquid) (Found : C, 17·8; H, 4·1. $C_{12}H_{30}Br_4P_2U$ requires C, 18·1; H, 3·8%).

*Tetrabromobis(tri-*n*-propylphosphine)uranium.* This *compound* was prepared and purified similarly to the previous compound, and obtained as yellow hygroscopic needles, m. p. 182—185° (decomp. to greenish-brown liquid) (Found : C, 24·3; H, 4·6. $C_{18}H_{42}Br_4P_2U$ requires C, 24·6; H, 4·8%).

No similar tetraiodo-compounds could be obtained either by treating the tetrachloro-compounds in alcoholic solution with sodium iodide, or by treating uranium tetrachloride in alcoholic solution with a considerable excess of sodium iodide and then with the tertiary phosphine.

*Tris-*2 : 2'-*dipyridyluranium hexathiocyanate.* A filtered solution of uranium tetrachloride (0·5 g.) in alcohol (20 c.c.) was added to one of dipyridyl (0·7 g., 3·3 mols.) also in alcohol (20 c.c.), and the mixture was boiled to coagulate the buff-coloured precipitate. The latter, when filtered from the cold mixture, became black; it was extracted with boiling water (3 c.c.), and the hot filtered extract treated with saturated aqueous potassium thiocyanate (*ca.* 0·3 c.c.). On cooling, a mixture of yellow crystals and a red oil separated : this mixture, when collected and recrystallised from a hot concentrated solution containing an excess of potassium thiocyanate, gave the above *hexathiocyanate* in low yield as very hygroscopic compact yellow crystals or as hexagonal plates (Found : C, 41·1; H, 2·3; N, 15·4, 15·2. $C_{36}H_{24}N_{12}S_6U$ requires C, 41·0; H, 2·3; N, 15·9%). When, however, the mixture was recrystallised from cooler and more dilute solutions containing a smaller excess of potassium thiocyanate, radial clusters of fine non-hygroscopic yellow needles, m. p. 178—183° (preliminary softening), were obtained; these were apparently the *monohydrate* of the above hexathiocyanate (Found: C, 40·7; H, 2·7; N, 15·3, 15·4. $C_{36}H_{24}N_{12}S_6U,H_2O$ requires C, 40·3; H, 2·4; N, 15·65%). The crystals of the anhydrous salt slowly become opaque on exposure to the air, apparently with the formation of the monohydrate. The salt is very soluble in methyl and ethyl alcohols, but insoluble in the usual non-polar organic liquids.

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