138. *Tetra-aryl-phosphonium, -arsonium and -stibonium Salts. Part II. The Mechanism of their Formation by the Aluminium Chloride Reaction.*

By Donald R. Lyon and Frederick G. Mann.

The tetraphenylarsonium ion can be formed by the following reactions : (*a*) Triphenylarsine with aluminium chloride gives an addition product $[Ph_3As\rightarrow AlCl_3]$ which is thermally stable to *ca.* 250°, but reacts readily with bromobenzene at *ca.* 200° to give the above ion. (*b*) Diphenylchloroarsine gives a product $[Ph_2ClAs\rightarrow AlCl_3]$ which conversely undergoes thermal decomposition when heated alone at 200° to give the arsonium ion and arsenic, but does not yield the ion with boiling bromobenzene. (*c*) Phenyldichloroarsine gives a product $[(PhCl_2As)_3AlCl_3]$ in which the arsine on heating undergoes disproportionation to $AsCl_3$ and $AsPh_2Cl$, the latter then reacting as in (*b*). (*d*) A mixture of benzene and arsenic chloride in the presence of aluminium chloride gives phenyldichloroarsine, which then reacts as in (*c*).

Tetra-*o*-tolyl-phosphonium and -arsonium compounds could not be prepared : the isomeric *m*- and *p*-compounds were obtained without difficulty.

In Part I (J., 1940, 1192) Chatt and Mann showed that tetraphenylarsonium salts, $AsPh_4X$, were formed when aluminium chloride was heated with (*a*) triphenylarsine, (*b*) diphenylchloroarsine, (*c*) phenyldichloroarsine, (*d*) a mixture of benzene and arsenic trichloride : the yield of the arsonium salt in (*a*) was increased if the arsine was previously mixed with moderate, and decreased if mixed with excessive, quantities of bromobenzene. In the reaction (*b*), benzene and elementary arsenic were also detected as products. Tetraphenylphosphonium and -stibonium salts were similarly prepared by the interaction of aluminium chloride with triphenyl-phosphine and -stibine respectively, bromobenzene being present in each case.

This initial exploratory work was performed with stock "resublimed" aluminium chloride which had not been specially purified. The mechanism of the above reactions, which have now been studied in detail with reagents of known purity, will be considered in turn.

(a) *Triphenylarsine.* This arsine combines readily with pure aluminium chloride to give the crystalline addition product *trichlorotriphenylarsinealuminium*, $[Ph_3As\rightarrow AlCl_3]$, a compound of 4-covalent aluminium similar in type to the well-known compounds $[H_3N\rightarrow AlCl_3]$ and $[C_5H_5N\rightarrow AlCl_3]$ (cf. Klemm, Clausen, and Jacobi, *Z. anorg. Chem.*, 1931, **200**, 343, 367; Plotnikov and Valjasny, *J. Gen. Chem. Russ.*, 1931, **1**, 823). This addition product, although chemically very reactive, is thermally stable in an inert atmosphere and can be heated to *ca.* 250° without change, and therefore does not give the arsonium salt when heated alone below this temperature. Its chemical reactivity * is shown by two reactions: (i) When a current of air at room temperature is passed through a suspension of the addition product in benzene, bromobenzene, or tetralin, smooth oxidation to triphenylarsine oxide occurs; triphenylarsine alone is not oxidised in these circumstances. (ii) When a mixture of the addition product and bromobenzene (1 mol.) is heated at 200° for 2 hours, a ready reaction occurs with production of the tetraphenylarsonium salt, no by-products being detected. There is little doubt, therefore, that this reaction consists in the direct union of the reactants,

$$[Ph_3As\rightarrow AlCl_3] + PhBr = [Ph_4As][AlCl_3Br] \longrightarrow Ph_4AsI \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and that the complex salt so formed, when subsequently extracted with hot water and treated with potassium iodide, thus gives the arsonium iodide. That the bromobenzene is a reagent, and is not acting solely as a solvent or flux, is shown by the facts that (1) no elementary arsenic is liberated, although conversion of the tertiary arsine addition product alone into the arsonium salt would probably necessitate arsenic formation and (2) the use of other aryl halides gives mixed arsonium salts. For instance, in the presence of aluminium chloride, triphenylarsine reacted with *p*-bromotoluene, and diphenyl-*p*-tolylarsine with bromobenzene, to give in each case the triphenyl-*p*-tolylarsonium ion, which was isolated as the *iodide* and the *thiocyanate*; diphenyl-*p*-tolylarsine similarly reacted with *p*-bromotoluene to give ultimately *diphenyldi-*p*-tolylarsonium iodide*, and tri-*p*-tolylarsine reacted with bromobenzene to give *phenyltri-*p*-tolylarsonium iodide*. The formation of compounds of type $[Ph_4As][AlCl_3Br]$ in these reactions is not unexpected: these are closely similar to compounds of type $R[AlCl_4]$ which are now known beyond reasonable doubt to occur in the Friedel–Crafts reaction (Wohl and Wertyporoch, *Ber.*, 1931, **64**, 1357, 1369; Fairbrother, *Trans. Faraday Soc.*, **1941**, **37**, 763) and demonstrate the readiness of aluminium chloride to pass into a complex $[AlX_4]$ anion.

The initial ready formation of the addition compound $[Ph_3As\rightarrow AlCl_3]$ and the fact that the reactions described under (i) and (ii) above will occur with either this compound or an equimolecular mixture of the tertiary arsine and aluminium chloride, but not in the absence of the chloride, prove that this compound is the essential reactive intermediate in the tertiary arsine reactions.

When, however, the pure resublimed aluminium chloride was exposed to the air in a shallow layer for 15 minutes, and then mixed with triphenylarsine and heated in the absence of bromobenzene, benzene was evolved from 120°, and the product then contained much tetraphenylarsonium salt. This marked difference attending the use of slightly hydrolysed aluminium chloride is undoubtedly due to the latter evolving hydrogen chloride, which then attacks the triphenylarsine giving benzene and diphenylchloroarsine; the latter then reacts directly with aluminium chloride to give the tetraphenylarsonium salt as described below (see b).

$$Ph_3As + HCl = Ph_2AsCl + C_6H_6$$

It is noteworthy that, although Blicke and Monroe (*J. Amer. Chem. Soc.*, 1935, **57**, 720) have shown that triphenylarsine oxide treated with phenylmagnesium bromide gives the tetraphenylarsonium ion, the arsine oxide cannot be an intermediate in the reactions we have studied, since, when heated with aluminium chloride and bromobenzene under many varied conditions, it always gave ultimately after the usual extraction only triphenylarsine hydroxy-salts.

(b) *Diphenylchloroarsine.* The mechanism of the formation of the arsonium salts from this arsine is entirely different from that from the tertiary arsine. Diphenylchloroarsine similarly combines with pure aluminium chloride to give *trichlorodiphenylchloroarsinealuminium*, $[Ph_2ClAs\rightarrow AlCl_3]$, which we have isolated only as a viscous syrup. It is, however, very reactive, and even a few seconds' exposure to the air causes formation of a solid surface film. When the addition product is refluxed with bromobenzene no tetraphenylarsonium ion is formed. When, however, the addition product alone is heated to 200°, decomposition occurs readily with the formation of the arsonium ion and of much elementary arsenic. This would appear to be initially a direct thermal decomposition (2): the fate of the chlorine formed is uncertain, but since Blicke and Monroe

$$2[Ph_2ClAs\rightarrow AlCl_3] = [Ph_4As]Cl + 2AlCl_3 + As + Cl \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

(*loc. cit.*) have shown that the arsonium ion readily forms stable trihalides of type $[PH_4As]X_3$, it is probable that the excess chlorine is absorbed to give $[Ph_4As]Cl_3$. The latter would be largely decomposed on extraction with boiling water, but it is significant that only in these experiments did the subsequent precipitation with

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* This great reactivity seems to be associated with the co-ordinate link; *e.g.*, Harley-Mason and Mann have shown that triphenylphosphine sulphide, $Ph_3P\rightarrow S$, when heated with excess of methyl iodide at 100° gives an almost theoretical yield of tetramethylphosphonium iodide, whereas triphenylphosphine similarly treated gives solely triphenylphosphine methiodide (unpublished work).

potassium iodide give arsonium iodide coloured yellow by traces of tri-iodide. No evidence that the chlorine combined with the arsenic to form arsenic trichloride could be obtained.

The above thermal decomposition of the pure addition product, or of an equimolecular mixture of the monochloroarsine and pure aluminium chloride, produces no benzene. When, however, a partly hydrolysed sample of aluminium chloride is used, benzene is freely evolved and the yield of the arsonium ion falls markedly. The explanation, as before, is that the hydrogen chloride produced on heating converts the monochloroarsine into phenyldichloroarsine and benzene; the high yield of benzene from a much hydrolysed sample indicates that this degradation may even proceed down to arsenic trichloride itself.

(c) *Phenyldichloroarsine.* A third mechanism occurs here. This arsine, even in the presence of an excess of aluminium chloride, gives *trichlorotris(phenyldichloroarsine)aluminium* * $[(PhCl_2As)_3AlCl_3]$, a non-ionic compound containing 6-covalent aluminium, as in the well-known compounds $[Al(H_2O)_6]Cl_3$ and $K_3[Al(C_2O_4)_3]$. This addition product, which has also been obtained only as a viscous but very reactive syrup, gives rise on heating to the arsonium ion, arsenic trichloride, and elementary arsenic. It follows that the essential reaction is the familiar disproportionation under the influence of the aluminium chloride (3, *a*), and that the diphenylchloroarsine thus produced then gives the arsonium ion and arsenic as discussed above (3, *b*). In these two equations, the co-ordinated aluminium chloride is omitted for simplicity. This mechanism is confirmed by the facts that (i) the arsenic trichloride was isolated, (ii) the elementary arsenic deposited was 21% (theoretical value, 25%) of that present in the original dichloroarsine.

$$(a)\ 4PhCl_2As = 2AsCl_3 + 2Ph_2AsCl \quad (b)\ 2Ph_2AsCl = Ph_4AsCl + As + Cl \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The use of partly hydrolysed aluminium chloride again furnished benzene by the usual mechanism.

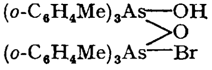
(d) *Benzene and arsenic trichloride.* A mixture of these compounds when heated with aluminium chloride is known to give phenyldichloroarsine, and then (in small quantity) diphenylchloroarsine. The reaction of the latter to give the arsonium ion will then, of course, be as under (b) above.

It follows from the foregoing work that the arsonium ion can arise in only two ways: by the interaction of $[Ph_3As\rightarrow AlCl_3]$ and bromobenzene, and by the thermal decomposition of $[Ph_2ClAs\rightarrow AlCl_3]$.

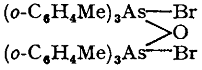
The mechanism of the formation of the tetraphenylphosphonium ion has not been investigated in detail. It is significant, however, that triphenylphosphine when mixed with aluminium chloride undergoes spontaneous oxidation at room temperature to triphenylphosphine oxide, although the pure phosphine alone is quite stable; this behaviour is strictly analogous to that of the arsine and is almost certainly due to the formation of an addition product $[Ph_3P\rightarrow AlCl_3]$.

The influence of substituents in the benzene ring upon the ease of formation of the tetra-arylarsonium ion has been briefly investigated. Theoretical considerations would indicate that a highly stable tetra-*o*-tolylarsonium ion should be readily formed, because the electromeric effect of the four *o*-methyl groups would cause strong electron pressure on the $\overset{+}{As}$ atom and so stabilise the ion. In the *p*-tolyl series, the effect of the *p*-methyl groups should be similar but weaker owing to their greater distance from the $\overset{+}{As}$ atom, whereas the tetra-*m*-tolylarsonium ion, in which the electromeric effect is reversed, should be less stable and less easily prepared than the unsubstituted ion. All attempts, over a wide variety of conditions, to prepare tetra-*o*-tolylarsonium salts failed, however; in all cases oxidation occurred, and the usual hot aqueous extraction of the product, followed by precipitation with sodium bromide, gave the *tri*-o-*tolylarsine hydroxy-oxybromide* (I) or the *oxydibromide* (II) according to the conditions employed. This failure to prepare the ion must presumably be due to the powerful steric effect of the four *o*-methyl groups. The tetra-*p*-tolylarsonium ion was readily formed in accordance with theory, whereas the formation of the tetra-*m*-tolylarsonium ion was not noticeably more difficult than that of the tetraphenylarsonium ion itself. Similar results were obtained with the phosphorus analogues: tetra-*o*-tolylphosphonium salts could not be prepared, the *tetra*-p-*tolyl* salts were readily formed, and the *tetra*-m-*tolyl* salts were prepared under similar conditions to the phenyl salts themselves.

(I.)



$$\begin{array}{l}(o\text{-}C_6H_4Me)_3As\text{—}OH\\ \qquad\qquad\qquad >O\\ (o\text{-}C_6H_4Me)_3As\text{—}Br\end{array}$$



$$\begin{array}{l}(o\text{-}C_6H_4Me)_3As\text{—}Br\\ \qquad\qquad\qquad >O\\ (o\text{-}C_6H_4Me)_3As\text{—}Br\end{array}$$

(II.)

The tetra-arylarsonium ions prepared in this work could usually be precipitated as their highly crystalline, slightly soluble thiocyanates; these frequently formed hydrates, an abnormal property of thiocyanates.

In view of the insecticidal value of triphenylbenzyl- and other quaternary phosphonium salts (D.R.P. 528,704; B.P. 312,163; U.S.P. 1,921,364) and the known toxic action of certain alkyl thiocyanates on lice, the action of tetraphenyl-phosphonium and -arsonium thiocyanates and other salts on lice has been investigated by Prof. P. A. Buxton and Dr. J. R. Busvine at the London School of Hygiene and Tropical Medicine, but the toxic action was too mild to be useful.

EXPERIMENTAL.

The names of solvents used for recrystallisation are given in parenthesis immediately after the names of the compounds concerned. "Pure" aluminium chloride referred to below was always material which had been freshly sub-

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* Hunt and Turner (J., 1925, **127**, 998) have described a crystalline addition compound, $PhCl_2As,AlCl_3$. Their analytical value (Al, 38·3%) indicates, however, an error in the identification of this compound, which actually requires Al, 7·6%.

limed in an atmosphere of hydrogen chloride and then stored in a vacuum until required; "impure" material refers to this pure material which had been exposed to air and partly hydrolysed as described on p. 667.

(A) *Trichlorotriphenylarsinealuminium.*—Pure powdered aluminium chloride (2·25 g.) was added to a solution of triphenylarsine (5 g., 1 mol.) in pure carbon disulphide (50 c.c.). On vigorous shaking, the chloride largely dissolved and a fine white sludge separated and rapidly solidified. The clear supernatant solution was quickly decanted and concentrated in a vacuum at room temperature. The colourless crystals of the above *addition product* which separated were rapidly collected with minimum exposure to the air, and dried in a vacuum (Found: C, 45·8; H, 3·8; Cl, 24·2; Al, 6·3. $C_{18}H_{15}Cl_3AlAs$ requires C, 49·1; H, 3·4; Cl, 24·2; Al, 6·1%. Low and inconsistent carbon values were always obtained). The solidified sludge was an impure sample of this material and gave many of its reactions.

(a) *Oxidation to triphenylarsine oxide.* Dry air was passed through a mixture of powdered triphenylarsine (2 g.) and pure aluminium chloride (0·9 g., 1 mol.) in bromobenzene (15 g.) at room temperature for 15 hours. The product, when extracted with hot water (100 c.c.), filtered, and treated with potassium iodide (10 g.) and acetic acid, gave triphenylarsine hydroxy-iodide (1 g.), m. p. 161—164° (mixed and unmixed); this iodide when treated with picric acid gave the hydroxy-picrate, m. p. 168—169° (mixed and unmixed), and when boiled with water gave the crystalline dihydroxide, which melted at 118°, resolidified, and remelted at 193—195° [Michaelis (*Annalen*, 1902, **321**, 164) gives $Ph_3As(OH)_2$, m. p. 116° and Ph_3AsO, m. p. 189°]. This experiment was repeated successfully by using benzene or tetralin in place of the bromobenzene; the omission of the aluminium chloride, or replacement of the air by hydrogen, caused the arsine to remain unchanged. When the above mixture (using, however, 7·5 g. bromobenzene) was kept for 24 hours in a flask open to the air through a calcium chloride tube, and then heated at 180° for 1 hour, the hydroxy-iodide was again obtained. Repetition of these experiments with the pure addition product, $[Ph_3As{\rightarrow}AlCl_3]$, instead of the mixture of arsine and aluminium chloride gave precisely similar results.

(b) *Conversion into tetraphenylarsonium salts.* The tetraphenylarsonium iodide described by Chatt and Mann has an indefinite m. p. (decomp.), and the arsonium ion was therefore identified as the picrate and thiocyanate. When hot alcoholic solutions of the arsonium bromide or iodide and of picric acid were mixed and cooled, *tetraphenylarsonium picrate* separated as yellow crystals (alcohol), m. p. 201—202° (Found: C, 58·8; H, 3·8; N, 7·0. $C_{30}H_{22}O_7N_3As$ requires C, 58·9; H, 3·6; N, 6·9%). Addition of potassium thiocyanate to hot aqueous solutions of the bromide or iodide gave on cooling long colourless needles of the *thiocyanate*; these were redissolved in hot water, reprecipitated with potassium thiocyanate, and crystallised from water; m. p. 268—270° with preliminary softening (Found: C, 68·3; H, 4·9; N, 3·3. $C_{25}H_{20}NSAs$ requires C, 68·0; H, 4·6; N, 3·2%).

Reaction in Absence of Bromobenzene.—Many experiments were performed in which equimolecular mixtures of triphenylarsine and pure aluminium chloride were heated for various periods at various temperatures. Below *ca.* 250° no free arsenic and only traces of arsonium salt and of benzene were detected even after 2·5 hours' heating; the usual aqueous extraction of the almost colourless product furnished unchanged arsine and sometimes traces of arsine oxide formed by atmospheric oxidation. At temperatures above 280°, thermal decomposition became increasingly prominent; *e.g.*, a mixture of the arsine (10 g.) and aluminium chloride (4·5 g., 1 mol.) was slowly heated to 300°, no change being perceptible to *ca.* 280°; during 3 hours' heating at 300° effervescence and charring with deposition of arsenic proceeded, and the final product yielded benzene (2·3 g., identified by b. p. and as *m*-dinitrobenzene, m. p. 91°) and the arsonium iodide (0·5 g.).

When a similar mixture prepared, however, with impure aluminium chloride was heated, brisk evolution of benzene (identified as before) started at 120° and all reaction appeared complete after 0·5 hour's heating at 210—220°; the dark product now yielded the arsonium iodide (4·1 g.), identified as the picrate, m. p. 200—201°. In a repetition of the latter experiment, steam-distillation of the dark product did not produce any diphenyl.

Reaction in Presence of Bromobenzene.—(i) A mixture of the arsine (10 g.), pure aluminium chloride (4·5 g., 1 mol.), and bromobenzene (6·0 g., 1·2 mols.) was heated at 200° for 2 hours. No benzene was evolved and the product remained colourless. The usual extraction gave the arsonium iodide (12 g., 72% of theory on equation 1), which afforded the picrate, m. p. 201—202°. (ii) When the proportion of aluminium chloride was doubled, much decomposition occurred and the yield of iodide fell to 7·2 g. (43%). (iii) When the proportion of aluminium chloride was unchanged and that of bromobenzene increased to 10 mols., heating in a bath at 200° gave little decomposition and the yield of iodide was 9·2 g. (55%). (iv) When experiment (i) was repeated using impure aluminium chloride (10 g., to allow for hydrolysis), much decomposition and benzene evolution occurred, and the yield of iodide was 0·3 g. (v) Repetition of experiment (i) using, however, aluminium bromide instead of the chloride gave the same result as in (i).

All the above experiments involving mixtures of the arsine and pure aluminium chloride were repeated upon the pure addition product $[Ph_3As{\rightarrow}AlCl_3]$, and precisely similar results were obtained.

Mixed Arsonium Salts.—(i) After mixtures of triphenylarsine (2 g.), pure aluminium chloride (0·9 g., 1 mol.), and *p*-bromotoluene (2 g., 1·8 mol), or of diphenyl-*p*-tolylarsine (2 g.), the pure trichloride (0·83 g., 1 mol.), and bromobenzene (3·0 g., 3 mols.), had been heated at 180° for 1 hour, the usual extraction gave *triphenyl*-p-*tolylarsonium iodide* as a white crystalline stable *monohydrate*, m. p. 186—187°, which, however, on heating at 130°/15 mm. for 8 hours gave the anhydrous iodide (Found, for the hydrate: C, 55·3; H, 4·6; I, 23·6. $C_{25}H_{22}IAs,H_2O$ requires C, 55·3; H, 4·5; I, 23·4%. Found, for the anhydrous salt: C, 57·5; H, 4·6; I, 24·1. $C_{25}H_{22}IAs$ requires C, 57·3; H, 4·2; I, 24·2%). The iodide in turn gave a *thiocyanate* (water), long colourless needles of a polyhydrate which, in a vacuum over phosphoric anhydride, rapidly decrepitated to a stable *monohydrate* (m. p. 147—148°), which when kept at 130°/15 mm. for 10 hours gave the anhydrous thiocyanate (Found, for the monohydrate: C, 65·7; H, 5·1. $C_{26}H_{22}NSAs,H_2O$ requires C, 65·9; H, 5·1%. Found, for the anhydrous salt: C, 69·0; H, 4·8. $C_{26}H_{22}NSAs$ requires C, 68·6; H, 4·9%).

(ii) A mixture of diphenyl-*p*-tolylarsine (2 g.), pure trichloride (0·83 g.), and *p*-bromotoluene (2 g., 1·8 mol.), heated at 180° for 1 hour, similarly gave *diphenyldi*-p-*tolylarsonium iodide*, m. p. 194—195°, as a *hydrate* stable in a vacuum over phosphoric anhydride but giving the anhydrous salt at 130°/15 mm. (Found, for the hydrate: C, 55·0; H, 4·8; I, 22·2. $C_{26}H_{24}IAs,1{\cdot}5H_2O$ requires C, 55·2; H, 4·8; I, 22·5%. Found, for the anhydrous salt: I, 23·7. $C_{26}H_{24}IAs$ requires I, 23·6%).

(iii) A mixture tri-*p*-tolylarsine (2 g.), the pure trichloride (1 g., 1·3 mols.), and bromobenzene (15 g., 16·6 mols.), refluxed for 1 hour, gave *phenyltri*-p-*tolylarsonium iodide* (water), m. p. 205—206° after drying at 130°/15 mm. (Found: C, 58·5; H, 4·6; I, 22·8. $C_{27}H_{26}IAs$ requires C, 58·7; H, 4·7; I, 23·0%). This gave a hydrated thiocyanate (water), which after 8 hrs. at 80°/15 mm. gave the anhydrous *thiocyanate*, m. p. 143—144° (Found: C, 69·8; H, 5·6; N, 3·0. $C_{28}H_{26}NSAs$ requires C, 69·6; H, 5·4; N, 2·9%).

(B) *Trichlorodiphenylchloroarsinealuminium* $[Ph_2ClAs{\rightarrow}AlCl_3]$.—Pure powdered aluminium chloride (3 g., 1·2 mols.) was added to a solution of the chloroarsine (5·0 g., 1 mol.) in pure carbon disulphide (50 c.c.). On vigorous shaking, the aluminium chloride almost completely dissolved and a heavy pale brown oil separated. The supernatant disulphide was decanted, and the oil filtered rapidly under pressure, washed with carbon disulphide, and finally confined in a vacuum until free from the disulphide. The *addition product* formed a viscous syrup which was rapidly attacked by air, and hence the above operations were conducted as speedily as possible (Found: C, 34·6; H, 2·7; Cl, 35·8. $C_{12}H_{10}Cl_4AsAl$ requires C, 36·2; H, 2·5; Cl, 35·7%. Consistent carbon analyses could not be obtained).

(i) A mixture of diphenylchloroarsine (5 g.) and pure aluminium chloride (2·5 g., 1 mol.) was heated at 200° for 2 hours. No benzene was evolved but arsenic (0·6 g.) was deposited. Extraction gave a yellow sample of the arsonium iodide (3·7 g.), which after recrystallisation gave the pure arsonium picrate; the yields of arsenic and arsonium iodide were 84% and 77% of those required by equation (2). Steam-distillation of the reaction product gave no diphenyl. (ii) A repetition of (i) with heating at 150—160° for 2 hours gave a low yield of arsonium iodide (1·2 g., 25%) and much unchanged arsine. (iii) A repetition of (i) in which the temperature was increased slowly to 280° gave an evolution of benzene which was slight at 220° and copious at 280°; purification of the arsonium iodide required, however, many recrystallisations. (iv) Repetition of (i) with addition of bromobenzene (6 g., 2 mols.) to the mixture gave a product which furnished no arsonium salt and very little arsenic. (v) On repetition of (i) but with impure aluminium chloride which had been exposed for 10 mins., benzene (0·7 g.) was evolved as the temperature reached 100—120°; final heating at 200° for 2 hours gave arsenic (0·4 g., 57%) and the arsonium iodide (2·7 g., 56%). (vi) Another repetition using the trichloride which had been exposed for 0·5 hour gave benzene (1·8 g.), some arsenic trichloride, but no arsonium iodide.

When the addition product [$Ph_2ClAs\rightarrow AlCl_3$] replaced the monochloro-arsine and pure trichloride in experiments (i), (ii), and (iii), the same results were obtained.

(C) *Trichlorotris(phenyldichloroarsine)aluminium*, [$(PhCl_2As)_3AlCl_3$].—When pure powdered aluminium chloride (6·0 g., 1 mol.) was shaken with a solution of the dichloroarsine (10 g., 1 mol.) in carbon disulphide (50 c.c.), a dark brown oil separated but much aluminium chloride remained unchanged. The clear supernatant solvent was removed, and the oil filtered rapidly under suction to remove excess aluminium chloride, and confined in a vacuum until free from disulphide (Found: C, 26·1; H, 2·3; Cl, 39·9. $C_{18}H_{15}Cl_9As_3Al$ requires C, 26·9; H, 1·9; Cl, 39·8%). The oil undergoes rapid surface oxidation when exposed to air. The same product was obtained when the oil was thoroughly washed with carbon disulphide before vacuum treatment (Cl, 39·9%) and when an excess of aluminium chloride (3 mols.) was used in the above preparation (Cl, 40·0%). When, however, an excess of arsine was used, the addition product retained some free arsine in solution; *e.g.*, the use of 2 and 4 mols. of arsine gave products having Cl, 37·9 and 34·2%, respectively.

(i) A mixture of phenyldichloroarsine (5 g.) and pure aluminium trichloride (3 g., 1 mol.) was heated at 200° for 2 hours. At 160—180° arsenic chloride was evolved and arsenic liberated. The arsenic chloride was collected and redistilled; b. p. 129—130° (Found: Cl, 58·5. Calc. for $AsCl_3$: Cl, 58·7%). The main product, extracted as usual, gave a crude yellow arsonium iodide (2·5 g., 88% of that indicated by equation 3; picrate, m. p. 200°) and elementary arsenic (0·35 g., 21% of that present in the original arsine). No benzene could be detected. (ii) When the above mixture, after being heated as described, was heated at 280° for another hour, the products were the same but the iodide less pure. (iii) Repetition of (i) but with impure aluminium chloride gave vigorous evolution of benzene (1·1 g.) from 100° upwards. (iv) Repetition of (i) and (ii) upon the pure addition product gave identical results.

It is noteworthy that tetraphenylarsonium bromide, after being heated with aluminium chloride (4 mols., pure or impure) at 200° for 2 hours and then 280° for 1 hour, was recovered unchanged.

Triphenylarsine Oxide and Hydroxybromide.—When (i) a mixture of triphenylarsine oxide (2 g.) and aluminium chloride (2 g.) was heated at 250° for 3 hours, (ii) the same mixture was boiled with bromobenzene (15 g.) under reflux for 3 hours, (iii) the hydroxybromide (2 g.), aluminium chloride (2 g.), and bromobenzene (3 g. or 15 g.) were heated at *ca.* 200° for 3 hours, the product in each case, extracted as usual, gave the arsine hydroxy-iodide, which in turn gave the hydroxy-picrate, m. p. 168° (mixed and unmixed).

*Tri-*o*-tolylarsine.*—A mixture of the arsine (2 g.), aluminium chloride (2 g., 2·6 mols.), and *o*-bromotoluene was heated at 100° for 5 hours. Extraction with water, followed by sodium bromide treatment, gave the *hydroxy-oxy-bromide* (I) (water), m. p. 148—152° (preliminary softening) (Found: C, 62·0; H, 5·5; Br, 9·8. $C_{42}H_{43}O_2BrAs_2$ requires C, 62·3; H, 5·3; Br, 9·9%). Crystallisation of (I) from hot dilute hydrobromic acid gave the *oxydibromide* (II), colourless plates, m. p. 232° (preliminary softening) (Found: C, 57·7; H, 5·0; Br, 18·2. $C_{42}H_{42}OBr_2As_2$ requires C, 57·8; H, 4·9; Br, 18·3%). Treatment of (I) or (II) in hot alcoholic solution with picric acid gave the *oxydipicrate*, m. p. 169—171° (alcohol) (Found: N, 7·2. $C_{54}H_{46}O_{15}N_6As_2$ requires N, 7·2%). The above bromides were precipitated because the iodides separated as viscous solids which only slowly crystallised; the pure (I), treated in aqueous solution with potassium iodide, gave the *hydroxy-oxyiodide*, which was recrystallised from dilute potassium iodide solution containing sodium sulphite; colourless crystals, decomp. on heating (Found: I, 14·8. $C_{42}H_{43}O_2IAs_2$ requires I, 14·8%).

The experiment was repeated with variations of the aluminium chloride and *o*-bromotoluene proportions, the temperature, and the time of heating. Either the above oxidation or (particularly at higher temperatures) extensive decomposition occurred.

*Tri-*p*-tolylarsine.*—A mixture of the arsine (2 g.), pure aluminium chloride (0·8 g., 1 mol.), and *p*-bromotoluene (3·0 g., 3 mols.) was heated at 180—200° for 1 hour. The usual extraction followed by potassium iodide treatment gave *tetra-*p*-tolylarsonium iodide*, colourless needles (water), m. p. 253—255° (Found: C, 59·6; H, 5·0; I, 22·0. $C_{28}H_{28}IAs$ requires C, 59·4; H, 5·0; I, 22·4%). This compound, treated with excess potassium thiocyanate, gave the *thiocyanate* as a *monohydrate* (water), m. p. 207—209°, which lost water when heated at 130°/15 mm. for 10 hours (Found, for the hydrate: C, 67·2; H, 5·8; N, 2·8. $C_{29}H_{28}NSAs,H_2O$ requires C, 67·5; H, 5·8; N, 2·7%. Found, for the anhydrous salt: C, 69·8; H, 5·7. $C_{29}H_{28}NSAs$ requires C, 70·0; H, 5·6%).

*Tri-*m*-tolylarsine.*—Repetition of the previous experiment but with *m*-tolylarsine and heating for 2·5 hours gave *tetra-*m*-tolylarsonium iodide* (water), m. p. 155—156° (Found: C, 59·4; H, 5·2; I, 22·7%). Heating the mixture at 120° for 4 hours and subsequent treatment with sodium bromide gave only tri-*m*-tolylarsine hydroxybromide (crystallised from dilute hydrobromic acid), m. p. 188° (Found: Br, 18·6. Calc. for $C_{21}H_{22}OBrAs$: Br, 18·0%).

*Tri-*o*-tolylphosphine.*—Mixtures of this phosphine with aluminium chloride and *o*-bromotoluene in various proportions, heated under widely different conditions, appeared to undergo almost complete decomposition, neither the phosphine hydroxy-halide nor the phosphonium salt being isolated.

*Tri-*p*-tolylphosphine.*—A mixture of the phosphine (3 g.), pure aluminium chloride (3 g., 2·3 mols.), and excess *p*-bromotoluene (15 g., 9 mols.), boiled under reflux for 1 hour, gave ultimately *tetra-*p*-tolylphosphonium iodide*, colourless needles (water), m. p. 260—264° (Found: C, 64·4; H, 5·7; I, 24·2. $C_{28}H_{28}IP$ requires C, 64·3; H, 5·4; I, 24·3%).

*Tri-*m*-tolylphosphine.*—A mixture of the phosphine (3 g.), pure aluminium chloride (1·3 g., 1 mol.), and *m*-bromotoluene (4 g., 2·4 mols.), heated at 190—200° for 2 hours, gave the *phosphonium iodide*, colourless crystals (water), m. p. 175—176° (Found: C, 64·5; H, 5·2; I, 24·5%). The m. p.'s of both these iodides must be determined by rapid heating: slow heating causes darkening, which will occur even on exposure to the light at room temperature. The phosphonium iodides are all markedly less stable than their arsonium analogues in this respect.

Tetraphenylphosphonium thiocyanate (water), colourless needles, unaffected by heating to 270°, was prepared from the iodide (Found: C, 75·3; H, 5·0; N, 3·5. $C_{25}H_{20}NSP$ requires C, 75·5; H, 5·1; N, 3·5%).

Toxic Properties.—Dr. Busvine reports: " The samples, which were white crystalline powders, were not readily soluble in mineral oil which would be the most satisfactory vehicle. Volatile solvents would leave them deposited as solids, so they were tested rather crudely in this form. Tapes thoroughly dusted with the crushed crystals were put into tins with lice. Some samples killed a high proportion of lice but all were slow in comparison to ordinary naphthalene. A proportion of eggs laid on the tapes hatched in all cases.

Results.—

	Deaths of 6 adult lice.			Eggs.	
Compound. Day :	1.	2.	3.	No. laid.	% hatched.
Tetraphenylphosphonium thiocyanate	0	1	0	10	80
Tetraphenylphosphonium iodide	0	5	1	31	52
Tetraphenylarsonium thiocyanate	2	3	0	19	58
Tetraphenylarsonium iodide	1	4	0	5	40
Tetraphenylstibonium iodide	0	3	3	16	75
Naphthalene	6	—	—	0	—

Although the tests were rather crude, they show that the compounds are not good insecticides for lice."

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