628. *Arsinophosphonium Salts.*

By J. M. F. BRADDOCK and G. E. COATES.

Many tertiary phosphines, R'_3P, react with halogenoarsines, R_2AsX, forming salts, $[R'_3P{\cdot}AsR_2]^+X^-$. Triphenylphosphine does not react. Though analogous salts are formed by some nitrogen bases, conductimetric titration shows pyridine to be a much weaker donor than triethylphosphine or dimethylphenylphosphine, to iododimethylarsine. Methoxydimethyl- and dimethylphenoxy-arsine have been prepared.

DIMETHYLARSINOPHOSPHONIUM salts, from halogenodimethylarsines and tertiary phosphines, *e.g.*, $Me_2AsI + Et_3P \longrightarrow [Me_2As{\cdot}PEt_3]^+I^-$, have been mentioned in a note.[1] We now report the scope of this reaction and some properties of the products. While this work was in progress a related series of compounds, derived from chloramine and tertiary phosphines (*e.g.*, $[Ph_3P{\cdot}NH_2]^+Cl^-$), was described.[2]

The salts prepared during the present work are listed in the Table. They are insoluble in non-polar solvents such as benzene and hexane and often slightly soluble in weakly

---

[1] Coates and Livingstone, *Chem. and Ind.*, 1958, 1366.

[2] Sisler, Sarkis, Ahuja, Drago, and Smith, *J. Amer. Chem. Soc.*, 1959, **81**, 2982.

				Found (%)			Required (%)	
Arsine	Phosphine	Salt	M. p.	C	H	Formula	C	H
Me_2AsCl	PEt_3	$[Me_2As{\cdot}PEt_3]Cl$ [a]	73—75° [b]	37·3	8·2	$C_8H_{21}AsClP$	37·2	8·1
,,	$PPhMe_2$	$[Me_2As{\cdot}PPhMe_2]Cl$ [a]	115—116 [c]	43·6	6·2	$C_{10}H_{17}AsClP$	43·3	6·1
Me_2AsBr	PEt_3	$[Me_2As{\cdot}PEt_3]Br$	142—145 [d]	31·8	7·1	$C_8H_{21}AsBrP$	31·8	7·0
,,	$PPhMe_2$	$[Me_2As{\cdot}PPhMe_2]Br$	178 [d]	37·3	5·6	$C_{10}H_{17}AsBrP$	37·3	5·3
,,	$PPhEt_2$	$[Me_2As{\cdot}PPhEt_2]Br$	142—148 [e]	41·3	6·3	$C_{12}H_{21}AsBrP$	41·1	6·0
Me_2AsI	PMe_3	$[Me_2As{\cdot}PMe_3]I$	270—273 [f]	20·2	5·1	$C_5H_{15}AsIP$	19·6	4·9
,,	PEt_3	$[Me_2As{\cdot}PEt_3]I$ [a]	132—135 [d]	27·7	6·0	$C_8H_{21}AsIP$	27·6	6·0
,,	PPr^n_3	$[Me_2As{\cdot}PPr_3]I$	100 [e]	33·2	6·9	$C_{11}H_{27}AsIP$	33·7	6·9
,,	$PPhMe_2$	$[Me_2As{\cdot}PPhMe_2]I$ [a]	147 [d]	32·3	4·6	$C_{10}H_{17}AsIP$	32·4	4·6
,,	PPh_2Me	$[Me_2As{\cdot}PPh_2Me]I$	115—117 [d]	42·1	4·5	$C_{15}H_{19}AsIP$	41·7	4·4
Et_2AsI	$PPhMe_2$	$[Et_2As{\cdot}PPhMe_2]I$	112—118 [d]	36·4	5·5	$C_{12}H_{21}AsIP$	36·3	5·3
Ph_2AsI	PEt_3	$[Ph_2As{\cdot}PEt_3]I$	85—87 [d]	45·4	5·6	$C_{18}H_{25}AsIP$	45·4	5·3

[a] Previously described (ref. 1). [b] Crystallized from ethanol–ether, [c] from acetone, [d] from ethanol, [e] from propan-1-ol, [f] from ethanol–water.

polar solvents (ether or tetrahydrofuran), and can generally by crystallized from acetone, ethanol, or propanol. Of the salts studied only dimethylarsinotrimethylphosphonium iodide, $[Me_2As{\cdot}PMe_3]I$, was stable to air and water; the rest decomposed (sometimes rapidly) in air by hydrolysis and oxidation, but remained undecomposed when stored under nitrogen. Some of the iodides, for example the methyl compound just mentioned, can be sublimed in a vacuum, presumably by reversible dissociation like the ammonium and phosphonium halides.

Although the aminophosphonium halides [2] are hydrolysed to phosphine oxides:

$$R_3P{\cdot}NH_2^+ + OH^- \longrightarrow R_3PO + NH_3,$$

and phosphine oxides are also formed by attack of base on quaternary phosphonium salts: [3]

$$R_4P^+ + OR'^- \longrightarrow R_3PO$$

the arsinophosphonium salts are hydrolysed to the tertiary phosphine and the arsenoxide:

$$[R_2As{\cdot}PR'_3]^+ + OH^- \longrightarrow (R_2As)_2O + PR'_3$$

We attribute this to reversible dissociation of the arsinophosphonium salt,

$$R_2As{\cdot}PR'_3{}^+X^- \rightleftharpoons R_2AsX + PR'_3$$

which is apparent from conductimetric titrations (see below), followed by rapid hydrolysis of the halogenoarsine, $2R_2AsX + 2OH^- \longrightarrow (R_2As)_2O + 2X^- + H_2O$. Reactions with MeO^- and PhO^- anions again yield the tertiary phosphine, with methoxy- and phenoxydimethylarsine:

$$[Me_2As{\cdot}PEt_3]I + NaOMe \longrightarrow Me_2AsOMe + PEt_3 + NaI$$

Since no reference could be found to compounds $Me_2As{\cdot}OR$ (R = Me or Ph), both these very readily hydrolysed compounds were prepared from iododimethylarsine, *e.g.*:

$$Me_2AsI + NaOMe \longrightarrow Me_2As{\cdot}OMe$$

The apparent molecular weights of the salts $[Me_2As{\cdot}PEt_3]I$ and $[Me_2As{\cdot}PPr_3]I$, measured cryoscopically in nitrobenzene, were rather more than half the formula weights.

Conductances.—In nitrobenzene at 25° the molar conductances of the iodides $[Me_2As{\cdot}PEt_3]I$ and $[Me_2As{\cdot}PPhMe_2]I$ were practically linear functions of the square root of the molar concentration M, according to the equations $\Lambda = 35{\cdot}6 - 197M^{\frac{1}{2}}$ and $\Lambda = 30{\cdot}6 - 142M^{\frac{1}{2}}$, respectively. These values of Λ_0, 35·6 and 30·6, are appropriate for a 1 : 1 electrolyte in nitrobenzene.

Conductimetric titration (Fig. A) of triethylphosphine with iododimethylarsine shows a well-defined discontinuity close to the theoretical equivalence point. When dimethylphenylphosphine (Fig. B) or methyldiphenylphosphine (Fig. C) are titrated with iododimethylarsine, the equivalence point is not well marked (see particularly Fig. C). We

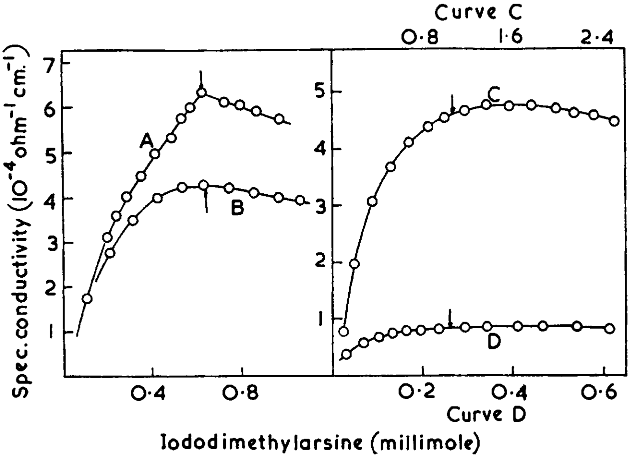
---

[3] Berlin and Butler, *Chem. Rev.*, 1960, **60**, 243.

attribute these results to the reversibility of the reaction, and the diarylphosphine PPh_2Me is clearly a weaker donor to iododimethylarsine than is $PPhMe_2$ in the sense that the equilibrium, $Me_2AsI + PR_3 \rightleftharpoons Me_2As{\cdot}PR_3^+ + I^-$, lies further to the left. The titration with pyridine (Fig. D) shows that this base is considerably weaker still; in fact, the very unstable pyridinium salt $[C_5H_5N{\cdot}AsMe_2]I$ was difficult to isolate, could not be purified satisfactorily, and slowly decomposed into its components even when kept in a vacuum at room temperature. Towards iododimethylarsine the donor character of the bases studied is in the order: $PEt_3 > PPhMe_2 > PPh_2Me > C_5H_5N > PPh_3 = 0$.

Halogenodiphenylarsines do not react with tertiary phosphines as readily as the dialkylhalogenoarsines. Though the iodide $[Ph_2As{\cdot}PEt_3]I$ was the only diphenylarsino-derivative that could be isolated, its instability was shown by a marked curvature of the conductimetric plot in the vicinity of the end-point. Evidence for the formation of the chloride, which could not be isolated in a pure state, was obtained only from a conductimetric titration. Similarly, unstable salts were formed from triethylphosphine and iododiphenyl-antimony and -bismuth, but in neither instance could a pure product be isolated.

Conductimetric titration of tertiary phosphines, (A) PEt_3, (B) $PPhMe_2$, *and* (C) PPh_2Me, *and of pyridine* (D) *with iododimethylarsine. Arrows indicate equivalence points.*



Co-ordination between phosphorus and arsenic occurs in the halide complexes described by Holmes,[4] *e.g.*, Me_3As,PCl_3, but in such a compound it is likely that arsenic is the donor.

EXPERIMENTAL

All the compounds were prepared under an inert atmosphere. The preparation of only one phosphonium salt is described since all the others were prepared by a very similar method.

Dimethylarsinodimethylphenylphosphonium Iodide.—Dimethylphenylphosphine (27·6 c.c., 0·2 mole) in ether (70 c.c.) was slowly (10 min.) added to a stirred solution of iododimethylarsine (33·2 c.c., 0·2 mole) in ether (250 c.c.). The *phosphonium salt* was precipitated in a rapid and exothermic reaction. After 2 hours' stirring the salt was separated and crystallized from ethanol (2 l.) as white square plates (48·5 g., 62%), m. p. 147° (see Table).

Dimethylarsinopyridinium Iodide.—Dry pyridine (8·0 g.) was added to iododimethylarsine (23 g.) in ether (50 c.c.). The ether was removed by evacuation for a few minutes at room temperature; the pale yellow solid residual *iodide* crystallised from ethanol as colourless leaflets, m. p. 194° (decomp.) (Found: C, 28·6; H, 3·3; I, 39·0. $C_7H_{11}AsIN$ requires C, 27·1; H, 3·5; I, 40·9%).

Methoxydimethylarsine.—Sodium methoxide (9·5 g.) and iododimethylarsine (18·5 g.) were

---

[4] Holmes, *J. Amer. Chem. Soc.*, 1960, **82**, 5285; *J. Phys. Chem.*, 1960, **64**, 1295.

boiled in xylene under reflux until the yellow colour of the iododimethylarsine had disappeared (4 hr.). Distillation followed by three fractional distillations (nitrogen atmosphere) yielded a colourless *arsine*, b. p. 79° (1·276 g., on hydrolysis and oxidation with hydrogen peroxide, gave 1·289 g. of dimethylarsinic acid. C_3H_9AsO requires 1·292 g.).

Dimethylphenoxyarsine.—Iododimethylarsine (18·5 g.) was added to sodium phenoxide (11·6 g., 0·1 mol.; excess of phenol had been removed by sublimation) in tetrahydrofuran (65 c.c.). A white solid was precipitated and the yellow colour of iododimethylarsine almost disappeared. The *phenoxyarsine* was isolated by distillation and had b. p. 204° (slight decomp.), 101°/12 mm. (Found: C, 49·5; H, 5·6. $C_8H_{11}AsO$ requires C, 48·5; H, 5·8%. 1·312 g. after hydrolysis and bromination gave 2·183 g. tribromophenol. $C_8H_{11}AsO$ requires 2·183 g.).

Chemistry Department, The Durham Colleges,
South Road, Durham.

[*Received, February* 10*th*, 1961.]