1015. *Iodomercurate Complexes with Group V Quaternary Iodides. Part II.*[1] *Reactions with Triphenylphosphine.*

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Triphenylphosphine reacts with a representative of each of the main stoicheiometric classes of the "quaternary" iodomercurates * in acetone or ethanol, with the formation of an iodo(triphenylphosphine)-mercury(II) complex, and either a "quaternary" iodomercurate with a higher iodine : mercury ratio than the reactant or a "quaternary" iodide.

Gallais[2] prepared the compounds $MHgI_3,H_2O$ (where M is K or NH_4) and suggested that they were not solvates but contained the tetraco-ordinate ion $[HgI_3,H_2O]^-$. Recently the preparation of the nickel complexes $[NEt_4][Ph_3P,NiX_3]$ (where X is Br or I) has been reported.[3] We have attempted to provide an unequivocal example of a mercury complex of the type $[HgI_3Y]^-$ (where Y is a neutral molecule) by the reaction between equimolar amounts of pyridinium tri-iodomercurate(II) and triphenylphosphine in acetone. The expected complex $[PyH][Ph_3P,HgI_3]$ was not isolated, the products being di-iodobis(triphenylphosphine)mercury(II)[4] and dipyridinium tetraiodomercurate(II).[1,5] The former product was still obtained when the ratio of iodomercurate to phosphine was 2 : 1.

The reaction of triphenylphosphine (2 mol.) with dipyridinium tetraiodomercurate (1 mol.) also gave di-iodobis(triphenylphosphine)mercury(II) as one product and pyridinium iodide as the other. However, compounds representing the other two classes of iodomercurates, *viz.*, $[PyH]_2Hg_3I_8$ and $[PMe_4][Hg_2I_5]$, gave different phosphine–mercuric iodide complexes depending on the ratio of triphenylphosphine to iodomercurate. With a 2 : 1 ratio of phosphine to iodomercurate the di-iodobis(triphenylphosphine)mercury complex was obtained while with a 1 : 1 ratio the new compound di-iodotriphenylphosphinemercury(II) was formed. The appropriate tri-iodomercurate was formed as the second product in each reaction.

The reactions may be represented:

$$2[PyH][HgI_3] + 2Ph_3P \longrightarrow (Ph_3P)_2HgI_2 + [PyH]_2[HgI_4] \quad \ldots\ldots \quad (i)$$

$$[PyH]_2[HgI_4] + 2Ph_3P \longrightarrow (Ph_3P)_2HgI_2 + PyH\cdot I \quad \ldots\ldots \quad (ii)$$

$$[PyH]_2[Hg_3I_8] + nPh_3P \longrightarrow (Ph_3P)_nHgI_2 + 2[PyH][HgI_3] \quad \ldots\ldots \quad (iii)$$

$$[PMe_4][Hg_2I_5] + nPh_3P \longrightarrow (Ph_3P)_nHgI_2 + [PMe_4][HgI_3] \quad \ldots\ldots \quad (iv)$$

where $n = 1$ or 2.

The compound di-iodotriphenylphosphinemercury(II) is assumed to be a dimer by

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* M_2HgI_4, $MHgI_3$, MHg_2I_5, and $M_2Hg_3I_8$, where M is a quaternary cation.

[1] Part I, Deacon and West, *J.*, 1961, 3929.

[2] Gallais, *Ann. Chim.* (*France*), 1938, **10**, 117.

[3] Cotton and Goodgame, *J. Amer. Chem. Soc.*, 1960, **82**, 2967.

[4] Evans, Mann, Peiser, and Purdie, *J.*, 1940, 1209.

[5] Lal Datta, *J. Amer. Chem. Soc.*, 1913, **35**, 949; Francois, *Compt. rend.*, 1905, **140**, 861.

analogy with the compounds R_3P,HgI_2 prepared by Evans *et al.*[4] which had molecular weights corresponding to dimers. The triphenylphosphine complex was not sufficiently soluble in suitable solvents for its molecular weight to be measured.

The slightly soluble compounds $(Ph_3P)_2HgI_2$ and $(Ph_3P,HgI_2)_2$ can be directly prepared by mixing triphenylphosphine and mercuric iodide in the correct molar proportions in benzene, the complexes being rapidly precipitated. Since the various iodomercurates are known to dissociate into mercuric iodide and iodine in solution a partial explanation of the triphenylphosphine–iodomercurate reactions can be made by assuming that the reaction product, $(Ph_3P)_2HgI_2$ or $(Ph_3P,HgI_2)_2$, is formed by the direct reaction between triphenylphosphine and free mercuric iodide in solution. Formation constants for the various ions in acetone have not been measured but the values in acetonitrile found by Ellendt and Cruse [6] are assumed to indicate the relative stabilities of the species.

$$HgI_2 + I^- \rightleftharpoons [HgI_3]^- \quad K_3 = 9 \times 10^5$$

$$[HgI_3]^- + I^- \rightleftharpoons [HgI_4]^{2-} \quad K_4 = 40$$

$$[HgI_3]^- + HgI_2 \rightleftharpoons [Hg_2I_5]^- \quad K_5 = 10$$

Ellendt and Cruse did not detect the formation of the $[Hg_3I_8]^{2-}$ species in solution, which indicates its extensive dissociation $[Hg_3I_8]^{2-} \rightleftharpoons HgI_2 + 2[HgI_3]^-$. Spectroscopic evidence was presented in Part I [1] to confirm extensive dissociation for this complex ion in ethanol.

Thus in the reactions between triphenylphosphine and either the tri-iodo- or the tetra-iodo-mercurate complexes, since there would be only a small concentration of "free" mercuric iodide in solutions of either complex, the ratio of mercuric iodide to added triphenylphosphine in each of the experiments performed was considerably smaller than the maximum 1 : 2 figure required to afford $(Ph_3P)_2HgI_2$ and therefore that complex was obtained.

Pentaiodo- and octaiodo-complexes dissociate into mercuric iodide and tri-iodomercurate ions so extensively as to produce virtually one molar equivalent of "free" mercuric iodide for every mole of iodomercurate complex; therefore, in these cases the particular triphenylphosphine-mercuric iodide complex formed will depend on the molar ratio of triphenylphosphine to iodomercurate, *i.e.*, 1 : 1 ratios give $(Ph_3PHgI_2)_2$, 2 : 1 give $(Ph_3P)_2HgI_2$.

This hypothesis alone does not account for the low yields of triphenylphosphine–mercuric iodide complexes in all the reactions—the yields are generally lower than those calculated on the basis of equations (i—iv). This may indicate that $[HgI_3,PPh_3]^-$ ions or other, more complex species exist in solution in equilibrium with the precipitated complexes. The reaction between triphenylphosphine and pyridinium tetraiodomercurate requires further investigation in this respect because the product finally obtained, *viz.*, $(Ph_3P)_2HgI_2$, is not immediately precipitated when the reactants are mixed despite its known low solubility in acetone but is only produced on boiling. This behaviour is not shown by any of the other iodomercurates, with which immediate precipitation of the final phosphine–mercuric iodide complex occurs on mixing. The solution of the tetraiodomercurate will contain a much lower concentration of "free" mercuric iodide than that of any of the other compounds because the iodide ions released in the first stage of dissociation, $[HgI_4]^{2-} \rightleftharpoons [HgI_3]^- + I^-$, restrict further dissociation of the $[HgI_3]^-$ ion. Thus, in this case, triphenylphosphine reacts at room temperature with mainly $[HgI_3]^-$ ions and this system should provide the best opportunity for formation of $[HgI_3PPh_3]^-$ ions if indeed they can exist at all.

When triphenylphosphine in excess was treated with each of the compounds, triphenylmethylphosphonium tri-iodomercurate, dipyridinium octaiodotrimercurate, and tetramethylphosphonium pentaiododimercurate in boiling ethanol, the mercuric iodide in the

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[6] Ellendt and Cruse, *Z. phys. Chem. (Leipzig)*, 1952, **201**, 130.

compounds was quantitatively precipitated as di-iodobis(triphenylphosphine)mercury(II). The reaction may thus be used as an analytical method for the determination of the mercuric iodide content of members of the $MHgI_3$, MHg_2I_5, and $M_2Hg_3I_8$ classes of Group VB quaternary iodomercurates. Since the tetraiodomercurate complex is an intermediate in the total decomposition of the tri-iodomercurate complex (reaction i), the method should be satisfactory also for tetraiodomercurate complexes. The liberated quaternary iodide was recovered in each case. Iodomercurates are useful derivatives for the isolation of Group VB quaternary cations from reaction mixtures, and decomposition with triphenylphosphine provides a satisfactory method for the recovery of the quaternary iodide.

EXPERIMENTAL

Reaction of Quaternary Iodomercurates with Triphenylphosphine.—The preparation of the quaternary iodomercurates has been reported.[1] After reactions 1, 5, 7, 8 (below) the products were shown to be identical with authentic samples of the appropriate compounds by comparison of *X*-ray powder photographs.

In reactions 1—6, solutions of the required amounts of triphenylphosphine and the quaternary iodomercurate, each in *ca.* 10 ml. of acetone, were mixed. Rapid precipitation of an iodo(triphenylphosphine)mercury(II) complex occurred. The mixture was left for an hour, then the precipitate was filtered off (fraction A). The filtrate was evaporated and the residue leached with a small quantity of cold acetone. This dissolved the iodomercurate, leaving undissolved some additional iodo(triphenylphosphine)mercury(II) complex (fraction B). Complete removal of the latter complex from the iodomercurate proved difficult, presumably since triphenylphosphine was reacting further in the extract. A further evaporation and extraction, followed by two or more recrystallizations of the iodomercurate from ethanol [ethanol–ether in the case of pyridinium tri-iodomercurate(II)], were generally necessary to achieve satisfactory purity. The two crops of the iodo(triphenylphosphine)-mercury(II) complex were either mixed and recrystallized from boiling benzene or were recrystallized and characterized separately. The stated yields of this complex refer to fraction (A).

Di-iodobis(triphenylphosphine)mercury(II) was synthesized by reaction between stoicheiometric quantities of mercuric iodide and triphenylphosphine in benzene (lit.,[4] ethanol used) and, recrystallized from benzene, had m. p. 246—247° (lit.,[4] *ca.* 250°) (Found: C, 44·0; H, 3·3; I, 26·4. Calc. for $C_{36}H_{30}HgI_2P_2$: C, 44·1; H, 3·1; I, 26·0%).

Di-iodo(triphenylphosphine)mercury(II) was synthesized by the reaction between stoicheiometric amounts of mercuric iodide and triphenylphosphine in benzene and, recrystallized from benzene, had m. p. 242—242·5° (Found: C, 30·6; H, 2·2; I, 35·4. $C_{18}H_{15}HgI_2P$ requires C, 30·2; H, 2·1; I, 35·4%). Di-iodo(triphenylphosphine)mercury(II), m. p. 242° (Found: C, 30·0; H, 2·3; I, 35·3%), was also obtained when triphenylphosphine and mercuric iodide reacted in benzene in the stoicheiometric ratio required for the formation of the complex, $(Ph_3P)_2(HgI_2)_3$. It was almost insoluble in cold acetone and benzene, insoluble in cold ethanol, and sparingly soluble in boiling benzene and acetone. Decomposition occurred during a Rast molecular-weight determination, and the solubility of the complex in boiling chloroform was not sufficient to afford a meaningful value of the molecular weight.

Reactions.—(1) Pyridinium tri-iodomercurate(II) (1·32 g., 2·0 mmoles) with triphenylphosphine (0·52 g., 2·0 mmoles) yielded di-iodobis(triphenylphosphine)mercury(II) (0·55 g., 0·56 mmole, 56%). The mixture of fractions (A) and (B) had m. p. 250° (Found: C, 44·1; H, 3·0; I, 26·0%). The other product was dipyridinium tetraiodomercurate(II), m. p. 168° (lit.,[1] *ca.* 168°), mixed m. p. 166·5—167°.

(2) Pyridinium tri-iodomercurate(II) (0·66 g., 1·0 mmole) with triphenylphosphine (0·13 g., 0·50 mmole) yielded di-iodobis(triphenylphosphine)mercury(II) (0·10 g., 0·10 mmole, 40%), m. p. and mixed m. p. 245° (Found: C, 44·6; H, 3·2%). The reaction mixture was not further investigated.

(3) Dipyridinium octaiodotrimercurate(II) (0·44 g., 0·25 mmole) with triphenylphosphine (0·13 g., 0·50 mmole) yielded di-iodobis(triphenylphosphine)mercury(II) {0·20 g., 0·20 mmole, 80% based on the reaction $[PyH]_2[Hg_3I_8] + 2Ph_3P \longrightarrow (Ph_3P)_2HgI_2 + 2[PyH][HgI_3]$}, m. p. and mixed m. p. 247—248° (Found: C, 44·4; H, 3·2%). The product obtained as fraction B was not investigated. The other product was pyridinium tri-iodomercurate(II), m. p. and

mixed m. p. 149—150° (lit.,[1] 149·5°) (Found: C, 9·2; H, 1·0; Hg, 29·9. Calc. for $C_5H_6HgI_3N$: C, 9·1; H, 0·9; Hg, 30·3%).

(4) Dipyridinium octaiodotrimercurate(II) (0·89 g., 0·50 mmole) with triphenylphosphine (0·13 g., 0·50 mmole) yielded di-iodo(triphenylphosphine)mercury(II) {0·19 g., 0·27 mmole, 54% based on the reaction $[PyH]_2[Hg_3I_8] + Ph_3P \longrightarrow (Ph_3P,HgI_2) + 2[PyH][HgI_3]$}, m. p. and mixed m. p. 242—242·5° (Found: C, 30·2; H, 2·1%). The product obtained as fraction (B) had m. p. and mixed m. p. 240—240·5° (Found: C, 29·9; H, 2·3%). The other product was pyridinium tri-iodomercurate(II), m. p. and mixed m. p. 149—150° (Found: C, 9·6; H, 1·1; Hg, 29·9%).

The reaction was repeated with double the concentration of each reactant to find whether any di-iodobis(triphenylphosphine)mercury(II) was present in the initially precipitated product. Di-iodo(triphenylphosphine)mercury(II) obtained as fraction (A) was twice recrystallized from benzene, then having m. p. and mixed m. p. 241—241·5° (Found: C, 30·2; H, 2·15%). The mother liquors from each recrystallization were combined, and crystallization from this solution gave white crystals (*ca.* 30 mg.), m. p. 238° (Found: C, 37·1; H, 2·8%), that may be a mixture of the two iodo(triphenylphosphine)mercury(II) complexes.

(5) Tetramethylphosphonium pentaiododimercurate(II) (1·13 g., 1·0 mmole) with triphenylphosphine (0·52 g., 2·0 mmoles) yielded di-iodobis(triphenylphosphine)mercury(II) {0·80 g., 0·82 mmole, 82% based on the reaction $[PMe_4][Hg_2I_5] + 2Ph_3P \longrightarrow (Ph_3P)_2HgI_2 + [PMe_4][HgI_3]$}. The combined products (A) and (B) had m. p. and mixed m. p. 248—249°. The other product was tetramethylphosphonium tri-iodomercurate(II), m. p. and mixed m. p. 196°.

(6) Tetramethylphosphonium pentaiododimercurate(II) (1·13 g., 1·0 mmole) with triphenylphosphine (0·26 g., 1·0 mmole) yielded di-iodo(triphenylphosphine)mercury(II) {0·36 g., 0·50 mmole, 50% based on the reaction $[PMe_4][Hg_2I_5] + Ph_3P \longrightarrow (Ph_3P,HgI_2) + [PMe_4][HgI_3]$}, m. p. 241—241·5°, mixed m. p. 240—241° (Found: C, 30·1; H, 2·3%). The same product obtained as fraction (B) had m. p. 239—241° (Found: C, 30·1; H, 2·2%). The other product was tetramethylphosphonium tri-iodomercurate(II), m. p. and mixed m. p. 196·5—197° [Found: HgI_2, 66·9 (by decomposition with excess of triphenylphosphine as described below). Calc. for $C_4H_{12}HgI_3P$: HgI_2, 67·6%].

(7) When acetone solutions of dipyridinium tetraiodomercurate(II) (0·44 g., 0·51 mmole) and triphenylphosphine (0·26 g., 1·0 mmole) were mixed no precipitate was obtained. The solution was evaporated to dryness, white crystals being deposited as the volume decreased. After the residue had been extracted with warm ethanol, di-iodobis(triphenylphosphine)-mercury(II) (0·34 g., 0·35 mmole, 70%) remained; recrystallized three times from benzene, it had m. p. and mixed m. p. 248—249°. No crystals were obtained from the ethanol, but it was shown to contain a pyridinium salt by evolution of pyridine on addition of warm aqueous sodium hydroxide.

(8) Dipyridinium tetraiodomercurate(II) (0·44 g., 0·51 mmole) was partially dissolved in ethanol (10 ml.), and a solution of triphenylphosphine (0·26 g., 1·00 mmole) in ethanol (10 ml.) was added. A slight cloudiness developed in the supernatant liquid. The mixture was heated at *ca.* 60°, white crystals being deposited, until the yellow colour of the iodomercurate disappeared from the suspension. The precipitated crystals consisted of di-iodobis(triphenylphosphine)mercury(II) (0·38 g., 0·39 mmole, 78%); twice recrystallized from benzene, this had m. p. and mixed m. p. 249—249·5°. Evaporation of the ethanol yielded an oil which, on addition of ether, gave crystals of impure pyridinium iodide that recrystallized with difficulty from acetone [m. p. 171—173° (decomp.)] (Found: I, 61·1. Calc. for C_5H_6IN: I, 61·4%). The ether used to crystallize the pyridinium iodide yielded a small amount of unchanged triphenylphosphine on evaporation.

Decomposition of Quaternary Iodomercurates by Excess of Triphenylphosphine.—Triphenylmethylphosphonium tri-iodomercurate(II) was prepared by reaction between stoicheiometric amounts of bis(triphenylmethylphosphonium) tetraiodomercurate(II)[7] and mercuric iodide and, recrystallized from acetone–ethanol, had m. p. 146—146·5° (Found: C, 26·2; H, 2·1; Hg, 22·9. $C_{19}H_{18}HgI_3P$ requires C, 26·5; H, 2·1; Hg, 23·4%).

In reactions (*a*—*c*), boiling ethanol solutions of the iodomercurate and triphenylphosphine [in excess of that required to precipitate all the mercuric iodide of the iodomercurate as $(Ph_3P)_2HgI_2$] were mixed, and di-iodobis(triphenylphosphine)mercury(II) was precipitated. The suspension was maintained at the b. p. of the solvent until the yellow colour disappeared.

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[7] Deacon and West, *J. Inorg. Nuclear Chem.*, in the press.

After cooling, the precipitate was filtered off, washed several times with ethanol, dried, and weighed. The filtrate was evaporated to dryness, and ether was added to crystallize the liberated quaternary iodide and dissolve the excess of triphenylphosphine. The quaternary iodide was recrystallized from ethanol–ether or acetone–ether.

(*a*) Triphenylmethylphosphonium tri-iodomercurate(II) (0·256 g., 0·298 mmole) with triphenylphosphine (0·509 g., 1·93 mmoles) yielded di-iodobis(triphenylphosphine)mercury(II) (0·291 g., 0·297 mmole; 100% yield requires 0·292 g.), m. p. (not recrystallized) and mixed m. p. 249—250° (Found: C, 44·6; H, 3·6%). The other product was triphenylmethylphosphonium iodide, m. p. 183—183·5° (lit.,[8,9] 182—183°, 176—181°) (Found: C, 56·5; H, 4·6; I, 30·8. Calc. for $C_{19}H_{18}IP$: C, 56·4; H, 4·5; I, 31·4%).

(*b*) Dipyridinium octaiodotrimercurate(II) (0·482 g., 0·271 mmole) with triphenylphosphine (1·03 g., 3·94 mmoles) yielded di-iodobis(triphenylphosphinemercury(II) (0·792 g., 0·809 mmole; 100% reaction requires 0·796 g.), m. p. (not recrystallized) and mixed m. p. 245—246° (Found: C, 44·1; H, 3·0%). The other product was slightly impure pyridinium iodide, m. p. 171—173° (decomp.) (Found: C, 29·5; H, 3·1; I, 60·2. Calc. for C_5H_6IN: C, 29·0; H, 2·9; I, 61·35%).

(*c*) Tetramethylphosphonium pentaiododimercurate(II) (0·455 g., 0·404 mmole) with triphenylphosphine (1·04 g., 3·97 mmoles) yielded di-iodobis(triphenylphosphine)mercury(II) (0·788 g., 0·805 mmole; 100% reaction requires 0·790 g.), m. p. (unrecrystallized) and mixed m. p. 248—249·5° (Found: C, 44·2; H, 3·1%). The other product was tetramethylphosphonium iodide, m. p. >300° (Found: C, 22·5; H, 5·4; I, 57·7. Calc. for $C_4H_{12}IP$: C, 22·0; H, 5·5; I, 58·3%).

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[8] Michaelis and Gleichmann, *Chem. Ber.*, 1882, **15**, 801.

[9] Blount, *J.*, 1932, 337.