339. Complex Salts Derived from Organomercury Halides and Related Compounds, and their Disproportionation

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Alkylmercury halides react with tertiary alkyl phosphines giving salts, $[RHgPR'_3]X$, which slowly disproportionate. Some methylmercury complexes with a variety of ligands, and anions other than halide, *e.g.*, $[MeHg\,py]ClO_4$, are also described. Reaction between arylmercury halides and tertiary phosphines results in rapid disproportionation, with formation of bisarylmercury. The relatively fast reaction of $[PhHgPEt_3]NO_3$ with sodium iodide, in which Ph_2Hg and $(PEt_3)_2HgI_2$ are formed, was followed photometrically. Dichlorobis(triethylphosphine)mercury(II) is extensively ionised in water, and several similar complexes are also appreciably ionised in alcoholic solution.

About twelve years ago one of us noticed that the reaction between methylmercury iodide and triethylphosphine in ethanol gave a crystalline complex which slowly changed into a product (bistriethylphosphinedi-iodomercury) of the disproportionation reaction,

$$2MeHgI + 2Et_3P \longrightarrow \text{intermediate} \longrightarrow Me_2Hg + (Et_3P)_2HgI_2$$

when allowed to remain several days at room temperature. The disproportionation brought about by tertiary phosphines was mentioned only briefly [1] but has since been used as a method for preparing various mercurials, R_2Hg, from the halides, RHgX, particular examples being where $R = CCl{:}CCl_2$ [2] and CO_2Me.[3] The formation of organomercury co-ordination complexes as intermediates was supported by the observation [4] that addition of triphenylphosphine increases the conductance of dilute solutions of phenylmercury chloride in dioxan–water to an extent consistent with the formation of a 1 : 1 complex. However, phenylmercury chloride was the only mercury compound isolated from the reaction mixture.

The isolation of the complex $[MeHgPEt_3]Br$, and the conductometric titration of ethylmercury bromide with phenyldimethylphosphine, were described in a preliminary Communication.[5]

We now describe a range of organomercury complexes, mainly with tertiary phosphines, and indicate some of the factors affecting the rate of the disproportionation reaction. Since reaction between trichlorovinyl- [2] or methoxycarbonyl-mercury chloride [3] and

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[1] G. E. Coates, " Organometallic Compounds," 1st edn., Methuen, London, 1956.

[2] D. Seyferth and R. H. Towe, *Inorg. Chem.*, 1962, **1**, 185.

[3] F. E. Paulik and R. E. Dessy, *Chem. and Ind.*, 1962, 1650.

[4] R. E. Dessy, W. L. Budde, and C. Woodruff, *J. Amer. Chem. Soc.*, 1962, **84**, 1172.

[5] R. J. Cross, A. Lauder, and G. E. Coates, *Chem. and Ind.*, 1962, 2013.

triphenylphosphine giving the disproportionation products, R_2Hg and $(Ph_3P)_2HgCl_2$, is fast, whereas methylmercury bromide yields the isolable complex, $[MeHgPR_3]Br$, it appears that the disproportionation is favoured when the organic group bound to the mercury is relatively electron-attracting.

We have succeeded in preparing organomercury tertiary phosphine halides only from alkylmercury halides, and even these complexes gradually decompose at room temperature over a period of weeks when stored under nitrogen. We were unable to prepare salts from methylmercury halides and triphenylphosphine, and could isolate only the dihalogeno-complex, $(Ph_3P)_2HgX_2$. The rate of the disproportionation of the Ph_3P–MeHgX system, which was not studied quantitatively by us, increases with the atomic weight of the halogen, $Cl < Br < I$, and with the dielectric constant of the solvent, benzene $<$ tetrahydrofuran $<$ acetone $<$ methanol.

The alkylmercury halide complexes listed in Table 1 were prepared by mixing solutions of the mercurial and of the tertiary phosphine in a solvent, frequently acetone, from which the complex crystallised within about an hour (sometimes after evaporation of some solvent under reduced pressure), or by precipitation of the complex from ether solutions of the reactants followed without delay by crystallisation from another solvent. Delay in isolation and characterisation of products can result in the isolation of dihalogeno-complexes; for example, methyl(triethylphosphine)mercury bromide (IV) crystallises as needles, m. p. 92—93°, soon after solutions of methylmercury bromide and triethylphosphine in acetone are mixed, but after several days at room temperature this product disappears and the solution slowly deposits large prismatic crystals of dibromobistriethylphosphinemercury, m. p. 155°.

The melting points listed in Table 1 should be regarded as decomposition temperatures (recorded under the usual conditions for measuring melting points of organic compounds). These are affected by the rate at which the compound is heated, and the length of time since its preparation. The temperatures listed in Table 1 refer to freshly prepared compounds. A quantitative investigation of the decomposition of (V), which liquefies after 30 min. at 80°, giving dimethylmercury and di-iodobis(phenyldimethylphosphine)mercury as main products, is described in the Experimental section.

Several salts containing methylmercury cations complexed with various ligands, and anions other than halide, are listed in Table 2. These salts were prepared by addition of the desired ligand to an aqueous solution of, for example, methylmercury perchlorate, known to contain the cation[6] $[MeHgOH_2]^+$. Their melting or decomposition temperatures are significantly higher than those of the analogous halides, and they do not appear to decompose when allowed to stand at room temperature for periods during which the halides decompose appreciably.

The reineckate (XIX) calls for some comment, since the possible constitution $[MeHgOH_2][Cr(NH_3)_2(SCN)_4]$ has to be considered. The compound is just perceptibly soluble in acetone, but is insoluble in all solvents investigated (except when it is decomposed). The anhydrous formulation is supported not only by analysis, but also by the presence of three infrared absorptions (2092, 2117, and 2174 $cm.^{-1}$). Salts containing the reineckate ion normally have a strong and rather broad absorption in the region 2060—2120 $cm.^{-1}$, and the presence of three distinct absorptions (2062, 2088, and 2151 $cm.^{-1}$) in the spectrum of mercury(II) reineckate has been ascribed to the effect of mercury–sulphur bonds.[7] The very similar appearance of the spectrum of (XIX) in this region suggests that Hg–S bonds are present in this compound also.

Although the pyridine complex (XXII) was obtained without difficulty, the complex $[MeHgNMe_3]ClO_4$, which we believe crystallised when trimethylamine was added to an aqueous acetone solution of methylmercury perchlorate, lost amine so rapidly that we were not able to analyse it. We do not know whether the bipyridyl complex, [MeHg bipy]NO_3,

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[6] P. Goggin and L. A. Woodward, *Trans. Faraday Soc.*, 1962, **58**, 1495.

[7] J. Fujita, K. Nakamoto, and M. Kobayashi, *J. Amer. Chem. Soc.*, 1956, **78**, 3295.

TABLE 1

Alkyl(tertiary phosphine)mercury halides

	Salt	Formula	M. p.[a]	ν(Hg–C)[b]	Found (%)			Required (%)		
					C	H		C	H	
(I)	[MeHgPMe$_3$]Cl	$C_4H_{12}ClHgP$	86°	528s	14·7	3·7	Cl, 10·95	14·5	3·7	Cl, 10·8
(II)	[MeHgPEt$_3$]Cl	$C_7H_{18}ClHgP$	84—85	—	22·8	5·0	Hg, 53·0	22·8	4·9	Hg, 54·3
(III)	[MeHgPMe$_2$Ph]Cl[d]	$C_9H_{14}ClHgP$	95—97	515·5s	27·5	3·7	Cl, 9·2	27·8	3·6	Cl, 9·2
(IV)	[MeHgPEt$_3$]Br	$C_7H_{18}BrHgP$	92—93[e]	516s[c]	20·5	4·5		20·3	4·4	
(V)	[MeHgPMe$_2$Ph]I[d]	$C_9H_{14}HgIP$	107	524s	22·5	2·9		22·5	2·9	
(VI)	[EtHgPMe$_3$]Cl	$C_5H_{14}ClHgP$	86	504s	17·4	4·2	Cl, 10·8	17·6	4·1	Cl, 10·4
(VII)	[EtHgPEt$_3$]Br[f]	$C_5H_{14}BrHgP$	87	508m[c]	22·5	4·8		22·5	4·7	
(VIII)	[Pr^{n}HgPMe$_3$]Cl	$C_6H_{16}ClHgP$	121—124	504m	20·2	4·6	Cl, 10·0	20·3	4·5	Cl, 10·0
(IX)	[Pr^{n}HgPMe$_2$Ph]Cl[d]	$C_{11}H_{18}ClHgP$	76—77	Absent	31·5	4·3	Cl, 8·4	31·7	4·35	Cl, 8·5
(X)	[Bu^{n}HgPMe$_3$]Cl	$C_7H_{18}ClHgP$	107—108	504w	22·75	4·8	Cl, 9·6	22·8	4·9	Cl, 9·6
(XI)	[Bu^{n}HgPMe$_2$Ph]Cl[d]	$C_{12}H_{20}ClHgP$	86—88	—	33·4	4·7	Cl, 8·2	33·4	4·7	Cl, 8·2
(XII)	[Bu^{n}HgPMe$_3$]I	$C_7H_{18}HgIP$	87—88	517s	18·1	3·9		18·25	3·9	

[a] With decomposition. [b] Nujol mull. [c] KBr disc. [d] Darkens when exposed to light. [e] Lit.,[5] m. p. 90—91°. [f] Molar conductance in water (25°) Λ_0 = 100·5 mole^{-1} ohm^{-1} cm.^{2}.

TABLE 2

Methylmercury salts of anions other than halide

	Salt	Formula	M. p.[a]	Found (%)	Required (%)
(XIII)	[MeHgPMe$_3$]ClO$_4$[b]	$C_4H_{12}ClHgO_4P$	215°	Hg, 49·8; ClO$_4$, 25·1	Hg, 51·3; ClO$_4$, 25·4
(XIV)	[MeHgPEt$_3$]ClO$_4$[b]	$C_7H_{18}ClHgO_4P$	137	Hg, 46·2; ClO$_4$, 22·8	Hg, 46·3; ClO$_4$, 23·0
(XV)	[MeHgPPh$_3$]ClO$_4$[b]	$C_{19}H_{18}ClHgO_4P$	213—218	Hg, 34·4	Hg, 34·7
(XVI)	[MeHgAsEt$_3$]ClO$_4$[b]	$C_7H_{18}AsClHgO_4$	120	Hg, 41·5	Hg, 42·0
(XVII)	[MeHgAsPh$_3$]ClO$_4$	$C_{19}H_{18}AsClHgO_4$	224—225	C, 36·95; H, 2·9	C, 36·7; H, 2·9
(XVIII)	[MeHgPEt$_3$]BF$_4$	$C_7H_{18}BF_4HgP$	120—125	C, 20·5; Hg, 47·4; BF$_4$, 21·2	C, 20·0; Hg, 47·7; BF$_4$, 20·65
(XIX)	[MeHgCr(NH$_3$)$_2$(SCN)$_4$]	$C_5H_9CrHgN_6S_4$	Decomp. from 190	C, 11·2; H, 1·74; Hg, 36·1	C, 11·25; H, 1·70; Hg, 36·4
(XX)	[MeHgPEt$_3$][Cr(NH$_3$)$_2$(SCN)$_4$]	$C_{11}H_{24}CrHgN_6PS_4$	,, 135	Cr, 7·9; Hg, 28·9	Cr, 8·0; Hg, 30·8
(XXI)	[MeHgPPh$_3$][Cr(NH$_3$)$_2$(SCN)$_4$]	$C_{23}H_{24}CrHgN_6PS_4$	,, 145	C, 34·9; Hg, 3·15; Cr, 6·4; Hg, 24·2	C, 34·8; H, 3·05; Cr, 6·5; Hg, 25·2
(XXII)	[MeHg py]ClO$_4$	$C_7H_8ClHgNO_4$	210—260	C, 18·6; H, 2·1; ClO$_4$, 25·7	C, 18·3; H, 2·05; ClO$_4$, 25·2

With decomposition. [b] Darkens when exposed to light.

contains a chelate ligand or the methylmercury group co-ordinated to one of the nitrogen atoms of the bipyridyl.

The formation of a salt, [$PhHgPPh_3$]Cl, from phenylmercury chloride and triphenylphosphine in dilute solution has been reported.[4] That phenylmercury chloride was the only mercury compound isolated from the mixture can be attributed to its unusually low solubility. Reaction between the much more soluble *m*-tolylmercury chloride and either triethyl- or triphenyl-phosphine is rapid in acetone solution and gives di-*m*-tolylmercury and the dichlorobisphosphine mercury complex in high yield. Reaction between triethylphosphine and an aqueous-acetone solution of phenylmercury nitrate (from the chloride and silver nitrate, and presumably containing $PhHgOH_2^+$ cations) yields phenyl(triethylphosphine)mercury nitrate, [$PhHgPEt_3$]NO_3, which is the only complexed arylmercury cation we have prepared. An attempt at the preparation of the triphenylphosphine analogue, [$PhHgPPh_3$]NO_3, yielded instead the dinitrato-complex, $(Ph_3P)_2Hg(NO_3)_2$, which has not previously been described. Thus, the presence of halogen is not essential for the disproportionation process to take place, though the halides disproportionate very much faster than the salts of other anions studied. In support of this we found that addition of aqueous sodium bromide to an acetone solution of [$PhHgPEt_3$]NO_3 resulted in the crystallisation of diphenylmercury:

$$[PhHgPEt_3]NO_3 + NaBr \longrightarrow \tfrac{1}{2}Ph_2Hg + \tfrac{1}{2}(Et_3P)_2HgBr_2 + NaNO_3$$

Though we have not made a proper kinetic study of reactions of the above type, it was possible to obtain some quantitative information about reaction rates by taking advantage of the fact that the spectrum of the iodide $(PEt_3)_2HgI_2$ in methanol solution has a shoulder at 2700 Å (ε 10,700; 9400 at 2800 Å). Of the other compounds that could possibly result from the addition of sodium iodide to [$PhHgPEt_3$]NO_3, *viz.* $NaNO_3$, NaI, PEt_3, Ph_2Hg, and PhHgI, only the last had a slight absorption at 2700 Å and caused negligible interference with measurements of the concentration of $(PEt_3)_2HgI_2$ derived from optical densities at 2800 Å. Solutions (1—4 $\times 10^{-5}$ mole $l.^{-1}$) of this complex in methanol obey Beer's law.

Sodium iodide (5·40 $\times 10^{-7}$ mole) in methanol (0·1 c.c.) was mixed with a solution of [$PhHgPEt_3$]NO_3 (4·72 $\times 10^{-7}$ mole) in methanol (4·9 c.c.) and the mixture at once transferred to a spectrometer. The optical density of the solution (2800 Å) rose rapidly, and became constant after 30 min. at room temperature (*ca.* 25°) at a value corresponding to 84·5% towards completion of the reaction:

$$[PhHgPEt_3]NO_3 + NaI \longrightarrow \tfrac{1}{2}Ph_2Hg + \tfrac{1}{2}(Et_3P)_2HgI_2 + NaNO_3$$

The concentration of the di-iodide had reached 74·5% of its equilibrium value 4 min. after the reagents were mixed. The reversibility of the reaction was shown by adding diphenylmercury to a methanol solution (originally containing 10·81 $\times 10^{-5}$ mole $l.^{-1}$ NaI and 9·42 $\times 10^{-5}$ mole $l.^{-1}$ [$PhHgPEt_3$]NO_3) and measuring the concentration of $(PEt_3)_2HgI_2$ optically after 1 hr. As the concentration of diphenylmercury was raised to 3·8, 7·5, 11·0, 18·6, and 368 $\times 10^{-5}$ mole $l.^{-1}$, that of $(PEt_3)_2HgI_2$ fell to 3·83, 3·72, 3·39, 3·33, and 1·83 $\times 10^{-5}$ mole $l.^{-1}$.

The conductometric titration of ethylmercury bromide with triethyl- and phenyldimethyl-phosphine in methanol, in which the conductance rose to a maximum at a 1 : 1 molar ratio corresponding to formation of the complex salt, [$EtHgPR_3$]Br, has been reported earlier.[5] Addition of 1 mol. triphenylphosphine to methanolic methylmercury chloride does not result in complete displacement of chloride by tertiary phosphine, and in 0·006M-solution in methanol (25°) a conductance maximum is not reached until the ratio Ph_3P : Hg is 1·25 : 1. Under similar conditions the conductance maxima for the bromide and iodide occur at ratios of 1·73 and 2·87 (0·0056 and 0·0044 molar in mercury, respectively). The specific conductances at the maxima for the three halides are chloride 17 $\times 10^{-5}$, bromide 7·3 $\times 10^{-5}$, and iodide 2·6 $\times 10^{-5}$. The relative affinities of halide ions for the methylmercury group have been shown, by partition measurements,[8] to be in the order $Cl^- < Br^- < I^-$.

At higher concentrations (*ca.* 0·1M), which can be realised using acetone as solvent, addition of triphenylphosphine to *m*-tolymercury chloride results in an immediate large increase in conductance as the reagents are mixed, followed after about ½ min. by a steady fall as dichlorobistriphenylphosphinemercury crystallises during about 6 min. Under similar conditions the dibromo-complex, from *m*-tolylmercury bromide, begins to precipitate after about 20 sec. and the conductance falls to a steady value after 2½ min. The high conductances observed immediately after the reagents were mixed are not necessarily due to the arylmercury salt, [*m*-tolyl $HgPPh_3$]X, since it is possible that the equilibria

$$m\text{-tolyl HgX} + PPh_3 \rightleftharpoons [m\text{-tolyl HgPPh}_3]X \rightleftharpoons m\text{-tolyl}_2\,Hg + (Ph_3P)_2HgX_2$$

are established rapidly. Solutions of bistertiary phosphine mercury(II) chloride and bromide complexes are themselves conducting, and the observed conductances could have been due to the presence of these complexes in ionised form and in supersaturated solution, as well as to the intermediate salt. Conductances did not fall to zero when crystallisation of the dihalogeno-complexes had ceased, and, again, the residual conductances could have been due to the small amount of dihalogeno-complex in solution as well as to the presence of *m*-tolyl(triphenylphosphine)mercury halide. However, the reversibility of the second stage of the above equilibrium is also indicated by the rise in conductance of a saturated methanolic solution of $(Ph_3P)_2HgCl_2$ from $3{\cdot}8 \times 10^{-5}$ to 10×10^{-5} ohm^{-1} $cm.^{-1}$ observed when a concentrated methanolic solution (1 mol.) of di-*m*-tolylmercury was added. Bis(triethylphosphine)mercury(II) chloride and bromide, which do not appear to have been described previously, are soluble in water, in which they are highly ionised. The molar conductance of the chloride in water, extrapolated to zero concentration (25°), is 200 $mole^{-1}$ $ohm,^{-1}$ $cm.^2$, a little less than might be expected for a 1 : 2 salt, presumably $[(Et_3P)_2Hg(H_2O)_2]Cl_2$.

EXPERIMENTAL

Combustion analyses were carried out by Mr. T. F. Holmes of this department. Transport of metallic mercury, from the combustion of organomercury compounds, into the magnesium perchlorate tube was prevented by the insertion of a tube containing asbestos wool on which gold had been deposited.

Infrared spectra were recorded using Grubb–Parsons prism-grating spectrometers, specimens generally being examined in the form of Nujol mulls. Ultraviolet spectra were recorded using an Optica CF4DR spectrometer.

Preparations involving tertiary phosphines and arsines, other than the triphenyl derivatives, were carried out under a nitrogen atmosphere.

Analytical data and general preparative data for most of the compounds described have already been given, and the following additional details concerning, for example, solvents used for preparation or crystallisation refer to compounds numbered in Tables 1 and 2. Compounds (I), (VI), (VIII), and (X): trimethylphosphine in diethyl ether was added to the mercurial in acetone; the salt crystallised when the filtrate was cooled in an acetone–CO_2 bath. Compounds (II) and (IV): from the components in acetone, or by precipitation from ether followed by crystallisation from chloroform–ether. Compound (III) crystallised when the components in acetone were cooled in an acetone–CO_2 bath. Compound (V): the phosphine (2 c.c.) was added to methylmercury iodide (3·2 g.) in acetone (40 c.c.), colourless needles being deposited soon after the reagents were mixed; it was also prepared by precipitation from ether followed by crystallisation from propan-2-ol. Compound (VII): addition of the phosphine (1 mol.) caused the complete solution of ethylmercury bromide (4·0 g.) in acetone (40 c.c.); the complex crystallised when the solution was concentrated to about 20 c.c. and cooled. Compound (IX): the phosphine (1·5 c.c.) was added to n-propylmercury chloride (2·2 g.) in ether (100 c.c.); evaporation of solvent under reduced pressure caused the separation of an oil which crystallised when the reaction mixture was shaken; the salt is extremely soluble in most polar solvents.

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[8] R. B. Simpson, *J. Amer. Chem. Soc.*, 1961, **83**, 4711.

Compound (XI): this was similarly prepared, and was also difficult to crystallise. Compound (XII): trimethylphosphine (0·6 g.) in ether (10 c.c.) was added to n-butylmercury iodide (1·9 g.) in acetone (70 c.c.); the clear solution was cooled to −20° and the cooling bath removed; the complex crystallised as fine colourless needles when the solution was shaken.

Compound (XIII): trimethylphosphine (slightly over 1 mol.) in ether–acetone was added to an equal volume of aqueous methylmercury perchlorate (from methylmercury chloride and silver perchlorate); the mixture became slightly warm and a small amount of mercury was precipitated; the complex crystallised as colourless needles when the solution, after filtration, was concentrated by evaporation under reduced pressure. Compound (XIV): this was prepared as (XIII) but the phosphine was not dissolved in a solvent. Compound (XV): aqueous methylmercury perchlorate was added to triphenylphosphine (1 mol.) in acetone; the complex, which became yellow when exposed to light for several hours, crystallised when the solvent was evaporated under reduced pressure [ν(Hg–Me) 523 cm.$^{-1}$ in Nujol]. Compound (XVI): triethylarsine (slightly over 1 mol.) in ether was added to an equal volume of methylmercury perchlorate in a mixture of water and acetone; the complex crystallised when about half of the solvent had been removed by evaporation under reduced pressure. Compound (XVII): this was precipitated when aqueous methylmercury perchlorate was added to triphenylarsine (1 mol.) in acetone. Compound (XVIII): addition of triethylphosphine (a slight excess over 1 mol.) to an aqueous-methanolic solution of methylmercury tetrafluoroborate (from methylmercury bromide and silver tetrafluoroborate) caused heat evolution and the deposition of a little mercury; the reaction mixture was filtered and the filtrate evporated to dryness under reduced pressure; the residue, which was very soluble in water, was dissolved in propan-2-ol and the complex crystallised when the solution was cooled to about −100° [Found: *M* (cryoscopically in water), 215, 218, 212. $C_7H_{18}BF_4HgP$ requires *M*, 421, or 210 for complete dissociation]. Compound (XIX): slow addition of aqueous ammonium tetrathiocyanatodiamminechromate(III) (reineckate) to methylmercury chloride in aqueous acetone gave a pink microcrystalline precipitate of (XIX), which is insoluble in water and sparingly soluble in acetone [ν(Hg–Me) 532 cm.$^{-1}$ in Nujol]. Compound (XX): this was precipitated when aqueous ammonium reineckate was added to methanolic (II); it is insoluble in water and in ether, and crystallised as red needles from acetone–water [ν(Hg–Me) 530 cm.$^{-1}$ in KBr]. Compound (XXI): this was prepared by adding the reineckate (XIX) to a solution of triphenylphosphine (1 mol.) in acetone with vigorous stirring; the suspended reineckate quickly dissolved, giving a deep purple solution which yielded the phosphine complex when concentrated; recrystallisation from aqueous acetone gave *methyl(triphenylphosphine)mercury tetrathiocyanatodiamminechromate*(III) as red needles containing 1 mol. of acetone of crystallisation, $[MeHgPPh_3][Cr(NH_3)_2(SCN)_4]Me_2CO$ (Found: C, 36·3; H, 3·7. $C_{28}H_{30}CrHgN_6OPS_4$ requires C, 36·55; H, 3·5%); the presence of acetone resulted in an infrared absorption at 1701 cm.$^{-1}$, which disappeared after the salt had been kept for 24 hr. at 60° *in vacuo*; the red needles thereby turned into a pink powder.

Phenyl(triethylphosphine)mercury Nitrate, $[PhHgPEt_3]NO_3$.—Triethylphosphine (1·2 c.c.) was added to phenylmercury nitrate (2·7 g.; from silver nitrate and phenylmercury chloride) in aqueous acetone (100 c.c.). After concentration to 20 c.c. the *complex* crystallised as long colourless needles, m. p. 120—121°, when the solution cooled (Found: C, 31·5; H, 4·7; NO_3, 13·5. $C_{12}H_{20}HgNO_3P$ requires C, 31·5; H, 4·4; NO_3, 13·5%). In methanol at 25°, $\Lambda^0 = 86·6$ ohm^{-1} mole^{-1} cm.^{2}.

Sodium bromide (0·1 g.; slightly more than 1 mol.) in water (10 c.c.) was added to a solution of the nitrate (0·43 g.) in acetone (30 c.c.). Next day the mixture was concentrated to 20 c.c., and, when cold, had deposited diphenylmercury (0·13 g., 78%, identified by mixed m. p. and infrared spectrum). The filtrate was evaporated to dryness under reduced pressure, and acetone (15 c.c.) added to the residue. Sodium nitrate (0·06 g., m. p. 305°) was separated by filtration, and evaporation of the filtrate yielded dibromobistriethylphosphinemercury (0·19 g., 68%), m. p. 158°, infrared spectrum identical with that of an authentic specimen.

Disproportionation of Methylmercury Halides.—Triphenylphosphine (2·50 g.) in benzene (10 c.c.) was added to methylmercury chloride (2·39 g., 1 mol.) in benzene (20 c.c.) and the mixture boiled with reflux for 20 hr. Dichlorobistriphenylphosphinemercury (1·52 g., 40%), m. p. 276—280° (lit.,[9] 273° with decomp.), was separated from the cooled mixture. The filtrate was distilled to dryness, benzene (10 c.c.) added to the solid residue, and the mixture again

[9] R. C. Evans, F. G. Mann, H. S. Peiser, and D. Purdie, *J.*, 1940, 1209.

distilled to dryness. The residue (2·205 g.), m. p. 274—279°, consisted of more of the dichloro-compex, and the dimethylmercury content of the combined distillates was determined by reaction with iodine and titration of excess with sodium thiosulphate. The total recovery of dichloro-complex was 98·2%, that of dimethylmercury 85·3%. Similar reactions with methylmercury bromide and iodide resulted in 99·9 and 99·7% yields of the dihalogeno-complexes, and 90·7 and 89·4% yields of dimethylmercury.

Reactions with Triethylphosphine.—When solutions of methylmercury chloride and triethylphosphine (1 mol.) in acetone were mixed and immediately concentrated to crystallisation, small colourless crystals of the salt (II) were deposited, m. p. 84—85° (decomp.). When a similar reaction mixture was allowed to remain for several days at room temperature, large colourless prisms of *dichlorobistriethylphosphinemercury*, m. p. 161° (decomp.), were slowly deposited [Found: C, 28·45; H, 6·0; Cl, 13·85; Hg, 38·7%; *M* (cryoscopically in 1·8, 2·7, 4·7, 6·0 wt. % water), 296, 315, 352, 399. $C_{12}H_{30}Cl_2HgP_2$ requires C, 28·4; H, 5·95; Cl, 14·0; Hg, 39·5%; *M*, 508]. The infrared spectrum corresponded to that of co-ordinated triethylphosphine, but contained two weak bands at 3413 and 1649 cm.$^{-1}$, suggesting the presence of a trace of water which was not revealed by elemental analysis.

A similar reaction between methylmercury bromide and triethylphosphine yielded large prismatic crystals of *dibromobistriethylphosphinemercury*, m. p. 155° (decomp.) (Found: C, 24·0; H, 5·1. $C_{12}H_{30}Br_2HgP_2$ requires C, 24·15; H, 5·1%). The dibromo-complex was also formed by slow crystallisation from solutions of triethylphosphine and ethyl-, n-propyl-, and n-butylmercury bromide in acetone.

Thermal Decomposition of Methyl(phenyldimethylphosphine)mercury Iodide (V).—The salt (1·1332 g.) contained in a 20-c.c. 2-neck flask fitted with a sintered disc, and attached to a vacuum line suitable for the quantitative manipulation of volatile substances, was heated to 80°. After ½ hr. the solid salt had liquefied to a viscous melt which bubbled as dimethylmercury was slowly evolved for a further ½ hr. The residue (0·8809 g. after a further 4 hr. heating at 80°) solidified overnight at room temperature and consisted mainly of di-iodobis-(phenyldimethylphosphine)mercury, m. p. 120—121° (from methanol), identified by mixed m. p. 120—121° and infrared spectrum identical with that of an authentic specimen.[10]

The volatile matter was condensed on an excess of methyl iodide, and after formation of phosphonium iodide, from the small amount of phenyldimethylphosphine that had been present, was complete, the excess of methyl iodide together with dimethylmercury was condensed into 0·1N-iodine solution and allowed to remain overnight. Next morning the mixture was gently boiled with reflux, and excess iodine determined. The dimethylmercury amounted to 0·2303 g. (85% of the theoretical), and the weight of phenyltrimethylphosphonium iodide was 0·0436 g., corresponding to 0·0215 g. tertiary phosphine.

Disproportionation of Arylmercury Halides.—(a) *Triethylphosphine.* The phosphine (1·7 g.) was added to a solution of *m*-tolylmercury chloride (4·18 g.) in acetone (160 c.c.), and the volume of solution reduced to 20 c.c. by evaporation under reduced pressure. Dichlorobistriethylphosphinemercury (1·1 g., 34%) was separated by filtration (Found: C, 28·9; H, 5·9; Hg, 39·0. Calc. for $C_{12}H_{30}Cl_2HgP_2$: C, 28·4; H, 5·95; Hg, 39·5%). After addition of water to the filtrate, followed by concentration and extraction with ether, di-*m*-tolymercury was recovered (2·22 g., 90%), m. p. 98—100° (mixed m. p. 98—101°).

(b) *Triphenylphosphine.* The phosphine (2·36 g.) in acetone (20 c.c.) was added to a solution of *m*-tolylmercury chloride (2·94 g., 1 mol.) in hot acetone (60 c.c.). Crystallisation began after about ½ min. After ½ hr. at room temperature dichlorobistriphenylphosphinemercury (2·14 g., 59·8%), m. p. 274—276° (decomp.) [lit.,[9] 273° (decomp.)], was separated. Solvent was distilled from the filtrate, and the di-*m*-tolylmercury (1·57 g., 91·3%), m. p. 99—101°, mixed m. p. 99—101°, was separated by ether extraction, leaving a residue of more of the dichloro-complex, m. p. 274—278° (1·20 g.). In all 3·34 g. (93·4%) of dichloro-complex was recovered.

Dinitratobistriphenylphosphinemercury, $(Ph_3P)_2Hg(NO_3)_2$.—Triphenylphosphine (1·4 g.) in acetone (20 c.c.) was added to a solution of phenylmercury nitrate (1·8 g., 1 mol.) in acetone (65 c.c.) and the mixture allowed to remain at room temperature for 1 week. The colourless prisms which slowly formed were collected (0·70 g., 22%), m. p. 190° (Found: C, 50·5; H, 3·6. $C_{36}H_{30}HgN_2O_6P_2$ requires C, 50·9; H, 3·6%). In another experiment, the phosphine (1·4 g., 1 mol.) in acetone (10 c.c.) was added to phenylmercury nitrate (1·8 g.) in acetone (65 c.c.). The solution was immediately concentrated to a volume of about 50 c.c. by evaporation under

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[10] R. C. Cass, G. E. Coates, and R. G. Hayter, *J.*, 1955, 4007.

reduced pressure, when the dinitrato-complex (0·6 g., 26%) crystallised (Found: C, 50·6; H, 3·7%), infrared spectrum identical with that of the earlier preparation.

Compound (XXI).—This crystallised when pyridine (1 c.c., an excess over 1 mol.) was added to methylmercury perchlorate (3 g.) in acetone–water (9 : 1; 25 c.c.). The infrared spectrum (Nujol) included a strong sharp band at 423 cm.$^{-1}$ characteristic of co-ordinated pyridine, and a weak absorption at 538 cm.$^{-1}$ due to ν(Hg–Me).

Methyl(bipyridyl)mercury Nitrate.—This was precipitated when bipyridyl (1 mol.) was added to methylmercury nitrate, both dissolved in acetone. It crystallised from methanol or ethanol as long fine colourless needles, m. p. 200—201° (decomp.) (Found: C, 30·4; H, 2·55; NO_3, 14·5. $C_{11}H_{11}HgN_3O_3$ requires C, 30·45; H, 2·55; NO_3, 14·3%), ν(Hg–Me), 545 cm.$^{-1}$ in Nujol.

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