

NOTE

ORGANOMERCURY COMPOUNDS

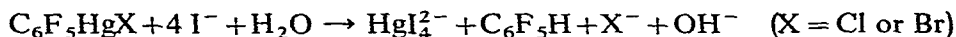
VI*. DISPROPORTIONATION REACTIONS OF (PENTAHALOPHENYL)-MERCURIC HALIDES WITH HALIDE IONS

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A preliminary report has been given of the cleavage reactions of (pentafluorophenyl)mercury compounds with iodide ions in aqueous ethanol^{2, **}. For the cleavage of (pentafluorophenyl)mercuric chloride or bromide,

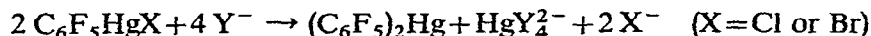


there are two possible reaction paths; (a) direct cleavage of the (pentafluorophenyl)-mercuric halide, or (b) disproportionation



followed by the known² iodide cleavage of bis(pentafluorophenyl)mercury. To distinguish between these routes, reactions of (pentafluorophenyl)mercuric chloride and bromide with iodide ions using milder conditions than those needed for cleavage have been investigated, and the study has been extended to reactions with other halide ions and to analogous reactions of (pentachlorophenyl)mercuric chloride. Disproportionation reactions of these (pentahalophenyl)mercuric halides with halide ions have not previously been studied. However, related reactions of other organomercuric halides are well known^{3,4}.

The reactions studied and the products obtained are given in Table 1. Tetrahalogenomercurate(II) ions were isolated as the methyltriphenylarsonium salts. (Pentafluorophenyl)mercuric chloride and bromide undergo disproportionation with halide ions



in aqueous ethanol at room temperature when Y = Br, or I (Table 1, reactions 1-4),

* For Part V see ref. 1.

** In this communication, the entries in the column of Table 1 headed NaI (mmole) are incorrectly given, and should read successively 13, 33, 33, 33, 8.3, 17, 17. However, the yields in the reactions are only marginally affected (ca. 5%) by using the incorrect quantities previously given.

TABLE 1

DISPROPORTIONATION REACTIONS OF (PENTAHALOPHENYL)MERCURIC HALIDES WITH HALIDE IONS IN AQUEOUS ETHANOL^a

No.	Compound	Mmole	Alkali metal halide	Mmole	Reaction time (min)	Yield of (C ₆ F ₅) ₂ Hg or (C ₆ Cl ₅) ₂ Hg (%)	Yield of (MePh ₃ As) ₂ HgY ₄ ^b (%)
1	C ₆ F ₅ HgCl	0.250	NaI	8.33	< 5	85	87
2	C ₆ F ₅ HgBr	0.250	NaI	8.33	< 5	93	92
3	C ₆ F ₅ HgCl	0.252	LiBr	14.7	< 5	84	60
4	C ₆ F ₅ HgBr	0.251	LiBr	14.7	< 5	89	84
5	C ₆ F ₅ HgCl	0.250	LiCl	14.9	< 5	trace	not obtained
6	C ₆ F ₅ HgBr	0.252	LiCl	14.9	< 5	trace	
7	C ₆ F ₅ HgCl	0.251	LiCl	14.9	5	49 ^c	
8	C ₆ F ₅ HgBr	0.247	LiCl	14.9	5	53 ^c	
9	C ₆ Cl ₅ HgCl	0.253	NaI	33.3	60	86	75
10	C ₆ Cl ₅ HgCl	0.262	LiBr	49.0	120	25	27
11	C ₆ Cl ₅ HgCl	0.253	LiCl	117.9	300	65	76

^a Reactions 1–8 in 10 ml aqueous ethanol, 1 : 4 (v/v). Reactions 9–11 in 10 ml aqueous ethanol, 1 : 1 (v/v). Reactions 1–6 at room temperature (*ca.* 22°). Reactions 7–11 at b.p. of solvent. ^b Y = halogen of the alkali metal halide, except for reaction 11 in which the product (HgCl₂²⁻) was converted to HgI₂²⁻ for convenience in isolation (see *experimental*). ^c Yield of crude product *ca.* 70% in each case (see *experimental*).

but little reaction is observed when Y = Cl*. Partial halide exchange occurs between (pentafluorophenyl)mercuric bromide and chloride ions, (pentafluorophenyl)mercuric chloride being detected in the product. However, disproportionation of (pentafluorophenyl)mercuric halides by chloride ions is readily induced on heating (Table 1, reactions 5 and 6). No cleavage of pentafluorophenyl groups occurs in the reactions, since base formation, which accompanies cleavage (see above), was not observed. Thus iodide cleavage of (pentafluorophenyl)mercuric halides takes place by route (*b*) in which disproportionation precedes cleavage. (Pentachlorophenyl)mercuric chloride undergoes similar disproportionation reactions with halide ions (Table 1, reactions 9–11). Negligible cleavage of pentachlorophenyl groups was observed (see *experimental*). Since both (pentachlorophenyl)mercuric chloride and bis(pentachlorophenyl)mercury have low solubilities in aqueous ethanol, the reactions could not be carried out using conditions similar to those for the (pentafluorophenyl)mercuric halides. An attempt to prepare (pentachlorophenyl)mercuric bromide was unsuccessful. Other organomercuric halides having highly electronegative organic groups, *e.g.* C₆F₅HgI⁵ and CCl₂=CClHgI⁺ have not been isolated owing to ready disproportionation into bisorganomercurial and mercuric iodide.

Disproportionation of (pentafluorophenyl)mercuric halides with iodide or bromide ions proceeds more readily than with chloride ions, and decomposition of (pentachlorophenyl)mercuric chloride proceeds more readily with iodide ions than bromide ions (Table 1, reactions 9 and 10). The overall reactivity I⁻ > Br⁻ > Cl⁻ can

* It is possible that both C₆F₅HgX and (C₆F₅)₂Hg form anionic complexes in the presence of excess halide ions, but it obviously does not prevent isolation of the disproportionation products. Qualitative evidence that (C₆F₅)₂Hg forms complexes with iodide and bromide has been obtained and this is being further studied.

be attributed to the relative stabilities⁶ $\text{HgI}_4^{2-} > \text{HgBr}_4^{2-} > \text{HgCl}_4^{2-}$ of the tetrahalogenomercurate(II) products. Since the electronegativity of the pentafluorophenyl group is between the values for chlorine and bromine⁷, the ready disproportionation of the (pentafluorophenyl)mercuric halides is consistent with the observation⁴ that the stability of unsymmetrical mercurials towards disproportionation decreases as the electronegativity difference between the substituents decreases.

EXPERIMENTAL

Infrared spectra

Spectra (4000–650 cm^{-1}) of compounds as Nujol and hexachlorobutadiene mulls were recorded with Perkin–Elmer 257 and Unicam SP 200 spectrophotometers. Far infrared spectra (400–220 cm^{-1}) of Nujol mulls between polyethylene plates were recorded with a Beckman IR 7 instrument.

Reagents and independent syntheses of reaction products

(Pentafluorophenyl)mercuric chloride⁸, (pentafluorophenyl)mercuric bromide⁵, (pentachlorophenyl)mercuric chloride⁹, bis(pentafluorophenyl)mercury⁵, bis(pentachlorophenyl)mercury⁹, and bis(methyltriphenylarsonium) tetraiodomercurate(II)¹⁰ were prepared by the reported methods. An attempt to prepare (pentachlorophenyl)mercuric bromide by reaction of equimolar amounts of bis(pentachlorophenyl)mercury and mercuric bromide in nitrobenzene (as for $\text{C}_6\text{Cl}_5\text{HgCl}$)⁹ was unsuccessful, the original mercurial being recovered.

Bis(methyltriphenylarsonium) tetrabromomercurate(II). On addition of a solution of methyltriphenylarsonium bromide (0.435 g, 1.09 mmole) in 5 ml aqueous ethanol (1:4, v/v) to a solution of mercuric bromide (0.180 g, 0.499 mmole) and lithium bromide (2.66 g, 30.2 mmole) in 5 ml aqueous ethanol, the required compound was precipitated as a white powder (0.499 g, 0.429 mmole, 86%), m.p. 137–138°. (Found: C, 38.9; H, 3.4. $\text{C}_{38}\text{H}_{36}\text{As}_2\text{Br}_4\text{Hg}$ calcd.: C, 39.3; H, 3.1 %.) Infrared absorption (2000–650 cm^{-1}): 1632m, 1580w, 1488m, 1442s, 1409w, 1345w, 1318w, 1193w, 1165w, 1088s, 1074w, 1025w, 1000s, 930w, 894vs, 751vs, 694s, and 681m cm^{-1} . It was often difficult to initiate precipitation from more dilute solutions and deposition of the complex was often slow. The identity of the complex was confirmed by conversion to the corresponding tetraiodomercurate complex, m.p. 166°, mixed m.p. 166° (lit.¹⁰ m.p. 167°) on refluxing with methyl iodide in acetone.

Disproportionation reactions

Identification of products. Bis(pentafluorophenyl)mercury and bis(methyltriphenylarsonium) tetraiodomercurate(II) and tetrabromomercurate(II) were identified by their infrared spectra, melting points, and mixed melting points with the authentic compounds. As the infrared spectrum (4000–400 cm^{-1}) of bis(pentachlorophenyl)mercury is very similar to that of (pentachlorophenyl)mercuric chloride¹¹, the compounds were distinguished by their far infrared spectra (400–300 cm^{-1}). The spectra (400–220 cm^{-1}) of the authentic compounds are: $(\text{C}_6\text{Cl}_5)_2\text{Hg}$: 353w, br, 343s, and 240m cm^{-1} ; $\text{C}_6\text{Cl}_5\text{HgCl}$: 357vs, br $[\nu(\text{Hg}-\text{Cl})]$, 348s, sh, 339sh, 330s, and 227w(?) cm^{-1} .

Reactions 1–8 (Table 1). Solutions of the (pentafluorophenyl)mercuric halide

and the metal halide in aqueous ethanol (1 : 4, v/v) were mixed (total volume, 10 ml) and allowed to react (for conditions see Table 1). Water (15 ml) was then added precipitating bis(pentafluorophenyl)mercury (reactions 1–4, 7 and 8; the products of the last two reactions had to be crystallised from aqueous methanol before satisfactory purity was achieved), crude (pentafluorophenyl)mercuric chloride (reaction 5), or a mixture of (pentafluorophenyl)mercury compounds (reaction 6). Crystallisation of the product of reaction 5 from petrol (b.p. 40–60°) gave successively (pentafluorophenyl)mercuric chloride (0.022 g, 0.055 mmole, 22 %), m.p. 162–164°, lit.⁵ m.p. 165° (infrared identification), crude C₆F₅HgCl, and crude bis(pentafluorophenyl)mercury (ca. 0.005 g; infrared identification). The product from reaction 6 on similar treatment gave firstly white crystals (0.022 g), m.p. 153–154°, identified by the far infrared spectrum as a mixture of (pentafluorophenyl)mercuric chloride [$\nu(\text{Hg}-\text{Cl})$ 341 cm⁻¹; lit.⁸ 344 cm⁻¹] and (pentafluorophenyl)mercuric bromide [$\nu(\text{Hg}-\text{Br})$ 246 cm⁻¹; lit.⁸ 246 cm⁻¹], and ultimately crude bis(pentafluorophenyl)mercury (ca. 0.004 g; infrared identification). After collection of bis(pentafluorophenyl)mercury (reactions 1–4), the filtrate was added to a solution of methyltriphenylarsonium iodide (reactions 1 and 2) or bromide (reactions 3 and 4) (0.250–0.254 mmole) in 5 ml of aqueous ethanol, precipitating the appropriate bis(methyltriphenylarsonium) tetrahalogenomercurate(II) complex. Other products of reactions 5–8 were not studied.

Reactions 9–11 (Table 1). A stirred suspension of (pentachlorophenyl)mercuric chloride in a solution of the alkali metal halide in 10 ml aqueous ethanol (1 : 1, v/v) was heated under reflux. After reaction the resultant suspension was filtered off, and was identified as bis(pentachlorophenyl)mercury (reaction 9) or a mixture of this mercurial and (pentachlorophenyl)mercuric chloride (reactions 10 and 11). After washing the products of reactions 10 and 11 with boiling benzene, bis(pentachlorophenyl)mercury was obtained. The tetrahalogenomercurate(II) products from reactions 9 and 10 were isolated as for reactions 1–4. Very slow precipitation of the methyltriphenylarsonium derivatives was observed. The aqueous ethanol solution of tetrachloromercurate complex from reaction 11 was treated with methyl iodide (50 ml) and the resulting suspension was stirred and refluxed for 2 h. After reaction, the resultant tetraiodomercurate complex was isolated as before. All reaction mixtures gave a negative test for alkali formation, except for reaction 9 in which a trace of base (< 4% for the reaction, $\text{C}_6\text{Cl}_5\text{HgCl} + 4 \text{I}^- + \text{H}_2\text{O} \rightarrow \text{HgI}_4^{2-} + \text{C}_6\text{Cl}_5\text{H} + \text{Cl}^- + \text{OH}^-$) was obtained.

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