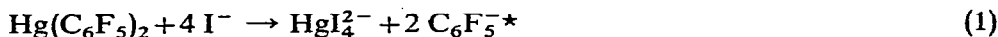


PRELIMINARY NOTE

Facile cleavage of pentafluorophenylmercury compounds

Bis(pentafluorophenyl)mercury has high thermal stability, can be recrystallised unchanged from concentrated sulphuric acid, and is only slowly cleaved by bromine in hot carbon tetrachloride¹. It has now been found that this compound and other pentafluorophenylmercurials are readily cleaved by iodide ions in boiling aqueous ethanol.

On addition of a solution of methyltriphenylarsonium iodide in 95% ethanol to a solution of bis(pentafluorophenyl)mercury and sodium iodide (mole ratio *ca.* 1:24) in the same solvent in an attempt to precipitate $[\text{MePh}_3\text{As}]_2[(\text{C}_6\text{F}_5)_2\text{HgI}_2]$ (*cf.* preparations of halogenoperfluoroalkylmercurate(II) complexes²), no reaction was observed. However, on boiling, the solution became yellow, and on cooling bis(methyltriphenylarsonium)tetraiodomercurate(II) crystallised, m.p. 167.5° (lit. m.p. 167°³; 175°⁴) (Found: C, 33.4; H, 2.9. $\text{C}_{38}\text{H}_{36}\text{As}_2\text{HgI}_4$ calcd.: C, 33.8; H, 2.7%), the infrared spectrum being in good agreement with reported data⁵. The cleavage reaction may be formulated:



Pentafluorobenzene was detected by infrared spectroscopy in the distillate from a typical reaction and the solution became alkaline, hence the formation of C_6F_5^- may be inferred.

Further experiments to establish yields and their variation with reaction conditions were carried out and details of some of these are given in Table 1. In all

TABLE 1
 REACTIONS OF PENTAFLUOROPHENYLMERCURY COMPOUNDS WITH IODIDE

Compound	mmole	NaI (mmole)	Solution volume (ml)	Reaction time (min)	Yield ^a ($[\text{MePh}_3\text{As}]_2\text{HgI}_4$) (%)	m.p. (°C)	Yield base (%)
1 $(\text{C}_6\text{F}_5)_2\text{Hg}$	0.50	12	15	5 ^b	50	165	40
2 $(\text{C}_6\text{F}_5)_2\text{Hg}$	0.50	29	25	5 ^b	70	166–166.5	52
3 $(\text{C}_6\text{F}_5)_2\text{Hg}$	0.50	29	20	10 ^c	78	165–166	61
4 $(\text{C}_6\text{F}_5)_2\text{Hg}$	0.50	29	20	5 ^{c,d}	97	166–167	
5 $(\text{C}_6\text{F}_5)_2\text{Hg}$ bipy	0.125	7.4	10	10 ^c	74	166	67
6 $\text{C}_6\text{F}_5\text{HgCl}$	0.25	15	10	10 ^c	85	166–166.5	75
7 $\text{C}_6\text{F}_5\text{HgBr}$	0.25	15	10	10 ^c	90	166–167	75

^a The identity of all products was confirmed by IR spectroscopy. ^b In 95% ethanol. ^c In aqueous ethanol, 1:4, v/v. ^d 1 ml of 0.991 M HCl added.

* An analogous carbanion displacement is suggested as the first stage in the reaction of phenyltrichloromethylmercury with iodide⁶.

reactions the solution of bis(pentafluorophenyl)mercury and sodium iodide was boiled for the reaction time, was cooled and filtered, then a solution of sufficient methyltriphenylarsonium iodide to precipitate all mercury as $(\text{MePh}_3\text{As})_2\text{HgI}_4$ was added. (An independent experiment, using a solution of mercuric iodide in ethanolic sodium iodide under similar conditions, showed the precipitation procedure gave yields of at least 92%.) The complex was filtered off, and the filtrate was titrated with hydrochloric acid. Yields of tetraiodomercurate complex were consistently higher than those of base. Explanations are possible based on either alternative decomposition of the carbanion or further reaction of base. Extended heating times caused deposition of small amounts of mercury and gave negligible further reaction. For example, after reaction (2), the neutralised filtrate was boiled for 30 min, giving a further yield of base of only 6%. A near quantitative yield of $(\text{MePh}_3\text{As})_2\text{HgI}_4$ was obtained when the cleavage reaction was carried out in the presence of sufficient acid to neutralise the liberated base (Table 1). From reaction of bis(pentafluorophenyl)mercury with HCl for 10 min under similar conditions, the mercurial was recovered in 89% yield, hence acid cleavage of the mercurial does not contribute significantly to the reaction using acidified iodide. Reaction of bis(pentafluorophenyl)-2,2'-bipyridylmercury, pentafluorophenylmercuric chloride, and pentafluorophenylmercuric bromide with iodide also resulted in cleavage of the pentafluorophenyl group (Table 1), but bis(pentachlorophenyl)mercury failed to react in 7 h probably owing to its negligible solubility.

This study is now being extended to reactions of other halide ions with pentafluorophenylmercurials, and preliminary experiments⁷ indicate that bis(pentafluorophenyl)thallium(III) compounds are also cleaved by iodide. Pentafluorophenyltin compounds undergo cleavage with fluoride in anhydrous ethanol, but halide catalysed hydrolysis occurs in aqueous ethanol⁸.

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