ORGANOTHALLIUM COMPOUNDS
V*. REACTIONS OF BIS(PENTAFLUOROPHENYL)THALLIUM(III) COMPOUNDS WITH IODIDE IONS

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SUMMARY

Bis(pentafluorophenyl)thallium(III) compounds, $(C_6F_5)_2TlX$ (X = Br, Cl, $\frac{1}{2}SO_4$, OAc, etc.), are decomposed by iodide ions in boiling aqueous ethanol, aqueous methanol, or water with the formation of thallous iodide and pentafluorobenzene. Analogous reactions are possible with bromide or cyanide ions. However, reaction with acidified iodide or bromide ions gives the corresponding tetrahalothallate(III) complex. The formation of thallous iodide in reactions without added acid is attributed to intermediate formation of the tetraiodothallate(III) complex and base, which then interact to give thallous iodide. The ready decomposition of $MTlI_4$ (M = Bu_4N or $MePh_3As$) complexes by base to give thallous iodide has been demonstrated. Under suitable conditions, cleavage of bromobis(pentafluorophenyl)thallium(III) with iodide ions gives the triiodopentafluorophenylthallate(III) complex, which has been isolated as the tetrabutylammonium or the methyltriphenylarsonium salt. The new compounds $(C_6F_5)_2TlX$ (X = I or CN) have been prepared by metathesis between sulphatodi[bis(pentafluorophenyl)thallium(III)] and iodide or cyanide ions in water. They are considered to be dimeric with bridging iodide or cyanide groups.

INTRODUCTION

It has recently been shown that pentafluorophenylmercury compounds are decomposed by iodide ions in aqueous ethanol[2], *e.g.*

$$(C_6F_5)_2Hg + 4\,I^- + 2\,H_2O \rightarrow 2\,C_6F_5H + HgI_4^{2-} + 2\,OH^- \qquad (1)$$
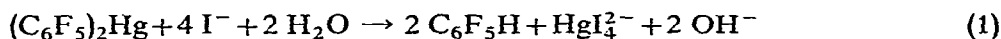
and related reactions of trifluoromethyl-[3] and trichloromethyl-mercury[4] compounds are known. Pentafluorophenyltin compounds are also decomposed in the presence of halide ions[5]: potassium fluoride reacts with pentafluorophenyltrimethyltin in anhydrous ethanol to give trimethyltin fluoride and pentafluorobenzene, and pentafluorophenyltin compounds undergo halide catalysed hydrolysis in aqueous ethanol. This paper reports an investigation of the reactions of bis(pentafluorophenyl)thallium(III) compounds with iodide ions and of bromobis(pentafluorophenyl)thallium-(III) with bromide and cyanide ions. It has previously been shown that the compounds

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* For Part IV see ref. 1.

TABLE 1

CLEAVAGE REACTIONS OF BROMO- AND CHLORO-BIS(PENTAFLUOROPHENYL)THALLIUM(III) WITH IODIDE IONS[a]

Solvents (1) aqueous ethanol, 1/1(v/v); (2) aqueous methanol, 1/1(v/v); (3) water.

Compound	mmole	Solvent	Reaction time (Reflux, h)	Yield			Further reaction time[c] (Room temp., days)	Final yield (%TlI)
				$(\%TlI)^b$	$(\%C_6F_5H)$	$(\%C_6F_5I)$		
$(C_6F_5)_2TlBr$	0.405	(1)	1.25	64			7	85
$(C_6F_5)_2TlBr$	0.255	(1)	4.75	94			2	100
$(C_6F_5)_2TlBr$	0.510	(1)	4.75		77	ca. 5[d]		
$(C_6F_5)_2TlBr$	0.255	(2)	2.75	92		ca. 5[d]	2	99
$(C_6F_5)_2TlBr$	0.510	(2)	2.75	93	77			
$(C_6F_5)_2TlBr$	0.239	(3)	1.00	97				
$(C_6F_5)_2TlBr$	0.766	(3)	3.00		60			
$(C_6F_5)_2TlBr$	0.510	(3)	3.00			ca. 9[d]		
$(C_6F_5)_2TlCl$	0.283	(1)	1.25	67			6	91
$(C_6F_5)_2TlCl$	0.291	(1)	4.75	87			4	96
$(C_6F_5)_2TlCl$	0.282	(2)	2.75	90			2	100

[a] All reactions with 67 mmole of NaI in 10 ml solvent. [b] Although TlI is slightly soluble[7], this is unlikely to have a significant effect on the yields, since the solubility would be greatly lowered by the excess iodide ions present. [c] The filtrates after initial isolation of TlI deposited further product on standing. [d] Although the absolute yields are approximate, the yield for the reaction in aqueous solution is definitely the highest.

$(C_6F_5)_2TlX$ ($X = Br$ or Cl) form the complexes $(C_6F_5)_2TlX_2^-$ with bromide or chloride ions, and an unsuccessful attempt to prepare $(C_6F_5)_2TlI$ by reaction of $(C_6F_5)_2TlBr$ with sodium iodide in acetone has been reported[6].

RESULTS AND DISCUSSION

A. Reaction with excess iodide ions ($I^-/Tl > 50/1$)

Bromo- and chloro-bis(pentafluorophenyl)thallium(III) are decomposed by iodide ions in boiling aqueous ethanol, aqueous methanol, or water with the formation of thallous iodide and pentafluorobenzene. A small amount of iodopentafluorobenzene is also obtained. Details of representative reactions are given in Table 1.

$$(C_6F_5)_2TlX \xrightarrow{I^-} TlI + C_6F_5H \qquad (2)$$

Use of extended reaction times gives near quantitative yields of thallous iodide. Similar reactions or qualitative tests have shown that other bis(pentafluorophenyl)-thallium(III) compounds, $(C_6F_5)_2TlX$ ($X = F$, I, NO_3, $\frac{1}{2} SO_4$, CN, OAc, OCOPh, or $OCOC_6F_5$) are also converted into thallous iodide by iodide ions in aqueous ethanol. Bromobis(pentafluorophenyl)thallium(III) undergoes a similar decomposition with bromide or cyanide ions, thallous bromide or thallous cyanide being formed. In the absence of added iodide, bromide, or cyanide ions, decomposition of $(C_6F_5)_2TlBr$ in boiling aqueous ethanol is slight (see Experimental).

When the reactions are carried out in the presence of acid ($Tl/HCl \simeq 1/2$), little reduction to the thallous state occurs. Thus bromobis(pentafluorophenyl)-thallium(III) reacts with acidified iodide to give the tetraiodothallate(III) complex, which may be precipitated as the tetrabutylammonium or the methyltriphenylarsonium salt.

$$(C_6F_5)_2TlBr \xrightarrow[HCl]{I^-} TlI_4^- + C_6F_5H \qquad (3)$$

An analogous reaction is observed with acidified bromide ions.

To establish the relation between reactions (2) and (3), the decomposition of the tetraiodothallate(III) complex has been investigated*. It is readily converted into thallous iodide in near quantitative yield on reaction with base in boiling aqueous ethanol.

$$TlI_4^- + 2\,OH^- \rightarrow TlI + 2\,I^- + OI^- + H_2O \qquad (4)$$
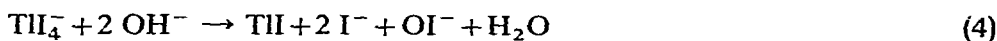
Further information comes from a study of the decomposition of tetrabutylammonium and methyltriphenylarsonium tetraiodothallate(III) and tetrabutylammonium tetrabromothallate(III) (Table 2). Because of the low solubilities of the complexes in aqueous ethanol, aqueous acetone was used as solvent. The results show that the tetraiodothallate(III)complex is only slightly decomposed to thallous iodide in neutral or acid solution, but is virtually quantitatively decomposed in basic solution. The tetrabromothallate(III) complex is similarly decomposed in basic iodide solution.

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* The reaction between Tl^{3+} and iodide ions can result either in complex formation, or in reduction to the thallous state, iodine also being formed[8,9]. Depending on the conditions, TlI_4^-, TlI, Tl_3I_4, or Tl^II_3 may be obtained.

TABLE 2

DECOMPOSITION REACTIONS OF TETRAHALOTHALLATE(III) COMPLEXES IN AQUEOUS ACETONE

Compound	mmole	Reagents NaI (mmole)		Solvent		Reaction time (h)	Yield (% TlI)
				% acetone (by volume)	Volume (ml)		
Bu_4NTlI_4	0.355	67	—	65	30	0.25^e	3
Bu_4NTlI_4	0.343	67	HCl^a	65	30	0.25^e	—
Bu_4NTlI_4	0.314	67	$NaOH^b$	65	30	0.25^e	100
$Bu_4NTlIBr_4$	0.275	67	$NaOH^b$	60	25	0.75^e	100
$MePh_3AsTlI_4$	0.398	—	—	33	30	48^f	30
$MePh_3AsTlI_4$	0.384	—	HCl^c	50	30	48^f	27
$MePh_3AsTlI_4$	0.236	67	$NaOH^b$	^{d}	25	48^f	98

^{a} $Tl/H^+ \simeq 1/2.$ ^{b} $Tl/OH \simeq 1/2.$ ^{c} $Tl/H^+ \simeq 1/3.$ ^{d} Solvent: water/ethanol/acetone (1/1/3, by volume). ^{e} Heated under reflux. ^{f} At room temperature.

(The reaction proceeds via TlI_4^-, since the conversion of $TlBr_4^-$ to TlI_4^- by reaction with iodide ions is known[10]).

Thus, the formation of thallous iodide [reaction (2)] is readily explained if cleavage of bis(pentafluorophenyl)thallium(III) compounds in the absence of acid gives the tetraiodothallate(III) complex and base [cf. reaction (1)],

$$(C_6F_5)_2TlX + 4\ I^- + 2\ H_2O \rightarrow 2\ C_6F_5H + X^- + TlI_4^- + 2\ OH^- \qquad (5)$$
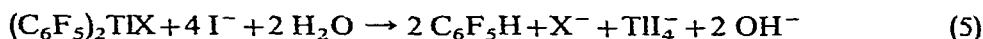
which then react to give thallous iodide [reaction (4)]. Low yields of base and TlI_4^- (isolated as Bu_4NTlI_4) are obtained from cleavage reactions in water (see Experimental). Isolation of the tetraiodothallate(III) complex in high yield from reactions with acidified iodide is possible because base formation [reaction (5)] is suppressed.
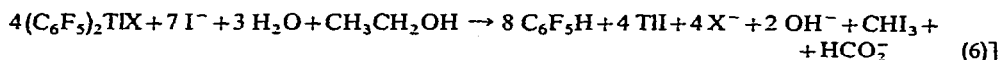
The hypoiodite ions [reaction (4)] can decompose by well established routes, *viz.* disproportionation into iodate and iodide ions, or reduction to iodide by methanol or ethanol, which are converted into aldehydes and, in the case of ethanol, iodoform. The formation of iodate in cleavage reactions in aqueous solution has been established, and a low yield of iodoform has been obtained from a typical reaction in aqueous ethanol★.

The formation of iodopentafluorobenzene in low yield (Table 1) can be explained by the reaction sequence:

$$TlI_4^- \rightleftharpoons TlI + I_2 + I^- \qquad (7)$$

$$(C_6F_5)_2TlBr + I_2 + I^- \rightarrow TlI + 2\ C_6F_5I + Br^- \qquad (8)$$
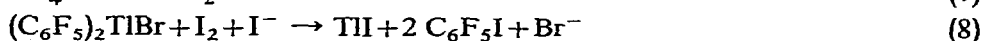
Reaction (7) is well-known[9], and is probably the first stage of reaction (4). Bromobis-(pentafluorophenyl)thallium(III) is cleaved by iodine in aqueous ethanol to give

★ An independent experiment has shown that when iodine and base ($I_2/OH^- = 1/2$, the required ratio for the formation of hypoiodite ions) are refluxed together in aqueous ethanolic sodium iodide, only a low yield of iodoform is obtained. Furthermore, when iodoform and base [$CHI_3/OH^- = 1/2$, corresponding to the ratio produced in the overall equation,

$$4(C_6F_5)_2TlX + 7\ I^- + 3\ H_2O + CH_3CH_2OH \rightarrow 8\ C_6F_5H + 4\ TlI + 4\ X^- + 2\ OH^- + CHI_3 + + HCO_2^- \qquad (6)]$$

are refluxed under similar conditions, substantial consumption of both reagents occurs.

iodopentafluorobenzene (see Experimental), hence reaction (8) is possible. Formation of thallous iodide and pentafluorobenzene via reactions (5) and (4) should give a neutral reaction mixture, whereas formation of pentafluorobenzene, thallous iodide, and iodopentafluorobenzene via reactions (5), (7), and (8) should give an alkaline solution. Although an alkaline reaction mixture can also be explained by incomplete decomposition of TlI_4^- and base in reaction (4), the yields of these species [in terms of reaction (5)] should be equal. However, for reactions in water, which give a higher yield of iodopentafluorobenzene than reactions in other media (Table 1), the yield of base is significantly higher than that of TlI_4^- (see Experimental). The yields of pentafluorophenylaromatic compounds are lower than those of thallous iodide for similar reactions. If this difference does not arise simply from loss of the fluoroaromatic compounds in the isolation procedure, some of the pentafluorobenzene must be decomposed. The susceptibility of this compound to nucleophilic substitution is well-known[11].

   Attempted isolation of intermediates in the cleavage reactions. The decomposition of bromobis(pentafluorophenyl)thallium(III) with excess iodide ions has also been investigated using milder conditions than those required to give high yields of TlI_4^- or TlI, in an attempt to isolate precursors of the tetraiodothallate(III) complex, *e.g.* $(C_6F_5)_2TlI_2^-$, analogous to the known $(C_6F_5)_2TlBr_2^-$ and $(C_6F_5)_2TlCl_2^-$ complexes[6], or $C_6F_5TlI_3^-$. Addition of a solution of tetrabutylammonium or methyltriphenylarsonium iodide to the reaction mixtures caused deposition of orange-yellow oils or precipitates, the infrared spectra of which were consistent with the presence of iodopentafluorophenylthallate(III) complexes (see Experimental). Many attempts have been made to crystallise and purify these products, generally without success. However, solids of composition $[Bu_4N][C_6F_5TlI_3]$ and $[MePh_3As][C_6F_5TlI_3]$ have been isolated, the former from a reaction with acidified iodide ions, the latter from a reaction without added acid. X-ray powder photography established that these products did not contain the corresponding tetraiodothallate(III) complexes, thus eliminating the possibility of equimolar mixtures of TlI_4^- and $(C_6F_5)_2TlI_2^-$ complexes. If the compounds are correctly formulated as triiodopentafluorophenylthallate(III) complexes, they are the first monopentafluorophenylthallium(III) derivatives to be prepared. The difficulty in crystallising and purifying the intermediates may be attributed to two causes. Firstly, small amounts of thallous iodide are readily formed in reactions in the absence of acid and on attempted recrystallisation. Secondly, Bu_4NTlI_4 and $MePh_3AsTlI_4$ appear to be less soluble than the corresponding iodopentafluorophenylthallate(III) complexes, hence the tetraiodothallate(III) complexes tend to deposit preferentially especially from reactions with acidified iodide. Qualitative evidence has also been obtained for intermediate formation of a bromopentafluorophenylthallate(III) species in the reaction of $(C_6F_5)_2TlBr$ with acidified bromide ions (see Experimental).

B. *Reactions with iodide ions* $(I^-/Tl = 1/1)$

   Reactions between equimolar amounts of $(C_6F_5)_2TlBr$ and MI (M = Na, Cs, or Bu_4N) have been investigated in an attempt to prepare either complexes of the type $M[(C_6F_5)_2TlBrI]$ or the previously unknown iodobis(pentafluorophenyl)-thallium(III). Yellow oils were obtained which decomposed to thallous iodide on dissolution prior to attempted recrystallisation. However, iodobis(pentafluorophenyl)-thallium(III) and the corresponding cyano derivative are readily prepared from the

water-soluble[6] sulphatodi[bis(pentafluorophenyl)thallium(III)] by metathesis reactions in cold water.

$$[(C_6F_5)_2Tl]_2SO_4 + 2\,NaX \rightarrow Na_2SO_4 + 2\,(C_6F_5)_2TlX\downarrow \qquad (X = I\ or\ CN)$$
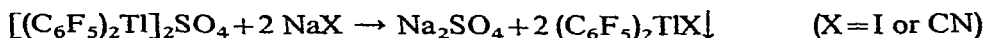
Iodobis(pentafluorophenyl)thallium(III) is white when freshly prepared, but slowly becomes yellow on standing, presumably owing to thallous iodide formation, and solutions of the compound in organic solvents *e.g.* benzene or ether deposit thallous iodide on standing or heating. Owing to this instability, it is unlikely that syntheses using Grignard or organolithium reagents would be successful. The cyano derivative is much more stable.

Iodobis(pentafluorophenyl)thallium(III) probably has a dimeric structure:
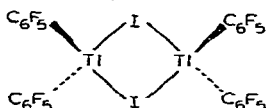
by analogy with the structures of other halobis(pentafluorophenyl)thallium(III) compounds[6,12,13]. The instability of the iodo compound precludes molecular weight measurements. X-ray powder photographs of the iodo and bromo compounds show similarities, but the compounds are not isostructural. Some evidence for a dimeric constitution is provided by the close similarity between the infrared spectra (4000–400 cm^{-1}) of the iodo compound (see Experimental) and the other halobis(pentafluorophenyl)thallium(III) compounds[6,14], and especially by the similarity in the stereochemically important 810–765 cm^{-1} region in which a mode involving C–Tl stretching is observed[14]. For the cyano compound, ν(CN) is observed at 2189 cm^{-1}, which is consistent with the presence of bridging cyano groups [ν(CN)$_{bridging}$ is generally near 2200 cm^{-1} and ν(CN)$_{terminal}$ near 2100 cm^{-1})[15], and the compound probably has a dimeric structure analogous to that proposed for $(C_6F_5)_2$TlI. The cyano derivative is not sufficiently soluble in benzene for molecular weight measurements; more polar solvents were not used, since they are known to rupture the bridging bonds of dimeric bis(pentafluorophenyl)thallium(III) compounds[6].

C. Possible mechanisms of the cleavage reactions

Two possible mechanisms can be considered for the cleavage of pentafluorophenyl groups from thallium: nucleophilic attack of iodide on thallium followed by solvolytic decomposition of the pentafluorophenyl carbanion,

$$C_6F_5Tl- + I^- \rightarrow C_6F_5^- + ITl-$$
$$C_6F_5^- + H_2O \rightarrow C_6F_5H + OH^-$$
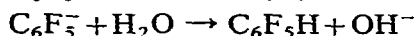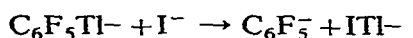
or solvolytic attack on the C–Tl bond followed by coordination of iodide.

$$C_6F_5Tl- + H_2O \rightarrow C_6F_5H + Tl^+- + OH^-$$
$$I^- + Tl^+- \rightarrow ITl-$$
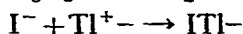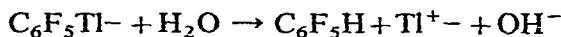
At this stage no conclusive choice can be made between the mechanisms for reactions with excess iodide ions. However, since the second mechanism requires either a protonic solvent or the presence of acid, the decomposition of $(C_6F_5)_2$TlI in aprotic solvents (section B) may involve nucleophilic attack of iodide on thallium. (It has also been observed that a low yield of thallous iodide is obtained when a suspension of

sodium iodide is refluxed with a solution of $(C_6F_5)_2TlBr$ in dry ether).

In cleavage reactions of $(C_6F_5)_2TlX$ compounds with excess iodide, the reacting species is probably the complex $(C_6F_5)_2TlI_2^-*$. Although it was not possible to isolate this complex, qualitative evidence has been obtained for the presence of iodopentafluorophenylthallate(III) complexes in the reaction mixtures. and intermediate formation of the related complex $C_6F_5TlI_3^-$, has been demonstrated (section A). Moreover, $(C_6F_5)_2TlX$ (X = Br or Cl) derivatives form $(C_6F_5)_2TlX_2^-$ complexes[6] in reactions in which Tl/X^- is only 1/2. Certainly, if the second mechanism obtains, the reacting species cannot be the original $(C_6F_5)_2TlX$ compound, since solvolytic decomposition of $(C_6F_5)_2TlBr$ is slight (section A).

EXPERIMENTAL

Microanalyses were carried out by the Australian Microanalytical Service, Melbourne. Infrared spectra (4000–400 cm^{-1}) of new compounds as Nujol and hexachlorobutadiene mulls were recorded with a Perkin–Elmer 521 spectrophotometer. The spectrum of $(C_6F_5)_2TlCN$ was obtained using potassium bromide plates covered by polystyrene film[18] to avoid the possibility of group exchange with the plates. Other spectra (4000–650 cm^{-1}) were recorded with Perkin-Elmer 257 and Unicam SP 200 instruments. Ultraviolet spectra were recorded with a Unicam SP 700 spectrophotometer, ethanol or methanol being used as solvent. X-ray powder photographs of compounds were obtained with a Philips–Debye–Scherrer 114.6 mm powder camera. using nickel filtered $CuK\alpha$ radiation. Unless stated otherwise aqueous ethanol and aqueous methanol have the composition 1/1(v/v). Pentafluorobenzene and iodopentafluorobenzene were obtained from the Imperial Smelting Corporation.

Preparations of bis(pentafluorophenyl)thallium(III) compounds

The compounds $(C_6F_5)_2TlX$ (X = Br, Cl, F, NO_3, $\frac{1}{2}$ SO_4. OAc, OCOPh, or $OCOC_6F_5$) were prepared by the reported methods[1,6], and were characterized by their melting points and infrared spectra[1,6,14].

Iodobis(pentafluorophenyl)thallium(III). On addition of a solution of sodium iodide (0.40 mmole) in water (1 ml) to a solution of sulphatodi[bis(pentafluorophenyl)-thallium(III)] (0.17 mmole) in water (5 ml), the required compound was obtained as a white precipitate, which was rapidly collected, washed with cold water, and dried *in vacuo* over phosphorus pentoxide (yield, 0.075 mmole, 22%) (Found: C, 21.2, $C_{12}F_{10}ITl$ calcd.: C, 21.7%). The preparation was carried out with almost complete exclusion of light, as the compound slowly becomes yellow on exposure to light. Continuous decomposition occurs on heating. The compound is soluble in benzene, ether, methanol, ethanol, and acetone, but decomposition to thallous iodide occurs soon after dissolution and is accelerated on heating. Infrared absorption: 1638s, 1582w, 1556w, 1514vs, 1481vs, 1455(sh), 1412w, 1389(sh), 1381s, 1369(sh), 1326w, 1283m, 1274(sh), 1141(sh), 1137m, 1087(sh), 1082vs, 1068vs, 1048m, 1015(sh), 1011m, 1003m, 973(sh), 966vs, 795s, 779m, 742w, 717m, 607m, 584w, and 486w, br cm^{-1}. Attempts to prepare the compound by metathesis between $(C_6F_5)_2TlBr$ and

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* The complex $(C_6F_5)_2TlI_3^{2-}$ is also possible: bis(pentafluorophenyl)thallium(III) compounds give five coordinate complexes[1,6,16], and the complex $Me_2TlI_3^{2-}$ has recently been reported[17].

equimolar amounts of sodium, caesium, or tetrabutylammonium iodide in ethanol or aqueous ethanol gave oils, which readily decomposed to thallous iodide.

Cyanobis(pentafluorophenyl)thallium(III). The compound was similarly prepared by reaction of sodium cyanide and sulphatodi[bis(pentafluorophenyl)-thallium(III)] in water (yield 72%), m.p. 190° (softens without complete melting) (Found: C, 27.55; F, 33.9; N, 2.4. $C_{13}F_{10}NTl$ calcd.: C, 27.7; F, 33.7; N, 2.5%). The compound is almost insoluble in benzene; otherwise the solubilities are similar to those of the iodo derivative. Infrared absorption: 2189s, 1640s, 1555w, 1512vs, 1472vs,br, 1455(sh), 1412w, 1383s, 1374s, 1328w, 1287m, 1272(sh), 1140w, 1083vs, 1078vs, 1059(sh), 1030(sh), 1016(sh), 1011m, 974(sh), 965vs, 803(sh), 795s, 790(sh), 743w, 719m, 614m, 589w, and 490w, br cm⁻¹.

Preparations of tetrahalothallate(III) complexes

The compounds were prepared by a method similar to that reported for methyl-triphenylarsonium tetraiodothallate(III)[10], and were recrystallised from acetone or acetone/ether. The melting points of the tetraiodothallate(III) complexes, which were confirmed in duplicate preparations, differ significantly from reported values[10]. Possibly more than one crystalline form of each complex may exist. Alternatively, the ready decomposition of the complexes (section A and Table 2) suggests that traces of thallous iodide could be deposited with the complexes and may have a significant effect on the melting points.

Tetrabutylammonium tetraiodothallate(III). m.p. 138° (lit.[10] m.p. 117–118°) (Found: C, 20.3; H, 3.9; N, 1.5; Tl, 21.3. $C_{16}H_{36}I_4NTl$ calcd.: C, 20.1; H, 3.8; N, 1.5; Tl, 21.4%). For the thallium analysis, the compound was first decomposed to Tl^{3+} by boiling with concentrated sulphuric acid, iodine being evolved, then with concentrated nitric acid. After boiling off the nitric acid, reduction to the thallous state was effected by sulphur dioxide[19], and thallium was determined by titration with potassium iodate using Andrew's conditions[20].

Tetrabutylammonium tetrabromothallate(III). m.p. 135° (lit.[10] m.p. 127–128°) (Found: C, 25.4; H, 4.8. $C_{16}H_{36}Br_4NTl$ calcd.: C, 25.1; H, 4.7%).

Methyltriphenylarsonium tetraiodothallate(III). m.p. 162–163° (lit.[10] m.p. 141–142°) (Found: C, 22.4; H, 2.0. $C_{19}H_{18}AsI_4Tl$ calcd.: C, 22.1; H, 1.8%).

Cleavage Reactions of bis(pentafluorophenyl)thallium(III) compounds

(1) *Reactions giving thallous iodide*

Procedure, and isolation of thallous iodide. Details of reagents, solvents, reaction times, and yields of thallous iodide for reactions of $(C_6F_5)_2TlBr$ and $(C_6F_5)_2TlCl$ are given in Table 1. For reactions in aqueous ethanol or aqueous methanol, a solution of the reagents in the appropriate solvent was gently refluxed (steam bath). Thallous iodide was deposited and the solution colour lightened from orange-yellow to pale yellow. After cooling and standing at room temperature for *ca.* 1 h, the precipitate was collected quantitatively, washed with aqueous ethanol and acetone, and dried *in vacuo* at 125°. The filtrates from incomplete reactions deposited further thallous iodide on standing, which was also collected (Table 1). Reactions of $(C_6F_5)_2TlX$ (X = I, CN, ½SO₄, or OAc) were carried out in a similar way and gave yields of thallous iodide in the range 45–100%. The X-ray powder photographs of the products of representa-

tive reactions were identical to that of authentic thallous iodide. For reactions in water, a suspension of $(C_6F_5)_2TlBr$ in aqueous sodium iodide was stirred and heated under reflux. An orange-yellow solution and a similar oil formed (Since $(C_6F_5)_2TlBr$ is insoluble in water[6], dissolution presumably involves formation of an anionic complex, *e.g.* $(C_6F_5)_2TlI_2^-$), which decomposed with precipitation of thallous iodide. This was collected as above, except that washings with organic solvents were not added to the aqueous filtrate. The yellow colour of the latter was shown to be due to the tetraiodothallate(III) ion: addition of excess aqueous tetrabutylammonium iodide to the aqueous filtrate from a typical reaction [that using 0.766 mmole of $(C_6F_5)_2TlBr$, Table 1], gave a yellow colloidal precipitate, which, on crystallisation from acetone, yielded tetrabutylammonium tetraiodothallate(III) [Yield $<3\%$; identified by the infrared spectrum and by decomposition to thallous iodide on reaction with sodium hydroxide in boiling aqueous acetone (see Section A)].

Cleavage of $(C_6F_5)_2TlBr$ with bromide or cyanide ions was effected in a similar manner. Bromide cleavage: A solution of $(C_6F_5)_2TlBr$ (0.383 mmole) and lithium bromide (115 mmole) in 10 ml of aqueous ethanol was refluxed for 2 h giving a precipitate of thallous bromide (0.285 mmole, 74%), which was identified by X-ray powder photography. Cyanide cleavage: A solution of $(C_6F_5)_2TlBr$ (0.360 mmole) and sodium cyanide (204 mmole) in 40 ml of aqueous ethanol (2/1, v/v) was refluxed for 1.5 h. The resultant solution was shown to contain thallous cyanide by addition of aqueous potassium chromate, when thallous chromate[19] (0.144 mmole, 80%) was precipitated.

Characterization of other products. The infrared spectra of the first 1–3 ml of distillates from representative reaction mixtures were identical to that of authentic pentafluorobenzene in methanol or ethanol. However, the ultraviolet spectra differed somewhat from that of pentafluorobenzene and were more similar to that of a mixture of pentafluorobenzene and iodopentafluorobenzene (mole ratio $\simeq 8/1$). There was no evidence[21] for the presence of pentafluorophenol. Gas chromatography (on silicone gum) confirmed the formation of pentafluorobenzene and iodopentafluorobenzene, and was also used to obtain yields of these compounds (Table 1). After the reaction in water, ethanol was added prior to distillation to facilitate removal of the fluoroaromatic compounds from the reaction mixture. (Since a satisfactory separation of pentafluorobenzene by gas chromatography could be achieved only when the concentration of water in the distillate was low ($<10\%$), only fractions distilling below *ca.* 85° were investigated). From one typical distillate, pentafluorobenzene was isolated by preparative gas chromatography and identified by infrared spectroscopy.

A number of reaction mixtures were tested for base formation. Those from reactions in aqueous ethanol were either neutral or only a low yield of base was obtained [$<10\%$ based on $(C_6F_5)_2TlX \rightarrow 2\ OH^-$, see equation (5)]. Somewhat higher yields (11–18%) were obtained from reactions in water.

The formation of iodate in cleavage reactions in water was established by qualitative tests[22].

Iodoform was detected after the following typical cleavage reaction in aqueous ethanol. A solution of $(C_6F_5)_2TlCl$ (0.725 mmole) and sodium iodide (67 mmole) in 10 ml aq. ethanol was refluxed for 1 h. After filtration, water (10 ml) was added to the filtrate. Ether extraction, evaporation of the solvent, and sublimation of the residue *in vacuo* gave crude iodoform [0.020 mmole, 11% based on $(C_6F_5)_2TlCl$, see equation

(6)], which was identified by infrared spectroscopy and thin layer chromatography. Under similar conditions, iodine (0.511 mmole) and sodium hydroxide (1.02 mmole) in aqueous ethanolic sodium iodide gave iodoform (0.029 mmole, 23 % based on I_2), the base being completely consumed. When iodoform (0.127 mmole) and sodium hydroxide (0.251 mmole) [$CHI_3/OH^- = 1/2$, corresponding to equation (6)] were similarly refluxed in aqueous ethanolic sodium iodide, 70 % of both reagents was consumed.

Decomposition of $(C_6F_5)_2TlBr$ in aqueous ethanol in the absence of added iodide, bromide or cyanide ions: when a solution of $(C_6F_5)_2TlBr$ (0.381 mmole) in aqueous ethanol (10 ml) was refluxed for 2 h, a trace amount of brown colloidal precipitate was formed, and, on cooling, a trace of cream solid also deposited. The infrared spectrum of the combined precipitates showed a sharp hydroxyl absorption at 3550 cm^{-1} and bands characteristic of a bis(pentafluorophenyl)thallium(III)compound[6,14], though the latter did not correspond exactly to bands of $(C_6F_5)_2TlBr$. Possibly the precipitate contained $(C_6F_5)_2TlOH$ or a mixture of this compound and $(C_6F_5)_2TlBr$. The brown colour may derive from the presence of Tl_2O_3 ($Tl(OH)_3$ is unknown[23]), whilst the presence of a trace of thallous bromide cannot be excluded. Unreacted $(C_6F_5)_2TlBr$ was recovered from solution as the complex, bromobis(pentafluorophenyl)-1,10-phenanthrolinethallium(III)[6] (Yield 0.274 mmole, 72%), which on recrystallisation from aqueous methanol had m.p. 140°, mixed m.p. 141–141.5° (lit.[6] m.p. 141–141.5°) and infrared absorption in agreement with reported data[6,14]. (Satisfactory crystallisation of $(C_6F_5)_2TlBr$ from aqueous ethanol could not be achieved. The phenanthroline complex can be crystallised from aqueous methanol in 80 % yield[6] and a similar recovery is likely from aqueous ethanol).

When a similar decomposition was carried out in the presence of base (Tl/ $OH^- = 1/2$), deposition of Tl_2O_3 commenced after 5 min.

(2) *Reactions giving tetrahalothallate(III) complexes*

Tetrabutylammonium tetraiodothallate(III). When a solution of $(C_6F_5)_2TlBr$ (0.37 mmole), sodium iodide (67 mmole), and HCl (1.0 mmole) in 20 ml of aqueous ethanol was refluxed, the solution became red after 5 min. After heating for 30 min, the solution was filtered to remove a small amount of thallous iodide, and a solution of tetrabutylammonium iodide (0.49 mmole) in 5 ml of ethanol was added giving a cloudy suspension. On standing at *ca.* −23° tetrabutylammonium tetraiodothallate-(III) crystallised (0.33 mmole, 89 %) m.p. 138–138.5°, mixed m.p. 138° (infrared identification).

Methyltriphenylarsonium tetraiodothallate(III). From a similar reaction in which the heating time was 3 min, use of methyltriphenylarsonium iodide as the precipitant gave the required complex (51 %), m.p. 162–163°, mixed m.p. 161–163°. The infrared spectrum was identical to that of the authentic compound, except for absorption indicating the presence of a trace of a C_6F_5Tl species.

Tetrabutylammonium tetrabromothallate(III). A solution of $(C_6F_5)_2TlBr$ (0.16 mmole), lithium bromide (58 mmole), and HCl (1.0 mmole) in 11 ml of aqueous ethanol was refluxed for 9 h. After filtration, addition of tetrabutylammonium bromide (0.16 mmole) in 2 ml of ethanol precipitated the required complex (*ca.* 0.16 mmole, 100 %) m.p. 135°. However, the infrared spectrum showed the product to be slightly hydrated. Recrystallisation from acetone/ethanol gave the anhydrous compound

m.p. 135–136°, mixed m.p. 135° (infrared identification).

(3) *Reactions giving iodopentafluorophenylthallate(III) complexes*

After reaction of $(C_6F_5)_2TlBr$ and sodium iodide (with or without acidification) under milder conditions than used for formation of TlI_4^- (above), addition of ethanolic Bu_4NI or $MePh_3AsI$ gave orange-yellow oils or precipitates, which were generally contaminated with the corresponding orange tetraiodothallate(III) complex. The infrared spectra of the products showed bands characteristic of the appropriate cation and of C_6F_5Tl groups[6,14], hence the presence of iodopentafluorophenylthallate(III) complexes was indicated. Analyses of the products generally indicated mixtures of complexes, and attempts to recrystallise usually gave thallous iodide and the corresponding tetraiodothallate(III) complex. However, two iodopentafluorophenylthallate(III) complexes were obtained in a reasonably pure state.

Tetrabutylammonium triiodopentafluorophenylthallate(III). A solution of $(C_6F_5)_2TlBr$ (0.40 mmole), sodium iodide (67 mmole), and HCl (1.0 mmole) in aqueous ethanol (20 ml) was heated on a steam bath for 30 sec. After filtration, a solution of tetrabutylammonium iodide (0.49 mmole) in ethanol (2 ml) was added, and the reaction mixture was kept at *ca.* $-23°$ for 1 h. The resulting precipitate (0.13 mmole, 33% as $[Bu_4N][C_6F_5TlI_3]$), m.p. 62–63° was orange and hence contained trace of the tetraiodothallate(III) complex. The filtrate deposited firstly (after 2 days) orange-yellow crystals (0.030 mmole, 8% as $[Bu_4N][C_6F_5TlI_3]$) m.p. 62–64°, then (after a further 2 days) the required complex as yellow needles (0.030 mmole, 8%) m.p. 61–63° (Found: C, 25.8; H, 3.7; F, 9.6. $C_{22}H_{36}F_5I_3NTl$ calcd.: C, 26.6; H, 3.65; F, 9.55%). No Bu_4NTlI_4 could be detected in the yellow crystals by X-ray powder photography. Infrared absorption: 2967vs, 2936m, 2899(sh), 2878s, 1632m, 1504vs, 1468vs, 1441m, 1399w, 1381m, 1362s, 1308w, 1266m, 1168m, 1128w, 1108w, 1068vs, 1059(sh), 1045m, 1036(sh), 1004m, 995m, 962vs, 925m, 896m, 881m, 791w,br, 770m, 737s, 715w, 598m, and 482w,br cm⁻¹. Since the melting points of all three products are virtually identical, the first two must contain mainly the triiodopentafluorophenylthallate(III) complex.

Methyltriphenylarsonium triiodopentafluorophenylthallate(III). A solution of $(C_6F_5)_2TlBr$ (0.39 mmole) and sodium iodide (67 mmole) in 11 ml of aqueous ethanol was shaken for 5 min, then methyltriphenylarsonium iodide (0.43 mmole) in ethanol (2 ml) was added giving a thick yellow oil. This was separated and extracted with acetone, evaporation of which gave an orange-yellow oil. After washing with water to remove traces of sodium iodide, ethanol (1 ml) was added, and, on scratching, the oil solidified to a yellow powder (0.094 mmole, 24%), m.p. (dec.) 109–110° (Found: C, 27.7; H, 2.1; F, 10.0. $C_{25}H_{18}AsF_5I_3Tl$ calcd.: C, 28.0; H, 1.7; F, 8.85%). No $MePh_3$-$AsTlI_4$ could be detected in the product by X-ray powder photography. Infrared absorption: 3058w, 3003w, 2924w, 1635m, 1582w, 1507vs, 1485m, 1464vs, 1440vs, 1413m, 1403m, 1365s, 1348m, 1342m, 1312w, 1264m, 1186w, 1163w, 1124w, 1087s, 1072vs, 1065(sh), 1061(sh), 1046m, 1026w, 1000s, 980(sh), 958vs, 923w, 891s, 883s, 844m, 768m, 739vs, 687vs, 625m, 599m, 471s, and 457s cm⁻¹.

Reaction of $(C_6F_5)_2TlBr$ with acidified bromide ions under milder conditions than required to give $TlBr_4^-$ (above), followed by addition of tetrabutylammonium bromide in ethanol, gave a cream precipitate, the infrared spectrum of which suggested the presence of a tetrabutylammonium bromopentafluorophenylthallate(III)

complex, but analyses and X-ray powder photography showed the product was contaminated with Bu_4NTlBr_4.

Decomposition reactions of tetrahalothallate(III) complexes

Decomposition of TlI$_4^-$ in aqueous ethanol. Sodium iodide (67 mmole) in aqueous ethanol (10 ml) was added to a solution of thallic chloride (0.834 mmole) in water (10 ml) giving an orange-red solution of the tetraiodothallate(III) complex. The solution was refluxed for 0.5 h, very little thallous iodide being deposited. Refluxing was continued for a further 3.0 h, and sodium hydroxide (1.75 mmole) and sodium iodide (20 mmole) in water (30 ml) were added in 5 ml amounts during the first 2.5 h. The solution colour was virtually discharged, and thallous iodide was deposited (0.821 mmole, 98%).

Decomposition of tetrahalothallate(III) complexes in aqueous acetone. Details of reagents, reaction times, and yields of thallous iodide are given in Table 2. The procedure was similar to that outlined for cleavage of $(C_6F_5)_2TlX$ compounds with iodide ions.

Cleavage of bromobis(pentafluorophenyl)thallium(III) with iodine

When equimolar amounts of $(C_6F_5)_2TlBr$ and iodine were refluxed in aqueous ethanol, thallous bromide was precipitated (identified by powder photography), and the distillate from the reaction mixture contained C_6F_5I (identified by the ultraviolet spectrum and gas chromatography).

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