Thallium(I) Carboxylate Modification of the Hunsdiecker Reaction

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Treatment of a thallium(I) carboxylate with 1 molar equivalent of bromine gives the corresponding thallium(III) carboxylate dibromide. High yields of primary alkyl bromides are obtained if the thallium(III) carboxylate dibromide is treated with 0.5 mol equiv. of bromine in refluxing carbon tetrachloride. Pyrolysis of the thallium(III) derivative in the absence of added bromine gives a low yield of the corresponding alkyl bromide. The use of thallium(I) carboxylates for the preparation of alkyl bromides in high yields is limited to the salts of primary carboxylic acids. A simple procedure for the preparation of alkyl bromides from carboxylic acids using thallium(I) carbonate has been developed.

HUNSDIECKER[1] and, more recently, McKillop and Taylor[2] have shown that thallium(I) carboxylates give satisfactory yields of alkyl bromides when treated with bromine (see also ref. 3). The method is an improvement on the classical Hunsdiecker reaction[4] since unlike silver(I) carboxylates, thallium(I) carboxylates are easily prepared and are stable crystalline compounds.[5] Since a 2 : 3 molar ratio of thallium(I) carboxylate to bromine was found to give optimum yields of alkyl bromide the sequence (1)—(4) was proposed for the reaction.[2] The

$$\begin{array}{lr}
2RCO_2Tl^{I} + 2Br_2 \longrightarrow 2RCO_2Tl^{III}Br_2 & (1)\\
2RCO_2Tl^{III}Br_2 + Br_2 \longrightarrow 2RCO_2Br + Tl_2Br_4 & (2)\\
2RCO_2Br \longrightarrow 2RBr + 2CO_2 & (3)\\
\hline
2RCO_2Tl^{I} + 3Br_2 \longrightarrow 2RBr + 2CO_2 + Tl_2Br_4 & (4)
\end{array}$$

proposal involves oxidation of a thallium(I) carboxylate to a thallium(III) species, conversion of this into an acyl hypobromite, and subsequent decarboxylation of the latter. The thallium residues were neither thallium(I) bromide nor thallium(III) bromide but exhibited the properties of the double salt $[Tl^+(TlBr_4)^-]$.[6]

However, Lee[7] has suggested that the *initial* products from reaction of a thallium(I) carboxylate and bromine could be the acyl hypobromite and thallium(I) bromide. An alternative bromodecarboxylation sequence [equations (5)—(8)] can then be proposed. Although the

$$\begin{array}{lr}
2RCO_2Tl^{I} + 2Br_2 \longrightarrow 2RCO_2Br + 2Tl^{I}Br & (5)\\
2RCO_2Br \longrightarrow 2RBr + 2CO_2 & (6)\\
2Tl^{I}Br + Br_2 \longrightarrow Tl_2Br_4 & (7)\\
\hline
2RCO_2Tl^{I} + 3Br_2 \longrightarrow 2RBr + 2CO_2 + Tl_2Br_4 & (8)
\end{array}$$

latter sequence still requires a molar ratio of 2 : 3 of thallium(I) carboxylate to bromine, it does not involve oxidation of the thallium(I) carboxylate by bromine and is still in accord with the fact that the end product of treatment of thallium(I) bromide with bromine is Tl_2Br_4.[8]

Although Cocton and Crastes de Paulet[9] found that oxidation of thallium(I) acetate by bromine in acetic acid gave thallium(III) acetate dibromide ($CH_3CO_2TlBr_2$), no other similar oxidations have been reported. A consideration of aqueous electrode potentials[10] for the oxidation of thallium(I) to thallium(III) by halogens shows that only chlorine ($E_{cell} = +0.14$ V) would be expected to effect this conversion. However, the calculated cell potential for bromine is only slightly negative ($E_{cell} = -0.17$ V) and since the standard reduction potential of thallium(III) varies with pH and the presence of complexing ions,[11] the electrode potential of thallium(I) in a thallium(I) carboxylate is likely to be different from that of an aquated thallium(I) ion. Therefore, the use of standard electrode potentials to deduce whether or not bromine will oxidise a compound of thallium(I) may not be valid. Indeed, the oxidation of thallium(I) acetate[9] and of thallium(I) halides[7b] by bromine has been reported but this does not constitute conclusive evidence for the proposed[2] intermediacy of a thallium(III) species in the bromodecarboxylation of a thallium(I) carboxylate. Thus, in order to provide experimental evidence on the nature of the intermediates involved in the bromodecarboxylation of thallium(I) carboxylates, the syntheses and reactions of the thallium(III) salts of some fatty acids and of a thallium(III) carboxylate dibromide were undertaken.

Initially, the thallium(III) salts of some fatty acids were prepared[12] by metathesis of thallium(III) triacetate with the acids in carbon tetrachloride. Although the thallium(III) tricarboxylates were obtained as flocculent white solids, their solubility in carbon tetrachloride increased as the chain length of the acid decreased, leading to lower yields. Therefore, rather than attempt to isolate the thallium(III) tricarboxylates, it was more convenient to treat a suspension of the trivalent salt in carbon tetrachloride with bromine (1 mol equiv.) at room temperature and then heat under reflux until the bromine colour was discharged (Table 1). In order to establish that the major bromodecarboxylation pathways were not *via* mixed ligand carboxylates, *i.e.* equation (9),

$$\begin{array}{c}
TlOAc_3 + nRCO_2H \rightleftharpoons Tl(OAc)_x(O_2CR)_y\\
(n = 1, x = 2, y = 1 \text{ or } n = 2, x = 1, y = 2) \qquad (9)
\end{array}$$

thallium(III) trioctadecanoate (5) was isolated (94%) from the reaction of thallium(III) triacetate with 10.0 mol equiv. of octadecanoic acid (1) and the presence of three octadecanoate residues in the product was confirmed by elemental analysis. Subsequent treatment of the thallium(III) tricarboxylate (5) with 3.0 mol equiv.

TABLE 1

Preparation of thallium(III) tricarboxylates and their bromodecarboxylations $3RCO_2H \xrightarrow{TlOAc_3} (RCO_2)_3Tl \xrightarrow{3Br_2} 3RBr$

Carboxylic acid (1 mol equiv.)	$TlOAc_3$ (mol (equiv.)	$(RCO_2)_3Tl$	Br_2 (mol equiv.)	RBr (%) [a]
(1)	2.5	(5)	1.0	78
(1)	2.5	(5)	2.0	81
(1)	2.5	(5)	2.5	82
(2)	2.5	(6)	1.0	72
(2)	3.0	(6)	1.0	84
(3)	2.5	(7)	1.0	79
(3)	3.0	(7)	1.0	80
(4)	3.0	(8)	1.0	78

[a] Isolated yields.

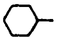
of bromine in refluxing carbon tetrachloride resulted in a clean conversion into 1-bromoheptadecane (9) in 70% yield, which compares favourably with that (78%) obtained when (5) was generated *in situ*. However, the yield of the bromide (9) from reaction of compound (5) with 1.5 mol equiv. of bromine was only 43%.

$CH_3[CH_2]_nCO_2H$	$(CH_3[CH_2]_nCO_2)_3Tl$	$CH_3[CH_2]_nBr$
(1) $n = 16$	(5) $n = 16$	(9) $n = 16$
(2) $n = 14$	(6) $n = 14$	(10) $n = 14$
(3) $n = 12$	(7) $n = 12$	(11) $n = 12$
(4) $n = 10$	(8) $n = 10$	(12) $n = 10$

$CH_3[CH_2]_{16}CO_2TlBr_2$

(13)

RCO_2Tl

(14) R = $CH_3[CH_2]_{16}-$
(15) R = Me_3CCH_2-
(16) R = Me_3C-
(17) R = $CH_3[CH_2]_{14}-$
(18) R = $CH_3[CH_2]_{12}-$
(19) R = $CH_3[CH_2]_{10}-$
(20) R = 

By analogy with the proposal of McKillop and Taylor[2] the sequence for the bromodecarboxylation of a thallium(III) tricarboxylate shown in equations (10)—(12) can be proposed. The decomposition of a thallium(III) tricarboxylate in the presence of bromine to give an acyl hypobromite can occur with or without reduction of trivalent thallium [equations (13) or (14). These two

$$2(RCO_2)_3Tl + 5Br_2 \longrightarrow 6RCO_2Br + Tl_2Br_4 \qquad (10)$$

$$\underline{6RCO_2Br \longrightarrow 6RBr + 6CO_2} \qquad (11)$$

$$2(RCO_2)_3Tl + 5Br_2 \longrightarrow 6RBr + 6CO_2 + Tl_2Br_4 \qquad (12)$$

$$(RCO_2)_3Tl^{III} + 2Br_2 \longrightarrow 3RCO_2Br + Tl^{I}Br \qquad (13)$$

$$\text{or } (RCO_2)_3Tl^{III} + 3Br_2 \longrightarrow 3RCO_2Br + Tl^{III}Br_3 \qquad (14)$$

equations differ in the amount of bromine used and in the final oxidation state of the thallium in the thallium bromide. However, thallium(I) bromide would not be expected to be stable in the presence of bromine while thallium(III) bromide would not be expected to be stable in refluxing carbon tetrachloride.[13] Therefore, the molar amount of bromine employed need not reflect the true stoicheiometry of the bromodecarboxylation.

An alternative possibility for the reaction pathway involves the trapping by bromine of alkyl radicals generated by thermolysis of the thallium(III) tricarboxylate [equations (15)—(17)]. Although Kochi and

$$(RCO_2)_3Tl^{III} \longrightarrow (RCO_2)_2Tl^{II} + R^{\bullet} + CO_2 \qquad (15)$$

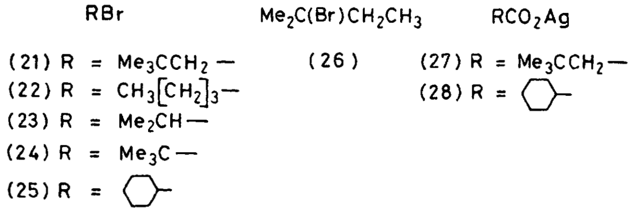
$$(RCO_2)_2Tl^{II} \longrightarrow (RCO_2)Tl^{I} + R^{\bullet} + CO_2 \qquad (16)$$

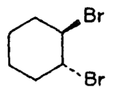
$$R^{\bullet} + Br_2 \longrightarrow RBr + Br^{\bullet} \qquad (17)$$

Bethea[12] have proposed the intermediacy of an unstable thallium(II) carboxylate in the photolytic decomposition of thallium(III) tricarboxylates, they found that thermally induced decomposition of these salts occurred only in the presence of strong acids. The formation of alkyl radicals and carbon dioxide in the present reactions seems unlikely since thallium(III) trioctadecanoate (5) was recovered quantitatively after it was heated at 100 °C under reduced pressure. Moreover, alkyl radicals, if formed, should have been trapped effectively with iodine; treatment of thallium(III) trioctadecanoate with iodine gave no 1-iodoheptadecane (^1H n.m.r. spectral analysis).

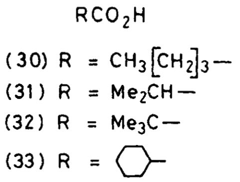
Although the present work shows that thallium(III) tricarboxylates can undergo bromodecarboxylation, this has not been demonstrated for a thallium(III) carboxylate dibromide. Therefore, a synthesis of such a mixed ligand compound was undertaken from thallium(III) acetate dibromide[9] and octadecanoic acid (1) since it was expected that the resulting thallium(III) compound (13) would be sufficiently insoluble in carbon tetrachloride to permit its isolation in high yield. The product was a pale yellow solid, m.p. 92—95 °C, but a satisfactory elemental analysis for $C_{18}H_{35}Br_2O_2Tl$ was not obtained. Presumably, the product was not pure because the equilibrium was not displaced sufficiently under the reaction conditions. However, reaction of the product with 0.5 mol equiv. of bromine in refluxing carbon tetrachloride gave 1-bromoheptadecane (9) in 74% yield. A direct synthesis of thallium(III) octadecanoate dibromide (13) from the reaction of thallium(I) octadecanoate (14) with bromine was also investigated since this would provide evidence for oxidation of thallium(I) salts by bromine. Treatment of thallium(I) octadecanoate (14) with 1.1 mol equiv. of bromine in carbon tetrachloride at room temperature gave a product, m.p. 86—91 °C, which analysed correctly for thallium(III) octadecanoate dibromide (13). Reaction of the dibromide (13) with 0.5 mol equiv. of bromine in refluxing carbon tetrachloride gave 1-bromoheptadecane (9) in a yield (83%) similar to that (79%) obtained from the reaction of thallium(I) octadecanoate (14) with 1.5 mol equiv. of bromine. No reaction occurred at room temperature and no detectable discharge of the bromine colour occurred after 24 h.

McKillop and Taylor[2] reported that reaction of equimolar amounts of a thallium(I) carboxylate and bromine led to only low yields (*ca.* 30%) of the alkyl bromide. Similarly, in the present study, 1-bromoheptadecane (9) was isolated consistently in yields of 25—30% when thallium(III) octadecanoate dibromide (13) was refluxed in carbon tetrachloride or heated in a Kugelrohr oven at reduced pressure. Thus the intermediacy of a thallium(III) species arising from the oxidation of a thallium(I) carboxylate by bromine, and the need for a further 0.5 mol equiv. of bromine if high yields of the alkyl bromide are to be obtained, have been confirmed for the bromodecarboxylation of thallium(I) carboxylates. Treatment of thallium(I) octadecanoate (14) with iodine gave no detectable reaction. The need for the halogen to oxidise the thallium(I) carboxylate to a thallium(III) carboxylate dihalide is consistent with this observation.





(29)



$Me_3CCO_2CMe_3$

(34)

Reaction of thallium(I) 3,3-dimethylbutanoate (15) with 1.5 mol equiv. of bromine afforded 1-bromo-2,2-dimethylpropane (21)[14] as the sole product. No 2-bromo-2-methylbutane (26) was detected which rules out a carbocationic intermediate and suggests that the bromide (21) arises *via* a one-electron transfer involving a radical intermediate. The bromide (21) was also obtained as the sole product when silver(I) 3,3-dimethylbutanoate (27) was treated with bromine.[15] These results can be taken as evidence for the involvement of an alkyl free radical intermediate in both the classical Hunsdiecker reaction (*cf.* ref. 16) and the thallium(I) modification. Such a radical intermediate can be formed either by homolysis of an acyl hypobromite [equation (18)] or directly from the thallium(III) carboxylate dibromide [equation (19)] (*cf.* ref. 17).

$$RCO_2TlBr_2 \longrightarrow RCO_2Br + Tl^{I}Br \qquad (18)$$

$$RCO_2TlBr_2 \longrightarrow R^{\cdot} + CO_2 + Tl^{II}Br_2 \qquad (19)$$

McKillop and Taylor[2] postulated formation of an acyl hypobromite when a thallium(III) carboxylate dibromide is treated with bromine. In the present work no discharge of the bromine colour was observed when thallium(III) octadecanoate dibromide (13) was treated with 0.5 mol equiv. of bromine at room temperature. However, when this mixture was refluxed in carbon tetrachloride rapid decolourisation of the bromine was observed and smooth bromodecarboxylation occurred. In the classical Hunsdiecker reaction acyl hypobromite formation usually occurs at 20 °C but elevated temperatures are required in order to decompose the intermediate. Attempts to generate acetyl hypobromite or thallium(III) acetate dibromide by treatment of thallium(I) acetate with bromine in carbon tetrachloride were unsuccessful, as shown by the quantitative isolation of the *trans*-dibromide (29)[18] after addition of cyclohexene to the reaction mixture. In contrast, when the reaction was carried out in glacial acetic acid it gave a low yield (21%) of diacetoxy(cyclopentyl)methane. Moreover, treatment of a solution of thallium(I) acetate in glacial acetic acid with an equimolar amount of bromine gave a straw-coloured solution, $\lambda_{max.}$ 275 nm, which was the same as that obtained from treatment of a suspension of thallium(I) bromide in glacial acetic acid with an equimolar amount of acetyl hypobromite. Solutions of thallium(I) acetate and thallium(III) triacetate in glacial acetic acid had $\lambda_{max.}$ at 255 and 252 nm respectively. McKillop and Taylor[13] report that acyl hypobromites react with thallium(I) bromide to give the sesquihalide, Tl_2Br_4, and cite the example of the thallium(I) Hunsdiecker reaction.[2] However, the latter paper contains no such evidence. The results of the present investigation indicate that the primary product obtained from treatment of thallium(I) bromide with an acyl hypobromite should be the thallium(III) carboxylate dibromide rather than Tl_2Br_4.

The present study indicates that equation (19) is the most likely decomposition pathway of the thallium(III) dicarboxylate dibromide in the absence of added bromine (see however, ref. 19). Bivalent thallium has never been isolated as a stable species, but its existence has been confirmed in γ-irradiated glasses by e.s.r. spectroscopy,[20] and from pulse radiolysis studies.[21] The electroreduction of thallium(III) at rotating disc electrodes of silver and platinum has been studied,[22,23] and a rate-determining step in the reduction was found[23] to be the transfer of one electron to give thallium(II). A one-electron transfer process as in equation (19) could lead to Tl_2Br_4 in the bromodecarboxylation of thallium(I) carboxylates,[2] since by analogy with thallium(II) dichloride,[24] thallium(II) dibromide is likely to be unstable and could disproportionate to a mixture of thallium(I) bromide and thallium(III) tribromide, $2Tl^{II}Br_2 \longrightarrow Tl^{I}Br + Tl^{III}Br_3$, or to thallium(I) bromide and bromine, $2Tl^{II}Br_2 \longrightarrow 2Tl^{I}Br + Br_2$; the action of bromine on thallium(II) bromide would then give Tl_2Br_4.[7] However, the above proposals do not explain why pyrolysis of thallium(III) octadecanoate dibromide (13) gave 1-bromoheptadecane (9) in only *ca.* 30% yield. When the solid residue obtained from this pyrolysis was treated with 0.5 mol equiv. of bromine, calculated on compound (13), the overall yield of the alkyl bromide (9) was raised to 70%. Furthermore, an increased yield of (9) was not obtained when the thallium(III) carboxylate dibromide (13) was heated in refluxing carbon tetrachloride with concurrent irradiation from a 100 W light bulb.

The bromodecarboxylation of thallium(I) carboxylates has been utilised for the preparation [2] of bromides derived only from primary aliphatic carboxylic acids. A study (Table 2) of the bromodecarboxylation of the thallium(I) carboxylates of pentanoic acid (30), 2-methylpropanoic acid (31), and 2,2-dimethylpropanoic acid (32), compared with the classical Hunsdiecker reaction and with the Cristol–Firth [25] modification, indicates that use of the thallium(I) salts is not suitable for the preparation of tertiary bromides. However, whereas the classical Hunsdiecker [26] or Cristol–Firth [27] reactions of the acid (32) lead to formation of the ester (34) *via* the alkyl bromide, no ester was detected when the thallium(I) carboxylate (16) was employed.

TABLE 2

Comparative studies

Acid	Method	RBr	Yield (%)
(30)	HgO,Br_2	(22)	63 [a]
	Hg^{II} salt, Br_2		81 [a]
	Ag^{I} salt, Br_2		86 [b]
	Tl^{I} salt, Br_2		100 [c]
(31)	HgO, Br_2	(23)	47 [a]
	Hg^{II} salt, Br_2		63 [a]
	Ag^{I} salt, Br_2		75 [b]
	Tl^{I} salt, Br_2		43 [c]
(32)	HgO, Br_2	(24)	<1 [a]
	Hg^{II} salt, Br_2		<1 [a]
	Ag^{I} salt, Br_2		<1 [b]
	Tl^{I} salt, Br_2		<1 [c]

[a] Ref. 27. [b] N. J. Bunce and N. C. Murray, *Tetrahedron*, 1971, **27**, 5323. [c] Present study.

Treatment of thallium(I) cyclohexylmethanoate (20) with 1.5 mol equiv. of bromine gave a mixture of bromocyclohexane, the free acid (33), and the *trans*-dibromide (29). It is unlikely that the last product arises from cyclohexene generated by disproportionation of a cyclohexyl radical since the dibromide (29) was not detected during preparation of bromocyclohexane using the Cristol–Firth procedure. Rather, the dibromide may arise by a pathway similar to that proposed by Cason *et al.* for the formation of dibromides and the free acid in the Hunsdiecker reaction with octanoic acid,[28] *viz.* equations (20)—(22). However, treatment of the silver(I) salt (28) of cyclohexylmethanoic acid with bromine gives a high yield of bromocyclohexane (25) [29] and thus it is not clear why dibromide formation only occurs with the procedure involving the thallium(I) carboxylate (20).

$$C_7H_{15}Br + {}^{\bullet}Br \longrightarrow {}^{\bullet}C_7H_{14}Br + HBr \qquad (20)$$

$${}^{\bullet}C_7H_{14}Br + Br_2 \longrightarrow C_7H_{14}Br_2 + Br^{\bullet} \qquad (21)$$

$$C_7H_{15}CO_2Ag + HBr \longrightarrow C_7H_{15}CO_2H + AgBr \qquad (22)$$

The preparation of the thallium(I) carboxylates in the present study was achieved initially by neutralisation of the appropriate carboxylic acid with thallium(I) ethoxide, prepared from the oxidation of thallium metal in the presence of anhydrous ethanol.[30] However, thallium(I) ethoxide is somewhat unstable. Accordingly, a simple one-pot procedure was developed for the preparation of alkyl bromides from the free carboxylic acid using the commercially available and stable thallium(I) carbonate [equation (23)]. The thallium(I) salts were not isolated

$$Tl_2CO_3 + 2RCO_2H \longrightarrow 2RCO_2Tl^{I} + H_2CO_3 \qquad (23)$$

but were treated with 1.5 mol equiv. of bromine in refluxing solvent to give the alkyl bromides (Table 3). The use of thallium(I) acetate [31] instead of thallium(I) carbonate was less successful. Thus, reaction of equimolar quantities of thallium(I) acetate and octadecanoic acid (1) in carbon tetrachloride, followed by treatment of the mixture with 1.5 mol equiv. of bromine under reflux gave a somewhat lower yield (63%) of the alkyl bromide (9).

TABLE 3

Preparation of alkyl bromides *via* thallium(I) salts

Acid (1 mol equiv.)	Tl_2CO_3	RCO_2Tl^{I}	Br_2	RBr	Yield (%) *a*	*b*	*c*
(1)	0.6	(14)	1.5	(9)	79	77	83
(2)	0.8	(17)	1.5	(10)	85	81	84
(3)	0.8	(18)	1.5	(11)	83	89	92
(4)	0.8	(19)	1.5	(12)	82	82	85

[a] Using Tl_2CO_3. [b] Using RCO_2Tl^{I} + 1.5 mol equiv. Br_2. [c] As in *b*, with yields taken from ref. 2.

EXPERIMENTAL

General experimental details are given in ref. 32. Analytical g.l.c. was carried out with a Varian Aerograph series 1400 instrument on a column (1.5 m × 3 mm) packed with 5% OV-17 on Chromosorb W (70—80 mesh). Nitrogen was used as carrier gas. Carbon tetrachloride was dried and purified by passage through a column of activated alumina followed by fractional distillation. It was then stored over activated molecular sieves. Glacial acetic acid was distilled from chromium(VI) oxide and then fractionally redistilled. Bromine (May and Baker) was distilled from potassium bromide. Thallium(III) triacetate was prepared from thallium(III) oxide (Fluka, AG) using the method of Kochi and Bethea.[12] Thallium(I) acetate, thallium(I) bromide, and thallium(I) carbonate (BDH, L.R.) were used without purification.

Preparation of Thallium(I) *Carboxylates.*—Thallium(I) ethoxide [30] (0.9 mol equiv.) was transferred by pipette into a stirred solution of the carboxylic acid (1.0 mol equiv.) in anhydrous hexane. The precipitated salt was filtered off and washed with hexane, dried, and recrystallized from an appropriate solvent to give the following compounds: thallium(I) octadecanoate (14) (94%), m.p. 116—119 °C (lit.,[2] 117—119 °C); thallium(I) hexadecanoate (17) (92%), m.p. 115—118 °C (lit.,[2] 116—118 °C); thallium(I) tetradecanoate (18) (59%), m.p. 121—123 °C (lit.,[2] 120—121 °C); thallium(I) dodecanoate (19) (30%), m.p. 127—130 °C (lit.,[2] 119—120 °C); *thallium*(I) *pentanoate* (100%), plates from hexane–methanol), m.p. 180—182 °C (Found: C, 19.3; H, 2.9. $C_5H_9O_2Tl$ requires C, 19.7; H, 2.9%); *thallium*(I) *2-methylpropanoate* (90%), plates (from hexane–methanol), m.p. 126—129 °C (Found: C, 16.5; H, 2.4. $C_4H_7O_2Tl$ requires C, 16.5; H, 2.4%); *thallium*(I) *2,2-dimethylpropanoate* (16) (82%), needles (from hexane–methanol), m.p. 160—163 °C (Found: C, 19.6; H, 2.9. $C_5H_9O_2Tl$ requires C, 19.7; H, 2.9%); and *thallium*(I) *cyclohexylmethanoate* (20) (97%), rods (from hexane–

methanol), m.p. 189—191 °C (Found: C, 24.9; H, 3.5. $C_7H_{11}O_2Tl$ requires C, 25.4; H, 3.3%).

Thallium(III) *Trioctadecanoate* (5).—Thallium(III) triacetate (0.46 g, 1.20 mmol) was added to a solution of octadecanoic acid (1) (3.42 g, 12.0 mmol) in carbon tetrachloride (60 ml) and the suspension was stirred at 20 °C for 8 h. The solid was filtered off, washed with carbon tetrachloride, and dried to give *thallium*(III) *trioctadecanoate* (1.19 g, 94%), m.p. 78—82 °C (Found: C, 61.8; H, 9.9. $C_{54}H_{105}O_6Tl$ requires C, 61.5; H, 10.0%).

Thallium(III) *Acetate Dibromide*.—Bromine (3.35 g, 21.0 mmol) was added dropwise to a solution of anhydrous thallium(I) acetate (5.0 g, 19.0 mmol) in dry glacial acetic acid (15 ml). The pale cream precipitate which formed initially dissolved on further addition of bromine to give a straw-coloured solution which was stirred at 20 °C for 10 min. The solvent was removed at 50 °C under reduced pressure (10 mmHg) to give thallium(III) acetate dibromide[9] (7.89 g, 98%), m.p. 151—155 °C after drying over potassium hydroxide pellets for 24 h.

Thallium(III) *Octadecanoate Dibromide* (13).—(a) *From thallium*(I) *octadecanoate*. Bromine (0.22 g, 1.38 mmol) was added to a stirred suspension of thallium(I) octadecanoate (14) (0.60 g, 1.23 mmol) in carbon tetrachloride (15 ml) in the absence of light. The mixture was kept at 20 °C for 21 h and the solvent was removed under reduced pressure at 20 °C to give *thallium*(III) *octadecanoate dibromide* (0.78 g, 98%), m.p. 88—91 °C (decomp.) (Found: C, 33.3; H, 5.2; Br, 25.1. $C_{18}H_{35}Br_2O_2Tl$ requires C, 33.4; H, 5.5; Br, 24.7%).

The oxidation was fast at 20 °C as indicated by the rapid discharge of the bromine colour but proceeded only slowly at −78 °C.

(b) *From thallium*(III) *acetate dibromide*. Thallium(III) acetate dibromide (1.50 g, 3.11 mmol) and a solution of octadecanoic acid (1) (1.35 g, 4.75 mmol) in carbon tetrachloride (30 ml) were stirred in the dark for 48 h. Filtration gave impure thallium(III) octadecanoate dibromide (1.37 g), m.p. 92—95 °C (decomp.) (Found: C, 31.2; H, 4.9; Br, 28.4. Calc. for $C_{18}H_{35}Br_2O_2Tl$: C, 33.4; H, 5.5; Br, 24.7%).

Preparation of Alkyl Bromides from Thallium(I) *Carboxylates*.—Bromine (1.5 mol equiv.) in carbon tetrachloride (5 ml) was added to a stirred suspension of the thallium(I) carboxylate (1.0 mol equiv.) in carbon tetrachloride (15 ml) under nitrogen at 20 °C. The suspension was stirred for 15 min at 20 °C and heated under reflux for 3 h. Precipitated thallium(I) salts were filtered off from the cooled solution, the carbon tetrachloride was evaporated off, and the crude product was percolated through a short column of alumina (benzene) to give the following pure alkyl bromides: 1-bromoheptadecane (9) (77%), m.p. 26—28 °C (lit.,[2] 27—29 °C), *m/z* 320 and 318 ($M^{+\bullet}$), from thallium(I) octadecanoate (14); 1-bromopentadecane (10) (81%), b.p. 122 °C (Kugelrohr) at 0.2 mmHg (lit.,[2] 171—176 °C at 5.0 mmHg), *m/z* 292 and 290 ($M^{+\bullet}$), from thallium(I) hexadecanoate (17); 1-bromotridecane (11) (89%), b.p. 104 °C (Kugelrohr) at 0.15 mmHg (lit.,[2] 160—162 °C at 5.0 mmHg), *m/z* 264 and 262 ($M^{+\bullet}$), from thallium(I) tetradecanoate (18); 1-bromoundecane (12) (82%), b.p. 92 °C (Kugelrohr) at 0.1 mmHg (lit.,[2] 102—105 °C at 2.0 mmHg), *m/z* 236 and 234 ($M^{+\bullet}$), from thallium(I) dodecanoate (19).

General Procedures for Preparation of Alkyl Bromides.—(a) *Using thallium*(I) *carbonate and bromine*. Thallium(I) carbonate (0.60—0.80 mol equiv.) and a solution of the carboxylic acid (1.0 mol equiv.) in carbon tetrachloride (20 ml) were stirred together under nitrogen at 20 °C for 1 h. Bromine (1.5 mol equiv.) was added and the solution was heated under reflux for 3 h. Work-up and purification of the product as above gave the alkyl bromide.

(b) *Using thallium*(III) *triacetate and bromine*. A solution of the carboxylic acid (1.0 mol equiv.) was stirred with thallium(III) triacetate (2.5 or 3.0 mol equiv.) in carbon tetrachloride (20 ml) at 20 °C for 4 h under nitrogen. Bromine (1.0 mol equiv.) was added and the solution was heated under reflux until the bromine colour was discharged (*ca.* 1.5 h). Work-up as in (a) gave the alkyl bromide. No bromodecarboxylation was detected when thallium(III) oxide was used in place of thallium(III) triacetate.

Treatment of octadecanoic acid (1) (0.25 g, 0.88 mmol) with thallium(I) acetate (0.58 g, 2.20 mmol) followed by bromine (0.21 g, 1.31 mmol) gave 1-bromoheptadecane (9) (0.24 g, 63%).

Reactions of Thallium(III) *Tris*(*octadecanoate*) (5).—(a) *With bromine*. Bromine (0.23 g, 1.44 mmol) was added to a suspension of thallium(III) tris(octadecanoate) (0.50 g, 0.47 mmol) in carbon tetrachloride (15 ml) under nitrogen and the suspension was refluxed for 3 h. Work-up gave 1-bromoheptadecane (9) (0.32 g, 70%).

Treatment of the tricarboxylate (5) with 2 mol equiv. of bromine gave 1-bromoheptadecane in 65% yield.

Replacement of bromine by an equivalent amount of iodine gave no alkyl iodide (^{1}H n.m.r. spectral analysis).

(b) *With lithium bromide*. Thallium(III) tris(octadecanoate) (0.20 g, 0.19 mmol) and anhydrous lithium bromide (40 mg, 0.46 mmol) was refluxed in carbon tetrachloride (6 ml) under nitrogen for 3 h. ^{1}H N.m.r. spectral analysis indicated that no alkyl bromide had formed.

(c) *Pyrolysis*. Thallium(III) tris(octadecanoate) (0.11 g, 0.10 mmol) was recovered after heating in a Kugelrohr oven at 100 °C and 0.01 mmHg for 3 h.

Reactions of Thallium(III) *Octadecanoate Dibromide* (13).—(a) *With bromine*. Thallium(III) octadecanoate dibromide (0.40 g, 0.62 mmol) and bromine (50 mg, 0.31 mmol) were refluxed in carbon tetrachloride (15 ml) under nitrogen for 2 h. Work-up gave 1-bromoheptadecane (9) (0.16 g, 83%). No discharge of the bromine colour or alkyl bromide formation occurred (^{1}H n.m.r., t.l.c.) when thallium(III) octadecanoate dibromide was stirred with bromine (0.5 mol equiv.) at 20 °C for 24 h.

(b) *Heating in carbon tetrachloride*. Thallium(III) octadecanoate dibromide (0.40 g, 0.62 mmol) was heated in refluxing carbon tetrachloride (15 ml) under nitrogen for 2 h. Centrifugation of the resulting suspension yielded a pale yellow solution and a yellow solid. Work-up of the solution gave 1-bromoheptadecane (9) (60 mg, 31%). Treatment of the yellow solid (0.27 g) with bromine (50 mg, 0.31 mmol) in refluxing carbon tetrachloride (10 ml) as in (a) gave 1-bromoheptadecane (60 mg, 31%) [overall 62% from (13)].

(c) *Pyrolysis*. Thallium(III) octadecanoate dibromide (0.40 g, 0.62 mmol) was heated in a Kugelrohr oven at 100 °C and 0.15 mmHg. The cooled residue was extracted with pentane to give 1-bromoheptadecane (50 mg, 25%). Treatment of the pentane-insoluble residue (0.32 g) with bromine (50 mg, 0.31 mmol) in refluxing carbon tetrachloride (15 ml) as in (b) gave 1-bromoheptadecane (90 mg, 47%) [overall 72% from (13)].

(d) *With irradiation*. Thallium(III) octadecanoate dibromide (0.41 g, 0.63 mmol) was refluxed in carbon tetrachloride (15 ml) under nitrogen for 1.5 h and irradiated by a 100 W light bulb. Work-up gave 1-bromoheptadecane (70 mg, 23%).

(e) The product from thallium(III) acetate dibromide and octadecanoic acid (1) (0.62 mmol) was treated with bromine (50 mg, 0.31 mmol) as in (a). Work-up gave 1-bromoheptadecane (0.15 g, 74%).

Estimation of Volatile Products obtained from Treatment of Thallium(I) *Carboxylates with Bromine.*—Yields were estimated relative to a known amount of a suitable standard (usually the corresponding alkyl iodide) by g.l.c. analysis of the crude reaction mixture. Product identities were confirmed by comparison of retention times (g.l.c.) or spectral parameters (^{1}H n.m.r.) with those of pure samples.

Thallium(I) pentanoate (0.30 g, 0.98 mmol) and bromine (0.24 g, 1.50 mmol) were heated under reflux in carbon tetrachloride (20 ml) under nitrogen for 3 h and 1-iodobutane (0.16 g, 0.87 mmol) was then added to the cooled mixture. G.l.c. (column temp. 45 °C) indicated a near quantitative yield of 1-bromobutane.

Thallium(I) 2-methylpropanoate (0.25 g, 0.86 mmol) and bromine (0.21 g, 1.31 mmol) in carbon tetrachloride (10 ml) were stirred at 20 °C for 20 min and heated under reflux for 2 h. 1-Iodobutane (0.16 g, 0.87 mmol) was then added to the cooled mixture. G.l.c. (40 °C) indicated the presence of 2-bromopropane (*ca.* 43%).

Thallium(I), 2,2-dimethylpropanoate (0.30 g, 0.98 mmol) and bromine (0.23 g, 1.44 mmol) in carbon tetrachloride (5 ml) were stirred at 0 °C for 1 h and the thick yellow slurry was then refluxed for 1 h under nitrogen. G.l.c. showed that the only detectable product was 2,2-dimethylpropanoic acid (32).

Thallium(I) cyclohexylmethanoate (0.15 g, 0.45 mmol) and bromine (70 mg, 0.44 mmol) were stirred in carbon tetrachloride (7 ml) at 0 °C for 1 h. G.l.c. (160 °C) indicated the presence of bromocyclohexane and cyclohexylmethanoic acid (33) in a ratio of *ca.* 1 : 1. More bromine (40 mg, 0.25 mmol) was added and the mixture was refluxed under nitrogen for 1 h. G.l.c. indicated the presence of bromocyclohexane (31%), cyclohexylmethanoic acid (30%), and *trans*-1,2-dibromocyclohexane (29) (39%). Addition of bromine (1.0 mol equiv.) to thallium(I) cyclohexylmethanoate at 20 °C resulted in the evolution of HBr and recovery of free acid (33) as the major product.

Thallium(I), 3,3-dimethylbutanoate (15) (0.32 g, 0.97 mmol) and bromine (0.24 g, 1.5 mmol) in carbon tetrachloride were stirred at 0 °C for 1 h, at 20 °C for 1 h, and finally refluxed for 1 h under nitrogen. Work-up gave 1-bromo-2,2-dimethylpropane (21)[15] (0.12 g, 82%), δ (CCl_4) 1.07 (s, Me_3) and 3.17 (CH_2Br). No products of skeletal rearrangement were detected by ^{1}H n.m.r. analyses before and after work-up.

Preparation of Bromocyclohexane using the Cristol–Firth Procedure.[25]—Bromine (0.50 g, 3.13 mmol) in carbon tetrachloride (5 ml) was added dropwise over 2 min to a suspension of cyclohexylmethanoic acid (33) (0.40 g, 2.90 mmol) and red mercury(II) oxide (0.34 g, 1.56 mmol) in carbon tetrachloride (20 ml) and the reflux was maintained for 2 h under nitrogen. The mixture was cooled and 1-iodobutane (0.16 g, 0.87 mmol) was added. G.l.c. indicated the presence of 1-bromocyclohexane (0.24 g, 47%) but no *trans*-1,2-dibromocyclohexane (29).

Treatment of Thallium(I) *Bromide with Acetyl Hypobromite.*—Thallium(I) bromide (0.93 g, 3.27 mmol) was added to a solution of acetyl hypobromite [3.26 mmol, prepared from bromine (0.52 g) and silver(I) acetate (0.60 g), $\lambda_{max.}$ 250 nm] in glacial acetic acid (10 ml) and the suspension was stirred. The thallium(I) bromide dissolved to give a straw-coloured solution, $\lambda_{max.}$ 275 nm.

Treatment of Thallium(I) *Acetate with Bromine in Acetic Acid.*—Bromine (0.56 g, 3.50 mmol) was added to a solution of thallium(I) acetate (0.86 g, 3.26 mmol) in glacial acetic acid (10 ml) to give a straw-coloured solution, $\lambda_{max.}$ 275 nm. A solution of thallium(I) acetate in glacial acetic acid had $\lambda_{max.}$ 255 nm.

Reactions of Thallium(I) *Acetate and Bromine with Cyclohexene.*—(a) *In carbon tetrachloride.* Bromine (0.16 g, 1.0 mmol) was added to a stirred suspension of thallium(I) acetate (0.50 g, 1.9 mmol) in carbon tetrachloride (10 ml) over 15 min and the solution was stirred at room temperature for 20 min. Cyclohexene (80 mg, 0.98 mmol) was added and the stirring was continued for 1 h. The mixture was filtered and the solvent was removed from the filtrate to give *trans*-1,2-dibromocyclohexane (29) (0.24 g, 100%) as an oil (correct ^{1}H n.m.r. spectrum[18]).

(b) *In glacial acetic acid.* Bromine (0.64 g, 4.0 mmol) was added to a stirred solution of thallium(I) acetate (1.05 g, 4.0 mmol) in glacial acetic acid (15 ml). Cyclohexene (0.33 g, 4.02 mmol) was added and the solution was stirred at room temperature for 12 h. The mixture was filtered, water was added, and the filtrate was extracted with ether. The extract was washed with sodium hydrogencarbonate solution and water and concentrated to give an oil (0.34 g) which darkened quickly on standing. The product was filtered through a column of Florisil (chloroform) to give diacetoxy(cyclopentyl)methane (0.17 g, 21%), $\nu_{max.}$ 1 670 cm^{-1} (CO), δ (CCl_4) 2.07 (s, $OCOCH_3$) and 6.17 [d, J 6.0 Hz, $CH(OAc)_2$], m/z 157 ($M^{+\bullet} - {}^{\bullet}C_2H_3O$), and 141 ($M^{+\bullet} - {}^{\bullet}C_2H_3O_2$).

A solution of the diacetate in methanol–water (10 : 1 v/v) and concentrated sulphuric acid (2 drops) was heated at 80 °C for 15 min. A 0.01M-solution of 2,4-dinitrophenylhydrazine in acidified methanol (20 ml) was added to the cooled solution which was concentrated to yield the 2,4-dinitrophenylhydrazone of cyclopentylmethanal (23 mg, 11% based on the diacetate), m.p. 154—158 °C (lit.,[33] 158—162 °C) (Found: $M^{+\bullet}$, 278.1008. Calc. for $C_{12}H_{14}N_4O_4$: M, 278.1015), $\nu_{max.}$ 3 200 (NH), 1 610, and 1 595 cm^{-1} (C=N and C=C), δ (CCl_4) 1.80 (m, CH_2), 7.51 (d, J 6.0 Hz, CH=N), 7.92 (d, J 10.0 Hz, 6′-H), 8.32 (dd, J 2.5 and 10.0 Hz, 5′-H), 9.15 (d, J 2.5 Hz, 3′-H), and 11.00 (m, NH).

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