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ORGANOTHALLIUM COMPOUNDS

XI *. REACTIONS OF THALLIC SALTS WITH SOME SODIUM ARENESULPHINATES

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Summary

Desulphination reactions between sodium mesitylenesulphinate and the thallic salts TlX_3 ($X = MeCO_2$, CF_3CO_2 or Cl) in aqueous acetic acid or water gave mesitylthallium(III) diacetate or the complexes $RTl(O_2SR)X$ ($R = 2,4,6\text{-}Me_3C_6H_2$; $X = MeCO_2$ or Cl) at room temperature and dimesitylthallium(III) mesitylenesulphinate at 100°C. The diacetate was independently synthesized by metathesis from mesitylthallium(III) dichloride, and was converted into $RTl(O_2SR)O_2CMe$ by sodium mesitylenesulphinate. The derivatives $RTl(O_2SR)X$ gave mesitylthallium(III) dichloride on treatment with HCl and rearranged into dimesitylthallium mesitylenesulphinate in boiling aqueous acetic acid or water. Thermal decomposition of $RTl(O_2SR)O_2CMe$ under vacuum yielded dimesitylthallium(III) acetate. The structures of the mesitylthallium sulphinate and acetate complexes are discussed. Reaction of thallic acetate or trifluoroacetate with sodium 2,4,6-triisopropylbenzenesulphinate in aqueous acetic acid gave $Tl^I[Tl^{III}(O_2SR^1)_4]$ [$R^1 = 2,4,6\text{-}(Me_2CH)_3C_6H_2$] at room temperature and the thiosulphonate $R^1SO_2SR^1$ at 100°C, whilst reactions with sodium benzenesulphinate and *p*-toluenesulphinate gave the diaryl disulphones.

Introduction

The first syntheses of Group III organometallics by sulphur dioxide elimination (desulphination) reactions have recently been described [1]. Acetatobis(polyfluorophenyl)thallium(III) compounds R_2TlO_2CMe ($R = C_6F_5$, $p\text{-}HC_6F_4$, or $m\text{-}HC_6F_4$) were obtained from reaction of thallic trifluoroacetate or acetate

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* Part X, Ref. [1].

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with the corresponding lithium polyfluorobenzenesulphinates. We now report reactions of thallic salts with some hydrocarbon arenesulphinate ions. Previous workers have shown that treatment of thallic chloride with sodium benzenesulphinate and *p*-toluenesulphinate yields *S*-arenesulphinatothallium(III) complexes [2].

Results and discussion

(a) Reactions of thallic salts with sodium mesitylenesulphinate

Sulphur dioxide elimination occurred on reaction of thallic trifluoroacetate with sodium mesitylenesulphinate (mol. ratio 3 : 2) * in aqueous acetic acid at room temperature, and mesitylthallium(III) diacetate was precipitated (eq. 1) ($R = 2,4,6\text{-}Me_3C_6H_2$ throughout section (a)). The compound was independently

$$Tl(O_2CCF_3)_3 + NaO_2SR + 2MeCO_2H \rightarrow RTl(O_2CMe)_2\downarrow + SO_2 + NaO_2CCF_3 + 2CF_3CO_2H \quad (1)$$

synthesized from the known [3] mesitylthallium(III) dichloride by metathesis (2). By contrast with (1), reaction of thallic acetate or trifluoroacetate ** with

$$RTlCl_2 + 2AgO_2CMe \rightarrow RTl(O_2CMe)_2 + 2AgCl\downarrow \quad (2)$$

sodium mesitylenesulphinate (mol. ratio 1 : 3) in aqueous acetic acid at room temperature gave mesitylthallium(III) mesitylenesulphinate acetate (e.g., reaction 3; $X = MeCO_2$). Probably the diacetate is formed first, by (1), and is then

$$TlX_3 + 2NaO_2SR \rightarrow RTl(O_2SR)X\downarrow + SO_2 + 2NaX \quad (3)$$

converted into the less soluble sulphinate acetate. In confirmation, mesityl-

$$RTl(O_2CMe)_2 + NaO_2SR \rightarrow RTl(O_2SR)O_2CMe\downarrow + NaO_2CMe \quad (4)$$

thallium(III) diacetate, which is appreciably soluble in acetic acid, was precipitated on reducing the amount of acetic acid in the solvent (from $MeCO_2H : H_2O$ = 1 : 5, v/v, for reaction 3 to 1 : 10) while maintaining the mol. ratio $TlX_3 : NaO_2SR$ = 1 : 3. In addition, reaction 4 has been independently carried out (Experimental section). Mesitylthallium(III) mesitylenesulphinate acetate was converted by hydrochloric acid into mesitylthallium(III) dichloride (reaction 5; $X = MeCO_2$), which has thallium—proton coupling constants (Experimental section) similar

$$RTl(O_2SR)X + 2HCl \rightarrow RTlCl_2 + RSO_2H + HX \quad (5)$$

to these reported [3] for the corresponding bistrifluoroacetate. Thermal decomposition of the sulphinate acetate at 185°C under vacuum resulted in sulphur dioxide elimination and formation of dimesitylthallium(III) acetate (eq. 6). Treatment of thallic chloride with sodium mesitylenesulphinate (mol.

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* In reactions of thallic salts with lithium polyfluorobenzenesulphinates [1], use of a mol. ratio of 3 : 2 gave maximum yields of acetatobis(polyfluorophenyl)thallium(III) complexes.

** An acetatothallium(III) species is formed on dissolution of thallic trifluoroacetate in aqueous acid, but complete conversion into thallic acetate does not occur [1].

$RTl(O_2SR)O_2CMe \rightarrow R_2TlO_2CMe + SO_2$ (6)

ratio 1 : 3) in aqueous solution at room temperature gave mesitylthallium(III) mesitylenesulphinate chloride (reaction 3; X = Cl), which could not be obtained analytically pure. However, the identification was certain, since the infrared spectrum (Experimental section) and reaction with HCl (equation 5; X = Cl) were similar to those of the sulphinate acetate.

Reaction of the thallic salts TlX_3 (X = CF_3CO_2, $MeCO_2$ or Cl) with sodium mesitylenesulphinate (mol. ratio 1 : 3) in hot (100°C) aqueous acetic acid (X = CF_3CO_2 or $MeCO_2$) or water (X = Cl) gave dimesitylthallium(III) mesitylenesulphinate (eq. 7). Monomesitylthallium(III) compounds, $RTl(O_2SR)X$ (X = $MeCO_2$ or Cl) were probably intermediates in the reaction, since they were obtained from the same reagents under milder conditions (reaction 3; X = $MeCO_2$ or Cl), and underwent rearrangement into dimesitylthallium(III) mesitylenesulphinate in boiling aqueous acetic acid (X = $MeCO_2$) or water (X = Cl) (eq. 8). Arylthallium(III) bistrifluoroacetates undergo similar symmetrization reactions in boiling acetone giving diarylthallium(III) trifluoroacetates [4]. Dimesitylthallium(III) mesitylenesulphinate was converted by potassium iodide into dimesitylthallium(III) iodide, which has thallium—proton coupling constants (Experimental section) similar to those [3] of dimesitylthallium(III) trifluoroacetate.

$TlX_3 + 3NaO_2SR \rightarrow R_2TlO_2SR\downarrow + 3NaX + 2SO_2$ (7)

$2RTl(O_2SR)X \rightarrow R_2TlO_2SR + Tl(O_2SR)X_2$ * (8)

$R_2TlO_2SR + KI \rightarrow R_2TlI + KO_2SR$

The desulphination reactions 1 and 6 are closely related to the preparation of organomercuric acetates by the Peters reaction [5] and the formation of diarylmercurials by thermal decomposition of arylmercuric arenesulphinates [6] respectively. There is also a similarity between reaction 7 and the preparations of diarylmercurials from mercuric acetate and arenesulphinate ions in boiling water [7].

Structures of mesitylthallium(III) sulphinates and acetates: The sulphur—oxygen stretching frequencies of $RTl(O_2SR)X$ (X = $MeCO_2$ or Cl) complexes (Table 1) are in the range (1100—800 cm^{-1}) for *O*-sulphinate complexes [6, 8—10], and the relatively large separation between $\nu_{as}(SO_2)$ and $\nu_s(SO_2)$ is indicative of unidentate *O*-sulphinate coordination [6,9]. Since the separation between the $\nu(CO_2)$ frequencies (Table 1) of $RTl(O_2SR)O_2CMe$ is similar to that [11] of sodium acetate (164 cm^{-1}), unidentate acetate groups can be ruled out, but the remaining possibilities, ionic, bidentate, or bridging bidentate cannot be distinguished on this basis [12,13,14]. The structure probably contains essentially ionic $[RTlO_2SR]^+$ groups with linear CTlO stereochemistry and

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* This may react further, by sulphur dioxide elimination, giving $RTlX_2$ (see also section (d)), then metathesis reforming $RTl(O_2SR)X$ (e.g. reaction 4), or by a redox reaction (see also section (b)).

$Tl(O_2SR)X_2 + H_2O \rightarrow RSO_3H + TlX + HX$

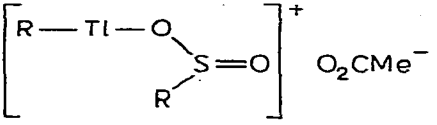
TABLE I

SULPHUR—OXYGEN AND CARBON—OXYGEN STRETCHING FREQUENCIES (cm^{-1}) OF SOME SULPHINATE AND CARBOXYLATE COMPLEXES

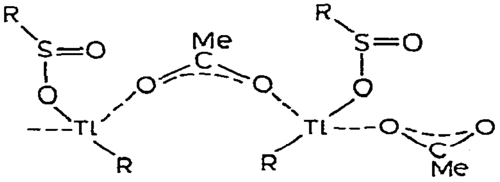
Compound [a]	$\nu_{as}(SO_2)$	$\nu_s(SO_2)$	Separation	$\nu_{as}(CO_2)$	$\nu_s(CO_2)$	Separation
$RTl(O_2SR)O_2CMe$	986	860	126	1557	1400	157
$RTl(O_2SR)Cl$	1004, 987	840	156			
$RTl(O_2CMe)_2$				1552	1387	165
$R_2Tl(O_2SR)$	979	941	38			
R_2TlO_2CMe				1529	1428	101

[a] $R = 2,4,6\text{-}Me_3C_6H_2$.

either ionic (structure I) or weakly bridging (structure II) acetate groups *. An analogous structure with bridging or ionic chloride is likely for $RTl(O_2SR)Cl$. Use of molecular weight or conductance measurements to distinguish between ionic and associated structures for $RTl(O_2SR)X$ complexes was prevented by decomposition on attempted dissolution.

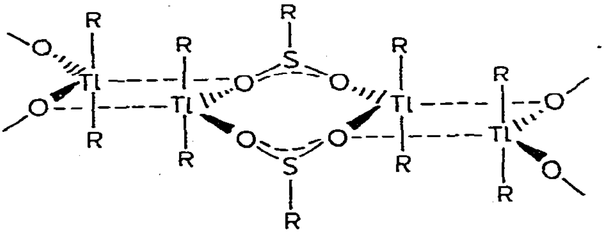


(I)



(II)

Dimesitylthallium(III) mesitylenesulphinate has $\nu(SO_2)$ frequencies (Table 1) similar to those of some known diorganothallium(III) arenesulphinates [18], hence an associated structure (III) similar to that proposed for these complexes is likely, and is consistent with the low solubility.



(III)

Molecular weight data (monomer ⇌ dimer equilibrium in chloroform) and conductance measurements (non-electrolyte in acetone) suggest that mesityl-

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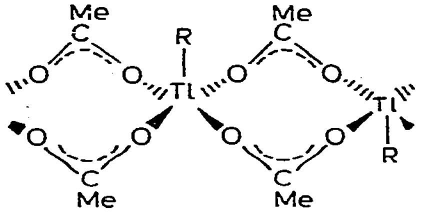
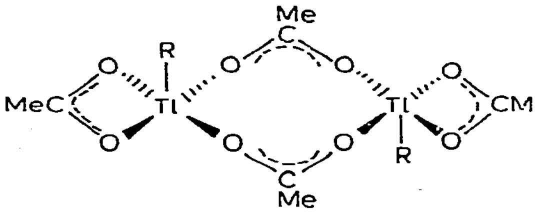
* X-ray crystallography has shown phenylthallium(III) dichloride to be essentially ionic [$PhTlCl^+$] Cl^-, but with weak interactions between chloride ions and the digonally coordinated complex cations [15]. This result has been overlooked in a recent infrared study [16], which concluded that the compound is monomeric with trigonal stereochemistry. Earlier infrared data have been correlated with the crystal structure [17].

thallium(III) diacetate has an associated structure. The separation between the $\nu(CO_2)$ frequencies (Table 1) is consistent [12—14] with bidentate or bridging bidentate carboxylate coordination. Accordingly, either a polymeric (IV) or a dimeric (V) structure with five coordinate thallium is likely.



(IV)



(V)

This coordination number is known for monoorganothallium(III) compounds [16,19]. Previous workers have suggested that other organothallium(III) dicarboxylates have either ionic structures with unidentate and ionic carboxylate groups and two coordinate thallium [3,20] or associated structures with unidentate and bridging bidentate carboxylate groups and four coordinate thallium [16,21], but infrared and conductance data exclude both for mesitylthallium(III) diacetate. The very low separation between the $\nu(CO_2)$ frequencies of dimesitylthallium(III) acetate (Table 1) is indicative [13,14] of bidentate or bridging bidentate acetate groups, and a dimeric or polymeric structure with bridging acetate ligands and four coordinate thallium is likely. Similar structures have been proposed [1,22,23] for other diorganothallium(III) carboxylates.

(b) Reactions of thallic salts with sodium 2,4,6-triisopropylbenzenesulphinate

Treatment of the thallic salts TlX_3 ($X = MeCO_2$ or CF_3CO_2) with sodium 2,4,6-triisopropylbenzenesulphinate (mol. ratio 1 : 3) in aqueous acetic acid gave a yellow precipitate of composition $Tl(O_2SR^1)_2$ ($R^1 = 2,4,6\text{-}(Me_2CH)_3C_6H_2$ throughout section (b)), considered to be the mixed oxidation state complex $Tl^I[Tl^{III}(O_2SR^1)_4]$, at room temperature (eq. 9), and *S*-2,4,6-triisopropylphenyl

$$2TlX_3 + 5NaO_2SR^1 + H_2O \rightarrow Tl[Tl(O_2SR^1)_4]\downarrow + NaO_3SR^1 + 2HX + 4NaX \qquad (9)$$

2,4,6-triisopropylbenzenethiosulphonate at 100°C (eq. 10). The observation of a

$$2TlX_3 + 5NaO_2SR^1 + H_2O \rightarrow R^1SO_2SR^1\downarrow + NaO_3SR^1 + 2HX + 4NaX + \\ + 2TlO_3SR^1 \qquad (10)$$

yellow precipitate in the initial stage of reaction 10 suggests that $Tl[Tl(O_2SR^1)_4]$ is an intermediate in the formation of the thiosulphonate. This was confirmed by the reaction of thallic trifluoroacetate with 2,4,6-triisopropylbenzenesulphinic acid in acetonitrile/acetic acid at room temperature, when the initially formed yellow precipitate of $Tl[Tl(O_2SR^1)_4]$ was converted into the thiosulphonate on continued stirring (eq. 11). Sulphinic acids [24] and bismuth tri-

$$Tl[Tl(O_2SR^1)_4] \rightarrow R^1SO_2SR^1 + 2TlO_3SR^1 \qquad (11)$$

p-chlorobenzenesulphinate [25] undergo disproportionation reactions similar to (11) on being heated.

Formulation of $Tl[Tl(O_2SR^1)_4]$ as a mixed oxidation state complex is supported by observation of an intense band, attributable [26] to intervalance electron transfer, at ca. 330 nm in the reflectance spectrum. A similar absorption is observed at 359 nm for $Tl^I[Tl^{III}Cl_4]$ [26]. The single $\nu(SO_2)$ frequency (918 cm^{-1}) for $Tl[Tl(O_2SR^1)_4]$ is consistent [9] with bidentate or bridging bidentate *O*-sulphinate coordination. An eight coordinate complex anion, in which four bidentate *O*-sulphinate ligands surround thallium in a pseudo-tetrahedral arrangement, seems likely. Similar eight coordinate anions are known in $K_3[Hg(NO_2)_4]NO_3$ [27] and $NO[Tl(NO_3)_4]$ [28].

(c) Reaction of thallic trifluoroacetate with sodium benzene- or p-toluene-sulphinate

The diaryl disulphones $R^2SO_2SO_2R^2$ (R^2 = Ph or *p*-MeC_6H_4) were formed on reaction of thallic trifluoroacetate with the sodium arenesulphinates (mol. ratio 1 : 3) in aqueous acetic acid at room temperature (eq. 12) (cf. precipitation of *S*-arenesulphinatothallium(III) complexes with $TlCl_3$ [2]). Since the yields were

$$Tl(O_2CCF_3)_3 + 2NaO_2SR^2 \rightarrow R^2SO_2SO_2R^2\downarrow + TlO_2CCF_3 + 2NaO_2CCF_3 \qquad (12)$$

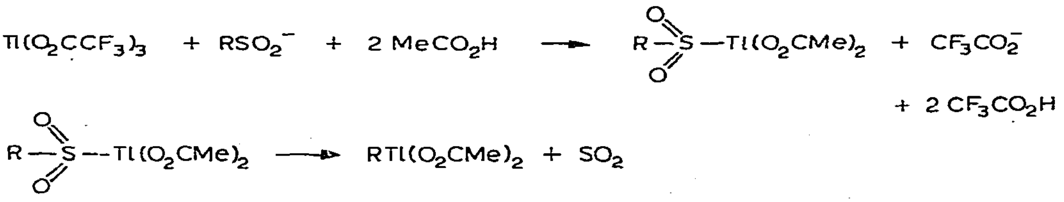
modest, simultaneous oxidation of sulphinate ions to sulphonate may also occur (eq. 13) (see also reaction 9). In the oxidation of sulphinate ions by

$$Tl(O_2CCF_3)_3 + NaO_2SR^2 + H_2O \rightarrow NaO_3SR^2 + TlO_2CCF_3 + 2CF_3CO_2H \qquad (13)$$

cerium(IV), sulphonate formation predominates over disulphone formation [29].

(d) General remarks and conclusions

Desulphination reactions of arenesulphinate ions with thallic salts are a simple route to mesitylthallium (section (a)) and polyfluorophenylthallium [1] compounds, but appear restricted to sulphinates with moderately bulky *ortho* substituents or electron withdrawing substituents. With other sulphinate ions, including those with very large *ortho* substituents (section (b)), redox reactions occur. It is likely that the sulphur dioxide elimination reaction 1 giving mesitylthallium(III) diacetate proceeds via formation and desulphination of an *S*-arenesulphinatothallium(III) complex. *S*-Arenesulphinatodichlorothallium(III) com-



($R = 2,4,6\text{-}Me_3C_6H_2$)

plexes have been isolated from reactions of thallic chloride with sodium benzene- and *p*-toluene-sulphinates in water [2], and a similar path has been proposed for desulphination syntheses of polyfluorophenylthallium compounds [1]. Steric destabilization of the *S*-mesitylenesulphinato intermediate accounts for the ready elimination of sulphur dioxide in reaction 1. Consistent with this explanation, the less hindered *O*-sulphinato complex $RTl(O_2SR)O_2CMe$ (R = 2,4,6-$Me_3C_6H_2$) has much greater thermal stability. The absence of elimination with the bulkier Me_2CH groups *ortho* to the $—SO_2$ group suggests that steric repulsion prevents formation of an *S*-sulphinate complex in this case. Accordingly, the less hindered *O*-sulphinate is obtained and undergoes oxidation (reaction 9) rather than elimination. By contrast with thallic salts, mercuric acetate induces desulphination more readily from sodium 2,4,6-triisopropylbenzenesulphinate than sodium mesitylenesulphinate [7]. Probably the reacting mercury(II) species has smaller steric requirements than the thallium(III) species, hence an *S*-sulphinate intermediate can be formed. The steric requirement of thallium is known to be large in thallation reactions [20].

Experimental

Microanalyses were by the Australian Microanalytical Service, Melbourne. Infrared spectra of compounds as Nujol and hexachlorobutadiene mulls were recorded with Perkin—Elmer 521 (4000—400 cm^{-1}) and 257 (4000—650 cm^{-1}) spectrophotometers. No exchange of sulphinate or carboxylate groups with KBr plates was observed. Very weak bands are not listed. Conductances were measured at ca. 15°C with a Wayne—Kerr B221A bridge using a cell of standard design fitted with shiny platinum electrodes. Molecular weights were determined at 25°C with a Mechrolab 301A osmometer. PMR spectra were obtained with a Varian A56/60 instrument.

Thallic acetate, mesitylenesulphonyl chloride, and 2,4,6-triisopropylbenzenesulphonyl chloride were from Aldrich, sodium benzenesulphinate dihydrate from B.D.H., sodium *p*-toluenesulphinate dihydrate from Eastman Organic Chemicals, and thallic trifluoroacetate from ROC/RIC. Mesitylthallium(III) dichloride [3], zinc mesitylenesulphinate [7] and 2,4,6-triisopropylbenzenesulphinic acid [7] were prepared by the literature methods. Solutions of sodium mesitylenesulphinate and 2,4,6-triisopropylbenzenesulphinate were prepared by neutralization of the corresponding arenesulphinic acids. Mesitylenesulphinic acid was precipitated (yield, 75%), m.p. 102—103°C, lit. [30] 98—99°C (Found: C, 58.8; H, 6.6. $C_9H_{12}O_2S$ calcd.: C, 58.7; H, 6.6%) on acidification of the solution obtained by treating the zinc sulphinate with an excess of sodium carbonate in boiling water.

New compounds were obtained as white solids unless indicated otherwise.

(a) Reaction of sodium mesitylenesulphinate with thallic acetate or trifluoroacetate at room temperature

Mesitylthallium(III) diacetate (nc). Thallic trifluoroacetate (2.0 mmol) in glacial CH_3COOH (7 ml) was added to a stirred solution of sodium mesitylenesulphinate (1.4 mmol) in H_2O (25 ml) giving an immediate white precipitate of the diacetate (yield, 50%; infrared identification). The authentic compound was prepared by heating silver acetate (3.8 mmol) and mesitylthallium(III) dichloride (1.3 mmol) for 1 h in refluxing methanol (15 ml) containing a few drops of glacial acetic acid, followed by filtration, evaporation to dryness, and recrystallization of the residue from chloroform/ether (yield, 80%), m.p. 208—209°C (Found: C, 35.5; H, 3.7; mol. wt. (in $CHCl_3$), 600 (1.01%, w/v); 618 (1.92%); 629 (2.34%). $C_{13}H_{17}O_4Tl$ calcd.: C, 35.4; H, 3.9%; mol. wt., 437). The compound had negligible conductivities in chloroform or acetone. Infrared absorption: 1552s(vbr), 1419(sh, br), 1387m(br), 1334m, 1298w, 1010m, 941m, 852w, 841m, 689 and 683s, 618w, and 536w cm^{-1}.

Mesitylthallium(III) mesitylenesulphinate acetate (nc). (i) By desulphination: Thallic acetate or trifluoroacetate (0.90 mmol) in glacial acetic acid (10 ml) was added to a stirred solution of sodium mesitylenesulphinate (2.7 mmol) in water (50 ml) giving an immediate precipitate of the title compound (yield, 42%, using thallic acetate), m.p. ca. 190°C (preliminary softening >150°C) (Found: C, 42.5; H, 4.3; S, 5.5. $C_{20}H_{25}O_4STl$ calcd.: C, 42.5; H, 4.5; S, 5.7%). Infrared absorption: 1597w, 1557s(br), 1400m(br), 1337w, 1296w, 1058w, 1018(sh), 986vs, 942w, 860vs, 845s, 684s, 630m, 592w, 562w, 540w, 496w and 432m cm^{-1}. A similar reaction in which the sole change was a reduction of the volume of acetic acid to 5 ml gave a precipitate of mesitylthallium(III) diacetate (infrared identification). When more than 10 ml of acetic acid was used, a mixture of the sulphinate acetate and mesitylenesulphinic acid was obtained (infrared identification). (ii) By metathesis: Sodium mesitylenesulphinate (0.40 mmol) in water (5 ml) was added to a stirred solution of mesitylthallium(III) diacetate (0.40 mmol) in glacial acetic acid (5 ml). After several minutes, water (10 ml) was added, precipitating mesitylthallium(III) mesitylenesulphinate acetate, which was collected after stirring for a further 15 min (yield, 44%; infrared identification).

(b) Reactions of mesitylthallium(III) mesitylenesulphinate acetate

(i) With HCl. The complex (0.20 g) was suspended in water (20 ml) containing 1 ml of methanol, and 10 drops of concentrated hydrochloric acid were added. After stirring for 1 h, sodium hydroxide was added until the mixture was just alkaline, and the precipitate of mesitylthallium(III) dichloride was filtered off (yield, 75%), m.p. >250°C, lit. [3] m.p. >300°C (Found: C, 27.8; H, 2.7. $C_9H_{11}Cl_2Tl$ calcd.: C, 27.4; H, 2.8%). The infrared spectrum was identical with that of an authentic sample (above). PMR spectrum ($(CD_3)_2CO$): 2.13 (d, J(Tl—H) 54 Hz, 3H, p-$\underline{CH_3}$), 2.39 (d, J(Tl—H) 99 Hz, 6 H, o-$\underline{CH_3}$), and 6.86 (d, J(Tl—H) 381 Hz, 2H, m-H) ppm downfield from external tetramethylsilane.

(ii) Thermal decomposition. The complex (0.20 g) was heated (20—185°C, 5 h) under vacuum (ca. 10^{-2} mmHg) in a sublimator with a water-cooled probe, giving a sublimate of dimesitylthallium(III) acetate (nc) (yield, 83%), m.p. 188—192°C (Found: C, 47.6; H, 5.0. $C_{20}H_{25}O_2Tl$ calcd.: C, 47.9; H, 5.0%). Infrared absorption: 1590(sh), 1566(sh), 1529s(br), 1447(sh, br), 1428s(br), 1377w, 1293s, 1030w, 978m, 834w, 849vs, 701m, 672vs, 616w, and 540m cm^{-1}.

(c) Reaction of sodium mesitylenesulphinate with thallic chloride at room temperature

Mesitylthallium(III) mesitylenesulphinate chloride (nc) was precipitated on mixing aqueous solutions of thallic chloride (0.90 mmol in 4 ml) and sodium mesitylenesulphinate (2.7 mmol in 50 ml). The compound was collected after

30 min, stirred with dilute sodium hydroxide, and was washed thoroughly with water (yield, ca. 40%), m.p. 135—146°C (with prelim. softening). Several preparations were carried out, the products having variable analyses (Found: C, 34.6—39.0; H, 3.6—3.8. $C_{18}H_{22}ClO_2STl$ calcd.: C, 39.9; H, 4.1%), but identical infrared spectra: 1602w, 1450w(br), 1376w, 1298m, 1060w, 1004s, 987vs, 843vs, 629s, 580m, 536w and 464w cm^{-1}. Reaction of an aqueous suspension of the product with HCl as in section (b) (i) above, gave mesitylthallium(III) dichloride (infrared identification).

(d) Reactions of sodium mesitylenesulphinate with thallic salts at 100°C

Dimesitylthallium(III) mesitylenesulphinate (nc). The thallic salt TlX_3 (X = CH_3CO_2, CF_3CO_2 or Cl) (0.90 mmol) in glacial acetic acid (10 ml) [X = CH_3CO_2 or CF_3CO_2] or water (4 ml) [X = Cl] was added with stirring to a boiling solution of sodium mesitylenesulphinate (2.7 mmol) in water (50 ml). The dimesitylthallium(III) derivative was precipitated immediately (yield, 46% (X = CH_3CO_2); 70% (X = Cl), based on reaction 7), m.p. >250°C (Found: C, 51.2; H, 5.2; S, 4.9. $C_{27}H_{33}O_2STl$ calcd.: C, 51.8; H, 5.3; S, 5.1%). Infrared absorption: 1602w, 1453w(br), 1374w, 1289m, 1060w, 1030w, 979vs, 941vs, 846s, 699w, 622m, 590w, 538w and 424m cm^{-1}.

Dimesitylthallium(III) iodide (nc). The addition of KI (3.0 mmol) to a suspension of dimesitylthallium(III) mesitylenesulphinate (0.80 mmol) in acetone (50 ml) gave a clear yellow solution, which was added to water (300 ml) precipitating dimesitylthallium(III) iodide (yield, 80%). An analytically pure sample was obtained as a pale yellow solid after several recrystallizations from acetone/water, m.p. 200—206°C (dec.) (Found: C, 37.6; H, 3.9. $C_{18}H_{22}ITl$ calcd.: C, 38.0; H, 3.9%). Infrared absorption: 1590w, 1567w, 1451m, 1440m, 1368w, 1298m, 1037m, 1028m, 845s and 697w cm^{-1}. PMR spectrum ($CDCl_3$): 2.32 (d, J(Tl—H) 22 Hz, 3H, p-$\underline{CH}_3$), 2.49 (d, J(Tl—H) 41 Hz, 6H, o-$\underline{CH}_3$), and 7.06 (d, J(Tl—H) 165 Hz, 2H, m-H) ppm downfield from internal tetramethylsilane. Suspensions of $RTl(O_2SR)X$ (R = 2,4,6-$Me_3C_6H_2$; X = CH_3CO_2 or Cl) in aqueous acetic acid (X = CH_3CO_2) or water (X = Cl) (ca. 0.10 g; 25 ml) were boiled and stirred for 20 min giving dimesitylthallium(III) mesitylenesulphinate (infrared identification).

(e) Reactions of sodium 2,4,6-triisopropylbenzenesulphinate with thallic salts

(i) At room temperature in aqueous acetic acid. Addition of the thallic salt TlX_3 (X = CH_3CO_2 or CF_3CO_2) (0.60 mmol) in aqueous acetic acid (H_2O : CH_3CO_2H = 9 : 1, v/v; 10 ml) to a solution of sodium 2,4,6-triisopropylbenzenesulphinate (1.9 mmol) in water (50 ml) gave an immediate yellow precipitate of thallium(I) tetrakis(2,4,6-triisopropylbenzenesulphinato)thallate(III) (nc) (yield, 70% for X = CH_3CO_2), m.p. 108—112°C (Found: C, 49.3; H, 6.3; S, 8.6; $C_{30}H_{46}O_4S_2Tl$ calcd.: C, 48.8; H, 6.3; S, 8.7%), Infrared absorption: 1596m, 1565w, 1460m, 1424w, 1383w, 1363w, 1040w, 929(sh), 918vs(br), 655m, 649m, 580w, 555w and 426w cm^{-1}. Use of a TlX_3 : NaO_2SR^1 mol. ratio of 3 : 2 gave the same complex (infrared identification).

(ii) At 100°C in aqueous acetic acid. On the same scale as in (i), the thallic salt was added to a vigorously stirred boiling solution of the sodium sulphinate, and the initially formed yellow precipitate became milky-white after ca. 1 min.

Continued boiling gave an oily solid, which was isolated by evaporation to dryness under reduced pressure. Crystallization from methanol gave *S*-2,4,6-triisopropylphenyl 2,4,6-triisopropylbenzenethiosulphonate (yield, 41%), m.p. 107—109°C, lit. [31] m.p. 108.5—110°C (Found: C, 72.2; H, 9.2. $C_{30}H_{46}O_2S_2$ calcd.: C, 71.7; H, 9.2%). Infrared absorption: 1598s, 1562w, 1463s, 1424m, 1385m, 1363m, 1323vs ($\nu_{as}(SO_2)$), 1254w, 1142vs ($\nu_s(SO_2)$), 1102w, 1070w, 1058w, 1030w, 939w, 884m, 757w, 650s, 624w, 576vs, 534s and 510w cm^{-1}.

(iii) In acetonitrile. On adding a solution of 2,4,6-triisopropylbenzenesulphinic acid (1.9 mmol) in acetonitrile (40 ml) to one of TlX_3 ($X = CF_3CO_2$ or CH_3CO_2) (0.60 mmol) in acetonitrile (10 ml) containing 1 ml of acetic acid at room temperature, thallium(I) tetrakis(2,4,6-triisopropylbenzenesulphinato)thallate(III) (54%; infrared identification) was precipitated immediately. If the solution was stirred for more than ca. 5 min, the yellow precipitate dissolved to give a clear solution. Evaporation to dryness and crystallization from methanol gave *S*-2,4,6-triisopropylphenyl 2,4,6-triisopropylbenzenethiosulphonate (61%; infrared identification).

(f) Reaction of sodium benzene- and p-toluene-sulphinate with thallic trifluoroacetate

Addition of thallic trifluoroacetate (1.6 mmol) in glacial acetic acid (6 ml) to a stirred solution of the sodium arenesulphinate dihydrate (4.8 mmol) in water (50 ml) at room temperature resulted in slow precipitation of diphenyl disulphone (yield, 22%, based on the thallic salt, after 30 min), m.p. 187—190°C, lit. [32] m.p. 193—194°C or di-*p*-tolyl disulphone (yield, 29%), m.p. 210—212°C, lit. [33] m.p. 212°C. The infrared spectra were identical with the reported spectra [34,35].

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