# ORGANOMERCURY COMPOUNDS

# IV.\* INFRARED SPECTRA, STRUCTURES, AND THERMAL DECOMPOSITION OF MERCURIC ARYLSULPHINATES

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#### Summary

The structures of mercuric benzenesulphinate and *p*-toluenesulphinate have been investigated by infrared spectroscopy, and it has been shown that the arylsulphinate ions are coordinated to mercury through sulphur and not through oxygen. Thermal decomposition of the benzenesulphinate, at the melting point or in toluene, gives good yields of diphenylmercury. No di-*p*-tolylmercury is obtained from pyrolysis of the *p*-toluenesulphinate in absence of a solvent, but a moderate yield is obtained when the compound is decomposed in boiling toluene.

## INTRODUCTION

Organomercury halides have been prepared by the sulphur dioxide elimination reaction  $^{1-3}$ 

$$RSO_2H + HgCl_2 \rightarrow RHgCl + SO_2 + HCl$$

but, except for the preparation of 10-dichloroarsinocamphor,<sup>4</sup> the method has not been used for the synthesis of organometallic derivatives of other elements. Of related interest are the recently reported insertion reactions of sulphur dioxide into metal-aryl and metal-alkyl bonds to give metal S-sulphinates;<sup>5,6</sup>



Iridium(III) S-sulphinates have been prepared by the reaction (1), and the p-toluenesulphinate undergoes sulphur dioxide elimination (2) to give the corresponding

\* Part III, Aust. J. Chem., 1966, 19, 2381.

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- <sup>1</sup> Peters, W., Chem. Ber., 1905, 38, 2567.
- <sup>2</sup> Kharasch, M. S., and Chalkley, L., J. Am. chem. Soc., 1921, 43, 607.

<sup>3</sup> Loudon, J. D., J. chem. Soc., 1933, 823; 1935, 535.

- <sup>4</sup> Loudon, J. D., J. chem. Soc., 1937, 391.
- <sup>5</sup> Bibler, J. P., and Wojcicki, A., J. Am. chem. Soc., 1964, 86, 5051; 1966, 88, 844.
- <sup>6</sup> Bibler, J. P., and Wojcicki, A., Abstr. 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965, p. 36M.

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p-tolyliridium compound.<sup>7</sup> Preparations of mercuric benzenesulphinate<sup>8</sup> and p-toluenesulphinate<sup>1</sup> have been reported, and it has been proposed<sup>1</sup> that the latter contains mercury-oxygen bonding (I):



but no structural data are available for these compounds. In the present study, the structures of the compounds have been investigated by infrared spectroscopy, and their thermal decomposition has been examined as a possible route to diarylmercury compounds.

# RESULTS AND DISCUSSION

# (a) Infrared Spectra and Structures

Mercuric benzenesulphinate and p-toluenesulphinate were obtained by a metathesis reaction between mercuric acetate and the appropriate sodium aryl-sulphinate in aqueous ethanol. The infrared absorption bands  $(1700-400 \text{ cm}^{-1})$  of mercuric benzenesulphinate and sodium benzenesulphinate are listed in Table 1. The majority of the absorption bands have similar positions and intensities in the two compounds and are attributed to modes of the Ph–S group. The assignments are based on those for chlorobenzene.<sup>9</sup> It is noteworthy that the "X-sensitive" modes, which involve Ph–S stretching (q, r, and t) or bending (y) coupled with phenyl ring vibrations, are at higher frequencies in the mercury compound than in the sodium salt. The very strong bands at frequencies unexpected for a monosubstituted benzene<sup>9</sup> are assigned to modes of the SO<sub>2</sub> group. The SO<sub>2</sub> stretching frequencies of sodium benzenesulphinate are near to those (1020 and 980 cm<sup>-1</sup>) of the potassium salt.<sup>10</sup>

Coordination of the benzenesulphinate anion through one oxygen (as in (I)) should shift  $\nu_{as}(SO_2)$  to higher and  $\nu_s(SO_2)$  to lower frequencies than in the free anion, as coordination removes the equivalence of the sulphur-oxygen bonds. These frequency shifts are observed for the esters

# Ph-S=O

<sup>7</sup> Collman, J. P., and Roper, W. R., J. Am. chem. Soc., 1966, 88, 180.

<sup>8</sup> Dubský, J. V., and Oravec, E., Spisy vydáv. přír. Fak. Masaryk. Univ., 1937, 232, 10 (Chem. Abstr., 1937, 31, 7858).

<sup>9</sup> Whiffen, D. H., J. chem. Soc., 1956, 1350.

<sup>10</sup> Detoni, S., and Hadži, D., J. chem. Soc., 1955, 3163.

 $(\nu_{as}(SO_2) \ c.\ 1130\ cm^{-1},\ \nu_s(SO_2) \ c.\ 960\ cm^{-1}),^{10}$  which may be regarded as an extreme case of coordination by the benzenesulphinate ion through oxygen. (Similar effects are well established for unidentate coordination by carboxylate ions.<sup>11</sup>) The SO<sub>2</sub>

#### TABLE 1

## VIBRATIONAL ASSIGNMENTS (1700-400 cm<sup>-1</sup>) FOR MERCURIC AND SODIUM BENZENESULPHINATES

For each compound, very weak bands and shoulders are omitted unless the other compound has a more intense absorption in a similar position

$Hg(SO_2Ph)_2$	$\mathrm{PhSO_2Na, 2H_2O}$	Assignment	
	1680w,vbr	δ(OH)	
	1610w,br	$\nu(CC)$	
1480m	1476m	$\nu(CC)$	
1449sh	1441		
1447s	1441V8	V(CC)	
2	1330w		
1315m	1304w	$\nu(CC)$	
1192vs,br		$\nu_{\rm as}({\rm SO}_2)$	
1100s	1084s	"X-sens" $q$	
1078w	1071m	β(CH)	
	1044vs,br	$v_{\rm as}({\rm SO}_2)$	
1037 vs, br		$\nu_{\rm s}({ m SO}_2)$	
1023m	c. 1020sh	β(CH)	
998m	1003 ک	ring wibration	
	995∫	ring vibration	
	978 we br	» (SO.)	
	972 ∫ <sup>vs,01</sup>	Vs(1502)	
925w	924m	$\gamma$ (CH)	
851vw	855w	w(CH)	
	848w∫	y(on)	
752s	759	v(CH)	
	754∫**		
708s	697vs	"X-sens" r	
686vs	689s	$\phi(CC)$	
614w	616w	$\alpha(CCC)$	
603vs	588vs,br	$\delta(SO_2)$	
507vs	492s	"X-sens" $y$	
472w ]	424m	"X-sens" t	
447vw ∫			

<sup>a</sup> Intensity uncertain, as situated between two very strong bands.

stretching frequencies of mercuric benzenesulphinate (Table 1) are accordingly inconsistent with mercury-oxygen bonding, but are similar to those observed for metal S-sulphinates  $(1250-1180 \text{ and } 1070-1050 \text{ cm}^{-1})^{5,7}$  and for metal-sulphur

<sup>11</sup> E.g. Cotton, F. A., in "Modern Coordination Chemistry." (Eds. J. Lewis and R. G. Wilkins.) p. 369. (Interscience: New York 1960.); Stephenson, T. A., Morehouse, S. M., Powell, A. R., Heffer, J. P., and Wilkinson, G., J. chem. Soc., 1965, 3632.

dioxide complexes (coordinated through sulphur).<sup>12</sup>



inated through sulphur).<sup>12</sup> Furthermore, the ratio  $\nu_{\rm as}({\rm SO}_2)/\nu_{\rm s}({\rm SO}_2) = 1.15$  for mercuric benzenesulphinate is almost equal to that (1.16) found for organic sulphones<sup>13</sup> and irridium(III) S-sulphinates.<sup>7</sup> Thus mercuric benzene-sulphinate must be formulated as the S-sulphinato complex (II).

The vibrational frequencies of the SO<sub>2</sub> group for mercuric and sodium *p*-toluenesulphinates (Table 2) are readily assigned as these compounds have intense absorption bands near the SO<sub>2</sub> frequencies of the corresponding benzenesulphinates. Thus mercuric *p*-toluenesulphinate has mercurysulphur bonding. The ratio  $\nu_{as}(SO_2)/\nu_s(SO_2) = 1.17$ . The splitting of the antisymmetric mode (Table 2) has also been observed in some irridium(III) *S*-sulphinates<sup>7</sup> and metal-sulphur dioxide complexes.<sup>12</sup>

 TABLE 2

 VIBRATIONAL FREQUENCIES FOR MERCURIC AND SODIUM p-TOLUENESULPHINATES

Compound	$v_{\rm as}({ m SO}_2)$	$\nu_{\rm S}({ m SO}_2)$	δ(SO <sub>2</sub> )
$Hg(SO_2-p-MeC_6H_4)_2$	1228s 1202vs.br	1040vs,br	585vs
p-MeC <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> Na,2H <sub>2</sub> O	1023 vs,br	973vs,br	554 vs, br

The  $\delta(SO_2)$  frequencies for  $Hg(SO_2Ph)_2$  and  $Hg(SO_2-p-MeC_6H_4)_2$  correspond closely to values for organic sulphones (600–520 cm<sup>-1</sup>),<sup>14</sup> but the  $\nu(SO_2)$  frequencies are considerably lower than in sulphones (1350–1300 and 1160–1120 cm<sup>-1</sup>)<sup>14</sup> as observed for other metal S-sulphinates.<sup>5,7</sup> This has been attributed to  $d_{\pi}-d_{\pi}$  back bonding from the metal to the SO<sub>2</sub> group. As Hg–S  $\pi$ -bonding is unlikely to be important in mercury S-sulphinates, another explanation is desirable and probably can be found in the difference between the S–Hg  $\sigma$ -bonding and the S–C  $\sigma$ -bonding of the organic sulphones. Charge transfer from the sulphinate ion to the mercuric ion is unlikely to produce as much covalent character in the S–Hg bonds as in the S–C bonds of sulphones, hence the SO<sub>2</sub> stretching frequencies of mercuric S-sulphinates, though shifted from values for the free sulphinate ions towards those for sulphones, still differ significantly from the latter. This effect must also apply in other metal S-sulphinates, whether or not  $\pi$ -bonding is important.

# (b) Thermal Decomposition

Mercuric benzenesulphinate and p-toluenesulphinate eliminate sulphur dioxide on heating. From decomposition of the former compound at the melting point, diphenylmercury is obtained in 37% yield:

$$Hg(SO_2Ph)_2 \rightarrow HgPh_2 + 2SO_2$$
 (3)

<sup>12</sup> Vaska, L., and Bath, S. S., J. Am. chem. Soc., 1966, 88, 1333.

<sup>13</sup> Bellamy, L. J., and Williams, R. L., J. chem. Soc., 1957, 863.

<sup>14</sup> Bellamy, L. J., "The Infrared Spectra of Complex Molecules." 2nd Edn, pp. 360, 361. (Methuen: London 1958.) A significantly higher yield is obtained when the compound is decomposed in boiling toluene, but no reaction is observed in boiling benzene and gross decomposition with elimination of mercury occurs in boiling xylene. Partial reversal of (3) is known, as diphenylmercury reacts with liquid sulphur dioxide to give phenylmercuric benzene-sulphinate.<sup>6</sup> An attempt to prepare and desulphonylate mercuric benzenesulphinate *in situ*, by heating mercuric acetate and sodium benzenesulphinate in acidified aqueous ethanol, gave only a very low yield of impure diphenylmercury. Di-*p*-tolylmercury is not isolated from decomposition of mercuric *p*-toluenesulphinate in the absence of solvent, but a 20% yield of the mercurial is obtained from the reaction in boiling toluene. Thus sulphur dioxide elimination reactions can be used for the synthesis of diarylmercurials, in addition to their known use as a route to organomercury halides.<sup>1-3</sup>

The pyrolysis of mercuric benzenesulphinate differs from that of mercuric benzoate. The latter does not decarboxylate on heating, but mercury substitutes in the phenyl ring ortho to the carboxyl group.<sup>15</sup> Mercuric carboxylates, Hg(OCOR)<sub>2</sub>, undergo thermal decarboxylation to give mercurials only if the group R contains substituents which prevent electrophilic substitution.<sup>16</sup> However, mercuric benzoate does eliminate carbon dioxide (giving a low yield of phenylmercuric benzoate) when conditions favouring free radical reactions are used.<sup>17</sup> The decomposition of Hg(SO<sub>2</sub>Ph)<sub>2</sub> and Hg(SO<sub>2</sub>-p-MeC<sub>6</sub>H<sub>4</sub>)<sub>2</sub> to give diarylmercurials evidently occurs at temperatures below those required for mercuration reactions, and may involve a free-radical mechanism.

#### EXPERIMENTAL

Microanalyses were carried out by the Australian Microanalytical Service, Melbourne. Melting points are uncorrected. Infrared spectra of sulphinates were recorded with a Perkin-Elmer 521 spectrophotometer. Spectra of other compounds were obtained with Perkin-Elmer 257 or Unicam SP 200 instruments. All compounds were examined as Nujol and hexachlorobutadiene mulls. Sodium benzenesulphinate dihydrate and sodium *p*-toluenesulphinate dihydrate, from Eastman Organic Chemicals, were used without further purification.

## (a) Preparations of Mercuric Arylsulphinates

# Mercuric Benzenesulphinate

On addition of a solution of sodium benzenesulphinate dihydrate  $(4 \cdot 0 \text{ g}, 20 \text{ mmole})$  in 30 ml aqueous ethanol (c. 2:1, v/v) to a solution of mercuric acetate  $(3 \cdot 2 \text{ g}, 10 \text{ mmole})$  in 30 ml aqueous ethanol acidified with a few drops of glacial acetic acid, a granular white precipitate was obtained. This was filtered off, washed with aqueous ethanol and then ethanol, and dried at 60°  $(3 \cdot 4 \text{ g}, 7 \cdot 1 \text{ mmole}, 71\%)$ , m.p. (dec.) 130° (some loss of SO<sub>2</sub> occurs below the melting point) (Found: C, 29 \cdot 8; H, 2 \cdot 1; S, 13 \cdot 35. Calc. for C<sub>12</sub>H<sub>10</sub>HgO<sub>4</sub>S<sub>2</sub>: C, 29 \cdot 8; H, 2 \cdot 1; S, 13 \cdot 3\%). Only slight decomposition occurs over a period of months at room temperature; it has been reported<sup>8</sup> that the compound decomposes and becomes black on standing.

<sup>15</sup> Goddard, A. E., and Goddard, D., in "Textbook of Inorganic Chemistry." (Ed. J. N. Friend.) Vol. XI, Part I, p. 163. (Griffen: London 1928.)

<sup>16</sup> Connett, J. E., Davies, A. G., Deacon, G. B., and Green, J. H. S., *J. chem. Soc.* C, 1966, 106.
<sup>17</sup> Maier, N. A., Gesel'berg, V. I., and Ol'dekop, Yu. A., *Zh. obshch. Khim.*, 1962, **32**, 2030 (*Chem. Abstr.*, 1963, **58**, 4398).

#### Mercuric p-Toluenesulphinate

This compound was similarly prepared and obtained as a gelatinous precipitate which was very difficult to filter off. It was dried under vacuum over phosphorus pentoxide, as slight loss of sulphur dioxide occurred at 60°. Yield 58% (Found: C, 33.0; H, 2.9; S, 12.3. Calc. for  $C_{14}H_{14}HgO_4S_2$ : C, 32.9; H, 2.7; S, 12.5%. Analytically pure samples were consistently obtained, contrary to an earlier report<sup>1</sup>). Vigorous decomposition with some melting commences at c. 170°, though loss of SO<sub>2</sub> is detectable at lower temperatures. Infrared absorption (1700-400 cm<sup>-1</sup>) (only bands of medium or greater intensity are given): 1593m, 1494m, 1399m, 1228s, 1202vs,br, 1183m, 1098vs, 1040vs,br, 1014s, 816vs, 705s, 647vs, 585vs, 497s, and 485m cm<sup>-1</sup>.

#### (b) Thermal Decomposition Reactions

#### Mercuric Benzenesulphinate

(1) At the melting point.—Highest yields were obtained when small amounts of the compound were pyrolysed. Mercuric benzenesulphinate  $(2 \cdot 21 \text{ g}, 4 \cdot 58 \text{ mmole})$  in five portions of c. 0.4 g was heated and stirred at  $130-135^{\circ}$  for 7 min, whereupon melting and evolution of sulphur dioxide occurred. The residue was extracted with boiling hexane which was then evaporated to dryness giving impure diphenylmercury. Recrystallized twice from aqueous methanol, the compound (0.60 g, 1.7 mmole, 37%), m.p.  $124 \cdot 5-125^{\circ}$ , lit.<sup>18</sup> m.p.  $125^{\circ}$  (Found: C,  $40 \cdot 4$ ; H,  $2 \cdot 9$ . Cale. for  $C_{12}H_{10}Hg$ : C,  $40 \cdot 6$ ; H,  $2 \cdot 8\%$ ) had an infrared spectrum identical with that of an authentic sample of the mercurial.

(2) In solvents.—No reaction was observed when a suspension of the compound in benzene was heated under reflux. In boiling xylene, evolution of sulphur dioxide, deposition of mercury, and blackening of the solvent occurred. No diphenylmercury was isolated.

In toluene.—Mercuric benzenesulphinate  $(2 \cdot 24 \text{ g}, 4 \cdot 64 \text{ mmole})$  as a suspension in AnalaR toluene (25 ml) was heated under reflux and stirred vigorously. Sulphur dioxide was evolved and most of the suspension dissolved. Gas evolution was complete after 45 min, the solution was filtered, and the solvent was removed under vacuum. Diphenylmercury was extracted from the residue and purified as in (1) (0.83 g, 2.3 mmole, 50%), m.p.  $123 \cdot 5-124^{\circ}$ , mixed m.p. (with product from (1))  $124-125^{\circ}$ . The infrared spectrum was identical with that of the product from (1). No hydrolysis of Hg(SO<sub>2</sub>Ph)<sub>2</sub> to mercuric oxide was observed, hence drying of the toluene was not necessary. (Ready hydrolysis of some mercuric carboxylates in organic solvents has been noted.<sup>16</sup>)

(3) Attempted in situ formation and desulphonylation.—A precipitate of mercuric benzenesulphinate in aqueous ethanol acidified with acetic acid, prepared as described above and on the same scale, was stirred vigorously and heated under reflux for 4 hr. Sulphur dioxide was evolved and mercury was deposited. After cooling, the mixture was extracted with petroleum (b.p. 40–60°), which was evaporated giving impure diphenylmercury (0.18 g, 0.51 mmole, 51%), m.p. c. 116– 120° (i.r. identification). Reaction between stoicheiometric amounts of mercuric acetate and sodium benzenesulphinate dihydrate in boiling toluene gave only c. 4% of crude diphenylmercury.

#### Mercuric p-Toluenesulphinate

(1) In absence of solvent.—The compound  $(1\cdot34 \text{ g}, 2\cdot62 \text{ mmole})$  in seven portions of  $c. 0\cdot2 \text{ g}$  was heated and stirred for 5 min at  $165-175^{\circ}$ . Sulphur dioxide and toluene (infrared spectrum identical with the reported spectrum<sup>19</sup>) were evolved. The residue was extracted with boiling benzene, evaporation of which gave  $0\cdot14$  g of pale brown crystals, which did not contain di-*p*-tolylmercury. Pyrolysis at 190-200° (10 min) also failed to give the mercurial.

(2) In toluene.—Mercuric p-toluenesulphinate  $(2 \cdot 43 \text{ g}, 4 \cdot 76 \text{ mmole})$  was decomposed in boiling toluene (30 ml) as for the benzenesulphinate. After 1 hr, evolution of sulphur dioxide was complete, the solution was filtered, and crude di-p-tolylmercury crystallized on evaporation

- <sup>18</sup> Coates, G. E., "Organometallic Compounds." 2nd Edn, p. 80. (Methuen: London 1960.)
   <sup>19</sup> "Catalog of Infrared Spectral Data." American Petroleum Institute Research Project
  - 44, Spectrum No. 308.

to small volume. Recrystallized from chloroform (twice), the mercurial (0.37 g, 0.97 mmole, 20%) had m.p. 240-242°, lit.<sup>20</sup> 241-243° (Found: C, 43.8; H, 3.8. Calc. for  $C_{14}H_{14}Hg$ : C, 43.9; H, 3.7%).

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<sup>20</sup> Morton, A. A., and Penner, H. P., J. Am. chem. Soc., 1951, 73, 3300.