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ORGANOMERCURY COMPOUNDS

XX* REACTIONS OF LITHIUM POLYFLUOROBENZENESULPHINATES WITH MERCURIC SALTS**

R. J. BERTINO, B. A. W. COLLER, G. B. DEACON, and in part
I. K. JOHNSON

Chemistry Department, Monash University, Clayton, Victoria, 3168
(Australia)

SUMMARY

The lithium polyfluorobenzenesulphinates, Li O_2SR ($R = C_6F_5$, $\underline{p}$-HC_6F_4, $\underline{m}$-HC_6F_4, or $\underline{o}$-HC_6F_4), and the dilithium tetrafluorobenzenedisulphinates, $\underline{p}$- and $\underline{o}$-$(LiO_2S)_2C_6F_4$, have been prepared by reaction of the appropriate polyfluoroaryllithium compounds with sulphur dioxide. All compounds were isolated as hydrates and gave the corresponding $\underline{S}$-benzylthiouronium salts on treatment with $\underline{S}$-benzylthiouronium chloride. From reactions of the lithium sulphinates with suitable mercuric salts in water, generally at room temperature, the derivatives RHgX ($R = C_6F_5$, X = Cl, Br, CH_3CO_2, or $PhSO_2$; R = $\underline{p}$-HC_6F_4, X = Cl, Br, or CH_3CO_2; R = $\underline{m}$-HC_6F_4, X = Cl or Br; R = $\underline{o}$-HC_6F_4, X = Cl), $\underline{p}$-$(XHg)_2C_6F_4$ (X = Cl, Br, or CH_3CO_2), and $\underline{o}$-$(XHg)_2C_6X_4$ (X = Cl or Br) have been prepared. Similarly, the bispolyfluorophenylmercurials R_2Hg ($R = C_6F_5$, $\underline{p}$-HC_6F_4, or $\underline{m}$-HC_6F_4) have been prepared from the corresponding lithium sulphinates and

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* Part XIX, Ref. [1]. ** Preliminary communication, Ref. [2].

either mercuric salts or polyfluorophenylmercuric halides in aqueous t-butanol. A possible mechanism for the sulphur dioxide elimination reactions is discussed.

INTRODUCTION

Only two syntheses of polyfluoroarylorganometallics by sulphur dioxide elimination (desulphination) have been reported [3], apart from examples in a preliminary report of this study [2]. Thermal decomposition of the S-sulphinato complex $(C_6F_5SO_2)Fe(\eta\text{-}C_5H_5)(CO)_2$ gives $C_6F_5Fe(\eta\text{-}C_5H_5)(CO)_2$ [4], and synthesis of $C_6F_5IrCl_2(Ph_3P)_2SO_2$ from $IrCl(Ph_3P)_2N_2$ and pentafluorobenzenesulphonyl chloride is considered to involve an intermediate S-pentafluorobenzenesulphinato complex, $(C_6F_5SO_2)IrCl_2(Ph_3P)_2$ [5]. The recent preparation of lithium pentafluorobenzenesulphinate [6] has raised the possibility of extending desulphination syntheses of monoaryl- [7,8] and diaryl-mercurials [9] to include analogous polyfluoroarylmercurials. We now report syntheses of a range of lithium polyfluorobenzenesulphinates and their sulphur dioxide elimination reactions with mercuric salts.

RESULTS and DISCUSSION

a. Preparations and Properties of Lithium Polyfluorobenzenesulphinates

The lithium polyfluorobenzenesulphinates, LiO_2SR (R = C_6F_5 [6], p-HC_6F_4, m-HC_6F_4, or o-HC_6F_4*), and the dilithium

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* For convenience, the positions of hydrogen substituents are indicated in formulae.

tetrafluorobenzenedisulphinates, p- and o-$(LiO_2S)_2C_6F_4$ have been prepared by reaction of appropriate organolithium compounds [10-15] with sulphur dioxide. Except for lithium 2,3,5,6-tetrafluorobenzenesulphinate, which contained 6% of dilithium 2,3,5,6-tetrafluorobenzenedisulphinate, mixtures of mono- and di-sulphinates were not isolated, provided the conditions used for synthesis of the organolithium compounds were closely controlled (see Experimental Section). Infrared spectra of the crude lithium sulphinates showed that all were hydrated. Analysis indicated that the pentafluorobenzenesulphinate was approximately a monohydrate, though it was obtained anhydrous in an earlier preparation [6]. As purification was very difficult owing to high solubilities and decomposition on being heated in hydroxylic solvents (see also [6]), the compounds were characterized by their ^{19}F NMR spectra (Experimental Section), and by conversion into analytically pure S-benzylthiouronium salts on treatment with aqueous S-benzylthiouronium chloride.

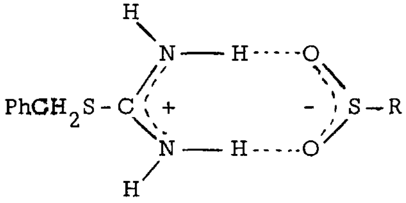
$$RLi + SO_2 \longrightarrow RSO_2Li$$

$$Li_2C_6F_4 + 2SO_2 \longrightarrow (LiO_2S)_2C_6F_4$$

Interpretation of the ^{19}F NMR spectra of $C_6F_5SO_2Li$ and o-$(LiO_2S)_2C_6F_4$ follows straightforwardly from data for comparable polyfluorobenzenes [6, 16] and perfluoroaromatic organometallics [17, 18]. For o- and p-$HC_6F_4SO_2Li$, the resonance at ca. 138 p.p.m. is attributed to fluorine ortho to hydrogen on the basis of data for o-$H_2C_6F_4$ [16], p-HC_6F_4OMe [16], and 2,3,4,5-tetrafluoro- [17, 18] and 2,3,5,6-tetrafluoro-phenylmercurials [19], whilst assignment of ca.

145-148 p.p.m. to fluorine ortho to $-SO_2Li$ is consistent with corresponding values for $C_6F_5SO_2Li$, o-$(LiO_2S)_2C_6F_4$, and p-$(LiO_2S)_2C_6F_4$. Assignment of F3 and F6 for lithium 2,3,4,6-tetrafluorobenzenesulphinate follows from the observation that in m-HC_6F_4X derivatives, F6 (ortho to H and to X) and F3 have the smallest and largest chemical shifts respectively [17, 18, 20], and the resonance at 130.6 p.p.m. is attributed to F4 (ortho to H and F) on the basis of data for m-HC_6F_4Cl [20], m-$H_2C_6F_4$ [16], and 2,3,4,6-tetrafluorophenylmercurials [17, 18].

Intense, often broad, infrared absorption at 1100-950 cm^{-1} in the spectra of the lithium and S-benzylthiouronium sulphinates is readily assigned to sulphur-oxygen stretching (Table 1). Where there are two fluorines ortho to the $-SO_2Li$ group, both $\nu(SO_2)$ frequencies are raised from values for lithium benzenesulphinate; otherwise significant shifts are not observed. Both $\nu(SO_2)$ frequencies of the S-benzylthiouronium salts are lowered from those of the corresponding lithium salts, possibly owing to hydrogen bonding between cation and anion, giving arrangements (I or II) related to bidentate or bridging bidentate sulphinate coordination. A number of compounds with the latter arrangement show similar shifts [21-23



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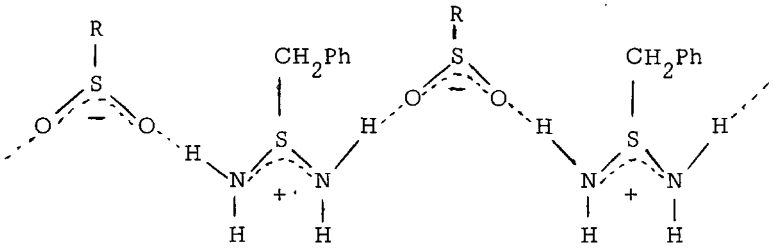

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TABLE 1

SULPHUR-OXYGEN STRETCHING FREQUENCIES (cm^{-1}) OF LITHIUM AND *S*-BENZYLTHIOURONIUM (SBT) POLYFLUOROBENZENESULPHINATES

Compound[a]	$\nu_{as}(SO_2)$	$\nu_s(SO_2)$	Compound	$\nu_{as}(SO_2)$	$\nu_s(SO_2)$
$C_6F_5SO_2Li$	1061	1029	$C_6F_5SO_2$(SBT)	1026	994
p-$HC_6F_4SO_2Li$	1060	1025	*p*-$HC_6F_4SO_2$(SBT)	1022	994
m-$HC_6F_4SO_2Li$	1061,[b] 1050[b]	1021	*m*-$HC_6F_4SO_2$(SBT)	1019	985
o-$HC_6F_4SO_2Li$	1038	1013[b]	*o*-$HC_6F_4SO_2$(SBT)	1012[b]	992[b]
p-$(LiO_2S)_2C_6F_4$	1064	1026	*p*-$[(SBT)O_2S]_2C_6F_4$	1013	976[b], 954[b]
o-$(LiO_2S)_2C_6F_4$	1027	994[b], 970	*o*-$[(SBT)O_2S]_2C_6F_4$	1012[b]	979
$PhSO_2Li$	1031	1011	$PhSO_2$(SBT)	1006	961

[a] All lithium sulphinates except $PhSO_2Li$ are hydrated (see text). [b] Coincident with ν(CF).

b. Reactions of Lithium Polyfluorobenzenesulphinates with Mercuric Salts

On reaction of mercuric salts with lithium polyfluorobenzenesulphinates (Table 2) or dilithium polyfluorobenzenedisulphinates (Table 3) in aqueous solution, sulphur dioxide elimination occurs [reaction (1), M = Li, or (2)], generally at room temperature, giving polyfluorophenylmercuric compounds RHgX (R = C_6F_5, X = Cl, Br, CH_3CO_2, or $PhSO_2$; R = *p*-HC_6F_4, X = Cl, Br, or CH_3CO_2; R = *m*-HC_6F_4, X = Cl or Br; R = *o*-HC_6F_4, X = Cl) or dimercurated tetrafluorobenzenes *p*-$(XHg)_2C_6F_4$ (X = Cl, Br, or CH_3CO_2) and *o*-$(XHg)_2C_6F_4$ (X = Cl or Br).

$$RSO_2M + HgX_2 \xrightarrow{H_2O} RHgX\downarrow + MX + SO_2\uparrow \qquad (1)$$

$$(LiO_2S)_2C_6F_4 + 2HgX_2 \xrightarrow{H_2O} (XHg)_2C_6F_4\downarrow + 2LiX + 2SO_2\uparrow \qquad (2)$$

Similarly, the bispolyfluorophenylmercurials R_2Hg (R = C_6F_5, *p*-HC_6F_4, or *m*-HC_6F_4) have been prepared by desulphination from the appropriate lithium sulphinates and mercuric chloride or acetate [reaction (3), M = Li] or suitable polyfluorophenylmercuric halides [reaction (4); R = C_6F_5, X = Cl; R = *p*-HC_6F_4, X = Br] in aqueous *t*-butanol at room temperature (Table 4).

$$2RSO_2M + HgX_2 \xrightarrow{H_2O/\underline{t}\text{-}BuOH} R_2Hg + 2MX + 2SO_2\uparrow \qquad (3)$$

$$RSO_2Li + RHgX \xrightarrow{H_2O/\underline{t}\text{-}BuOH} R_2Hg + LiX + SO_2\uparrow \qquad (4)$$

The formation of mercury, which accompanies (1) or (3) when X = CH_3CO_2, is attributed to reduction of mercuric acetate.

$$Hg(O_2CCH_3)_2 + LiO_2SR + H_2O \longrightarrow \dot{H}g + LiO_3SR + 2CH_3CO_2H$$

TABLE 2

PREPARATIONS OF MONO-ORGANOMERCURIALS, RHgX, IN WATER[a]

Reactants				Solution	Reaction	Product RHgX			[Ref]
LiO_2SR		HgX_2		Volume[b]	Time	Yield	m.p.	m.p.	
R	mmol	X	mmol	ml.	min.	(%)	(°C)	lit. (°C)	
C_6F_5	1.0	Cl	2.1	60	immed.[c]	46	164	165	[24]
C_6F_5	1.0	Br	1.1	90	2 [c]	52	155-156	155	[25]
C_6F_5	1.0	CH_3CO_2	2.1	50	immed.[c]	55	182-183	178	[26]
C_6F_5	1.2	$PhSO_2$	1.0	50	30	20	dec.[d]	165	[27]
p-HC_6F_4	1.1	Cl	2.3	50	0.5 [c]	47	188	186-188	[19]
p-HC_6F_4	1.1	Br	2.3	80	immed.[c,e]	69	180-181	179-180	[f]
p-HC_6F_4	2.1	CH_3CO_2	4.6	60	1 [c]	29	161	161-162	[19]
m-HC_6F_4	1.1	Cl	2.3	55	0.5 [c]	59	144-145	143-144	[18]
m-HC_6F_4	1.1	Br	2.3	80	0.5 [c,e]	79	137-138	138-140	[18]
o-HC_6F_4	2.2	Cl	4.6	60	300	15	151-152	150-152	[17, 18]
o-HC_6F_4	2.2	Cl	4.6	60	30 [g]	49	149-150	150-152	[17, 18]

[a] At room temperature unless indicated otherwise. [b] Total volume after mixing solutions of reactants. [c] Time for onset of precipitation. The product was filtered off ≤ 5 min after mixing. [d] Decomposition temperature and melting point dependent on rate of heating and immersion temperature; reported melting point [27] is considered incorrect. [e] At 40-50° because of the low solubility of mercuric bromide at room temperature. [f] Independent synthesis - this work. [g] Preheated (80°) solutions of reactants were mixed, some precipitation occurring, and the mixture was stirred for 30 min. without further heating.

TABLE 3

PREPARATIONS OF DIMERCURATED TETRAFLUOROBENZENES IN WATER [a]

Reactants			Solution	Reaction	Product				[Ref]
	HgX_2		Volume [b]	Time		Yield	m.p. [c]	m.p.	
mmol	X	mmol	ml.	min.		(%)	(°C)	lit. (°C)	
p-$(LiO_2S)_2C_6F_4$									
3.2	Cl	13.8	100	Immed. [d]	p-$(ClHg)_2C_6F_4$	61	>350	>300	[19]
1.6	Br [e]	3.4	100	60	p-$(BrHg)_2C_6F_4$	66	>350	>300	f
1.6	CH_3CO_2	6.9	65	5 [d]	p-$(CH_3CO_2Hg)_2C_6F_4$	47	>350	>300	[19]
o-$(LiO_2S)_2C_6F_4$									
1.6	Cl	3.4	70	1080	o-$(ClHg)_2C_6F_4$	38	>300	300	[18]
1.6	Br	6.9	150	60 [g]	o-$(BrHg)_2C_6F_4$	73	292-293	>300	[18]

[a] At room temperature, unless indicated otherwise. [b] Total volume after mixing solutions of reactants. [c] Some decomposition usually observed. [d] Time for onset of precipitation. The product was filtered off after 5 min. (X = Cl) and 10 min. (X = CH_3CO_2). [e] Not completely dissolved. [f] Independent synthesis - this work. [g] Preheated (60°) solutions of reactants were mixed, and were stirred for 60 min. without further heating.

TABLE 4

PREPARATIONS OF BISPOLYFLUOROPHENYLMERCURIALS IN AQUEOUS t-BUTANOL AT ROOM TEMPERATURE

Reactants				Solution	Reaction	Product R_2Hg			
LiO_2SR		Mercury		Volume[a]	Time	Yield	m.p.	m.p.	
R	mmol	Compound	mmol	ml.	min.	(%)	(°C)	lit. (°C)	[Ref]
C_6F_5	2.0	$Hg(O_2CCH_3)_2$	1.1	80[b]	5	27[f]	137-139	142	[25]
C_6F_5	2.0	$HgCl_2$	0.55	60[c]	5	66[f]	137	142	[25]
C_6F_5	1.2	C_6F_5HgCl	0.35	55[d]	10	92[g]	138	142	[25]
p-HC_6F_4	2.1	$HgCl_2$	0.58	60[c]	5	78[f]	141-142	146-147	[19]
p-HC_6F_4	0.84	p-HC_6F_4HgBr	0.23	40[b]	15	60[g]	146-147	146-147	[19]
m-HC_6F_4	4.2	$Hg(O_2CCH_3)_2$	2.3	50[e]	10	20[f]	86-87	84-85	[18]

[a] Total volume after mixing solutions of reactants. Solvent, H_2O/t-BuOH [b] 1:1 [c] 1:2 [d] 3:8, v/v.

[e] Water only. [f] Based on reaction (3). [g] Based on reaction (4).

By contrast with the present results, syntheses of hydrocarbon monoarylmercurials by (1) [8, 28] or diarylmercurials by (3) [9, 29] in aqueous media normally require heating. Reactions of sodium benzenesulphinate with mercuric acetate (mol. ratio 2:1 [29] or 1:2 [this work]), mercuric chloride [30], and mercuric bromide [30] in water at room temperature give di(S-benzenesulphinato)mercury(II), a mercuric chloride adduct of S-benzenesulphinatochloromercury (II), $(PhSO_2HgCl)_2HgCl_2$, and no observable reaction respectively. The same results are obtained with mercuric acetate and chloride in aqueous t-butanol (Experimental Section). When suspended in boiling water, $Hg(O_2SPh)_2$ and $(PhSO_2HgCl)_2HgCl_2$ decompose into diphenylmercury [9] and phenylmercuric chloride [30] respectively. Under the conditions of reaction (4), phenylmercuric chloride fails to react with sodium benzenesulphinate. There are few previous reports of reactions of disulphinates with mercuric salts, but preparations of m-$(XHg)_2C_6H_4$ ($X = CH_3CO_2$ or Cl) are known [8].

Two new mercurials, 2,3,5,6-tetrafluorophenylmercuric bromide and 1,4-dibromomercuritetrafluorobenzene, obtained by desulphination, were independently synthesized by redistribution (5) and metathesis (6) respectively.

$$(p\text{-}HC_6F_4)_2Hg + HgBr_2 \longrightarrow 2\,p\text{-}HC_6F_4HgBr \qquad (5)$$

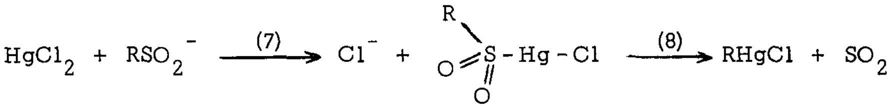
$$p\text{-}(CF_3CO_2Hg)_2C_6F_4 + 2\,HBr \longrightarrow p\text{-}(BrHg)_2C_6F_4 + 2\,CF_3CO_2H \qquad (6)$$

The other halogeno-derivatives (Tables 2 and 3) and $C_6F_5HgO_2SPh$ have previously been prepared by one or more of metathesis [18, 19], redistribution [17-19,24, 25, 27], and decarboxylation [19] methods, and the acetates by mercuration [26, 19]. There are numerous reported syntheses for the bispolyfluorophenylmercurials (Table 4), e. g. refs. [1, 17-19, 25].

As a synthetic route to polyfluorophenylmercurials, sulphur dioxide elimination has the disadvantage of the need for prior preparations of the lithium polyfluorobenzenesulphinates. However, the *solid* lithium salts are quite stable,[*] hence a single preparation can form the basis of a series of desulphination syntheses, and one lithium fluorocarbonsulphinate can give a range of mercurials (Tables 2 and 4).

c. Reaction Paths and Mechanism for Desulphination Reactions

The preparation of *hydrocarbon* arylmercuric chlorides by the Peters reaction (1) proceeds by formation (7) and decomposition (8) (slow step) of intermediate *S*-arenesulphinatochloromercury(II) complexes [30].



$$HgCl_2 + RSO_2^- \xrightarrow{(7)} Cl^- + R\text{-}S(=O)_2\text{-}Hg\text{-}Cl \xrightarrow{(8)} RHgCl + SO_2$$

A similar path is likely for the polyfluorophenylmercuric chlorides, the rapid rates preventing isolation of intermediate complexes. Since reaction (1) is faster for R = polyfluorophenyl than for R = Ph (section b), the transition state for decomposition of the sulphinate complexes in the slow step (8) probably has considerable carbanionic character [scheme I, $X = Cl$].

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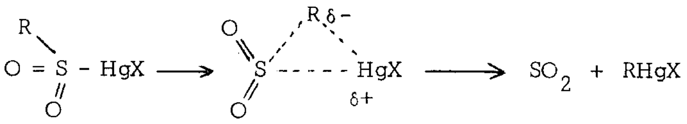
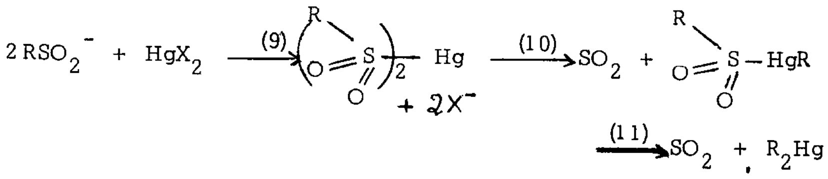
[*] After four months, lithium pentafluorobenzenesulphinate retains at least 50% of its reactivity in SO_2 elimination reactions.



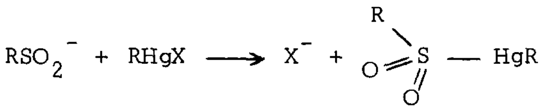
Scheme I

Decomposition of S-sulphinatoiridium complexes is considered to proceed in a similar manner, except that the eliminated sulphur dioxide remains coordinated to the metal [5]. Preparative data (Tables 2 and 3) indicate that removal of a fluorine ortho to the $-SO_2Li$ group slows elimination relative to $C_6F_5SO_2Li$, whereas removal of a meta or para fluorine has little effect. A qualitatively similar substituent effect is observed for hydrogen exchange reactions between polyfluorobenzenes and methoxide ions in methanol [31]. Polyfluorophenyl carbanions are intermediates in the exchange reactions, and the reduction in rate from pentafluorobenzene to 1,2,3,4-tetrafluorobenzene is much larger than that from pentafluorobenzene to 1,2,3,5- or 1,2,4,5-tetrafluorobenzene.

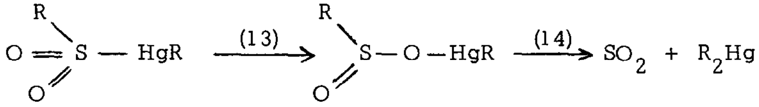
The reaction path for the formation of bispolyfluorophenylmercurials by reaction (3) is not yet established. There are two reasonable possibilities, viz. A. reactions (1) and (4), both of which have been independently carried out (section b), or B. formation (9) of a bis(S-arenesulphinato)mercury(II) complex, which undergoes stepwise elimination of sulphur dioxide, (10) and (11).



Reaction (4) (path A) can be envisaged as involving formation (12) and decomposition (11) (in common with path B) of an S-arenesulphinatoaryl-mercury(II) complex.


(12)

Preparations of *hydrocarbon* diarylmercurials by reaction (3) proceed via bis(*S*-arenesulphinato)mercury(II) and *O*-arenesulphinatoarylmercury(II) complexes [9, 32]. The latter are presumably formed by isomerization (13) of *S*-arenesulphinatoarylmercury(II) complexes (a known reaction [27] for R = Ph), and then undergo desulphination (14).



The overall reaction (3) is much faster for R = polyfluorophenyl than for R = Ph (section b), hence (14), which is aided by electron donor substituents,[*] is an unlikely step in the path to bispolyfluorophenylmercurials. Whichever path, *A* or *B*, obtains, rapid desulphination for R = polyfluorophenyl can be attributed to decomposition of *S*-sulphinate intermediates via transition states with considerable carbanionic character [e.g. scheme I, X = RSO$_2$ or R].

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[*] Preparative data [9; 32] suggest that this reaction becomes slower in the sequence R = 2,4,6-Me$_3$C$_6$H$_2$ > *p*-MeC$_6$H$_4$ or Ph > *p*-ClC$_6$H$_4$, 2,3,4-Cl$_3$C$_6$H$_2$, or 2-naphthyl. Related substituent effects are observed [27; see also discussion in 33] for the reverse reaction, insertion of sulphur dioxide into diarylmercurials. Molecular models and the fairly high thermal stability of tris(*O*-2,4,6-triisopropylbenzenesulphinato)bismuth(III) [34] suggest that steric destabilization is not markedly significant for 2,6-disubstituted *O*-benzenesulphinates, hence the rapid desulphination of *O*-mesitylenesulphinatomesitylmercury(II) cannot be explained in this way.

EXPERIMENTAL

Microanalyses were by the Australian Microanalytical Service, Melbourne. Infrared spectra of compounds as Nujol and either hexachlorobutadiene or perfluorokerosene mulls were recorded with Perkin-Elmer 521 (4000-400 cm^{-1}) or 257 (4000-700 cm^{-1}) spectrophotometers. ^{19}F NMR spectra of lithium sulphinates in deuterium oxide were recorded with a Varian A56/60 instrument. Chemical shifts are given in p.p.m. upfield from external trichlorofluoromethane. Perfluoroaromatic compound were from Bristol Organics, except for 1,2,3,4-tetrafluorobenzene (PCR, Inc.). _n_-Butyllithium (22%, w/v in hexane) was from ROC/RIC or Alpha Inorganics. Ether and tetrahydrofuran were dried over sodium wire and lithium aluminium hydride respectively.

Preparations of polyfluorophenyllithium compounds, based on reported methods [10-15], were carried out at _ca_. -78° under nitrogen. Specific details are given since yields from subsequent reactions with sulphur dioxide were affected by variation in the conditions. $\underline{p\text{-}HC_6F_4Li}$: 1,2,4,5-Tetrafluorobenzene (0.041 mol.) in ether (45 ml.) was added over 0.5 h. to a stirred precooled solution of _n_-butyllithium (0.041 mol.) in hexane (80 ml.), followed by further stirring (0.75 h.). This procedure gave, after treatment with sulphur dioxide, a smaller impurity of disulphinate than was obtained when _n_-butyllithium was added to the tetrafluorobenzene. $\underline{m\text{-}HC_6F_4Li}$: 1,2,3,5-Tetrafluorobenzene (0.10 mol.) in ether (100 ml.) was added over 2.75 h. to _n_-butyllithium (0.10 mol.) in hexane (48 ml.) and ether (50 ml.), with further stirring (0.5 h.).

<u>o-HC_6F_4Li:</u> n-Butyllithium (0.10 mol.) in hexane (48 ml.) was added over 15 min. to 1,2,3,4-tetrafluorobenzene (0.10 mol.) in tetrahydrofuran (100 ml.), with further stirring (25 min.). <u>p-$Li_2C_6F_4$:</u> 1,4-Dibromobenzene (0.050 mol.) in ether (50 ml.) was added over 50 min. to <u>n</u>-butyllithium (0.11 mol.) in hexane (52 ml.), with further stirring (35 min.). <u>o-$Li_2C_6F_4$:</u> n-Butyllithium (0.078 mol.) in hexane (37 ml.) was added over 23 min. to <u>o</u>-$Br_2C_6F_4$ (0.032 mol.) in ether (200 ml.), with further stirring (70 min.).

<u>Preparations of Lithium and</u> S-<u>Benzylthiouronium Polyfluorobenzenesulphinates</u>

<u>General:</u> Dry (silica gel, then P_2O_5) sulphur dioxide was bubbled for 0.5-1.0 h. through a solution of the polyfluorophenyllithium compound at -78°, the lithium sulphinate being precipitated. The product was filtered off, washed with ether, and dried over silica gel under vacuum at room temperature. For lithium 2,3,4,5-tetrafluorobenzenesulphinate, further product was obtained by partial evaporation of the filtrate. <u>S</u>-Benzylthiouronium derivatives were precipitated on reaction of stoicheiometric amounts of the lithium sulphinate and <u>S</u>-benzylthiouronium chloride in aqueous solution, and were dried as for the lithium salts.

<u>Lithium pentafluorobenzenesulphinate hydrate</u>. - Using the reported method [6], the compound was obtained hydrated (<u>ca</u>.$1H_2O/Li$),* dec.

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* The ν(OH) absorptions of all the lithium sulphinates are of comparable intensity, hence it is likely that they are all hydrated to a similar extent.

temp. > 260°; lit. [6] > 280° for the anhydrous form [Found: C, 27.0; H, 0.9; F, 37.3; S, 13.3. $C_6H_2F_5LiO_3S$ (monohydrate) requires C, 28.1; H, 0.8; F, 37.1; S, 12.5. $C_6F_5LiO_2S$ (anhydrous) requires C, 30.3; F, 39.9; S, 13.5. $C_6H_4F_5LiO_4S$ (dihydrate) requires C, 26.3; H, 1.5; F, 34.7; S, 11.7%]. Infrared absorption: 3430 and 3370m (br) [ν(OH)], 1642m, 1515sh, 1479vs, 1381m, 1297w, 1107 and 1102s, 1061vs, 1029s, 1008m, 988 and 977vs, 767m, and 727w cm^{-1}. ^{19}F NMR spectrum: 147.9 (m, 2F, F2, 6), 153.7 (m, 1F, F4), and 161.3 (m, 2F, F3, 5) p.p.m. S-<u>Benzylthiouronium pentafluorobenzenesulphinate</u> (nc), yield, 57%, m.p. 92-93° (Found: C, 42.2; H, 2.9; S, 15.8. $C_{14}H_{11}F_5N_2O_2S_2$ requires C, 42.2; H, 2.8; S, 16.1%). Infrared absorption: 3370sh, 3260s (br), 3045s (br), 1654s, 1509m, 1471s, 1089m, 1026vs, 994s, 972vs, 715s, 697s, 533w, 499m, 480w, and 450w cm^{-1}.

<u>Lithium</u> 2,3,5,6-<u>tetrafluorobenzenesulphinate hydrate</u> (nc), yield, <u>ca.</u> 60%, containing 6% (by ^{19}F NMR) of dilithium 2,3,5,6-tetrafluorobenzenedisulphinate. Infrared absorption: 3375 and 3330s (vbr) [ν(OH)], 1637m (br), 1605m, 1483vs, 1458m, 1405w, 1259sh, 1239s, 1184s, 1176s, 1113m, 1060vs (br), 1025vs (br), 1010sh, 929sh, 921vs, 857sh, 851s, 788m, and 739s cm^{-1}. ^{19}F NMR spectrum: 138.5 (m, 2F, F3, 5) and 147.9 (m, 2F, F2, 6) p.p.m. Impurity of disulphinate, 146.3 (s, 0.25 F) p.p.m. S-<u>Benzylthiouronium</u> 2,3,5,6-<u>tetrafluorobenzenesulphinate</u> (nc), yield, 43%, m.p. 115° (Found: C, 44.0; H, 3.2; F, 19.9; N, 7.5%. $C_{14}H_{12}F_4N_2O_2S_2$ requires C, 44.2; H, 3.2; F, 20.0; N, 7.4%). Infrared absorption: 3350sh, 3250s, 3015s, 1656s, 1602w, 1561w, 1512sh, 1475vs, 1458sh, 1375w, 1355w, 1253w, 1223m, 1170m, 1022vs, 994vs, 914s, 850m, 833w, 777w, 737sh, 710s, 694s, 527w, 498m, 478w,

and 460m cm^{-1}. Lithium 2, 3,4,6-tetrafluorobenzenesulphinate hydrate (nc), yield, 80%, dec. temp. > 260°. Infrared absorption: 3385s (br) [ν(OH)], 1626s, 1487vs, 1431m, 1360w, 1233m, 1153m, 1079sh, 1061 and 1050vs, 1021s, 1003w, 976w, 947m, 897w, 861w, 840m, and 688w cm^{-1}. ^{19}F NMR spectrum: 120.9 (m, 1F, F6), 130.6 (m, 1F, F4), 140.7 (m, 1F, F2), and 164.7 (m, 1F, F3) p.p.m. S-Benzylthiouronium 2,3,4,6-tetrafluorobenzenesulphinate (nc), yield, 43%, m.p. 121-122° (Found: C, 44.2; H, 3.2; F, 19.6; N, 7.3%). Infrared absorption: 3270s (br), 3025s (br), 1675s, 1628m, 1562w, 1501s, 1487sh, 1452w, 1430s, 1359w, 1233m, 1140m, 1064s, 1035sh, 1019vs, 985s, 855m, 838m, 829sh, 777w, 732sh, 710s, 691s, 570w, 530m, 498m, 478w, 457s, and 439s cm^{-1}. Lithium 2,3,4,5-tetrafluorobenzenesulphinate hydrate (nc), yield, 60%. Infrared absorption: 3420 and 3310s (br), [ν(OH)], 1623m, 1510s, 1470vs, 1331s, 1280w, 1188m, 1095vs, 1038 and 1013vs (br), 993sh, 862m, 835w, 727m, and 712s cm^{-1}. ^{19}F NMR spectrum: 137.9 (m, 1F, F5), 145.6 (m, 1F, F2), 153.4 and 154.8 (each m, total integration 2F, F3, 4) p.p.m. S-Benzylthiouronium 2,3,4,5-tetrafluorobenzenesulphinate (nc), yield, 58%, m.p. 167-168° (Found: C, 44.2; H, 3.2; F, 19.8; N, 7.4%. Infrared absorption: 3370sh, 3240s (br), 3020s (br), 1659vs, 1628sh, 1609sh, 1568w, 1512m, 1469vs, 1455sh, 1326m, 1260w, 1185m, 1091s, 1077sh, 1012 and 992vs (br), 924w, 869s, 823w, 781sh, 745sh, 717vs (br), 699sh, 600w, 568m, 534m, 525sh, 503s, 482w, 470w, and 460w cm^{-1}. Dilithium 3,4,5,6-tetrafluorobenzenedisulphinate hydrate (nc), yield, 80%. Infrared absorption: 3450m (vbr) [ν(OH)]', 1616m (br), 1490s, 1468vs, 1436s, 1299m, 1263m, 1108 and 1099s (sh), 1027, 994, and 970vs (br), 875w, 831w, and 768s cm^{-1}. ^{19}F NMR spectrum: 145.2 (m, 2F, F3, 6) and 151.7 (m, 2F, F4, 5) p.p.m. Di-S-benzylthiouronium 3,4,5,6-tetrafluorobenzenedisulphinate (nc), yield, 42%, m.p. 124-125° (Found: C, 43.3; H, 3.7; F, 12.5; N, 9.1; S, 20.6. $C_{22}H_{22}F_4N_4O_4S_4$ requires C, 43.3; H, 3.6; F, 12.5; N, 9.2; S, 21.0%). Infrared absorption: 3250s (br), 3040s (br), 1655vs, 1559w, 1491vs, 1455sh, 1436vs, 1296m, 1260m, 1101s, 1071m, 1012vs (br), 979s (br), 963sh, 773sh, 745sh, 710vs, 696s, 549m, 499m, 487m, 448sh, and 436s cm^{-1}. Dilithium 2,3,5,6-tetrafluorobenzenedisulphinate hydrate (nc), yield, 100%. Infrared absorption: 3400m (vbr) [ν(OH)], 1638m (br), 1490sh, 1455s, 1398w, 1278sh, 1253s, 1117m, 1064vs (br), 1026vs (br), 974 and 964s cm^{-1}. ^{19}F NMR spectrum: 146.3 (s) p.p.m. Di-S-benzylthiouronium 2,3,5,6-tetrafluorobenzenedisulphinate (nc), yield, 59%, m.p. 124-125° (Found: C, 44.8; H, 3.9; N, 8.9%). Infrared absorption: 3195s (br), 3020s (br), 1673s, 1552w, 1493m, 1451vs, 1252sh, 1239m, 1174w, 1013vs (br), 976s, 954vs, 764sh, 735sh, 710s, 693s, 621w, 568w, 543m, 494sh, 481m, and 473sh cm^{-1}. Lithium benzenesulphinate . A suspension of silver benzenesulphinate [35] (2.1 mmol) in an aqueous solution (30 ml.) of lithium chloride (2.1 mmol.) was stirred at room temperature for 30 min. After filtration, the required compound was isolated by evaporation of the filtrate to dryness under vacuum (yield, 92%). An analytically pure sample was obtained on recrystallization from ether/ethanol (Found: C, 48.6; H, 3.4. $C_6H_5LiO_2S$ requires C, 48.7; H, 3.4%). Infrared absorption: 3062m, 1447s, 1101m, 1031 and 1011vs (br), 994sh, 986sh, 767 and 764vs, 712 and 705vs cm^{-1}. The compound slowly hydrates on standing, as indicated by the appearance of intense broad infrared absorption at 3450 cm^{-1}.

S-Benzylthiouronium benzenesulphinate (nc) was obtained by the standard method (above) from the sodium salt (yield, 83%), mp. 152-153° (Found: C, 54.2; H, 5.1: N, 9.4. $C_{14}H_{16}N_2O_2S_2$ requires C, 54.5; H, 5.2; N, 9.1%). Infrared absorption: 3150s, 2980vs (br), 2790sh, 1681s (br), 1552m (br), 1490w, 1470w, 1451m, 1439s, 1157w, 1150w, 1080m, 1070w, 1006vs, 961vs, 917w, 812m (br), 752s, 693vs, 562m, 475s, 459m, 430w, and 418w cm^{-1}.

Reactions of Mercuric Salts with Lithium Polyfluorobenzenesulphinates

All products were identified by melting points (Tables 2-4) and infrared spectra [18,19,25-27]. The lithium sulphinates were assumed to be monohydrates.

(i) Preparations of mono(polyfluorophenyl)mercurials RHgX: An aqueous solution of the mercuric salt (a suspension for X = O_2SPh; acidified with a few drops of acetic acid for X = O_2CCH_3) was added to a stirred aqueous solution of the lithium polyfluorobenzenesulphinate, giving a white precipitate of the required mono-organomercurial. For X = O_2CCH_3, some mercury metal was also obtained. The product was collected and dissolved in ether, filtered through cellulose powder, was recovered by evaporation to dryness, and was dried under vacuum. Details are given in Table 2. Authentic 2,3,5,6-tetrafluorophenylmercuric bromide (nc) was prepared by fusing mercuric bromide (1.1 mmol) and bis(2,3,5,6-tetrafluorophenyl)mercury [19] (1.0 mmol) at 190°. The product was sublimed at 160°/0.2 mm., then at 100°/0.5 mm. giving the required compound (yield, 92%), m.p. 179-181° (Found: C, 16.8; H, 0.4; Br, 19.4; F, 18.0. C_6HBrF_4Hg requires C, 16.8; H, 0.2; Br, 18.6; F, 17.7%). Infrared absorption: 3100w, 3075w, 1601m, 1470vs (br), 1433s, 1363s, 1273m, 1230s, 1178vs, 929m, 895s, 867sh, 850s, 834sh, 709s, 697s, 678m, and 498w cm^{-1}. ^{19}F NMR spectrum (in acetone): 120.5 (m, 2F, F2, 6) and 138.0 (m, 2F, F3, 5) p.p.m. from internal $CFCl_3$.

(ii) Preparations of dimercurated tetrafluorobenzenes $(XHg)_2C_6F_4$: These were effected in a similar manner, details being given in Table 3. The precipitated products were not purified except for 1,4-bis(acetatomercuri)-tetrafluorobenzene, which was recrystallized from acetic acid, the process being accompanied by decomposition. Authentic 1,4-bis(bromomercuri)-tetrafluorobenzene (nc) was deposited on addition of 50% hydrobromic acid (4.5 mmol) to a solution of 1,4-bis(trifluoroacetatomercuri)tetrafluorobenzene [19] (2.0 mmol) in ethanol (5 ml.). Precipitation was completed by addition of water (30 ml.). After drying under vacuum at room temperature, the compound (yield, 92%) had m.p. > 300° (Found: C, 10.3; Br, 22.1; F, 10.5. $C_6Br_2F_4Hg_2$ requires C, 10.2; Br, 22.5; F, 10.7%). Infrared absorption: 1443vs, 1431vs, 1379m, 1272m, 1221s, 1008w, 980w, 930vs, 751s, 720sh, 560s, 418w, and 410w cm^{-1}.

(iii) Preparations of bispolyfluorophenylmercurials: An aqueous solution of the mercuric salt or a solution of the mono(polyfluorophenyl)mercurial in t-butanol, and a solution of the lithium polyfluorobenzenesulphinate in aqueous t-butanol, were mixed and stirred at room temperature.

Mercury was formed in reactions with mercuric acetate. The t-butanol was removed under vacuum giving a precipitate of the required mercurial, which was purified by ether extraction as in (i). Details are given in Table 4.

Reactions of Mercuric Salts with Sodium Benzenesulphinate

Sodium benzenesulphinate (7.4 mmol) in water (30 ml.) and t-butanol (40 ml.), and mercurio chloride(1.8 mmol.) in water (30 ml.) were mixed and stirred at room temperature for 30 min., then the t-butanol was removed under reduced pressure giving a precipitate of $(PhSO_2HgCl)_2HgCl_2$ (yield, 8%; infrared and far infrared identification [30]), containing a trace of mercuric benzenesulphinate [29].

Similarly, addition of sodium benzenesulphinate (3.1 mmol.) in water (20 ml.) and t-butanol (30 ml.) to mercuric acetate (1.6 mmol.) in water (20 ml.), acidified with a few drops of acetic acid, gave a precipitate of mercuric benzenesulphinate (72%, infrared identification [29]). A similar reaction in water (mol. ratio $NaO_2SPh : Hg(O_2CCH_3)_2 = 1 : 2.4$) gave the same product (yield, 54%). After a suspension of phenylmercuric chloride (3.9 mmol.) in a solution of sodium benzenesulphinate (15.5 mmol.) in water (15 ml.) and t-butanol (70 ml.) was stirred at room temperature for 1 h., phenylmercuric chloride was recovered (92%), m.p. 244-246°, lit. [36], 251° (infrared identification [37]).

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