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SULFUR DIOXIDE INSERTION
IX*. SULFINATO COMPLEXES OF DIVALENT MERCURY

PHILIP J. POLLICK, JANE P. BIBLER AND ANDREW WOJCICKI
The McPherson and Evans Chemical Laboratory, The Ohio State University, Columbus, Ohio 43210 (U.S.A.)

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SUMMARY

Interaction of HgR_2 (R = C_6H_5, C_2H_5, and $CH_2C_6H_5$) with liquid sulfur dioxide at −40° to −10° affords virtually quantitative yields of the corresponding monosulfinates, RSO_2HgR. At low temperatures (*ca.* −70°), $(C_2H_5Hg)_2SO_2$ usually becomes a by-product of the reaction between $Hg(C_2H_5)_2$ and SO_2. The new compounds have been characterized by chemical analyses, molecular weight measurements, and IR and NMR spectroscopy. The phenylsulfinate, $C_6H_5SO_2HgC_6H_5$, has been isolated in two isomeric forms which are *S*- and *O*-bonded. The latter arises from the former on crystallization; it also appears to be the prevalent species in solution, where it is monomeric. The ethylsulfinate, $C_2H_5SO_2HgC_2H_5$, is *S*-bonded in the solid but adopts a monomeric, *O*-bonded structure in solution; the benzylsulfinate, $C_6H_5CH_2SO_2HgCH_2C_6H_5$, has been assigned a monomeric, *O*-bonded structure both in the solid and in solution.

INTRODUCTION

Insertion reactions of sulfur dioxide with a number of transition metal alkyl[1-3], aryl[1,2], 2-alkenyl[4,5], and 2-alkynyl[6] complexes have been reported in the earlier papers of this series. With the exception of the 2-alkynyls, all of the above afford sulfur-bonded sulfinates.

To ascertain better the nature of the products resulting from interaction of SO_2 with alkyl and aryl complexes of some non-transition metals we have extended our studies to divalent mercury. Although reactions of SO_2 with some alkyls of lead[7,8], aluminum[9], and zinc[10] have been recently examined, the only literature report on behavior of organomercury compounds toward sulfur dioxide known to us at the outset of this investigation concerns the interaction between molten $Hg(C_6H_5)_2$ and gaseous SO_2[11].

Subsequent to our disclosure of preliminary results[12-14], two pertinent papers have appeared in the literature. Deacon and Felder[15] synthesized a number of arylmercuric arenesulfinates, $Ar'SO_2HgAr$ (Ar′ = C_6H_5 and p-$CH_3C_6H_4$), by reaction

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* For part VIII see ref. 3.

of $(Ar'SO_2)_2Hg$ with diarylmercury compounds, $Hg(Ar)_2$. Phenylmercuric benzenesulfinate was isolated in two isomeric forms, one being assigned an *S*-sulfinato structure and the other an *O*-sulfinato structure. Further, Carey and Clark[10] recently reported on the reaction between dimethylmercury and sulfur dioxide. They isolated a dinuclear $(CH_3Hg)_2SO_2$ and another compound, provisionally formulated as $CH_3HgS(O)OCH_3$.

Presented now in some detail are our investigations on sulfur dioxide insertion with diphenyl-, dibenzyl-, and diethylmercury. Spectroscopic studies aimed at elucidation of the structures of the resulting sulfinates represent a major part of this paper.

EXPERIMENTAL

Diphenylmercury and diethylmercury were purchased from Eastman Organic Chemicals; dibenzylmercury and thiophenol were obtained from Alfa Inorganics, Inc., and Matheson Coleman and Bell, respectively. All of these were used without further purification. Mercuric benzenesulfinate was prepared as described by Deacon[16]. Anhydrous grade sulfur dioxide, from Matheson, was passed through concentrated H_2SO_4 and a $P_4O_{10}/CaCl_2$ column before condensation. Chlorine (Matheson, high purity grade) was used as received. Tetrahydrofuran was distilled from $LiAlH_4$ under a nitrogen atmosphere immediately before use. Technical grade pentane was used without further purification. All other chemicals and solvents were of reagent grade or equivalent.

IR spectra were recorded using Beckman Model IR-9 and Perkin–Elmer Model 337 spectrophotometers. Since early studies demonstrated that $C_2H_5SO_2HgC_2H_5$ and $C_6H_5CH_2SO_2HgCH_2C_6H_5$ react with KBr, measurements on these and other related compounds in the solid phase were carried out using Nujol suspensions between Irtran-2 plates* (unless specified otherwise). Solution spectra were recorded using Irtran-2 cells of 1 mm thickness.

NMR spectra were obtained on Varian Associates A-60 and A-60A spectrometers using tetramethylsilane as a reference. Unless stated otherwise, the melting points were determined with a Fisher–Johns melting-point block and are uncorrected. Molecular weight measurements were made on *ca.* 10^{-2} *M* chloroform and 1,2-dichloroethane solutions with a Mechrolab Model 301-A osmometer. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn., and by Pascher Mikroanalytisches Laboratorium, Bonn, Germany.

Preparation of $C_6H_5SO_2HgC_6H_5$

Diphenylmercury (5 g, 0.014 mole) was introduced into a 50-ml flask fitted with a Dry Ice condenser which was attached to a vacuum line using standard techniques. Dry sulfur dioxide was condensed (40 ml) in the flask and the resulting solution was allowed to reflux for about 12 h before cooling to *ca.* −75° overnight. Excess SO_2 was then removed at −75° leaving 5.8 g (98%) of a brownish-white product (I). This was extracted with 40 ml of chloroform, the extract was filtered, and 200 ml of pentane was added with stirring to the filtrate. The resulting mixture was chilled at *ca.* −70° for 30 min and the white precipitate was collected on a filter and

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* Available from Wilks Scientific Co., P.O. Box 441, S. Norwalk, Conn. 06856.

redissolved in a minimum amount (~30 ml) of chloroform. Addition of 200 ml of pentane, followed by cooling, again yielded white crystals. The process was repeated (usually two or three times) until both the melting point (105°) and the IR spectrum of the product (II) remained constant. [Found: C, 34.63; H, 2.50; S, 7.87; mol.wt., 421 (0.0101 *M* $ClCH_2CH_2Cl$ soln.), 455 (0.0166 *M* $ClCH_2CH_2Cl$ soln.). $C_{12}H_{10}HgO_2S$ calcd.: C, 34.56; H, 2.39; S, 7.63%; mol.wt., 419.]

The sulfinate (II) may be also synthesized, in a virtually quantitative yield, by refluxing diphenylmercury in liquid SO_2 at atmospheric pressure, removal of excess SO_2 at reflux temperature, and crystallization from chloroform/pentane.

The compound is soluble in chloroform, tetrahydrofuran, methyl and ethyl alcohols, and liquid SO_2 but insoluble in pentane and water. It appears to be reasonably stable to air in the solid. After 2 h of refluxing in liquid SO_2, the sulfinate (II) is recovered unchanged (IR spectroscopy).

Preparation of $C_6H_5CH_2SO_2HgCH_2C_6H_5$

Dry sulfur dioxide was condensed (*ca.* 50 ml) onto dibenzylmercury (5 g, 0.013 mole) in a flask equipped with a magnetic stirring bar and a Dry Ice condenser and maintained at *ca.* −40°. The resulting bright orange solution was stirred for 48 h and then allowed to warm to room temperature. Excess SO_2 was removed in a stream of nitrogen and the residue was purified in a manner strictly analogous to that for $C_6H_5SO_2HgC_6H_5$ (*vide supra*). The yield of white crystals, m.p. 95°, was 5.62 g (96%). [Found: C, 37.59; H, 3.22; S, 7.03; mol.wt., 429 (0.0078 *M* $ClCH_2CH_2Cl$ soln.). $C_{14}H_{14}HgO_2S$ calcd.: C, 37.58; H, 3.13; S, 7.15%; mol.wt., 447.]

Solubility properties of this compound are very similar to those of $C_6H_5SO_2$-HgC_6H_5 (II). The solid sulfinate is rather unstable with respect to decomposition into elemental mercury and dibenzyl sulfone, even at 0°. Further, when normal laboratory light is excluded from a sample maintained at 27° under nitrogen, the decomposition proceeds noticeably slower (3 weeks) than in the case of a sample exposed to light (4 h). However, samples of $C_6H_5CH_2SO_2HgCH_2C_6H_5$ stored at Dry Ice temperatures showed no apparent change over extended periods of time.

The reaction of dibenzylmercury with refluxing SO_2 yielded a considerable amount of elemental mercury and a solid which was shown by IR and NMR spectroscopy not to contain the desired sulfinate. No attempt was made at characterization of this material.

Preparation of $C_2H_5SO_2HgC_2H_5$ *and* $(C_2H_5Hg)_2SO_2$

A 25-ml flask fitted with a Dry Ice condenser was charged with 5 g (0.019 mole) of diethylmercury and attached to a vacuum line using standard techniques. Dry sulfur dioxide was condensed (~20 ml) in the flask and the resulting mixture was allowed to reflux for about 6 h. Excess SO_2 was then removed leaving 6.10 g (98%) of the white sulfinate. [Found: C, 15.01; H, 3.27; S, 9.70; mol.wt., 346 (0.0105 *M* $CHCl_3$ soln.), 352 (0.0169 *M* $CHCl_3$ soln.), 279 (0.0120 *M* $ClCH_2CH_2Cl$ soln.). $C_4H_{10}HgO_2S$ calcd.: C, 14.15; H, 3.09; S, 9.92%; mol. wt., 323.]

To obtain the compound in high purity for spectral studies the above residue was dissolved in a minimum amount of chloroform (20–25 ml), treated with 200 ml of pentane, and cooled to *ca.* −70°. The resulting precipitate was filtered and air-dried. The procedure was repeated two more times, m.p. (sealed tube) 98–100°. The compound possesses solubility properties which are very similar to those of the other two sulfinates. It shows no decomposition on storage at room temperature for 3 months. Dissolution of the sulfinate in either chloroform or acetone, followed by cooling at −23° for 30 min and removal of the solvent, affords a solid whose IR spectrum is identical with that of the starting material.

In other experiments, 5 g (0.019 mole) of diethylmercury and 30 ml of liquid SO_2 were kept with occasional stirring at *ca.* −70° for 7 days. Excess solvent was then removed from a pale yellow solution and the white residue was treated with 15 ml of chloroform. The insoluble material was collected on a filter and washed with 5 ml of $CHCl_3$, m.p. 195° (dec.). (Found: C, 9.14; H, 2.00; S, 6.01. $C_4H_{10}Hg_2O_2S$ calcd.: C, 9.14; H, 1.91; S, 6.10%.) The compound is insoluble in common organic solvents and only sparingly soluble in liquid SO_2. Its yield varied with each preparation; in one case, no $(C_2H_5Hg)_2SO_2$ was detected.

Removal of $CHCl_3$ from the filtrate, followed by two recrystallizations of the residue from chloroform/pentane yielded 2.62 g (42%) of $C_2H_5SO_2HgC_2H_5$.

Preparation of $C_6H_5SO_2HgC_2H_5$

Diethylmercury (0.54 g, 2.07 mmoles) and $(C_6H_5SO_2)_2Hg$ (1 g, 2.07 mmoles) in 75 ml of chloroform were stirred at room temperature for about 4 h. The solution was then filtered and concentrated in a stream of nitrogen until the product just began to crystallize. Addition of 30 ml of pentane and cooling at *ca.* −70° afforded a precipitate which was filtered off and air-dried. The yield was 1.1 g (72%). The compound was characterized by proton magnetic resonance spectroscopy.

Preparation of $C_6H_5SHgC_6H_5$

This compound was prepared by the general method of Takagi *et al.*[17], with the specific experimental conditions having been elucidated in this study.

A solution of 1.10 g (0.01 mole) of thiophenol in 20 ml of absolute ethanol was added dropwise with stirring to a suspension of phenylmercuric chloride (3.14 g, 0.01 mole) in 200 ml of absolute ethanol at *ca.* −78°. The mixture was stirred for 30 min and then filtered. The volume of the filtrate was reduced to about 150 ml and the resulting solution was stored in Dry Ice for 24 h. A white precipitate, which appeared gradually, was collected on a filter and recrystallized from absolute ethanol. Yield, 1.55 g (40%); m.p. 100–102° (lit.[17] 103.5°). (Found: C, 37.35; H, 2.81; S, 8.45. $C_{12}H_{10}HgS$ calcd.: C, 37.21; H, 2.58; S, 8.27%.)

When the temperature of the reaction mixture was allowed to exceed −78°, the only product isolated was $(C_6H_5S)_2Hg$.

Reaction of $C_6H_5SO_2HgC_6H_5$ and $C_2H_5SO_2HgC_2H_5$ with chlorine

After chlorine had been bubbled for 15 min into a solution of $C_6H_5SO_2HgC_6H_5$ (II) (0.4 g, 0.001 mole) in tetrahydrofuran (50 ml) at 0°, removal of the solvent yielded *ca.* 0.1 g of benzenesulfonyl chloride and 0.3 g of phenylmercuric chloride. No formation of $BaSO_3$ was observed by passing the ensuing gases into aqueous $BaCl_2$. A similar treatment of $C_2H_5SO_2HgC_2H_5$ resulted in the isolation of $HgCl_2$ and $C_2H_5SO_2Cl$; no SO_2 was detected.

UV irradiation of $C_2H_5SO_2HgC_2H_5$ and $C_6H_5CH_2SO_2HgCH_2C_6H_5$

Irradiation of a benzene (90 ml)/tetrahydrofuran (10 ml) solution of $C_2H_5SO_2HgC_2H_5$ (1 g) for 72 h at *ca.* 30°, using photochemical equipment described previously[1], yielded some elemental mercury. Removal of the solvent, followed by crystallization of the residue from chloroform/pentane, gave 0.9 g of unreacted $C_2H_5SO_2HgC_2H_5$. A similar result was obtained with $C_6H_5CH_2SO_2HgCH_2C_6H_5$.

RESULTS AND DISCUSSION

Diphenyl- and diethylmercury react with refluxing sulfur dioxide to give virtually quantitative yields of compounds which analyze for $HgR_2 \cdot SO_2$. When the reaction of diethylmercury and sulfur dioxide is carried out at *ca.* −70° for 7 days, another product, $(C_2H_5Hg)_2SO_2$, may be usually isolated in addition to $Hg(C_2H_5)_2 \cdot SO_2$. Interaction of $Hg(CH_2C_6H_5)_2$ with refluxing sulfur dioxide affords elemental mercury and a solid which contains no $Hg(CH_2C_6H_5)_2 \cdot SO_2$; the latter is, however, obtained almost quantitatively by lowering the reaction temperature to *ca.* −40°.

Dissolution of dibenzyl- and diethylmercury in liquid SO_2 produces orange and pale yellow solutions, respectively. The above colors may indicate presence of free radicals; indeed, formation of free radicals in reactions of some organomercury compounds has been proposed in the literature[18]. However, in the absence of ESR data on these SO_2 solutions, the foregoing remains strictly a conjecture. Nevertheless, it is of interest that $(C_2H_5Hg)_2SO_2$ may be isolated from reaction of $Hg(C_2H_5)_2$ with SO_2 at −70°; this product should conceivably arise from interaction of C_2H_5Hg radicals with sulfur dioxide.

The reaction of sulfur dioxide with a dialkyl- or a diarylmercury (HgR_2) thus represents one of the two convenient preparative methods for compounds RSO_2HgR. The other is the reaction between HgR_2 and $(RSO_2)_2Hg$, reported by Deacon and Felder[15].

All of the SO_2-containing mercury compounds prepared in this study are

TABLE 1

PROTON MAGNETIC RESONANCE DATA[a,b]

Compound	Chemical shift, τ	Assignment
$C_2H_5SO_2HgC_2H_5$	7.50 (quartet, $J = 7.5$ cps)	CH_2SO_2
	8.00 [A_2 part of A_2B_3 (approx. quartet), $J(^1H-^{199}Hg) = 224$ cps]	$HgCH_2$
	8.75 (complex pattern)	CH_3
$C_6H_5SO_2HgC_2H_5$	*ca.* 8.2 [A_2 part of A_2B_3, $J(^1H-^{199}Hg) = 235$ cps]	CH_2
	ca. 8.8 (B_3 part of A_2B_3)	CH_3
$C_6H_5CH_2SO_2HgCH_2C_6H_5$[c]	6.29[d], 6.30[e] (6.22)[f], 6.32[g], 6.20[h], 6.23[i]	CH_2SO_2
	7.35[d], 7.25[e] (7.12)[f], 7.23[g], 7.20[h], 7.17[i]	$HgCH_2$

[a] In $CDCl_3$ solution and at room temperature unless noted otherwise. [b] Phenyl proton resonances are not tabulated. [c] All peaks are singlets; satellites due to $^1H-^{199}Hg$ spin–spin coupling are not descernible because of limited solubility. [d] At −40°. [e] At −20°. [f] At −20° in liquid SO_2. [g] At 0°. [h] At 40°. [i] At 100°.

TABLE 2

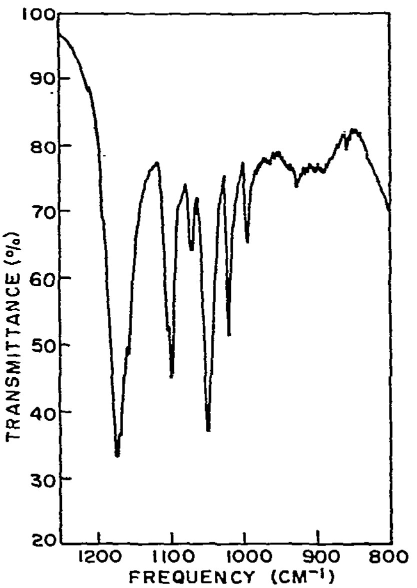
PROMINENT ABSORPTIONS (cm^{-1}) IN THE IR SPECTRA OF $C_6H_5SHgC_6H_5$ (1200–800 cm^{-1}) AND ISOMERS (I) AND (II) OF $C_6H_5SO_2HgC_6H_5$ (1250–800 cm^{-1})[a]

$C_6H_5SHgC_6H_5$	$C_6H_5SO_2HgC_6H_5$ [isomer (I)]	$C_6H_5SO_2HgC_6H_5$ [isomer (II)]			
Nujol mull	Nujol mull	Nujol mull	CH_2Cl_2 soln.[b]	$CHBr_3$ soln.[b]	$ClCH_2CH_2Cl$ soln.[b]
	1175 vs(br)($\nu_{as}SO_2$)				
1153 w[c]		1160 vw[c]	1151 m[d]		
1083 m	1099 m	1082 m			1100 s
1066 s	1070 w		1085 vs	1085 vs	
	1048 s (ν_sSO_2)	1048 vs(br)($\nu_{as}SO_2$)	1059 vs	1059 vs	1059 m
1022 s	1022 m	1024 s	1022 s	1022 s	
999 m	996 w	996 m	998 s	998 m	
			940 w	938 vw	
		912 vw[c]		919 vw	
903 s[c]		903 vw[c]			
		836 vs(br)(ν_sSO_2)	847 vs, br	849 vs (br)	~8.50 (sh)[e]

[a] Recorded on a Beckman Model IR-9 spectrophotometer; abbreviations: vs, very strong; s, strong; m, medium; w, weak; (br), broad; (sh), shoulder. [b] Measured only in the regions not masked by strong solvent absorptions; see the text. [c] The spectrum of Nujol mull between Irtran-2 plates contains weak but broad bands at 1180–1130 cm^{-1} and 970–870 cm^{-1}, which enhance the intensity of other absorptions in these regions. [d] Due in part to solvent absorption. [e] Partly covered by a strong solvent band.

colorless, crystalline solids. With the exception of $(C_2H_5Hg)_2SO_2$, they are soluble in a number of organic solvents (*vide supra*). Products derived from diphenyl- and diethylmercury appear to be reasonably stable in the solid; the benzyl derivative decomposes to elemental mercury and dibenzyl sulfone on storage at 0° and under the influence of light. Neither the benzyl nor the ethyl compound exhibits any tendency to lose SO_2 under photolytic conditions; moreover, none of these compounds react with additional SO_2 to yield $HgR_2 \cdot 2SO_2$.

Evidence for insertion of SO_2 between Hg–C bonds in $HgR_2 \cdot SO_2$ is derived from examination of the NMR spectra of the ethyl and benzyl derivatives and from the nature of products obtained in reaction of $HgR_2 \cdot SO_2$ ($R = C_2H_5$ and C_6H_5) with chlorine. The NMR spectra of both compounds (Table 1) show two kinds of methylene protons, thus reflecting a $R'CH_2SO_2HgCH_2R'$ ($R' = CH_3$ and C_6H_5) type of structure; the formation of RSO_2Cl from $HgR_2 \cdot SO_2$ and chlorine lends support to such a formulation.



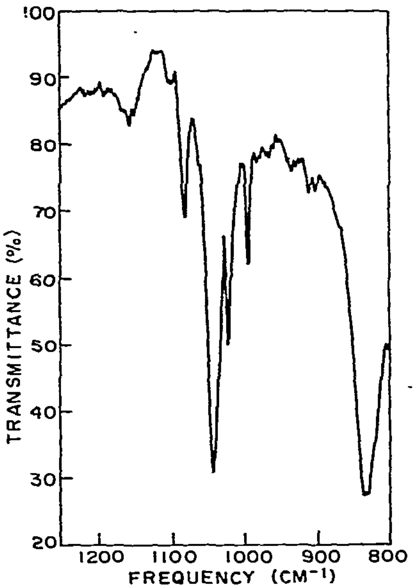


Fig. 1. The infrared spectrum (1250–800 cm^{-1}) of a Nujol dispersion of $C_6H_5SO_2HgC_6H_5$ [isomer (I)].

Fig. 2. The infrared spectrum (1250–800 cm^{-1}) of a Nujol dispersion of $C_6H_5SO_2HgC_6H_5$. [isomer (II)].

There are three possible monodentate modes of bonding in $HgSO_2R$ moieties —HgOS(O)R, $HgS(O)_2R$, and HgS(O)OR—in addition to several bidentate and bridging types of attachment. These will be considered next; because of the diversity of behavior displayed by $C_6H_5SO_2HgC_6H_5$, the structure of this compound will be examined first.

Removal of excess solvent at −75° from solutions of $Hg(C_6H_5)_2$ in liquid SO_2 yields an off-white solid, designated as (I). Crystallization of this material from chloroform/pentane affords a white substance, referred to as (II), which does not revert to (I) upon dissolution in SO_2, refluxing for 2 h, and subsequent removal of the solvent. Examination of the IR spectra (Nujol mull) of (I) and (II) in the 1250–800 cm^{-1} range

(Table 2, Figs. 1 and 2) reveals significant differences between them. In order to assign unequivocally bands due to the S–O stretching modes in these sulfinates, we have also synthesized the compound $C_6H_5HgSC_6H_5$. Its spectrum (1200–800 cm^{-1}, Nujol mull) is tabulated (Table 2) and reproduced in Fig. 3. Inspection of the three spectra clearly discloses that the asymmetric and symmetric SO_2 stretching frequencies occur at 1175 and 1048 cm^{-1}, respectively, for (I), and at 1048 and 836 cm^{-1}, respectively, for (II). These numbers are virtually identical with those reported recently by Deacon and Felder[15] for isomers B and A, respectively, of $C_6H_5SO_2HgC_6H_5$.

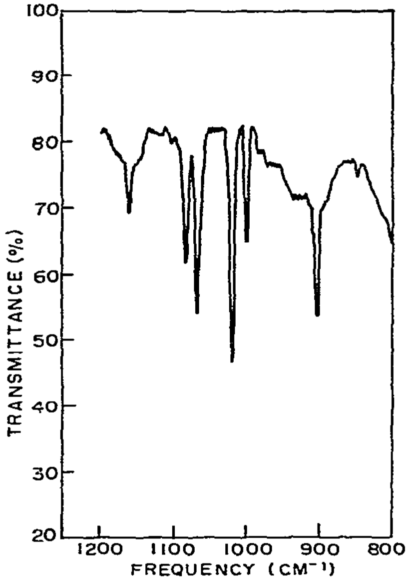


Fig. 3. The infrared spectrum (1200–800 cm^{-1}) of a Nujol dispersion of $C_6H_5SHgC_6H_5$.

There is little doubt that (I) is the *S*-sulfinate $C_6H_5S(O)_2HgC_6H_5$, since a closely related mercury(II) *S*-sulfinate, $(C_6H_5SO_2)_2Hg$, shows[16] S–O stretching bands at 1192 and 1037 cm^{-1}. Furthermore, in other *S*-sulfinato complexes[1–3] —$C_5H_5Fe(CO)_2S(O)_2R$, $Mn(CO)_5S(O)_2R$, $Mn(CO)_3L_2S(O)_2R$, and $Mn(CO)_3(L–L)S(O)_2R$ (L and L–L are monodentate and bidentate amines, respectively)—S–O stretching fundamentals give rise to absorptions in the regions 1218–1102 and 1061–1009 cm^{-1}.

The observed S–O stretching frequencies for (II)—at 1048 and 836 cm^{-1}— preclude its formulation either as an *S*-sulfinato or as the phenyl(oxy)sulfinyl, $C_6H_5HgS(O)OC_6H_5$*, derivative. This leaves for consideration several possible monomeric and polymeric structures containing oxygen-bonded $C_6H_5SO_2$.

Since molecular weight determinations have shown that (II) is monomeric in 1,2-dichloroethane, we examined its IR spectrum in the 1250–800 cm^{-1} region in this solvent. However, strong absorptions of $ClCH_2CH_2Cl$ rendered impossible complete identification of the sulfinate bands, the only clear regions in the spectrum

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* See ref. 6 for typical S–O stretching frequencies of complexes containing MS(O)OR moieties.

being 1190–1150, 1120–1040, 1000–970, and 850–800 cm^{-1}. Therefore, solution spectra of (II) were recorded also using CH_2Cl_2 and $CHBr_3$. The former solvent is virtually transparent in the regions 1210–920 and 880–830 cm^{-1}, and the latter is transparent in the region 1090–800 cm^{-1}. Hence the two complement each other; the regions that overlap provide a useful check on any similarities or differences between the solution spectra of the compound examined.

The relatively high and the relatively low respective vapor pressures of CH_2Cl_2 and $CHBr_3$ prevented us from measuring molecular weights of the sulfinates in these solvents by osmometry. Nevertheless, where lack of solvent absorption permits, the spectra of (II) in CH_2Cl_2 and $CHBr_3$ (Fig. 4), which are virtually identical, match quite well that of (II) in $ClCH_2CH_2Cl$ (Table 2). Since (II) is monomeric in the latter solvent, it appears safe to conclude that it is monomeric also in CH_2Cl_2 and $CHBr_3$. Thus the solution spectra, recorded using concentrations approximately equal to those employed for molecular weight measurements, are diagnostic of a monomeric $C_6H_5SO_2HgC_6H_5$.

Examination of Table 2 reveals that, aside from some differences in the relative intensities of the bands, the spectrum of (II) in Nujol mull is virtually the same as those in CH_2Cl_2 and $CHBr_3$ solutions. It therefore follows that (II) is almost certainly monomeric in the solid. Since dissolution of (I) in $ClCH_2CH_2Cl$, CH_2Cl_2, or $CHBr_3$ gives immediately (< 1 min) the same spectrum as that of (II), the two isomers must

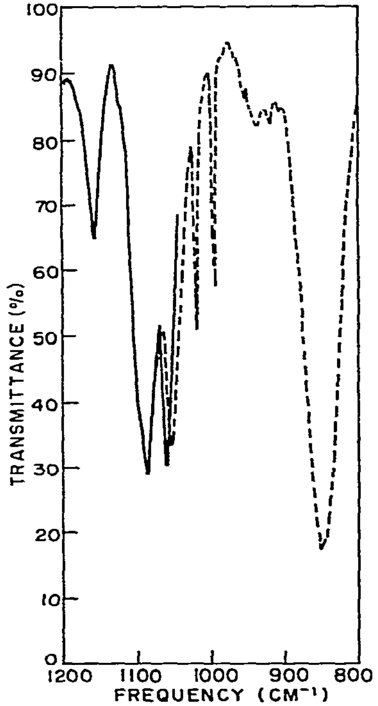
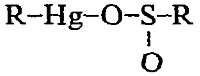


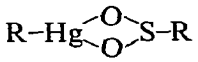
Fig. 4. The infrared spectrum (1200–800 cm^{-1}) of $C_6H_5SO_2HgC_6H_5$ in CH_2Cl_2 (————) and $CHBr_3$ (– – – – – –).

have an identical structure in solution, either (IIIa) or (IVa).



$$\mathrm{R{-}Hg{-}O{-}\underset{\underset{\displaystyle O}{|}}{S}{-}R}$$

(III)



(IV)

[(IIIa), R = C_6H_5; (IIIb), R = C_2H_5] [(IVa), R = C_6H_5; (IVb), R = C_2H_5]

At present differentiation between them does not appear possible from the data available.

TABLE 3

PROMINENT ABSORPTIONS (cm^{-1}) IN THE IR SPECTRA OF $C_2H_5SO_2HgC_2H_5$ AND $(C_2H_5Hg)_2SO_2$ IN THE 1255–800 cm^{-1} REGION

$C_2H_5SO_2HgC_2H_5$[a]				$(C_2H_5Hg)_2SO_2$[b]
Nujol mull	CH_2Cl_2 soln.[c]	$CHBr_3$ soln.[c]	$ClCH_2CH_2Cl$ soln.[c]	KBr pellet
1229 m				1251 s
	1194 s			1194 (sh)
1157 vs (br) (ν_{as} SO_2)				1185 m
	1133 m			1111 vs
1059 s	1059 vs (br)	1048 s (br)	1061 s	1094 vs
1033 vs (ν_s SO_2)				1020 s
	1015 m	1012 m		940 vs (br)
970 m				872 m
947 m	946 m	943 m	~965 (sh)[d]	801 s
	859 vs (br)	854 vs (br)	~950 (sh)[d]	
810 w				

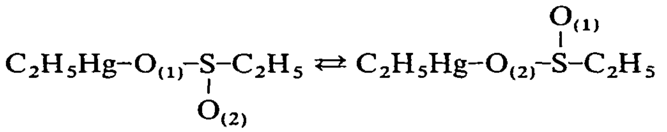
[a] Recorded on a Perkin–Elmer Model 337 spectrophotometer; for abbreviations see Table 2. [b] Recorded using a Beckman Model IR-9 spectrophotometer. [c] Measured only in the regions not masked by strong solvent absorptions; see the text. [d] Partly covered by a strong solvent band.

The IR spectrum of $C_2H_5SO_2HgC_2H_5$ in Nujol mull, listed in Table 3, exhibits two strong-intensity bands at 1157 and 1033 cm^{-1}, assigned to the asymmetric and symmetric SO_2 stretching modes. The spectrum is invariant to the method of purification and/or treatment of the compound; accordingly, it is the same for crude sulfinate, obtained by removal of SO_2 from the reaction mixture, for the sulfinate recrystallized from chloroform/pentane, and for samples which had been chilled to $-23°$ in chloroform or acetone before removal of the solvent. The positions of the S–O stretching bands indicate mercury–sulfur bonding for $C_2H_5SO_2HgC_2H_5$ in the solid.

Solution spectra of $C_2H_5SO_2HgC_2H_5$, summarized in Table 3, show the two S–O stretching bands to occur at frequencies comparable to those for $C_6H_5SO_2HgC_6H_5$ in the same solvents. Since the compound is monomeric in both $CHCl_3$ and $ClCH_2CH_2Cl$, it undoubtedly adopts one of the two types of structure already proposed for the phenylsulfinato analog. In order possibly to differentiate between them, we have examined the NMR spectrum of $C_2H_5SO_2HgC_2H_5$ in $CDCl_3$. If the sulfinate acts as a monodentate ligand [structure (IIIb)], then its methylene protons are expected to be magnetically nonequivalent because of the presence of asymmetric sulfur[19]. However, a bidentate sulfinate [structure (IVb)] should render the two hydrogens equivalent.

The NMR spectra of $C_2H_5SO_2HgC_2H_5$ and $C_6H_5SO_2HgC_2H_5$ are given in Table 1. The latter spectrum was recorded in order to aid unambiguous assignment of the two sets of methylene proton signals in the ethylsulfinato compound. In $C_6H_5SO_2HgC_2H_5$, the CH_2 hydrogen signal is centered at τ 8.2; from the position of this resonance we assign the absorption pattern at τ 7.50 to the $CH_3CH_2SO_2$ methylene protons and that at τ 8.00 to the $HgCH_2CH_3$ methylene protons of $C_2H_5SO_2HgC_2H_5$. This assignment is supported by the presence of satellite resonances due to ^1H–^{199}Hg spin–spin coupling ($J = 224$ cps) in the $HgCH_2CH_3$ moiety.

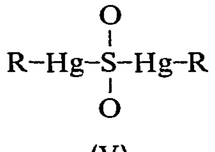
The appearance of the $CH_3CH_2SO_2$ methylene proton signal as a 1:3:3:1 quartet rather than an ABX_3 pattern is consistent with a bidentate, oxygen attachment of this ligand [structure (IVb)]. However, the possibility of a very rapid equilibrium (1)



$$C_2H_5Hg{-}O_{(1)}{-}\underset{O_{(2)}}{S}{-}C_2H_5 \rightleftarrows C_2H_5Hg{-}O_{(2)}{-}\overset{O_{(1)}}{S}{-}C_2H_5 \qquad (1)$$

or, alternatively, fast inversion at the asymmetric sulfur, which would make the two methylene protons of the ethylsulfinate ligand equivalent on the NMR time scale, cannot be dismissed.

The other compound isolated from reaction of diethylmercury and liquid SO_2 analyzes for $(C_2H_5Hg)_2SO_2$ and shows intense IR absorptions at 1251, 1111, 1094, and 940 cm^{-1} (Table 3). The bands at 1251, 1111, and 1094 cm^{-1} occur at frequencies comparable to those for $(CH_3Hg)_2SO_2$ (1245 and 1085 cm^{-1})[10], prepared recently by Carey and Clark and assigned structure (Va) on the basis of IR and NMR data. Both of these compounds



$$R{-}Hg{-}\overset{O}{\underset{O}{S}}{-}Hg{-}R$$

(V)

[(Va), $R{=}CH_3$; (Vb), $R{=}C_2H_5$]

show also an IR band at 940 cm^{-1}, consistent with the $\rangle S{-}O{\rightarrow}Hg$ type of association[20], which would account for their observed insolubility. On the basis of the close similarities in the spectra and physical behavior, it is safe to conclude that the two compounds have the same type of structure, probably (Va) and (Vb).

Inspection of the tabulated IR spectra (Table 4) of the benzylsulfinato compound, $C_6H_5CH_2SO_2HgCH_2C_6H_5$, shows that the pertinent absorptions occur virtually at the same wavenumbers irrespective of the medium employed. The bands at 1055–1048 and 877–844 cm^{-1} are assigned to the S–O stretching modes; their positions indicate the same type of bonding of the sulfinate ligand to mercury as that

TABLE 4

PROMINENT ABSORPTIONS IN THE IR SPECTRA OF $C_6H_5CH_2SO_2HgCH_2C_6H_5$ IN THE 1250–800 cm^{-1} REGION[a]

Nujol mull	CH_2Cl_2 soln.[b]	$CHBr_3$ soln.[b]	$ClCH_2CH_2Cl$ soln.[b]
1072 s	1072 s	1067 s	1074 s
1051 vs ($\nu_{as}SO_2$)	1055 s	1048 s	1055 s
1029 m			
		911 m	
877 m (ν_sSO_2?)		874 s(br)	
844 m (ν_sSO_2?)	853 s	848 m–s	

[a] Recorded on a Perkin–Elmer Model 337 spectrophotometer; for abbreviations see Table 2. [b] Measured only in the regions not masked by strong solvent absorptions; see the text.

found for $C_6H_5SO_2HgC_6H_5$ and $C_2H_5SO_2HgC_2H_5$ in solution. A monomeric nature of $C_6H_5CH_2SO_2HgCH_2C_6H_5$ in $ClCH_2CH_2Cl$ is consistent with these observations.

The NMR spectrum of $C_6H_5CH_2SO_2HgCH_2C_6H_5$ over the −40° to 100° temperature range (Table 1) shows signals due to protons of the two different methylene groups as sharp singlets. This observation is in accord with the NMR data obtained for the ethyl analog and provides additional support for the same type of structure in solution of the two sulfinates*.

It is noteworthy that the three sulfinates of the type RSO_2HgR investigated in this work exhibit such a striking diversity of structural behavior depending on the nature of the group R. We have no ready explanation for these differences.

The position of the S–O stretching bands for the *O*-bonded RSO_2HgR deserves special comment. There are few well-characterized metal sulfinates containing monodentate MOS(O)R linkages whose spectra have been reported. The compound $Cu(H_2O)_4[p\text{-}OS(O)C_6H_4CH_3]_2$, examined crystallographically[21], represents one of such *O*-sulfinates; its S–O stretching frequencies occur[15] at 998 and 938 cm^{-1}. The corresponding absorptions for $(C_6H_5)_3SnOS(O)C_6H_5$ are found[2] at 979–954 and 933 cm^{-1}. For $[(CH_3)_2MOS(C_6H_5)O]_2$ (M = Al and Ga), which presumably contain bridging $C_6H_5SO_2$ ligands, S–O stretching frequencies occur[22] at 1027–1005 and 980–941 cm^{-1}. It is to be noted that the separation between the two bands in each of the above compounds is significantly smaller than that found in *O*-bonded mercury sulfinates.

In analogy with the known behavior of complexes containing monodentate acetate ligands[23], one may suggest that the asymmetric SO_2 stretching frequency increases and the symmetric SO_2 stretching frequency decreases as the M–O bond in the sulfinate becomes stronger. This would then indicate that the Hg–O bonds in

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* It has been suggested by Dr. G. B. Deacon in personal correspondence that $C_6H_5CH_2SO_2HgCH_2C_6H_5$ may undergo a rapid but slight ionization

$$C_6H_5CH_2SO_2HgCH_2C_6H_5 \rightleftharpoons C_6H_5CH_2Hg^+ + C_6H_5CH_2SO_2^-$$

which would account for the observed magnetic equivalence of the $C_6H_5CH_2SO_2$ methylene protons. Supporting such a possibility is our observation that the sulfinate readily yields $C_6H_5CH_2HgX$ and $C_6H_5CH_2SO_2M$ when allowed to come in contact with MX (M = Na or K; X = Cl or Br). A similar argument may be also invoked to explain the NMR spectrum of the ethyl compound, $C_2H_5SO_2HgC_2H_5$ (*vide supra*).

the *O*-bonded RSO_2HgR are considerably stronger than the $Cu-OS(O)C_6H_4CH_3$ bonds in $Cu(H_2O)_4[p\text{-}OS(O)C_6H_4CH_3]_2$ and the $Sn-OS(O)C_6H_5$ bond in $(C_6H_5)_3SnOS(O)C_6H_5$. There are no thermodynamic data either to support or to refute such a supposition. Should this be the case, however, then the relatively facile interconversion between S- and O-bonded mercury sulfinates must be ascribed primarily to such factors as crystal packing and influence of the solvent.

Interaction of chlorine with tetrahydrofuran solutions of $C_6H_5SO_2HgC_6H_5$ or $C_2H_5SO_2HgC_2H_5$ results in the formation of the organic sulfonyl chlorides. This behavior contrasts[1,2] that of $C_5H_5Fe(CO)_2S(O)_2R$ and $Mn(CO)_5S(O)_2R$ toward Cl_2; there, sulfur dioxide is invariably produced and no RSO_2Cl has been detected. The observed variation may be attributed to the different mode of attachment of RSO_2 in these compounds. Assuming that RSO_2HgR are oxygen-bonded also in tetrahydrofuran, then electrophilic attack of chlorine at the uncoordinated sulfur and a subsequent rupture of the Hg–O bond(s) would give rise to the formation of RSO_2Cl. However, such a mechanism could not be operative for the *S*-bonded $C_5H_5Fe(CO)_2S(O)_2R$ and $Mn(CO)_5S(O)_2R$.

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