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Sulfur Dioxide Insertion Reactions of some Compounds containing Sn—C and Fe—Sn—C Bonds[1]

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The preparations of $[CpFe(CO)_2]_2Sn[OS(O)Ph]_2$, $CpFe(CO)_2SnPh[OS(O)Ph]_2$, $CpFe(CO)_2SnPh[OS(O)Ph]OH$, and $Ph_2Sn[OS(O)Ph]_2$ by sulfur dioxide insertion into the C—Sn bond and also by reaction of the sodium phenyl sulfinate with the corresponding chloro-compounds are reported. The infrared (i.r.) spectra and some reactions of these compounds are also discussed.

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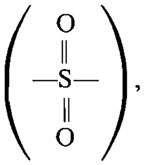
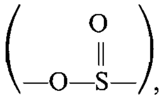
Introduction

Insertion reactions between sulfur dioxide and organometallic compounds have received much attention during the last few years (*e.g.*, refs. 1–6 and references therein). A wide variety of reactions and of types of insertion product has now been claimed. Thus, for a compound containing Fe—Sn—C bonds, insertion of sulfur dioxide between either the Fe—Sn and/or the Sn—C bonds might be expected. The product could also be an *S*-sulfinate



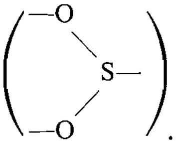
$\left(\underset{O}{\overset{O}{\overset{\|}{\underset{\|}{-S-}}}}\right)$,

O-sulfinate



$\left(-O-\overset{O}{\overset{\|}{S}}-\right)$,

or a polymeric O-bonded sulfinate



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The first insertion of sulfur dioxide into a C—Sn bond was briefly reported earlier by two of us (7). We now discuss this reaction and others in more detail.

Discussion

Bis(dicarbonyl-π-cyclopentadienyliron)diphenyltin(IV) reacts with sulfur dioxide, either in benzene solution or in liquid sulfur dioxide, giving $[CpFe(CO)_2]_2Sn[OS(O)Ph]_2$ in good yield (70 and 60%, respectively). The infrared spectrum shows no bands in the 1200–1300 and 1030–1150 cm^{-1} regions expected for the ν_{asym} S=O and ν_{sym} S=O of compounds containing the $\underset{O}{\overset{O}{\overset{\|}{\underset{\|}{-S-}}}}$ group (8, 9). Instead, a pattern is observed at 800–900 cm^{-1} (Fig. 1) which is assigned to $\nu_{S=O}$ and ν_{S-O} of an *O*-sulfinate and also the δ_{CH} of the cyclopentadienyl group. The same compound is also obtained using sodium phenylsulfinate

$$[CpFe(CO)_2]_2SnCl_2 + 2NaSO_2Ph \rightarrow [CpFe(CO)_2]_2Sn[OS(O)Ph]_2\ (60\%) + 2NaCl$$

This shows that the product is an *O*-sulfinate rather than an *S*-sulfinate or a sulfone. Ultimate proof of this structure has been obtained by X-ray analysis (10).

On heating at 180° for 48 h, $[CpFe(CO)_2]_2Sn[OS(O)Ph]_2$ decomposes to give diphenyldisulfide and a black non-volatile solid. Although organic sulfones and diphenyl-*O*-sulfinato-mercury evolve sulfur dioxide on thermal decomposition, no sulfur dioxide was detected in this case (11, 12), *cf.*

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[1] Presented in brief at the C.I.C.–A.C.S. Joint Conference, Toronto, 24–29 May, 1970. Abstract No. 30.

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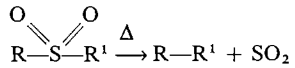
$$Hg(SO_2Ph)_2 \xrightarrow{\Delta} HgPh_2 + SO_2$$



$$R-\overset{O\quad O}{S}-R^1 \xrightarrow{\Delta} R-R^1 + SO_2$$

$(R = \text{alkyl}, R^1 = \text{alkyl or aryl})$

Reaction with hydrogen chloride likewise evolved no sulfur dioxide. The products were $[CpFe(CO)_2]_2SnCl_2$ and diphenylthiolsulfonate (13, 14), *cf.*

$$Mn(CO)_5SO_2Me \xrightarrow{Cl_2} Mn(CO)_5Cl + SO_2$$

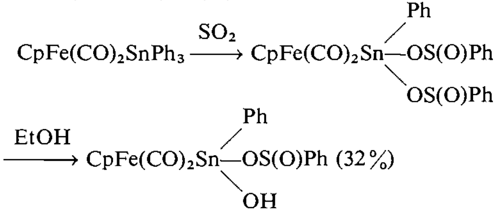
$$[CpFe(CO)_2]SnPh_3 \xrightarrow{HCl} [CpFe(CO)_2]SnCl_3$$

The diphenylthiosulfonate probably arises via decomposition of phenylsulfinic acid under acidic conditions (15) although no sulfonic acid was detected.

$$[CpFe(Co)]_2Sn[OS(O)Ph]_2 \xrightarrow{HCl} [CpFe(CO)_2]_2SnCl_2\ (79\%) + 2PhSO_2H$$

$$3\ PhSO_2H \xrightarrow{H^+} PhSO_2SPh\ (80\%) + PhSO_3H + H_2O$$

Treatment of (dicarbonyl-π-cyclopentadienyl-iron)triphenyltin(IV) with sulfur dioxide was expected to yield the analogous $[CpFe(CO)_2]Sn[OS(O)Ph]_3$. However, the initial yellow product was found to be $[CpFe(CO)_2]SnPh[OS(O)Ph]_2$ which decomposed on treatment with boiling ethanol to give orange crystals of $CpFe(CO)_2SnPh[OS(O)Ph]OH$.



$$CpFe(CO)_2SnPh_3 \xrightarrow{SO_2} CpFe(CO)_2Sn\begin{array}{l} Ph \\ OS(O)Ph \\ OS(O)Ph \end{array} \xrightarrow{EtOH} CpFe(CO)_2Sn\begin{array}{l} Ph \\ OS(O)Ph\ (32\%) \\ OH \end{array}$$

Fong and Kitching (3) have very recently shown that the insertion of sulfur dioxide into a carbon–tin bond is very likely an electrophilic substitution. A consequence of this in the present system is that insertion of sulfur dioxide is more difficult into the second Sn—Ph bond than into the first, and no insertion occurs into the third Sn—Ph bond. A similar product is obtained in the reaction between $(CO)_5MnSnPh_3$ and sulfur dioxide (16). Confirmation of the identity of the two iron compounds was provided by the synthesis using sodium phenylsulfinate

$$CpFe(CO)_2SnPhCl_2 + NaSO_2Ph \rightarrow CpFe(CO)_2SnPh[OS(O)Ph]_2\ (18\%) + CpFe(CO)_2SnPh[OS(O)Ph]OH\ (18\%)$$

The nuclear magnetic resonance (n.m.r.) and infrared (i.r.) spectra are consistent with these formulations. The $\nu_{S=O}$ and ν_{S-O} occur in the same region as for $[CpFe(CO)_2]_2Sn[OS(O)Ph]_2$ where the *O*-sulfinate structure is confirmed by X-ray analysis (Fig. 1).

Thermal decomposition of $CpFe(CO)_2SnPh[OS(O)Ph]OH$ at 190° yields diphenyldisulfide; no sulfur dioxide was evolved. Treatment with hydrogen chloride yields $[CpFe(CO)_2]SnCl_3$ and diphenylthiolsulfinate, again no sulfur dioxide was evolved.

The only product which was isolated when $[CpFe(CO)_2]_2SnMe_2$ was treated with sulfur dioxide was $CpFe(CO)_2SO_2Me$ (8). This may be a decomposition product of $[CpFe(CO)_2]_2Sn[OS(O)Me]_2$ although the reaction between $CpFe(CO)_2SnMe_3$ and sulfur dioxide is said to yield a product containing $Fe-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-Sn$ (4). The lack of reactivity of $[CpFe(CO)_2]_2SnCl_2$ towards sulfur dioxide at 50° for 5 days clearly reflects the stability of this compound. No insertion of sulfur dioxide between the Fe—Sn bond or substitution of sulfur dioxide for carbonyl groups was detected. The starting material was completely recovered in 97% yield.

Although diphenyltin dichloride and tetraphenyltin are recovered unchanged after 24 h at 20° in liquid sulfur dioxide (the latter probably owing to its insolubility), triphenyltin chloride readily reacts under identical conditions yielding diphenyltin dichloride and a white insoluble compound, diphenylbis(phenyl *O*-sulfinato)tin(IV).

$$2Ph_3SnCl \xrightarrow{SO_2} Ph_2SnCl_2\ (80\%) + Ph_2Sn[OS(O)Ph]_2\ (84\%)$$

The same product was also obtained from the reaction between diphenyltin dichloride and sodium phenylsulfinate

$$Ph_2SnCl_2 + 2PhSO_2Na \rightarrow Ph_2Sn[OS(O)Ph]_2\ (99\%) + 2NaCl$$

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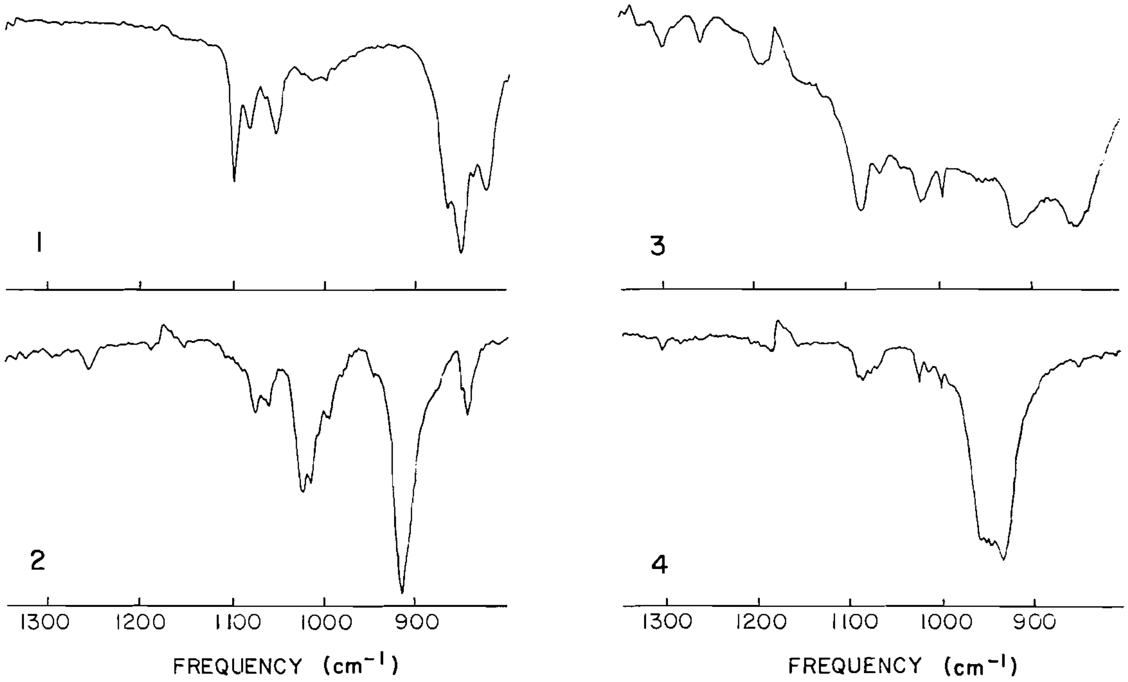
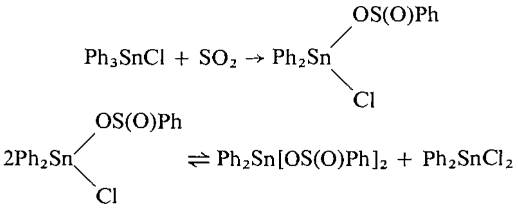


FIG. 1. Infrared spectra in the region 1350 to 800 cm^{-1}; (1), $[CpFe(CO)_2]_2Sn[OS(O)Ph]_2$; (2), $CpFe(CO)_2SnPh[OS(O)Ph]OH$; (3), $CpFe(CO)_2SnPh[OS(O)Ph]_2$; (4) $Ph_2Sn[OS(O)Ph]_2$.

Other workers have very recently reported similar results (5). The infrared spectrum of $Ph_2Sn[OS(O)Ph]_2$ showed ν_{SO} at 850 cm^{-1} which is consistent with the *O*-sulfinate linkage, probably in a hexacoordinate *O*-sulfinate-bridged polymer (5*b*) (Fig. 1).

It is possible that sulfur dioxide inserts into one Sn—Ph bond of triphenyltin chloride and that anion exchange then occurs between two such mono-substitution products



$$Ph_3SnCl + SO_2 \rightarrow Ph_2Sn\begin{matrix}\diagup OS(O)Ph \\ \diagdown Cl\end{matrix}$$

$$2Ph_2Sn\begin{matrix}\diagup OS(O)Ph \\ \diagdown Cl\end{matrix} \rightleftharpoons Ph_2Sn[OS(O)Ph]_2 + Ph_2SnCl_2$$

Further electrophilic substitution in either product is then probably unfavorable. An analogous reaction with sulfur trioxide has also been reported (17).

$$Me_3SnCl + SO_3 \rightarrow Me_2Sn(OSO_2Me)_2 + Me_2SnCl_2$$

Thermal decomposition of $Ph_2Sn[OS(O)Ph]_2$ at 225° yields diphenylsulfone; no sulfur dioxide is evolved. When $Ph_2Sn[OS(O)Ph]_2$ is treated with hydrogen chloride in methylene dichloride suspension, an oil is obtained which yields $Ph_2Sn[OS(O)Ph]_2$ on treatment with water. Presumably a hydrochloride is formed. Reaction with concentrated hydrochloric acid under reflux gives some diphenylthiolsulfonate and a hygroscopic oil, probably tin(IV) chloride.

Experimental

The starting materials were either purchased (Alfa Inorganics Ltd.) or prepared as reported in the literature. Anhydrous grade sulfur dioxide (*ex.* Matheson) was dried by passing through concentrated sulfuric acid and over phosphorus pentoxide/calcium chloride. All experiments were carried out under an atmosphere of nitrogen. Compounds containing iron and tin tended to be unstable in air especially when in solution. Infrared spectra were obtained as KBr discs using a Perkin–Elmer Model 457 spectrometer. Nuclear magnetic resonance spectra were recorded using a Varian A60 instrument operating at 60 Hz and for mass spectrometry a Perkin–Elmer Hitachi RMU6E spectrometer was employed. Element analyses were carried out by the A. Bernhardt Microanalytical Laboratory, West Germany, or the Schwarzkopf Microanalytical Laboratory, New York, except for the iron analyses which were performed in this laboratory using a Unicam S.P. 90 Atomic Absorption instrument.

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Reaction of Sulfur Dioxide with Bis(dicarbonyl-π-cyclopentadienyliron)diphenyltin(IV)

(*a*) Sulfur dioxide (*ca.* 15 ml) was condensed into a 100 ml Pyrex ampoule containing bis(dicarbonyl-π-cyclopentadienyliron)diphenyltin(IV) (18) (2.02 g, 3.22 mmol). The ampoule was sealed *in vacuo* and left for 24 h at 22°. The volatile products were removed under reduced pressure leaving a reddish tar which yielded bis(dicarbonyl-π-cyclopentadienyliron)bis(phenyl-*O*-sulfinato)tin(IV) (1.47 g, 1.95 mmol, 60%) as yellow crystals on crystallization from ethanol.

(*b*) In a similar reaction sulfur dioxide was passed through a solution of bis(dicarbonyl-π-cyclopentadienyliron)diphenyltin(IV) (3.3 g, 5.3 mmol) in benzene (400 ml) during 48 h. The solvent was removed under reduced pressure leaving a yellow oil which crystallized from ether/petroleum ether (b.p. 60–80°). Recrystallization from methylene chloride/petroleum ether (b.p. 30–40°) yielded yellow crystals of bis(dicarbonyl-π-cyclopentadienyliron)bis(phenyl-*O*-sulfinato)tin(IV) (2.8 g, 3.7 mmol, 70%) m.p. 153–155°.

Anal. Calcd. for $C_{26}H_{20}O_8S_2Fe_2Sn$: C, 41.4; H, 2.7; S, 8.5; $Fe_2O_3SnO_2$, 41.1. Found: C, 41.7; H, 2.8; S, 8.2; residue 40.4.

λ_{max}(KBr): 3112 vw, 3084 vw, 3067 vw, 2008 vs, 1968 vs, 1966 vs, 1953 vs, 1926 w, 1475 vw, 1442 w, 1429 w, 1414 w, 1358 vw, 1100 m, 1084 w, 1055 w, 1016 vw, 1000 vw, 866 m, 852 s, 840 m, 825 m, 754 m, 699 m, 630 m, 600 w, 580 s, 573 s, 454 vw, 425 vw, 384 vw, 298 vw, 263 vw, 235 vw cm^{-1}. $^1H_{n.m.r.}$ $\delta_{(CDCl_3)}$ 5.09 (singlet, C_5H_5), 2.4 (multiplet, C_6H_5) τ. Intensity 1:1.

(*c*) Bis(dicarbonyl-π-cyclopentadienyliron)bis(phenyl-*O*-sulfinato)tin(IV) was also prepared when dichlorobis(dicarbonyl-π-cyclopentadienyliron)tin(IV) (3.0 g, 5.5 mmol) and sodium phenylsulfinate dihydrate (1.86 g, 9.3 mmol) were heated under reflux (65°) in methanol (300 ml) during 22 h. The solvent was removed under reduced pressure leaving a yellow solid which recrystallized from methylene chloride/petroleum ether (b.p. 40–60°) to give bis(dicarbonyl-π-cyclopentadienyliron)bis(phenyl-*O*-sulfinato)tin(IV) (3.29 g, 4.4 mmol, 79% [based on $[CpFe(CO)_2]_2SnCl_2$]) m.p. 153–155°.

Anal. Calcd. for $C_{26}H_{20}O_8S_2Fe_2Sn$: C, 41.4; H, 2.7; S, 8.5; $Fe_2O_3.SnO_2$, 41.1. Found: C, 41.4; H, 3.0; S, 8.2; residue 41.0.

Reactions of Bis(dicarbonyl-π-cyclopentadienyliron)-bis(phenyl-O-sulfinato)tin(IV)

(*a*) *Effect of Heat*

Bis(dicarbonyl-π-cyclopentadienyliron)bis(phenyl-*O*-sulfinato)tin(IV) (0.29 g, 0.38 mmol) was placed in a sublimation apparatus fitted with a water-cooled finger and open to the atmosphere (fume hood) via a trap at −78° (solid CO_2/MeOH) and a calcium chloride tube. The sample was kept at 180° for 48 h. A white solid collected on the cold finger and was identified by i.r. (9) and mass spectrometry as diphenyldisulfide (0.026 g, 0.12 mmol, 31%) m.p. 58–60° (lit. (9) m.p. 61°). The nonvolatile residue was a black solid (0.23 g) which contained no carbonyl groups (i.r.) and was not identified. No sulfur dioxide was detected (19).

(*b*) *Effect of Hydrogen Chloride*

Hydrogen chloride was passed through a stirred solution of bis(dicarbonyl-π-cyclopentadienyliron)bis(phenyl-*O*-sulfinato)tin(IV) (0.37 g, 0.49 mmol) in benzene (40 ml) during 1 h. The exit gases from the reaction vessel were passed through a trap cooled to −78°. No sulfur dioxide was detected in the trap after the reaction. The solvent was removed under reduced pressure leaving a reddish tar. Treatment with petroleum ether (b.p. 30–60°) afforded a white solid identified by its i.r. (9) and mass spectra as diphenylthiosulfonate (0.10 g, 0.40 mmol, 80%). The residual red tar which was insoluble in the petroleum ether was crystallized from ethanol to yield (i.r. and mass spectral analysis) dichlorobis(dicarbonyl-π-cyclopentadienyliron)tin(IV) (0.21 g, 0.39 mmol, 79%) m.p. 166–168% (lit. (20) m.p. 166–168°).

Reaction of Sulphur Dioxide with (Dicarbonyl-π-cyclopentadienyliron)triphenyltin(IV)

(Dicarbonyl-π-cyclopentadienyliron)triphenyltin(IV) (15) (10.24 g, 19.4 mmol) was stirred under reflux (−10°) in sulfur dioxide (*ca.* 30 ml) for 10 h. The sulfur dioxide was removed in a stream of nitrogen leaving a sticky yellow residue which slowly solidified *in vacuo*. The solid was treated with petroleum ether (b.p. 60–80°) in a Soxhlet apparatus which extracted a pale yellow solid, (dicarbonyl-π-cyclopentadienyliron)triphenyltin(IV) (1.50 g, 2.85 mmol, 15% recovery). The residue, insoluble in petroleum ether, was a yellow solid which was identified by i.r. spectroscopy (see later) as $CpFe(CO)_2SnPh[OS(O)Ph]_2$. However, recrystallization from boiling ethanol gave yellow needles of $CpFe(CO)_2SnPh[OS(O)Ph]OH$ (3.30 g, 6.22 mmol, 32%), m.p. 149–151°.

Anal. Calcd. for $C_{19}H_{16}SSnFeO_5$: C, 42.97; H, 3.04; S, 6.04; Fe, 10.52; $Fe_2O_3.SnO_2$, 43.41. Found: C, 42.98; H, 2.97; S, 5.82; Fe, 10.7; residue, 42.71.

λ_{max}(KBr) 3400–2800 bw, 3112 w, 3079 vw, 3056 vw, 2018 vs, 1995 w, 1970 vs, 1928 w, 1576 vw, 1479 w, 1473 vw, 1442 w, 1436 vw, 1429 m, 1414 w, 1358 vw, 1301 vw, 1261 vw, 1194 vw, 1157 vw, 1114 vw, 1080 vw, 1065 vw, 1027 m, 1020 m, 1000 w, 997 w, 920 vs, 847 w, 771 m, 732 m, 703 sh, 697 m, 691 sh, 626 m, 590 s, 578 s, 496 m, 451 m, 389 vw, 375 vw, 359 vw, 303 vw, 265 w, cm^{-1}. $^1H_{n.m.r.}$ $\delta_{(CDCl_3)}$ 5.53 (singlet, C_5H_5), 2.5 (multiplet, C_6H_5) τ. Intensity 1:2. Molecular weight (benzene) 1050 ± 2% (calcd. 531).

An identical sample was obtained from the reaction between dichloro(dicarbonyl-π-cyclopentadienyliron)phenyltin(IV) and sodium phenylsulfinate:

Dichloro(dicarbonyl-π-cyclopentadienyliron)phenyltin(IV) (0.986 g, 2.22 mmol) and sodium phenylsulfinate (2.43 g, 14.8 mmol) were stirred under reflux in absolute ethanol (50 ml) for 24 h. The solvent was removed under reduced pressure and the residue treated with methylene chloride and filtered through celite. The filtrate was evaporated to yield a reddish oil which on crystallization from absolute ethanol yielded yellow crystals of $CpFe(CO)_2SnPh[OS(O)Ph]OH$ (0.214 g, 0.403 mmol, 18% yield).

Anal. Calcd. for $C_{19}H_{16}SSnFeO_5$: C, 42.97; H, 3.04; S, 6.04; $Fe_2O_3.SnO_2$ 43.41. Found: C, 42.93; H, 2.94; S, 6.09; residue 43.25.

Evaporation of the ethanol filtrate yielded a reddish oil which gave $CpFe(CO)_2SnPh[OS(O)Ph]_2$ as a yellow powdery solid on washing with ether (0.265 g, 0.404 mmol, 18% yield).

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Anal. Calcd. for $C_{25}H_{20}O_6S_2FeSn$: C, 45.83; H, 3.08; S, 9.79%. Found: C, 45.90; H, 3.24; S, 10.08.

λ_{max}(KBr) 3115 vw, 3053 w, 2018 vs, 1966 vs, 1575 vw, 1477 w, 1445 m, 1430 m, 1421 sh, 1303 vw, 1262 vw, 1089 m, 1067 vw, 1018 vw, 997 vw, 909 vw, 851 m, 753 m, 729 m, 694 m, 622 m, 584 s, 508 vw, 448 w, 308 vw, 263 vw cm^{-1}. $^1H_{n.m.r.}$ $\delta_{(CDCl_3)}$ 4.97 (singlet C_5H_5), 2.5 (multiplet C_6H_5) τ. Intensity 1:3.

Reactions of (Dicarbonyl-π-cyclopentadienyliron)-phenyl(phenyl-O-sulfinato)tin(IV) hydroxide

(a) Effect of Heat

$[C_5H_5Fe(CO)_2]SnPh[OS(O)Ph]OH$ (0.304 g, 0.572 mmol) was placed in a sublimation apparatus fitted with a water cooled finger and open to the atmosphere (fume hood) *via* a trap cooled to −78° and a calcium chloride tube. The sample was kept at 190° for 72 h. The apparatus was then evacuated and maintained at 190° for a further 6 h. No sulfur dioxide was detected. A white solid collected on the cold finger and was shown to be diphenyldisulfide (0.010 g, 0.046 mmol). The black tar-like residue contained no carbonyl groups (i.r.) and was not identified.

(b) Effect of Hydrogen Chloride

Hydrogen chloride was passed through a stirred solution of $[C_5H_5Fe(CO)_2]SnPh[OS(O)Ph]OH$ (0.597 g, 1.090 mmol) in benzene (40 ml) in 1 h. The exit gases from the reaction were passed through a trap cooled to −78°. No sulfur dioxide was detected. The solvent was removed under reduced pressure leaving a sticky yellow solid. Treatment with petroleum ether (b.p. 40–60°) and diethyl ether extracted a white solid identified by i.r. and mass spectroscopic analysis as diphenylthiosulfonate (0.116 g, 0.463 mmol). The yellow solid which was insoluble in the petroleum ether and diethyl ether was shown to be (i.r., mass spectroscopy) trichloro(dicarbonyl-π-cyclopentadienyliron)tin(IV) (14) (0.275 g, 0.684 mmol, 63%) m.p. 159–160° (from ethanol) (lit. (14) 150° decomp.).

Reaction of Sulfur Dioxide with Bis(dicarbonyl-π-cyclopentadienyliron)dimethyltin(IV)

Sulfur dioxide was passed through a stirred solution of bis(dicarbonyl-π-cyclopentadienyliron)dimethyltin(IV) (1.19 g 2.37 mmol) in diethylether (40 ml) in 3 h. The solvent was removed under reduced pressure leaving a dark red oily solid which proved difficult to crystallize. The oil was heated with methylene chloride (10 ml) and petroleum ether (b.p. 100–120°) (60 ml). The supernatant yellow solution was decanted and on cooling to 0° yielded pale yellow needles of dicarbonyl-π-cyclopentadienyl methyl-*S*-sulfinatoiron (8) (0.05 g, 0.20 mmol, 8%) m.p. 143–145° (lit. (8) 135°) identified by n.m.r., i.r. and mass spectrometry.

Reaction of Sulfur Dioxide with Dichlorobis(dicarbonyl-π-cyclopentadienyliron)tin(IV)

Sulfur dioxide (*ca.* 10 ml) was condensed into a 100 ml Pyrex ampoule containing dichlorobis(dicarbonyl-π-cyclopentadienyliron)tin(IV) (1.44 g 2.65 mmol). The ampoule was sealed *in vacuo* and left for 24 h at 22°. The reddish crystalline solid dissolved to give an orange red solution. The sulfur dioxide was removed under reduced pressure leaving a yellow solid, dichlorobis(dicarbonyl-π-cyclopentadienyliron)tin(IV) (1.37 g, 2.52 mmol, 95% recovery).

A similar experiment carried out at 50° for 5 days afforded only the dichlorobis(dicarbonyl-π-cyclopentadienyliron)tin(IV) (97% recovery).

Reaction of Sulfur Dioxide with Diphenyltin Dichloride

No reaction was observed between diphenyltin dichloride (5.79 g, 16.8 mmol) and sulfur dioxide (*ca.* 15 ml) after 24 h at 23°. On removal of the sulfur dioxide, a white solid was obtained, diphenyltin dichloride (5.56 g, 16.2 mmol, 96% recovery).

Reaction of Sulfur Dioxide with Triphenyltin Chloride

Sulfur dioxide (*ca.* 20 ml) was condensed into a 100 ml Pyrex ampoule containing triphenyltin chloride (2.27 g, 5.89 mmol). The ampoule was sealed *in vacuo* and left at 22° for 20 h. As the ampoule warmed up to 0° the colorless crystalline triphenyltin chloride dissolved to form a colorless solution. At 20° a white milky precipitate was formed and after 20 h at 22° the mixture was a stiff suspension. The sulfur dioxide was removed under reduced pressure and the white residue placed in a Soxhlet apparatus. Extraction with diethyl ether during 24 h afforded a colorless oily liquid which crystallized from petroleum ether (b.p. 30–60°) as a white crystalline solid identified by m.p. (41–42°) (lit (21) m.p. 40–41.5°), i.r., and mass spectroscopy as diphenyltin dichloride (0.81 g, 2.36 mmol, 80%). The white powdery residue which was insoluble in ether was $Ph_2Sn[OS(O)Ph]_2$ (1.38 g, 2.49 mmol, 84%) m.p. 218–219°.

Anal. Calcd. for $C_{24}H_{20}O_4S_2Sn$: C, 51.90; H, 3.64; S, 11.54; SnO_2, 27.14. Found: C, 52.00; H, 3.74; S, 11.46; residue, 26.89.

λ_{max}(KBr), 3082 vw, 3065 w, 1485 vw, 1475 w, 1442 w, 1429 m, 1083 w, 1079 w, 1060 sh, 1024 w, 1013 vw, 1001 w, 959 vs, 946 vs, 934 vs, 756 w, 741 sh, 737 m, 700 m, 691 m, 600 m, 590 m, 474 m, 459 m, 414 vw, 348 vw, 329 vw, 298 w cm^{-1}. $^1H_{n.m.r.}$ $\delta_{(dimethylsulfoxide)}$ 2.53 (broad singlet) τ.

An identical sample of diphenyldi[phenyl-*O*-sulfinato]tin(IV) was obtained from the reaction of diphenyltin dichloride with sodium phenylsulfinate.

Diphenyltin dichloride (2.09 g, 6.09 mmol) in 95% ethanol (20 ml) was added to a stirred solution of sodium phenylsulfinate (3.15 g, 19.2 mmol) in 95% ethanol (50 ml). A copious white precipitate was immediately formed. The mixture was stirred under reflux for 1 h before the white product was filtered, washed with water, and dried over phosphorous pentoxide *in vacuo* to yield diphenyldi[phenyl-*O*-sulfinato]tin(IV) (3.34 g, 6.01 mmol, 98% yield) m.p. 218–220°.

Found; C, 51.96; H, 3.77; S, 11.46; Residue, 26.84%. $C_{24}H_{20}O_4S_2Sn$ requires; C, 51.90; H, 3.64; S, 11.54; SnO_2, 27.14%.

Reactions of Diphenyldi[phenyl-O-sulfinato]tin(IV)

(i) Effect of Heat

$Ph_2Sn[OS(O)Ph]_2$ (0.95 g, 1.71 mmol) was placed in a water-cooled sublimation apparatus open to the atmosphere (fume hood) via a cold trap (−78°) and a calcium chloride tube. A white solid sublimed during 18 h at 225° which was identified as diphenylsulfone (0.32 g,

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1.47 mmol). The sublimation residue was a brownish solid (0.52 g). No sulfur dioxide was detected.

(ii) Effect of Hydrogen Chloride

Hydrogen chloride was passed through a stirred suspension of $Ph_2Sn[OS(O)Ph]_2$ (0.67 g, 1.21 mmol) in methylene chloride (40 ml) in 30 min. The exit gases from the reaction vessel were passed through a cold trap (−78°). After 10 min, the white suspension dissolved forming a colorless solution. The solvent was removed under reduced pressure yielding a colorless oil. On addition of water a white solid was formed. It was filtered, washed with water and diethylether to yield $Ph_2Sn[OS(O)Ph]_2$ (0.43 g, 0.77 mmol, 64% recovery), identical to the starting material (i.r.), m.p. 216–218°. No sulfur dioxide was detected.

(iii) Effect of Hydrochloric Acid

$Ph_2Sn[OS(O)Ph]_2$ (0.48 g, 0.86 mmol) and concentrated hydrochloric acid (40 ml) were heated under reflux during 20 h. A white oily solid was formed within 10 min, and became a white suspension in another 10 min. After 20 h a colorless solution was obtained containing a colorless oil ($d > 1$). Water (40 ml) was added and the mixture extracted with methylene chloride (3 × 40 ml) to yield a colorless oil (0.19 g), which was mostly diphenylthiolsulfonate containing probably some diphenyltin dichloride (i.r.). A foul odor was also detected. The aqueous solution was evaporated, yielding a white oily solid which, after 24 h *in vacuo* over phosphorus pentoxide and sodium hydroxide pellets, became an oily liquid. The liquid produced white fumes on contact with air with the formation of a white solid (0.13 g), probably $SnCl_4.nH_2O$.

Reaction of Sulfur Dioxide with Tetraphenyltin

No reaction was observed between tetraphenyltin (0.94 g, 2.20 mmol) and sulfur dioxide (*ca.* 15 ml) after 24 h at 22°. The tetraphenyltin appeared to be completely insoluble in the sulfur dioxide and was recovered after removal of the sulfur dioxide under reduced pressure (0.92 g, 2.15 mmol, 98% recovery).

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