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SULFUR DIOXIDE INSERTION INTO CARBON–TIN BONDS
I. SCOPE OF THE REACTION AND NATURE OF THE PRODUCTS

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SUMMARY

A range of tetraorganotin compounds, embodying extensive variety in the organic groups, have been shown to undergo insertion of sulfur dioxide into the carbon–tin bond. The structures of the insertion products have been arrived at from considerations of vibrational, nuclear magnetic resonance and mass spectroscopy. The products are *O*-sulfinate in type, but aggregated in the solid phase and solution so that tin generally achieves a coordination number of five, with an essentially planar R_3Sn moiety.

INTRODUCTION

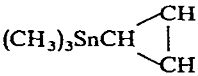
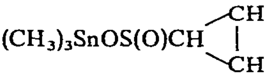
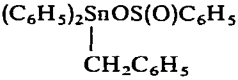
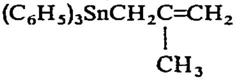
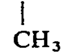
The insertion of sulfur dioxide into carbon–metal systems is a subject of considerable interest[1–10], and a number of such systems have been explored. We inclined to the view that SO_2 insertions into bonds between carbon and the more electropositive borderline metals such as tin[1–3], mercury[5–7], thallium[8] and lead[9,10] were examples, of electrophilic cleavage. At the outset we recognised the potential generality of the reaction with organometallic systems, but reserved our closest scrutiny for carbon–tin systems, since these combined convenient reactivities with ease of synthesis, stability and structural variety. Having isolated the major features of insertion into carbon–tin bonds, our expectation was that application of these notions to the other systems above would be especially meaningful. More distant extrapolation, particularly to the transition metal derived systems, we would view as unjustifiable and dangerous. Our studies with the organotin systems fall logically into several areas, and in this report we describe the scope of the reaction, and physical characterisation of the products. Subsequently we shall discuss rearrangements accompanying the insertion, followed by determinations of the stereochemistry with appropriate systems. Finally our kinetic studies, and their implications as to mechanism, will be reported.

Somewhat prior to our tactical study of these systems, a brief report[2] focussed on the adventitious insertion of SO_2 into a phenyl–tin bond, and reaction of an organotin hydride and benzenesulfinic acid has also been outlined[11], and both products were considered to be *O*-sulfinato in type. In the former case, this was subsequently proven for the solid phase by an actual X-ray determination[3], and the data now available (*vide infra*) is overwhelmingly in support of such structures, and evidence for *S*-sulfinato species in tin systems, is lacking.

RESULTS AND DISCUSSION

The organotin compounds and their insertion products (with analytical data and melting points) are located in Table 1. With few exceptions they are stable crystalline solids.

TABLE 1

Organotin compound	Insertion product	Calcd. (%)		Found (%)		M.p. (°C)
		C	H	C	H	
$(CH_3)_4Sn$	$(CH_3)SnOS(O)CH_3$	19.75	4.93	19.93	5.06	104–105
$(CH_3)_3SnC_6H_5$	$(CH_3)_3SnOS(O)C_6H_5$	35.44	4.63	35.93	4.60	80–81
$(CH_3)_3SnC_6H_4CH_3$-*p*	$(CH_3)_3SnOS(O)C_6H_4CH_3$-*p*	37.65	5.06	36.90	5.00	100–102
$(CH_3)_3SnC_6H_4F$-*p*	$(CH_3)_3SnOS(O)C_6H_4F$-*p*	33.33	4.01	33.44	4.11	71–72
$(CH_3)_3SnC_6H_4F$-*m*	$(CH_3)_3SnOS(O)C_6H_4F$-*m*	33.33	4.01	33.09	4.14	94–95
$(CH_3)_3SnCH_2C_6H_5$	$(CH_3)_3SnOS(O)CH_2C_6H_5$	37.65	5.02	37.70	5.09	109–110
$(CH_3)_3SnCH_2C_6H_4CH_3$-*p*	$(CH_3)_3SnOS(O)CH_2C_6H_4CH_3$-*p*	39.67	5.41	39.76	5.37	94–95
$(CH_3)_3SnCH_2C_6H_4F$-*p*	$(CH_3)_3SnOS(O)CH_2C_6H_4F$-*p*	35.64	4.45	35.44	4.53	84–85
$(CH_3)_3SnCH{=}CHC_6H_5$	$(CH_3)_3SnOS(O)CH{=}CHC_6H_5$	39.91	4.83	39.90	4.96	108–109[a]
		26.66	5.18	26.57	5.27	95–96
$(CH_3)_3SnC_6H_4$-*p*-C_6H_4F-*p*	$(CH_3)_3SnOS(O)C_6H_4$-*p*-C_6H_4F-*p*	45.00	4.25	45.27	4.38	150–152
$(C_6H_5)_3SnCH_2C_6H_5$	 $(C_6H_5)_2\underset{CH_2C_6H_5}{Sn}OS(O)C_6H_5$	59.44	4.34	60.00	4.49	79–80
$(CH_3)_3SnCH_2CH{=}CH_2$	$(CH_3)_3SnOS(O)CH_2CH{=}CH_2$	26.76	5.20	26.93	5.09	47–48
$(C_6H_5)_3SnCH_2CH{=}CH_2$	$(C_6H_5)_3SnOS(O)CH_2CH{=}CH_2$	55.42	4.38	55.78	4.56	177–178
$(CH_3)_3SnCH{=}C{=}CH_2$	$(CH_3)_3SnOS(O)CH_2C{\equiv}CH$	26.99	4.49	26.39	4.66	83–84
$(C_6H_5)_3SnCH_2C{\equiv}CH$	$(C_6H_5)_3SnOS(O)CH{=}C{=}CH_2$	55.62	3.97	55.65	4.01	110–111
$(C_6H_5)_3SnCH{=}C{=}CH_2$	$(C_6H_5)_3SnOS(O)CH_2C{\equiv}CH$	55.62	3.97	55.65	4.01	110–111
$(CH_3)_2Sn[CH{=}C{=}CH_2]_2$	$(CH_3)_2Sn[OS(O)CH_2C{\equiv}CH]_2$	27.06	3.38	26.63	3.58	85–86
 $(C_6H_5)_3SnCH_2\underset{CH_3}{C}{=}CH_2$	 $(C_6H_5)_3SnOS(O)CH_2\underset{CH_3}{C}{=}CH_2$	56.17	4.68	56.00	4.52	95–96

[a] Predominantly *trans* isomer after recrystallisation.

Proton magnetic resonance data

This data is assembled in Table 2 for the starting compounds and their insertion products. Where observable, spin coupling between the magnetically active ^{119}Sn and ^{117}Sn isotopes and protons has been indicated.

Molecular weight data

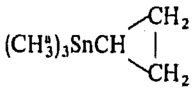
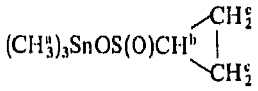
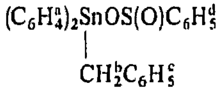
Molecular weights were recorded (Vapor pressure Osmometer) for a range of the suitably soluble products (benzene solution) and their degrees of aggregation (*n*) *i.e.* mol.wt. obs./formula wt. are recorded in Table 3.

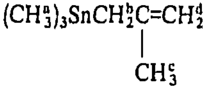
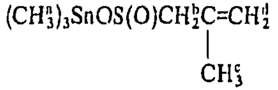
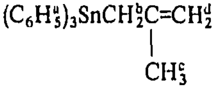
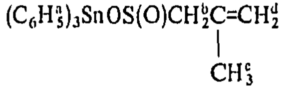
TABLE 2[a]

No.[b]	Organotin compound		Insertion compound	
1	$(CH_3^a)_4Sn$	(a) 9.94, 1, $J^1 = 54$	$(CH_3^a)_3SnOS(O)CH_3^b$	(a) 9.42, 1, $J^1 = 70$ (b) 7.70, 1, $J^1 = 0$
2	$(CH_3^a)_3SnC_6H_5^b$	(a) 10.00, 1, $J^1 = 55$ (b) 3.07, complex	$(CH_3^a)_3SnOS(O)C_6H_5^b$	(a) 9.45, 1, $J^1 = 70$ (b) 2.53, 1
3	$(CH_3^a)_3SnC_6H_4^bCH_3^c$-*p*	(a) 9.75, 1, $J^1 = 55$ (b) AA′BB′ quartet centre 2.76, $J = 8$ (c) 7.73, 1	$(CH_3^a)_3SnOS(O)C_6H_4^bCH_3$-*p*	(a) 9.45, 1, $J^1 = 70$ (b) AA′BB′ quartet centre 1.98, $J = 8$ (c) 7.60, 1
4	$(CH_3^a)_3SnC_6H_4^bF$-*p*	(a) 9.73, 1, $J^1 = 54$ (b) 2.74, complex	$(CH_3^a)_3SnOS(O)C_6H_4^bF$-*p*	(a) 9.45, 1, $J^1 = 70$ (b) 2.67, complex
5	$(CH_3^a)_3SnC_6H_4^bF$-*m*	(a) 9.72, 1, $J^1 = 54$ (b) 2.95, complex	$(CH_3^a)_3SnOS(O)C_6H_4^bF$-*m*	(a) 9.45, 1, $J^1 = 70$ (b) 2.77, complex
6	$(CH_3^a)_3SnCH_2^bC_6H_5^c$	(a) 10.00, 1, $J^1 = 53$ (b) 7.78, 1, $J^1 = 62.5$ (c) 2.92, complex	$(CH_3^a)_3SnOS(O)CH_2^bC_6H_5^c$	(a) 9.64, 1, $J^1 = 70$ (b) 6.48, 1, $J^1 = 0$ (c) 2.87, complex
7	$(CH_3^a)_3SnCH_2^bC_6H_4^cCH_3^d$-*p*	(a) 9.99, 1, $J^1 = 54$ (b) 7.76, 1, $J^1 = 62$ (c) 3.07, 1 (d) 7.76, 1	$(CH_3^a)_3SnOS(O)CH_2^bC_6H_4^cCH_3^d$-*p*	(a) 9.63, 1, $J^1 = 70$ (b) 6.47, 1, $J^1 = 0$ (c) 2.85, 1 (d) 7.65, 1
8	$(CH_3^a)_3SnCH_2^bC_6H_4^cF$-*p*	(a) 10.00, 1, $J^1 = 51.5$ (b) 7.77, 1, $J^1 = 60$ (c) 3.15, 2	$(CH_3^a)_3SnOS(O)CH_2^bC_6H_4^cF$-*p*	(a) 9.64, 1, $J^1 = 70$ (b) 6.49, 1, $J^1 = 0$ (c) 2.96, complex
9	$(CH_3^a)_3SnCH^b{=}CH^cC_6H_5^{d,c}$ (*trans*)	(a) 9.92, 1, $J^1 = 55$ (b,c) 3.30, 1, $J^1 = 75.5$ (d) 7.3, 1	$(CH_3^a)_3SnOS(O)CH^b{=}CH^cC_6H_5^d$ (*trans*)	(a) 9.40, 1, $J^1 = 70$ (b) 3.17, AB quartet $J = 16$ (c) 3.30, AB, $J = 16$ (d) 2.65, 1

(*Continued p.* 98)

TABLE 2 (*continued*)

No.^{b}	Organotin compound		Insertion compound	
10	(CH$_3^a$)$_3$SnCH^b=CH^{c}C$_6$H$_5^{d,e}$ (*cis*)	(a) 10.03, 1, $J^1=55$ (b) 2.50, 2, $J=14$ (c) 3.91, 2, $J=14$ (d) 2.85, 1	(CH$_3^a$)$_3$SnOS(O)CH^b=CH^{c}C$_6$H$_5$^{d} (*cis*)	(a) 9.40, 1, $J^1=70$ (b) 3.30, AB quartet $J=11$ (c) 3.87, AB, $J=11$
11		(a) 9.98, 1, $J^1=54$ (b) cyclopropyl protons complex		(a) 9.43, 1, $J^1=70$ (b) 8.08, complex (c) 9.30, complex
12	(CH$_3^a$)$_3$SnC$_6$H$_4^b$-*p*-C$_6$H$_4^c$F-*p*	(a) 9.64, 1, $J^1=56$ (b, c) 2.70, complex	(CH$_3^a$)$_3$SnOS(O)C$_6$H$_4^b$-*p*-C$_6$H$_4^b$F-*p*	(a) 9.35, 1, $J^1=70$ (b) 2.65, complex
13	(C$_6$H$_5^a$)$_3$SnCH$_2^b$C$_6$H$_5^c$	(a) 2.60, complex (b) 6.98, 1, $J^1=68.5$ (c) 2.88, 1	(C$_6$H$_4^a$)$_2$SnOS(O)C$_6$H$_5^d$ | CH$_2^b$C$_6$H$_5^c$	(a) 2.62, complex (b) 7.03, 1, $J^1=68.5$ (c) 2.93, 1 (d) 2.62, complex
14	(CH$_3^a$)$_3$SnCH$_2^b$CH^c=CH$_2^d$	(a) 9.98, 1, $J^1=54$ (b) 8.23, 2, $J=8.5$, $J^1=67$ (c) 4.07, complex (d) 5.25, complex	(CH$_3^a$)$_3$SnOS(O)CH$_2^b$CH^c=CH$_2^d$	(a) 9.43, 1, $J^1=70$ (b) 6.92, 2, $J=7$, $J^1=0$ (c,d) 4.45, complex
15	(C$_6$H$_5^a$)$_3$SnCH$_2^b$CH^c=CH$_2^d$	(a) 2.58, complex (b) 7.57, 2, $J=8.5$, $J^1=74$ (c) 3.88, complex (d) 5.08, complex	(C$_6$H$_5^a$)$_3$SnOS(O)CH$_2^b$CH^c=CH$_2^d$	(a) 2.58, complex (b) 7.70, 2, $J=6$, $J^1=0$ (c,d) 5.22, complex
16	(CH$_3^a$)$_3$SnCH^b=C=CH$_2^c$	(a) 9.80, 1, $J^1=56.5$ (b) 4.98, 3, $J=7.5$, $J^1=12$ (c) 5.85, 2, $J=7.5$, $J^1=40$	(CH$_3^a$)$_3$SnOS(O)CH$_2^b$C≡CH^c	(a) 9.38, 1, $J^1=69$ (b) 6.88, 2, $J=3$, $J^1=0$ (c) 7.69, 3, $J=3$, $J^1=0$

17	$(C_6H_5^a)_3SnCH^b{=}C{=}CH_2^c$	(a) 2.55, complex (b) 4.64, 3, $J=7.5$, $J^1=12$ (c) 5.72, 2, $J=7.5$, $J^1=44$	$(C_6H_5^a)_3SnOS(O)CH_2^bC{\equiv}CH^{c,d}$	(a) (b) 7.58, 2, $J=3$, $J^1=0$ (c)7.58, 3, $J=3$, $J^1=0$
18	$(C_6H_5^a)_3SnCH_2^bC{\equiv}CH^c$	(a) 2.55, complex (b) 7.88, 2, $J=3$, $J^1=63$ (c) 8.17, 3, $J=3$, $J^1=24$	$(C_6H_5^a)_3SnOS(O)CH^b{=}C{=}CH_2^{c,e}$	(a) 2.34, complex (b) 4.43, 3, $J=6.5$, $J^1=0$ (c) 5.18, 2, $J=6.5$, $J^1=0$
19	$(CH_3^a)_2Sn(CH^b{=}C{=}CH_2^c)_2$	(a) 9.68, 1, $J^1=59$ (b) 4.93, 3, $J=7.5$, $J^1=12$ (c) 5.78, 2, $J=7.5$, $J^1=44$	$(CH_3^a)_2Sn[OS(O)CH_2^bC{\equiv}CH^c]_2$	(a) 9.09, 1, $J^1=75$ (b) 6.92, 2, $J=3$, $J^1=0$ (c) 7.74, 3, $J=3$, $J^1=0$
20	 $(CH_3^a)_3SnCH_2^b\underset{\substack{\vert\\ CH_3^c}}{C}{=}CH_2^d$	(a) 9.99, 1, $J^1=54$ (b) 8.21, 1, $J^1=67$ (c) 8.32, 1, $J^1=12$ (d) 5.54, 1, $J^1=22$	 $(CH_3^a)_3SnOS(O)CH_2^b\underset{\substack{\vert\\ CH_3^c}}{C}{=}CH_2^d$	(a) 9.44, 1, $J^1=70$ (b) 6.98, 1, $J^1=0$ (c) 8.05, 1, $J^1=0$ (d) 5.05, 1, $J^1=0$ 5.15, 1, $J^1=0$
21	 $(C_6H_5^a)_3SnCH_2^b\underset{\substack{\vert\\ CH_3^c}}{C}{=}CH_2^d$	(a) 2.60 complex (b) 7.53, 1, $J^1=74$ (c) 8.33, 1, $J^1=13$ (d) 5.30, 1, $J^1=24$ 5.42, 1, $J^1=22$	 $(C_6H_5^a)_3SnOS(O)CH_2^b\underset{\substack{\vert\\ CH_3^c}}{C}{=}CH_2^d$	(a) 2.60, complex (b) 7.74, 1, $J^1=0$ (c) 9.04, 1, $J^1=0$ (d) 5.64, 1, $J^1=0$ 5.95, 1, $J^1=0$

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[a] Protons are indicated by superscripts and are tabulated in the order: τ value, multiplicity, J (proton–proton coupling, Hz), J^1 (^{119}Sn–proton coupling, Hz). All spectra were measured in $CDCl_3$ with internal TMS as standard. [b] System number. [c] See ref. 19. [d] Measured in pyridine solution. [e] Measured in DMSO/$CDCl_3$.

TABLE 3

Compound	Molality based on monomer	Dgree of aggregation (n)
p-$FC_6H_4CH_2S(O)OSn(CH_3)_3$	0.007	3.54
$C_6H_5CH_2S(O)OSn(CH_3)_3$	0.006	3.78
p-$CH_3C_6H_4CH_2S(O)OSn(CH_3)_3$	0.008	2.98
$HC{\equiv}CCH_2S(O)OSn(CH_3)_3$	0.0025	7.72
$CH_3S(O)OSn(CH_3)_3$	0.0055	4.0

Infrared data

This has not been tabulated since repetitive features emerge. Very strong bands in the 900–1000 cm^{-1} region are identified as ν_s(S–O) and ν_{as}(S–O) [Fig. 1(a)] while ν_{as}(Sn–C) in the 550 cm^{-1} region is readily assigned [Fig. 1(b)]. No band assignable with confidence to ν_s(Sn–C) was observed. In the allenic and propargylic cases, ν(C=C=C) and ν(≡C–H) were strong absorbers in the 1900 cm^{-1} and 3300 cm^{-1} regions respectively.

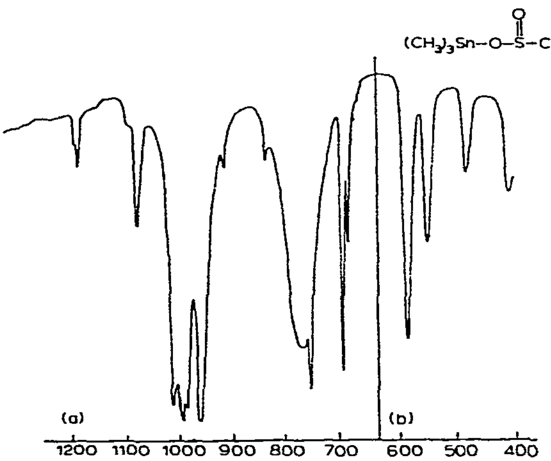


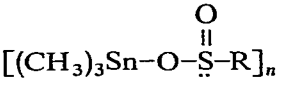
Fig. 1. (a). IR spectrum of trimethyltin benzenesulfinate showing the S–O stretching region at 950–1000 cm^{-1}. (b). Lower region of spectrum showing a ν_{as}(Sn–C) at 550 cm^{-1} and $\delta(SO_2)$ at 585 cm^{-1}. The band at 480 cm^{-1} is considered to be too low for ν_s(Sn–C) which normally arises in the 510–520 cm^{-1} region.

Structures of insertion products

The elemental analyses confirm the mono-insertion nature of the products, except in the case of system 19 (Table 2) where di-insertion is confirmed by analyses and spectra. Thus, generally, the products are to be formulated as $[(CH_3)_3SnR \cdot SO_2]_n$ and $[(C_6H_5)_3SnR \cdot SO_2]_n$ where n = degree of aggregation.

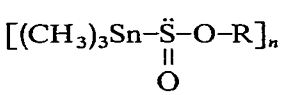
Location of the site of insertion in the trimethyltin derivatives $[(CH_3)_3SnR \cdot SO_2]_n$ is very straightforward since in every case (Table 2), the presence of satellites about the nine proton singlet at *ca.* 9.5 τ, assignable only to the three equivalent methyl groups, and the non-appearance of satellites about the resonances of R, necessitates the $[(CH_3)_3Sn(SO_2)R]_n$ structure. In the cases of the triphenyltin derivatives $[(C_6H_5)_3SnR \cdot SO_2]_n$, the R groups possessed the allyl, benzyl, allenyl and propargylic structures, so that the non-appearance of satellites (which were readily seen in the spectra of the starting compounds) about these resonances, demand the $[(C_6H_5)_3Sn(SO_2)R]_n$ formulation for R = allyl, propargyl and allenyl, but $(C_6H_5)_2Sn(SO_2C_6H_5)R$ for R = benzyl, since satellites about the CH_2 resonance were clear.

A decision on the *O* or *-S*-sulfinato nature of the products is facilitated by much recent IR data on these systems, and this has been summarised by Deacon and Felder[7]. Absorption in the range 900 cm^{-1}–1000 cm^{-1} is consistent with an *O*-sulfinato structure, while *S*-sulfinates absorb in the regions 1250–1150 cm^{-1} $[\nu_{as}(SO_2)]$ and 1100–1300 cm^{-1} $[\nu_s(SO_2)]$. In the present work, the range 1000–900 cm^{-1} was encountered in every case for solids and solution, so that *O*-sulfinato structures are favored most strongly. In addition, the small separation between the ν(S–O) modes is indicative of bidentate *O*-sulfinates, but it is of interest to note that in the compound $[C_5H_5Fe(CO)_2]_2Sn(O_2SC_6H_5)_2$, which definitely has an *O*-sulfinato structure, that there is substantial energy difference between the ν(S–O) modes (*cf.* 1100 and 860 cm^{-1}). A number of effects, peculiar to this system, may account for this. On this basis, then, we arrive at structures (I) and (II) below for the trimethyltin derivatives



$$[(CH_3)_3Sn{-}O{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\cdot\cdot}{S}}{-}R]_n$$

(I)



$$[(CH_3)_3Sn{-}\underset{\underset{\displaystyle O}{\|}}{\overset{\cdot\cdot}{S}}{-}O{-}R]_n$$

(II)

and similarly for the triphenyltin derivatives. Structure (II) seems highly unlikely as a general feature since

(*a*) the crystal structure[3] is in line with (I);

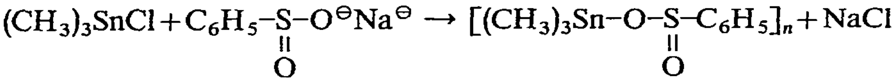
(*b*) only one (possible) example[12] of type (II) has been reported* but in this the S–O stretching frequencies were located at 1110 cm^{-1} and either 906 or 808 cm^{-1};

(*c*) a rational mechanistic approach indicts (I);

(*d*) Sn–O bonds are considered to be stronger than Sn–S bonds[13] by about 12.4 kcal/mole;

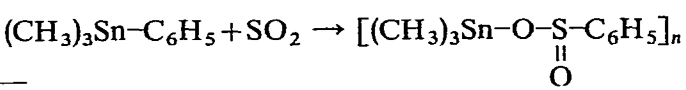
(*e*) intermolecular association seems more consistent with (I) since these are *S*-analogues of organotinacetates for which such behaviour is well known (*vide infra*).

In addition it has been possible to synthesise a number of examples (systems 2 and 3) of the type $[(CH_3)_3SnOS(O)R]_n$ by the alternate device of reacting $(CH_3)_3SnCl$ with the sodium salt of the appropriate arylsulfinic acid under conditions so mild that rearrangement would be exceedingly remote.



$$(CH_3)_3SnCl + C_6H_5{-}\underset{\underset{\displaystyle O}{\|}}{S}{-}O^{\ominus}Na^{\oplus} \rightarrow [(CH_3)_3Sn{-}O{-}\underset{\underset{\displaystyle O}{\|}}{S}{-}C_6H_5]_n + NaCl$$

In these cases, identity with the insertion products



$$(CH_3)_3Sn{-}C_6H_5 + SO_2 \rightarrow [(CH_3)_3Sn{-}O{-}\underset{\underset{\displaystyle O}{\|}}{S}{-}C_6H_5]_n$$

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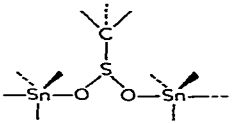
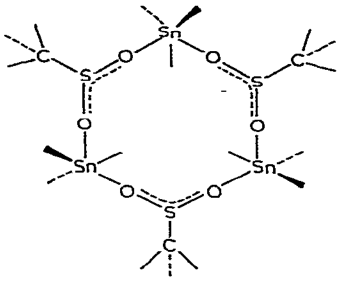
* Recent structural studies (A. Wojcicki, Private communication) indicate that in a compound analogous to the one in ref. 12, SO_2 has added to the hydrocarbon moiety rather than inserted into the M–C bond. Thus, other related compounds probably react in the same manner.

was established by near and far IR spectra, m.p., and PMR spectra. We conclude the *O*-sulfinato structure in the sense of (I) to be in accord with the data.

All trimethyltin derivatives (Table 2) show $J(^{119}\text{Sn–CH}_3)$ 70 Hz ± 1, a value encountered in almost all pentacoordinate trimethyltin (IV) systems $[(\text{CH}_3)_3\text{SnCl}\cdot\text{L}]$ for which crystal structure and far IR data implicate an essentially planar $(\text{CH}_3)_3\text{Sn}$ moiety, when L is a reasonably good donor. Very recent evidence[14] supports the view that the *J* value above is related to *s* character in the orbitals utilised by Sn to bond the methyl groups. The far IR spectra, in which only $\nu_{as}(\text{Sn–C})$ at 550 cm^{-1} is discernible, is also in agreement with the $(\text{CH}_3)_3\text{Sn}$ moiety being planar. These conclusions can be accommodated in terms of a five coordinate structure for $[(\text{CH}_3)_3\text{SnOS(O)R}]_n$ since the RSO_2– group may play a bridging role, as does RCO_2– in certain organotincarboxylates. Two basic structures may be considered, which account for the solution aggregation.





Inspection of the PMR data (Table 2) for the triphenyltin systems 13, 15, 17 and 21 and comparison then with the corresponding trimethyltin systems 6, 14, 16 and 20, indicates the operation of a pronounced shielding effect, particularly of protons α to sulfur, in the triphenyltin derivatives. As outlined in our report on organo-lead systems, we believe such an effect to have its origin in diamagnetic shielding associated with the proximity of such protons to the faces of phenyl rings in an essentially planar $(\text{C}_6\text{H}_5)_3\text{Sn}$ moiety. (Fig. 2).

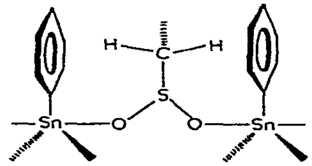


Fig. 2. Suggested representation of essentially planar $(\text{C}_6\text{H}_5)_3\text{Sn}$ group, with the proximity of indicated hydrogens to the faces of the phenyl rings probably accounting for shielding phenomenon discussed in the text.

The linear variety appears more probable for systems possessing unsaturated organic groups, (*e.g.* systems 9, 10, 14, 15 etc.) and further association via these unsaturated centers may be occurring.

In a monomeric version of (I) (tetrahedral S) in which R = benzyl, the methylene protons are in principle, inequivalent. There are several ways in which this inequivalence can be removed, a partial (even very slight) dissociation would suffice. This would, however, seem unlikely for chloroform solution and is contrary to the molecular weight data. The aggregated structures above, which involve planar (sp^2) sulfur, appear as far superior alternatives in explaining methylene proton equivalence in appropriate cases. A plane of symmetry passing through S and C and bisecting the O–S–O angle is present.

Mass spectra

The mass spectrum of trimethyltin-*O*-sulfinate (Fig. 3) shows a base peak at *m/e* 185. A very weak monomeric M^+ at *m/e* 244 (< 1%) and peaks at *m/e* 247, 277

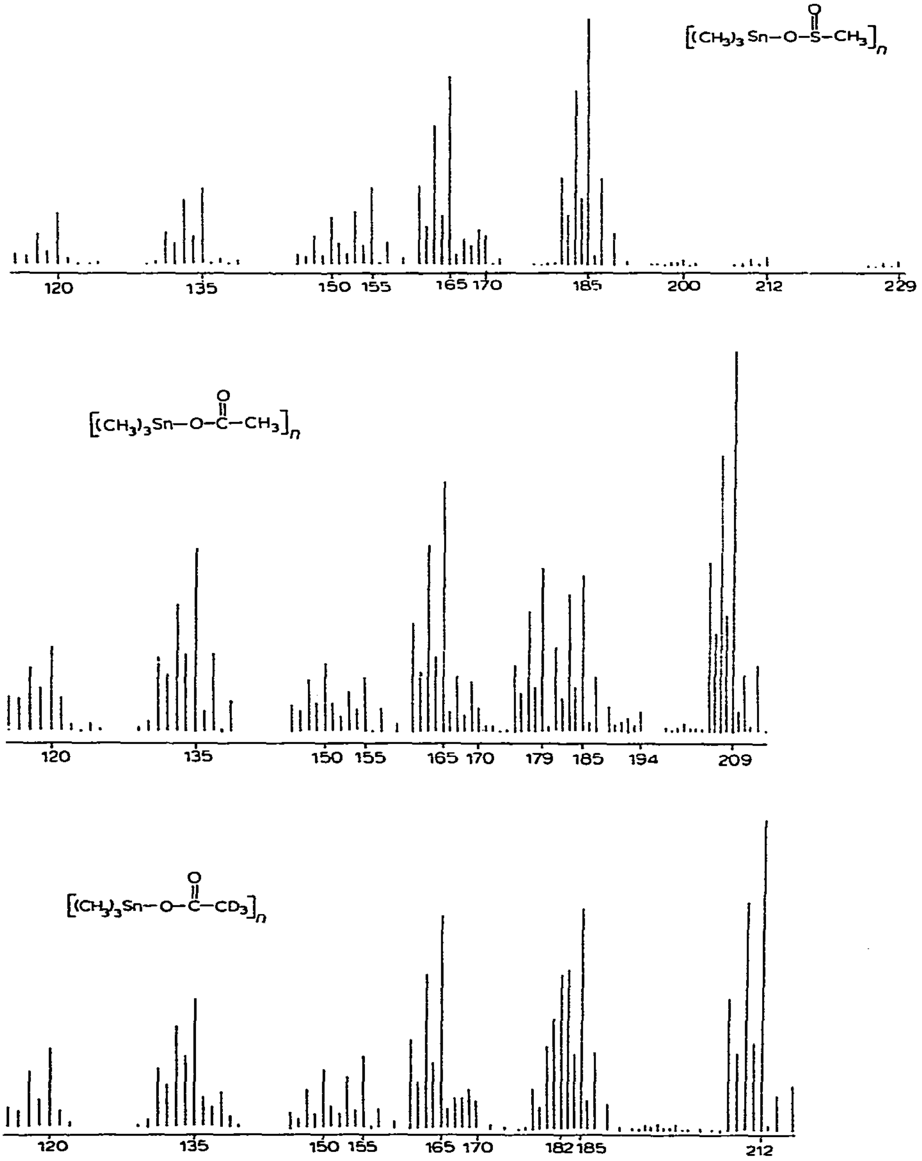
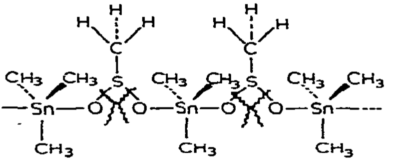


Fig. 3. (a). Mass spectrum of $[(CH_3)_3SnOS(O)CH_3]_n$ (b). Mass spectrum of $[(CH_3)_3SnOC(O)CH_3]_n$ (c). Mass spectrum of $[(CH_3)_3SnOC(O)CD_3]_n$.

and 292 (all < 1%, but exhibiting the tin isotopic distribution) are present. The latter peaks are evidence for the persistence of aggregation in the vapor phase, but some thermal reversion to monomer apparently occurs.

Since the evidence strongly suggests structural similarity between the present *O*-sulfinate and the well investigated trimethyltin acetate, which almost certainly has bridging carboxylato functions[15], it appeared instructive to compare mass spectral features. The spectrum of $[(CH_3)_3SnOC(O)CH_3]_n$ exhibits a base peak at *m/e* 209, ($[(CH_3)_3SnOC(O)CD_3]_n$ at *m/e* 212), but both show peaks at *m/e* 185 (41.6% and 71.6% respectively), as was observed for the *O*-sulfinate. The presence of the *m/e* 185 peak in the spectra of the above three compounds would appear to demand the absence of (CCH_3), (SCH_3) and (CCD_3) from the bridging groups in the ion responsible (*i.e. m/e* 185). A corollary is that the Sn–O bonds survive ahead of O–C or S–C bonds as indicated below, and further we tentatively assign this peak to $\left[(CH_3)_2Sn\begin{smallmatrix}OH\\OH_2\end{smallmatrix}\right]^+$. It thus seems that aggregated species only can account for the common occurrence of the *m/e* 185 ion.



Both tin acetates show no $M^{+\cdot}$ (*i.e. m/e* 214 and 217) corresponding to a monomer, but yield peaks at *m/e* 247, 262, 277 and 292, with the appropriate tin isotopic pattern. These results again point to vapor phase aggregation, but the identity of the ions responsible is not clear, except that $C–CH_3$ and $C–CD_3$ cannot of course, be involved.

All three compounds show similar patterns below *m/e* 185: peaks at *m/e* 120, 135, 150 and 165 which can be assigned to Sn^+, $SnCH_3^{+\cdot}$, $Sn(CH_3)_2^{+\cdot}$ and $Sn(CH_3)_3^{+\cdot}$, whilst various hydride species of these fragments are observable; ions at *m/e* 139, 154, 155, 169 and 170 are also common to these compounds. The sulfinate shows no significant peaks below *m/e* 100.

The close similarity of spectral patterns of the readily sublimable acetates and less thermally stable sulfinate would point to aggregation as a common feature of their vapor phases.

Scope of the reaction

The structural variety in the starting $(CH_3)_3SnR$ and $(C_6H_5)_3SnR'$ compounds, and their ready reaction with sulfur dioxide, indicates this insertion to be a general reaction of tetraorganotin compounds. Di-insertion occurs only when groups are present which are particularly susceptible to electrophilic assault *e.g.* allenyl. This constrasts with the organolead systems, where tetramethyllead will undergo ready di-insertion, and examples of tri-insertion are also fairly common in aryllead systems. Reasons for this contrast have been given[8].

From Table 1, it is clear that the order of reactivity is allyl ~ allenyl ~ propargyl > phenyl > benzyl > methyl, while vinyl and cyclopropyl react faster than methyl.

Suffice to say at this stage, that these orders are the expected ones for an electrophilic description of the insertion process, but details of the mechanism will be discussed in later papers focussing on stereochemistry and kinetics.

EXPERIMENTAL

All organotin compounds discussed have been previously reported, and physical properties of all compounds were in agreement with literature values.

Analyses, where performed, were satisfactory. Organotin compounds (system number, Table 2) and literature source are indicated as superscripts: 1 (commercially available), 2^{16}, 3^{17}, 6^{18}, 9^{19}, 10^{19}, 11^{20}, 13^{21}, 14^{22}, 15^{23}, 16^{24}, 17^{24}, 18^{24}, 19^{25}, 20^{22}, 21^{26}.

We are grateful to A Smith for donations of compounds (system number, Table 2) 4, 5, 8 and 12.

The systems 14–21 underwent rapid insertion with gaseous sulphur dioxides. When prolonged reaction times were necessary, the compounds were stored in liquid SO_2 solution at $-20°$ for the requisite periods. Insertion compounds were generally recrystallized from absolute ethanol, or chloroform/pentane mixtures.

Preparation of insertion compounds 2 and 3 by the alternative route were achieved by mixing an acetone or aqueous solution of $(CH_3)_3SnCl$ to an aqueous solution of the sodium arylsulfinate in the molar ratio of 1/1.5; the products slowly crystallized from solution, and were recrystallized from absolute ethanol.

Mass spectra were run on an Atlas CH4 Mass Spectrometer with a TO4 ion source. $(CH_3)_3SnOC(O)CH_3$ and $(CH_3)_3SnOC(O)CD_3$ were prepared by reacting CH_3COOH and CD_3COOD with $(CH_3)_3SnCH{=}C{=}CH_2$, and purified by repeated sublimation under vacuum. Conditions under which samples were run: $(CH_3)_3SnOC(O)CH_3$ and $(CH_3)_3SnOC(O)CD_3$, ion source temperature 168°, trap current 20 μA; $(CH_3)_3SnOS(O)CH_3$, ion source temp. 108°, trap current 20 μA.

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