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SULFUR DIOXIDE INSERTION INTO ARYL CARBON–TIN BONDS: KINETICS AND MECHANISM

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SUMMARY

A kinetic study of the insertion of sulfur dioxide into the aryl carbon–tin bond of a series of 3- and 4-substituted phenyltrimethyl stannanes in anhydrous methanol has been conducted. The reaction is cleanly second order in this solvent (first order in each of stannane and sulfur dioxide) and the second order rate constants show an excellent correlation with σ^+, indicating an electrophilic insertion reaction. The low ρ value and a positive salt effect on the rate of insertion suggests a four centred S_Ei transition state with some polar character. Sulfur dioxide is located in the electrophile reactivity series, $CH_3COOH < SO_2 < HCl << I_2 << Br_2$ for this particular system. Whilst the insertion reaction in methanol is a second order process, the kinetic situation in benzene is more complex, with k_2(obs) increasing with $[SO_2]$, and may be attributable to changes in the dielectric properties of the medium. The stereochemistry of insertion into a vinyl–tin bond is shown to involve essentially complete retention of configuration at carbon, as demanded by an S_Ei process.

INTRODUCTION

We have previously suggested[1] that sulfur dioxide insertion into carbon–tin bonds is an electrophilic process, a view in harmony with the relative reactivity of different organic groups attached to tin. The previously observed[2] relative reactivity sequences (allyl, allenyl, propargyl) $\gg$ phenyl $>$ benzyl $>$ methyl, and (vinyl, cyclopropyl) $>$ methyl are consistent with previous data for genuine electrophilic substitutions in these systems. The insertion reactions of allyl-, allenyl- and propargyl-tin systems have been shown[3] to involve essentially exclusive rearrangement of the organic moieties, and to react at greatly enhanced rates compared with their saturated counterparts. In previous studies, we have outlined the scope of the reaction and nature of the products[2], and discussed the rearrangements accompanying insertion[3]. In this paper we discuss some aspects of the reaction mechanism, based on a detailed kinetic study of the insertion reaction of phenyltrimethyltin in methanol and benzene,

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and a kinetic study of the substituent effect of 3- and 4-substituted phenyltrimethyltin compounds in methanol. The stereochemistry of the insertion reaction of β-styryltrimethyltin is also described. A preliminary account of this work had been previously given[4].

EXPERIMENTAL

(i) Synthesis of 3- and 4-substituted phenyltrimethyltin compounds.

The aryltrimethyltin compounds were synthesized according to literature methods by the addition of trimethyltin chloride to the appropriate arylmagnesium bromide in ether. Generally a slight excess of trimethyltin chloride was used, and the excess removed during workup as the insoluble trimethyltin fluoride. The following compounds (with the relevant literature references) were prepared: phenyltrimethyltin[5], 4-tolyltrimethyltin[5], 3-tolyltrimethyltin[6], 4-anisyltrimethyltin[6], 3-anisyltrimethyltin[7], 4-chlorophenyltrimethyltin[5], 3-chlorophenyltrimethyltin[5], 4-trifluoromethylphenyltrimethyltin[7], 3-trifluoromethylphenyltrimethyltin[7].

4-*N*,*N'*-Dimethylaminophenyltrimethyltin[7] was prepared from the organolithium derivative[8] of 4-bromo-*N*,*N'*-dimethylaniline and trimethyltin chloride.

[4-Trimethylstannyl]trimethylanilinium iodide[7] was obtained from 4-*N*,*N'*-dimethylaminophenyltrimethyltin and methyl iodide in absolute ethanol.

The physical constants (m.p. and b.p.) were in good agreement with the quoted literature values. The purity of all compounds was $>99\%$ as adjudged by vapour phase chromatography and proton magnetic resonance spectra of the liquid organotin compounds. These compounds were distilled immediately before use in the kinetic experiments. The solid (4-trimethylstannyl)trimethylanilinium iodide was recrystallized to constant melting point in agreement with the literature value[7].

(ii) β-Styryltrimethyltin[9] was obtained from β-bromostyrene and trimethyltin chloride via the Grignard method in tetrahydrofuran. Both *cis* and *trans* isomers were obtained (1/3.9 respectively).

(iii) The trimethyltin arylsulfinates showed very similar physical characteristics to the trimethyltin alkylsulfinates and trimethyltin arylsulfinates previously described[2], being aggregated *O*-sulfinates, bridging through the O–S–O group and having essentially planar $(CH_3)_3Sn$ groups. Compounds obtained from reaction in liquid sulfur dioxide and from sulfur dioxide–anhydrous methanol and sulfur dioxide–anhydrous benzene were identical in physical properties. Most insertion compounds were well defined solids, although some were oils which defied crystallization. Analytical data were satisfactory in all cases.

The isomeric *trans* and *cis* trimethyltin-β-styrylsulfinates have been previously described[2] though stereochemical implications were not discussed.

(iv) Anhydrous A.R. lithium chloride was dried overnight in a furnace at ca. 400° immediately before use. A.R. lithium perchlorate dihydrate was dehydrated by heating in a furnace at ca. 200° overnight and used immediately.

(v) Anhydrous methanol was prepared by drying A.R. grade methanol with magnesium methoxide generated *in situ*, and distilling from 2,4,6-trimethylbenzoic acid. The distillate was then fractionated.

Anhydrous benzene was obtained by drying A.R. grade benzene over lithium aluminium hydride, followed by distillation.

Sulfur dioxide, B.D.H. reagent grade, was twice washed with concentrated sulfuric acid, and passed up columns of fresh calcium chloride and 3A molecular sieves. The dried gas was then passed into a flask containing anhydrous methanol or anhydrous benzene. The sulfur dioxide concentrations were determined by adding aliquots of the SO_2/CH_3OH or SO_2/C_6H_6 to excess standard aqueous I_2/KI solution followed by back titration with standard sodium thiosulfate. Solutions of organotin and sulfur dioxide were pre-equilibrated in a constant temperature bath at the required temperature before use in the kinetic experiments. Kinetic experiments in benzene were conducted in sealed PMR tubes, whereas the kinetics in methanol were conducted in PMR tubes capped with plastic gas tight seals. Control experiments using up to 100 times the concentration range of SO_2 used in the kinetic experiments indicated no loss of SO_2 from methanol at the highest temperature used in the kinetics. As much higher temperatures were used in the benzene kinetics and solubility of SO_2 in benzene is not as great as in methanol, sealed tubes were used for all runs.

PMR tubes containing the reaction mixtures were kept in a constant temperature bath ($\pm 0.1°$) and periodically removed for measurement, each measurement taking an average of 2 minutes; measurements were generally made every 20–30 minutes, with most reaction half-lives being ca. 2–3 hours or longer. Errors produced in this fashion were considered negligible. Rate constants are considered to be accurate to 6–8% under varying conditions.

Rate constants were calculated from the following equation $(a-b)k_2t = \ln[b(a-x)/a(b-x)]$ where a and b represent the initial concentrations, and x is the concentration of product formed. In this study, the peak heights of the resonances due to the trimethyltin groups of the starting compound and product in the PMR spectrum were used as directly proportional to the molar concentration of reagents, as established by measurement of a series of known standards of starting compound and insertion product. Each kinetic measurement was the average of at least four measurements of peak heights.

A Varian A-60 spectrometer was used for the kinetic measurements.

RESULTS AND DISCUSSION

(a) *Kinetics in methanol*

The compound phenyltrimethyltin has been studied in most detail, and was observed to be cleanly first order in both sulfur dioxide and tin compound. No significant deviations from second order kinetics were observed up to ca. 70% reaction in any run. The reaction is easily monitored by observing the change in the PMR spectrum of the reaction mixture with time. The rate is followed by the disappearance of the sharp nine proton signal at ca. τ 10.0 of the trimethyltin moiety and the appearance of the signal due to the $(CH_3)_3SnSO_2$-moiety ca. 18 Hz downfield (at 60 MHz). This technique allows observations of the reaction mixture at all times during a kinetic run, and no evidence of any undesirable side reactions (such as insertion into the methyl–tin bond) was observed. The second-order rate constants, for phenyltrimethyltin in anhydrous methanol at various temperatures are given in Table 1.

An Arrhenius plot yields the activation energy, Ea, of 8.000 kcal·mole^{-1}. The calculated enthalpy of activation, $\Delta H^{\neq}$ is 7.40 kcal·mole^{-1}, whilst the entropy of

TABLE 1

SECOND-ORDER RATE CONSTANTS FOR PHENYLTRIMETHYLTIN IN ANHYDROUS METHANOL

Temp. (±0.1°)	[*Sn*][a] (*M*)	[*SO*$_2$] (*M*)	k_2[b,c]
25.0	0.1016	0.1261	0.0141
25.0	0.0677	0.1651	0.0142
30.0	0.1016	0.1261	0.0194
30.0	0.0677	0.1681	0.0197
30.0	0.1354	0.0841	0.0199
30.0	0.1016	0.0631	0.0199
35.0	0.0677	0.0841	0.0244
35.0	0.1016	0.1261	0.0241
45.0	0.1016	0.1261	0.0367

[a] Concentration of phenyltrimethyltin in moles·l^{-1}.
[b] l·mole^{-1}·sec^{-1}.
[c] Mean of two determinations.

TABLE 2

RATE CONSTANTS OF INSERTION OF SUBSTITUTED PHENYLTRIMETHYLTIN COMPOUNDS

R	k_{2av} (*i*·*mole*$^{-1}$·*min*$^{-1}$)	k_{rel}
H	0.1181	1
m-CH_3	0.1766	1.492
p-CH_3	0.5019	4.246
m-CF_3	0.0117	0.098
p-CF_3	0.0104	0.088
m-Cl	0.0264	0.223
p-Cl	0.0466	0.394
m-OCH_3	0.1443	1.221
p-OCH_3	4.66	39.42
p-$\overset{+}{N}(CH_3)_3$	0.0056	0.047

activation, $\Delta S^{\neq}$ is -43 e.u., both at 30.0°. ($\Delta F^{\neq} = 21$ kcal·mole^{-1})*. The large negative value of $\Delta S^{\neq}$ indicates a substantial restriction in translational and vibrational modes on passing to the transition state. The low activation energy and large negative entropy of activation are anticipated for insertion reactions generally. Trimethyltin benzenesulfinate has been found to be slightly dissociated in methanol (i=0.912 at 0.17 *M* concentrations)**, but this post-kinetic dissociation appears to be too small to produce kinetically significant medium changes, particularly in the early stages.

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* These values may be compared with those for SO_2 insertion into π-$C_5H_5Fe(CO)_2C_6H_5$, where $\Delta H^{\neq} =$ 7.3 kcal·mol^{-1} and $\Delta S^{\neq} = -52$ e.u. for liquid SO_2 solvent.

** i=Apparent molecular weight/Actual molecular weight.

To study the effect of substituents on the rate of insertion, the following system has been investigated:

where R = H, 3-CH_3, 4-CH_3, 3-Cl, 4-Cl, 3-CF_3, 4-CF_3, 3-OCH_3, 4-OCH_3, 4-$\overset{+}{N}(CH_3)_3$

The rates of insertion of the substituted phenyltrimethyltin compounds were measured in anhydrous methanol at 30.0±0.1°, individual rate constants being calculated for each substituent. In each case, the reaction enhibited clean second-order kinetics up to ca. 75% reaction, and no evidence of any side reactions was observed in any case. The results are given in Table 2.

It was noted that 4-*N*,*N*′-dimethylaminophenyltrimethyltin reacted too rapidly to obtain a second-order rate constant under these conditions.

Firstly, it can be seen that electron-donating substituents increase the rate whereas electron-withdrawing substituents retard the rate. Thus, there has been an increase in the positive character of the carbon attached to tin on proceeding to the transition state.

At this point, it is pertinent to discuss the work of Nasielski *et al.*[10–13] who have studied a number of authentic electrophilic cleavages of 3- and 4-substituted phenyltrimethylstannane compounds in anhydrous methanol. In each case, a linear relationship between the rate constants and Brown's σ^+ values[14] was observed. As σ^+ values are derived for aromatic electrophilic substitution reactions in which a positive charge capable of direct resonance interaction with the aromatic ring is generated, it has been reasoned that these reactions are examples of classical electrophilic substitutions. A notable feature of the reactions is the low sensitivity to substituent effects, ρ being -2.17, -2.24, -2.58 and -2.54 for HCl, CH_3COOH, Br_2 and I_2 cleavages, respectively.

By comparison with the electrophilic cleavages discussed above, it might be expected sulfur-dioxide insertion will display similar features. In fact, a plot of log k_{rel} against σ^+ shows a linear correlation ($r = 0.992$), with $\rho = -1.87$, determined by the method of least squares. The correlation with σ is much poorer ($r = 0.929$).

The data* are plotted in Fig. 1.

We have also observed a primary positive salt effect on the rate of insertion of phenyltrimethyltin in anhydrous methanol. The effect of the addition of anhydrous lithium perchlorate on the rate of insertion at 30.0° is given in Table 3.

Inspection of Table 3 reveals a significant salt effect, the rate increasing some 64% upon the addition of 0.541 *M* lithium perchlorate. Whilst the concentration is far too high for the application of the Debye-Hückel law, the data appears to fit the empi-

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* The σ^+ value for the 4-$N^+(CH_3)_3$ substituent has been quoted to be 0.408, a value[14] which appears anomalously small[15]. This is apparent when comparing values[16] of $\sigma^n = 0.80$ and $\sigma^1 = 0.90$; as this substituent should show minimal resonance ability, *e.g.* $\sigma_R = -0.02$, a σ^+ value about 0.80–0.90 should be a good indicator of its essentially inductive ability. Thus, we have used the σ^n value of 0.80 in Fig. 1. However, even using $\sigma^+ = 0.408$, an acceptable correlation ($r = 0.974$) is still obtained. Problems can arise for charged substituents in a solvent like methanol.

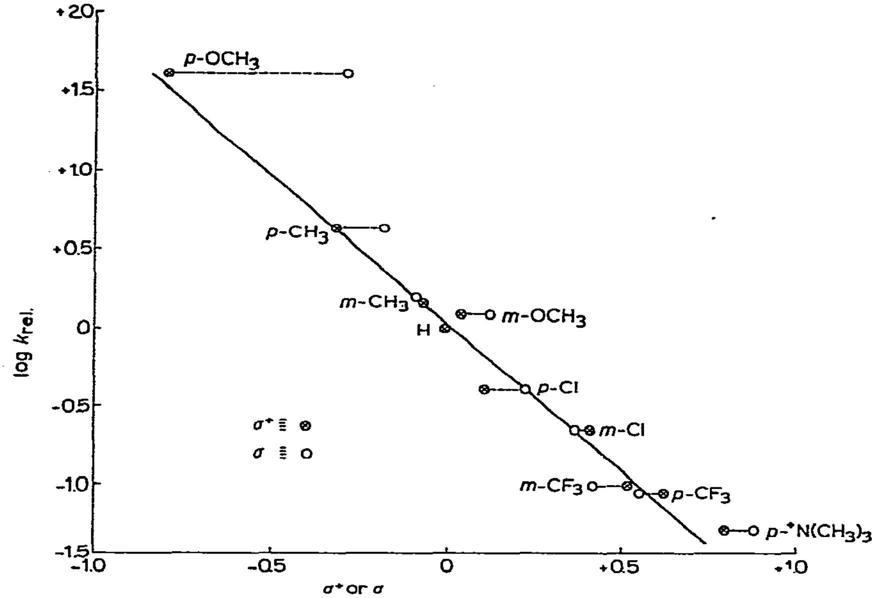


Fig. 1. A plot of log k_{rel} against σ and σ^+ for sulfur dioxide insertion into the aryl-carbon–tin bond of series of *m*- and *p*-substituted phenyltrimethylstannanes.

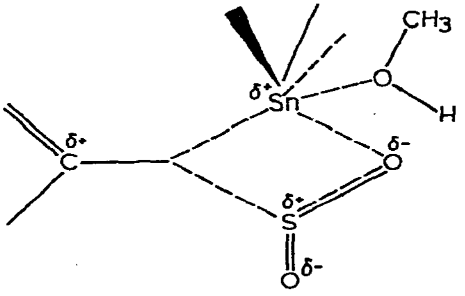
TABLE 3

EFFECT OF ANHYDROUS LITHIUM PERCHLORATE ADDITION ON THE RATE OF INSERTION AT 30°

[*Sn*] (*M*)	[SO_2] (*M*)	$LiClO_4$ (*M*)	$k_2 \times 10^3$ ($l \cdot mole^{-1} \cdot min^{-1}$)
0.0995	0.0722	0	1.970
0.0995	0.1060	0.1417	2.232
0.0995	0.0722	0.3513	2.560
0.0771	0.0541	0.4058	2.985
0.0995	0.0722	0.5410	3.232

rical expression, a modification of the Debye-Hückel law[17], which has been used for concentrations of added salt about 0.1 *M*; log $k = \log k_0 + \alpha\,\mu$, where k_0 is the rate constant without added salt, α_0 is a constant, and μ is the ionic strength. Thus a plot of log k_2 against μ is linear with $\alpha = 0.395$.

We have also measured the rate acceleration caused by added lithium chloride to see whether changing the anion from perchlorate to the potentially stronger donor chloride anion has any effect. However, the second-order rate constant under the conditions used, [Sn] = 0.1031 *M*, [SO_2] = 0.1147 *M*, [LiCl] = 0.6396 *M*, shows only a 22% rate increase. This is compared to a rate increase of 79% for the corresponding lithium perchlorate concentration. Observation of the PMR spectra during the kinetic runs indicating the absence of any complicating side reactions, all runs showing clean second order kinetics. Although the reaction is best viewed as a four centre S_Ei process, the positive salt effect indicates the transition state to have some polar character. The low ρ value (-1.87) suggests the classical σ-complex of electrophilic aromatic substitution reactions involving an sp^3 hybridized carbon may be an inadequate description of the transition state and that the π-electron system is experiencing a very modest perturbation. The following representation appears to have merit in that such a transition state, involving an essentially sp^2 hybridized aromatic carbon, would account for the small sensitivity to substituent effects and that the polar character of the transition state arises from SO_2 attack on the Sn–C bond. Stabilization of positive charge on tin and possibly sulfur by coordination of methanol may partly offset unfavourable charge effects. The possibility of bridging transition states involving some polar character has been foreseen by Jensen and Rickborn[18].



(*b*) *Kinetics in benzene*

A study of the insertion reaction of phenyltrimethyltin in a non-polar solvent, anhydrous benzene, was conducted to expose any differences due to solvent polarity or coordination ability. Whilst first order dependence on organotin substrate and sulfur dioxide were observed for phenyl- and substituted phenyltrimethyltin compounds in methanol, the situation appears more complicated in benzene.

As for the methanol system, the reaction was followed by the rate of disappearance of the $(CH_3)_3Sn$ resonance and rate of simultaneous appearance of the

TABLE 4

SECOND-ORDER RATE CONSTANTS DEPENDENCE ON ORGANOTIN COMPOUND

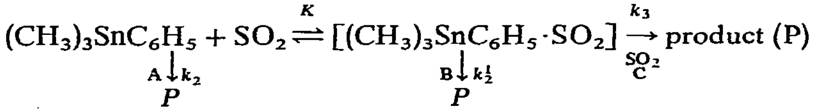
Temp. (±0.1°)	[*Sn*] (*M*)	[SO_2] (*M*)	k_2 (*obs*) × 10^3 ($l \cdot mole^{-1} \cdot min^{-1}$)
60.0	0.191	0.281	1.55
60.0	0.323	0.281	1.53
60.0	0.596	0.281	1.53
70.0	0.243	0.294	2.06
70.0	0.362	0.294	2.00
70.0	0.461	0.294	1.92

resonance due to $(CH_3)_3SnSO_2$ in the PMR spectrum. No evidence for any side reaction during any kinetic run in benzene was observed.

The most striking difference is that the rate in benzene was much lower than in methanol. For example at 35° for comparable concentrations of reactants, the methanol reaction is faster by a factor of ca. 10^3. Initially it was found that in benzene with similar reactant concentrations, the reaction appeared to follow reproducible second-order kinetics. However, when reactant concentrations were varied the observed second-order rate constant changed significantly. By maintaining the concentration of sulfur dioxide constant and varying the organotin concentration, the apparent second-order rate constant remained essentially the same, indicating a first-order dependence on organotin compound. The data are given in Table 4. Also under conditions of a very large excess of sulfur dioxide the reaction followed pseudo first-order kinetics, confirming the first-order dependence on organotin compound.

With the concentration of organotin constant, and the sulfur dioxide concentration varied, the apparent second-order rate constants were linearly dependent on SO_2 concentration. Again the reactions exhibited second-order kinetics for at least one half life. The data are tabulated in Table 5.

There appear to be two reasonable explanations for this increase in k_2(obs) with increasing SO_2 concentration. Firstly, concurrent second-order and third-order reaction pathways may be involved and a model incorporating such behaviour is shown below.



$$(CH_3)_3SnC_6H_5 + SO_2 \overset{K}{\rightleftharpoons} [(CH_3)_3SnC_6H_5 \cdot SO_2] \xrightarrow[SO_2 \atop C]{k_3} \text{product (P)}$$

$$\text{A}\downarrow k_2 \;\; P \qquad \text{B}\downarrow k_2^1 \;\; P$$

$$\therefore \frac{dP}{dt} = k_2[Sn][SO_2] + k_2^1 K[Sn][SO_2] + k_3 K[Sn][SO_2]^2$$

$$= [Sn][SO_2](k_2 + k'_2 K + k_3 K[SO_2])$$

and

$$\frac{dP}{dt}(\text{obs}) = k_2(\text{obs})[Sn][SO_2]$$

$$\therefore \; k_2\,(\text{obs}) = k_2 + k'_2 K + k_3 K[SO_2] \text{ if } [SO_2] \gg [Sn]$$

Thus, a plot of k_2(obs) against SO_2 concentration should be linear, with slope k_3K and intercept $(k_2+k'_2K)$*. Hence, it is possible to derive the following data from Table 5.

(i) at 35°: $k_3K = 4.44 \times 10^{-4}\, l^2 \cdot \text{mole}^{-2} \cdot \text{min}^{-1}$
$k_2 + k'_2K = 1.80 \times 10^{-4}\, l \cdot \text{mole}^{-1} \cdot \text{min}^{-1}$

(ii) at 60°: $k_3K = 1.495 \times 10^{-3}\, l^2 \cdot \text{mole}^{-2} \cdot \text{min}^{-1}$
$k_2 + k'_2K = 8.50 \times 10^{-4}\, l \cdot \text{mole}^{-1} \cdot \text{min}^{-1}$

(iii) at 70°: $k_3K = 2.50 \times 10^{-3}\, l^2 \cdot \text{mole}^{-2} \cdot \text{min}^{-1}$
$k_2 + k'_2K = 1.20 \times 10^{-3}\, l \cdot \text{mole}^{-1} \cdot \text{min}^{-1}$

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* The slope, k_3K, will have units of $(l \cdot \text{mole}^{-1} \cdot \text{min}^{-1})/l^{-1} \cdot \text{mole} = l^2 \cdot \text{mole}^{-2} \cdot \text{min}^{-1}$ and the intercept (on the k_2(obs) axis) (of $k_2 + k'_2K$) will be in $l \cdot \text{mole}^{-1} \cdot \text{min}^{-1}$.

The nature of the intermediate complex is not known, but could involve a π-complex of SO_2 with the aromatic ring; such a π-complex between benzene and SO_2 is well known[19], $K_c=0.0436$ at 35°.

TABLE 5

SECOND-ORDER RATE CONSTANTS DEPENDENCE ON SO_2 CONCENTRATION

Temp. (±0.1°)	[*Sn*] (*M*)	[SO_2] (*M*)	k_2 (*obs*) × 10^3 ($l\cdot mole^{-1}\cdot min^{-1}$)
35.0	0.231	0.310	0.333
35.0	0.230	0.765	0.493
35.0	0.230	1.385	0.820
35.0	0.231	1.610	0.900
35.0	0.230	2.550	1.290
60.0	0.230	0.450	1.500
60.0	0.231	0.670	1.870
60.0	0.231	1.230	2.671
60.0	0.231	2.015	3.859
70.0	0.231	0.725	3.178
70.0	0.232	1.515	4.893
70.0	0.231	1.970	5.786
70.0	0.230	2.480	7.626

Since the $(CH_3)_3Sn$ group does not exert a strong substituent effect, a value of K of ~0.04 l·mole^{-1} seems very reasonable to adopt and utilising the 35° data,

$$k_3 = \frac{4.44\times10^{-4}\ (\text{l}^2\text{mole}^{-2}\text{min}^{-1})}{4\times10^{-2}\ (\text{l mole}^{-1})} \approx 1.1\times10^{-2}\ \text{l}\cdot\text{mole}^{-1}\cdot\text{min}^{-1}$$

$\therefore\ k_3 > k_2 + k_2'K$ (each of these terms is in units of l·mole^{-1}·min^{-1})*.

$\therefore\ k_3 > k_2$

(This inequality holds even for $K \leqslant 2.4$).

This situation seems very unlikely since donor action by the π-system must reduce its reactivity towards electrophiles. Hence analysis of this model leads to predictions at variance with chemical reasonableness, and the operation of a third-order pathway in benzene is probably of marginal importance.

Since the reaction is quite sensitive to solvent polarity and dielectric, and does exhibit a salt effect in methanol (where complete dissociation is unlikely) it seems plausible that substantial changes in SO_2 concentration (eg. at 35° from 0.31 *M* to 2.55 *M*, Table 5) will influence the gross dielectric constant of the benzene-SO_2 medium, and hence the reaction rate. ($\varepsilon(C_6H_6)$ 2.27 at 25° and $\varepsilon(SO_2)$ 14 at 20°).

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* Note that the specific rate constant k_3, for reaction between SO_2 and $Sn\cdot SO_2$ complex is a second order constant, but that involvement of K (in l·mole^{-1}) gives k_3K units of l^2·mole^{-2}·min^{-1}.

Since no measurements in the benzene–SO_2 medium were available, a gross dielectric constant was calculated on the basis of the mole fractions of the components and their respective ε values. While this approach is only approximate (since it neglects any changes in polarity etc. of SO_2 when interacting with benzene) it does allow a crude evaluation of the rate change with medium. A plot of log k_2(obs) against $1/D$ (D=computed gross dielectric constant of medium) was satisfactorily linear and does suggest that medium change related to dielectric, may be responsible for the escalation of k_2(obs) with increasing SO_2 concentration.

A detailed study of substituent effects on the rate was not conducted for solvent benzene. However, 4-anisyltrimethyltin was cursorily investigated. For the conditions, $[Sn]=0.300\,M$, $[SO_2]=0.591\,M$, $k_2(\text{obs})=0.067$ l·mole^{-1}·min^{-1} at 35°. Using the same reactant concentration and conditions, $k_2(\text{obs})=5.26\times10^{-3}$ l·mole^{-1}·min^{-1} for phenyltrimethyltin. Thus, the apparent rate constant for the 4-OCH_3 substituent is 128 times as great as that for the parent compound.

(*c*) *Stereochemistry*

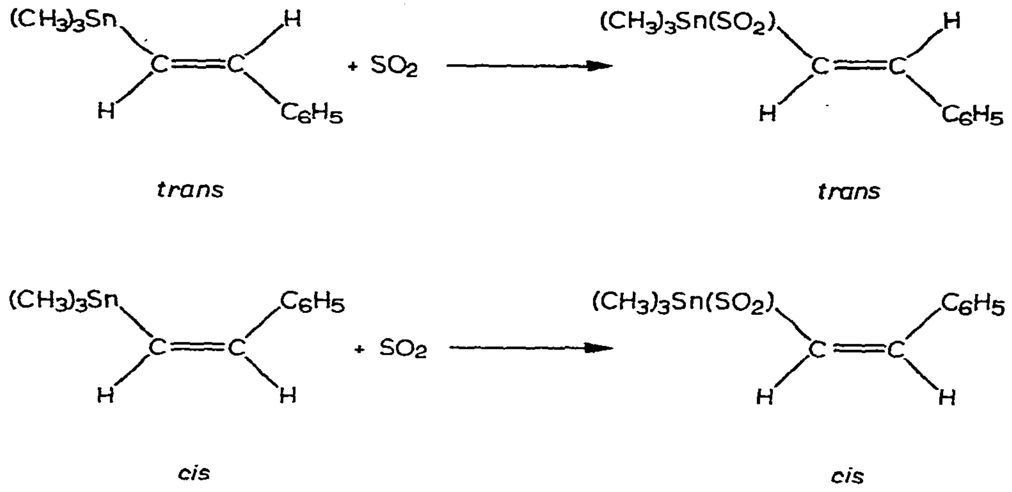
The only system found readily amenable to stereochemical study was the insertion reaction of β-styryltrimethyltin:

$$(CH_3)_3Sn{-}CH{=}CH{-}C_6H_5 + SO_2 \rightarrow (CH_3)_3SnOS(O)CH{=}CH{-}C_6H_5$$

β-styryltrimethyltin has been previously synthesized, both *cis* and *trans* isomers were separated, and identified by IR, UV, and PMR spectroscopy[20]. The PMR spectrum ($CDCl_3$) of a 3/1 mixture of *trans/cis* isomers exhibits a sharp singlet at τ 3.30 with $J(^{119}Sn{-}CH)$ 75.5 Hz identified[23] as the magnetically equivalent vinyl protons of the *trans* isomer, (an example of what would normally be two strongly coupled inequivalent protons). The vinyl protons of the *cis* isomer appear as the more general four line AB pattern, resonating at τ 2.50 and 3.91, J_{AB} 14 Hz.

After reacting in liquid SO_2 for 3–4 hours at ca. −25°, the mixture undergoes complete monoinsertion into the tin–vinyl bond as evidenced by the nine proton singlet at τ 9.40, $J(^{119}Sn{-}CH)$ 70 Hz due to the $(CH_3)_3SnOS(O)$ moiety. The $^{119}Sn{-}^1H$ coupling of 70 Hz strongly indicates usual five coordinate *O*-sulfinate aggregated species, with an essentially planar $(CH_3)_3Sn$ group.

Investigation of the vinyl region of the mixture of insertion products reveals two AB patterns which integrate in the ratio 3/1. The more predominant isomer has protons resonating at τ 3.17 and 3.30, J 16 Hz. The other isomer has protons at τ 3.30 and 3.87, J 11 Hz. These values of J can be safely assigned to the *trans* and *cis* insertion products respectively, as *trans* vinyl proton–proton coupling is always larger than *cis* vinyl proton–proton coupling without exception[21]. Similarly, vinyl tin compounds obey this rule also[20]. Reaction of a fraction very rich in *trans* isomer (~95%) in a similar way yielded a product showing vinyl absorption as described above with J 16 Hz, and barely detectable (at higher gain) resonances for the *cis* insertion compound. Examination of a less pure fraction, but with about 40% *cis*, showed the *cis* insertion product to be quite stable to the conditions employed. Hence, within the accuracy of integration (±5%) insertion of SO_2 into the tin–carbon bond of β-styryltrimethyltin is stereospecific with retention of configuration at vinylic carbon, a result expected for an S_Ei process.



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