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SULFUR DIOXIDE INSERTION INTO BENZYLTRIMETHYLSTANNANES: KINETICS AND MECHANISM

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SUMMARY

A series of *meta*- and *para*-substituted benzyltrimethylstannanes have been prepared and their reactions with sulfur dioxide in methanol solvent at 30° have been studied kinetically by an ^{1}H NMR method. Insertion occurs exclusively into the benzyl–tin bond, irrespective of substituent (*m*- and *p*-CH_3, *m*- and *p*-CF_3, *m*- and *p*-Cl, *m*- and *p*-OCH_3), and the reaction exhibits good second-order kinetics for at least 70% reaction. The striking feature of the reaction is the relative insensitivity of rate to substituent, the greatest effect being a rate enhancement of 2.2 by *p*-CF_3. While this implies some development of carbanion character at the benzylic carbon in the transition state, the fact that electron donoting groups *m*- and *p*-CH_3 cause slight rate enhancements (1.2 and 1.07 respectively) also, suggests that the reaction mechanism is changing with substituent, with charge developing so as to be best dispersed by the substituent.

INTRODUCTION

In previous papers in this series, we have discussed various aspects of the reaction of organotin compounds with sulfur dioxide[1]. As regards the mechanism of the insertion process, the essentially complete allylic and allenic–propargylic rearrangements accompanying insertion[1], and the excellent correlation[2] of the rate constants in the *m* and *p* substituted phenyl series with σ^+, encouraged the view that the process was basically an electrophilic substitution at carbon. In order to learn more of the details of this insertion process, we have undertaken a study of the kinetics of the reactions of a series of *m*- and *p*-substituted benzyltrimethylstannanes with sulfur dioxide in anhydrous methanol at 30°. The results of that study are reported herein.

EXPERIMENTAL

(*a*). *Benzyltrimethylstannanes*

These compounds were prepared by the reaction of the appropriate benzyl-

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magnesium chloride or bromide with trimethyltin chloride (Method A) or by the reaction of the benzyl halide with trimethylstannyllithium in THF (Method B).

Benzyltrimethylstannane was prepared by Method A in 58% yield. B.p. 89–90°/9 mmHg (lit.[3] 90°/9 mmHg).

(p-Chlorobenzyl)trimethylstannane was prepared from *p*,α-dichlorotoluene by Method A in 75% yield. B.p. 88°/0.5 mmHg (lit.[4] 96°/2 mmHg).

(m-Chlorobenzyl)trimethylstannane was prepared from *m*-chlorobenzyl bromide (Method A) in 70% yield. B.p. 69–70°/1 mmHg (lit.[4] 89.5°/1.2 mmHg). (The bromide was prepared from *m*-chlorotoluene and *N*-bromosuccinimide in CCl_4.)

(p-Methylbenzyl)trimethylstannane was prepared from α-bromo-*p*-xylene (Aldrich) by Method A in 50% yield. B.p. 84–86°/3 mmHg (lit.[4] 62°/0.7 mmHg).

(p-Methoxybenzyl)trimethylstannane. *p*-Methoxybenzyl chloride was prepared by the action of thionyl chloride on *p*-methoxybenzyl alcohol. The chloride was reacted with $(CH_3)_3SnLi$ (Method B) to yield the desired compound in 55% yield. B.p. 128°/11 mmHg. (Found: C, 46.67; H, 6.65. $C_{10}H_{16}OSn$ calcd.: C, 46.36%; H, 6.3%.) PMR data: singlet at δ 0.02, 9 H, $(CH_3)_3Sn$; singlet at 2.2, 2 H, CH_2Sn; singlet at 3.71, 3 H, OCH_3; AB quartet at 6.74 ppm, 4 H, aromatic protons; $J(^{119}Sn–CH_3)$ 52.5 Hz; $J(^{119}Sn–CH_2)$ 61 Hz.

(m-Methoxybenzyl)trimethylstannane. *m*-Methoxybenzaldehyde was reduced to the alcohol (by $NaBH_4$ in absolute ethanol) which was converted to the chloride as described above for the *p*-isomer. The title compound was obtained (Method B) in 60% yield. B.p. 74°/1 mmHg. (Found: C, 46.47; H, 6.54. $C_{10}H_{16}OSn$ calcd.: C, 46.36; H, 6.3%.) PMR data: singlet at δ 0.04, 9 H, $Sn(CH_3)_3$; singlet 2.24, 2 H, CH_2Sn; singlet at 3.71, 3 H, OCH_3; multiplet at 6.73 ppm, 4 H, aromatic protons; $J(^{119}Sn–CH_3)$ 53 Hz; $J(^{119}Sn–CH_2)$ 62 Hz.

[p-(Trifluoromethyl)benzyl]trimethylstannane. *p*-Trifluoromethylbenzyl alcohol (b.p. 64°/1.5 mmHg; lit[6]. 86°/8 mmHg) was converted to the bromide by reaction with 48% aqueous HBr and concd. H_2SO_4. The title compound was prepared (Method A) in 50% yield. B.p. 104°/12 mmHg. (Found: C, 41.16; H, 4.48. $C_{10}H_{13}F_3Sn$ calcd.: C, 40.8; H, 4.64%.) PMR data: singlet at δ 0.06, 9 H, $Sn(CH_3)_3$; singlet at 2.34, 2 H, CH_2Sn; AB quartet at 7.21 ppm, 4 H, aromatic protons; $J(^{119}Sn–CH_3)$ 53 Hz; $J(^{119}Sn–CH_2)$ 62 Hz.

[m-(Trifluoromethyl)benzyl]trimethylstannane was prepared from the benzyl chloride (Pierce Chem. Coy.,) by Method A in 70% yield. B.p. 89–91°/5 mmHg. (Found: C, 41.10; H, 4.40. $C_{10}H_{13}F_3Sn$ calcd.: C, 40.8; H, 4.64%.) PMR data: singlet at δ 0.05, 9 H, $Sn(CH_3)_3$; singlet, 2.34, 2 H, CH_2Sn; multiplet at 7.16 ppm, 4 H, aromatic protons. $J(^{119}Sn–CH_3)$ 53 Hz; $J(^{119}Sn–CH_2)$ 61 Hz.

Dibenzyldimethylstannane was prepared by method A from benzyl Grignard (2 mole equivalents) and dimethyltin dichloride. Yield 80%. M.p. 47°. (Found: C, 58.14; H, 6.01. $C_{16}H_{20}Sn$ calcd.: C, 58.05; H, 6.04%.)

Many of the above reactions led to the formation of significant quantities of white, crystalline by-products, identified by their PMR spectra (and in those cases where the solids were known compounds, by melting points) as substituted bibenzyls.

The above benzylstannanes have also been characterised by their proton-decoupled, (natural abundance) ^{13}C spectra[7].

TABLE 1

ANALYTICAL DATA AND MELTING POINTS OF ORGANOTIN SULFINATES, $R{-}C_6H_4{-}CH_2{-}S(O){-}O{-}Sn(CH_3)_3$

R^a	*Calcd.* (%)		*Found* (%)		*M.p.* (°C)^b
	C	*H*	*C*	*H*	
m-CH_3	39.68	5.41	39.80	5.46	93–95
p-CH_3	39.68	5.41	39.95	5.51	111–114
m-Cl	33.95	4.24	33.58	4.22	83–87
p-Cl	33.95	4.24	33.86	4.28	134–136
m-CF_3	34.11	3.88	34.54	3.97	67–70
p-CF_3	34.11	3.88	34.19	3.83	133–137

[a] The data for the insertion product of benzyltrimethylstannane has been reported previously[8]. [b] All compounds softened before melting.

(*b*) *Reaction products: sulfinates* $(CH_3)_3Sn{-}O{-}S(O){-}CH_2{-}C_6H_4{-}R$

The sulfinates were prepared by condensing gaseous SO_2 into small sample tubes containing *ca.* 0.5 g of the stannane, the lower half of the tube being immersed in liquid nitrogen. The tubes were sealed, placed in a deep freeze for 24 h then opened. Last traces of SO_2 were removed under vacuum. The sulfinates were recrystallised from ethanol, and had the analytical and m.p. characteristics as shown in Table 1. The ^1H NMR data were unexceptional and agreed with those for the products in the insertion reactions in methanol.

The (methoxybenzyl)trimethylstannanes, while exhibiting good second-order kinetics, and yielding product spectra consistent with the anticipated trimethyltin-methoxybenzylsulfinates, behaved anomalously in that pure samples of the insertion products were not obtainable. Crystalline materials of variable composition separated from the methanol, and some further reaction of the initial product with SO_2 was presumably occurring and not investigated further.

The structural features of the white crystalline sulfinates, as revealed by IR and PMR spectra were similar to those described by Fong and Kitching[8]. Each contained strong absorptions in 1000–900 cm^{-1} region, typical of *O*-sulfinate structures. The $^{119}Sn{-}CH_3$ coupling constants were consistently close to 70 Hz as seems to be the rule for five-coordinate $(CH_3)_3Sn^{IV}$ species with a planar $(CH_3)_3Sn$ array. In addition, the ^1H spectra of the products demonstrated, that within the limits of detection of the instrument at high gain, no insertion into $Sn{-}CH_3$ bonds was occurring. For example benzyltrimethylstannane [with $\delta(CH_3)$ 0, $J(^{119}Sn{-}CH_3)$ 53 Hz; and $\delta(CH_2)$ 2.22 ppm, $J(^{119}Sn{-}CH_2)$ 62.5 Hz] yields, with SO_2, a product besides analysing well for uptake of one molecule of SO_2, showing $\delta(CH_3)$ 0.36 ppm $J(^{119}Sn{-}CH_2)$ 70 Hz; and $\delta(CH_2)$ 3.52 ppm *with no coupling with* ^{119}Sn. No other CH_3 or CH_2 signals were observable, indicating clean insertion into the benzyl–tin bond. The small downfield movement for the CH_3 resonance (Δ 0.36 ppm) and larger movement for CH_2 (Δ 1.3 ppm) agree with trends noted previously[8].

(*c*). *Kinetic procedure*

This was essentially the same as described previously[9].

RESULTS AND DISCUSSION

The reaction studied can be represented as follows:

$$\text{R–C}_6\text{H}_4\text{–CH}_2\text{–Sn(CH}_3)_3 + \text{SO}_2 \xrightarrow[\text{methanol}]{\text{Anhydrous}} \text{R–C}_6\text{H}_4\text{–CH}_2\text{–S(O)–O–Sn(CH}_3)_3$$

where R = H, *m*- and *p*-CH_3, *m*- and *p*-Cl, *m*- and *p*-OCH_3, *m*- and *p*-CF_3.

Several characteristics of the reaction enabled it to be followed relatively easily by monitoring the peak heights of the sharp $(CH_3)_3Sn$ resonances in reactant and product, such resonances being separated by ca. 30 Hz at 60 MHz. The second-order rate expression

$$kt = \frac{2.303}{a-b} \cdot \log_{10} \frac{b(a-x)}{a(B-x)} \quad \text{with } x = \frac{q}{p+q}a$$

was employed where a = initial [Sn], b = initial [SO_2] and $p = (CH_3)_3$ peak height in substrate and $q = (CH_3)_3Sn$ peak height in product. The data for the compounds studied is presented in Table 2, and shows that the rate constants were generally reproducible to ca. 10%.

There is no reasonable doubt from the kinetic order that one molecule of SO_2 and of benzylstannane (and indeterminate molecules of methanol) are involved in the transition state. The absence of an induction period, the well-behaved and reproducible kinetics, and failure to detect products commonly associated with benzyl radicals

TABLE 2

KINETICS OF INSERTION OF SO_2 INTO SUBSTITUTED BENZYLTRIMETHYLTIN

Concentrations are expressed in mole · l^{-1}. Second-order rate constants, *k*, are expressed in l · $mole^{-1}$ · min^{-1}.

Substituent	*Organotin concn.*	*SO_2 concn.*	*k*	*k_{av}*	*k_{rel}*
H	0.1334	0.0629	0.0849	0.0900	1
	0.0667	0.1258	0.1007		
	0.1000	0.0944	0.0877		
m-CH_3	0.1284	0.0630	0.1074	0.1078	1.198
	0.0642	0.126	0.1100		
	0.0963	0.0942	0.1060		
p-CH_3	0.1327	0.1115	0.0956	0.0967	1.074
	0.0995	0.1672	0.0978		
m-Cl	0.1337	0.0688	0.1100	0.1178	1.309
	0.0669	0.1377	0.1259		
	0.1004	0.1033	0.1174		
p-Cl	0.1317	0.0609	0.1464	0.1465	1.628
	0.0658	0.1218	0.1500		
	0.0828	0.0914	0.1432		
m-CF_3	0.1328	0.0656	0.1224	0.1334	1.482
	0.0664	0.1313	0.1454		
	0.0996	0.0985	0.1324		
p-CF_3	0.1329	0.0664	0.1768	0.1973	2.192
	0.0664	0.1327	0.2150		
	0.0997	0.0996	0.2000		

argue against any significant radical pathway.

Of particular note is the extreme insensitivity of the reaction to substituent effects (Table 1) with the greatest rate enhancement being 2.2 caused by *p*-CF_3. Other small rate enhancements are due to *m*-CF_3, *m*- and *p*-Cl, while the normally electron-donating groups *m*- and *p*-CH_3 also seem to produce very marginal rate increases. The kinetic data for the *m*- and *p*-OCH_3 compounds has not been included in the Table, in view of the difficulties in obtaining pure samples of the insertion products. Nevertheless, we believe that the kinetic behaviour and product spectra recorded during a kinetic run, are consistent with a second-order insertion process for both compounds (exclusively into the benzyl–tin bond) with k_{rel} of 1.10.

This small rate spread strongly suggests that charge generation in the transition state is not pronounced and that almost concerted bond changes are involved. The results for CF_3 and Cl substituents which normally disperse negative charge, do suggest that some such charge, albeit small, is located on the benzylic carbon. This in turn would be consistent with Sn–O bond formation and C–Sn bond rupture being somewhat ahead of C–S bond formation. On the other hand the barely perceptible accelerations due to *m*- and *p*-CH_3, implying a lesser degree of negative charge in the transition state compared with the ground state, indicates C–S bond formation to be significant with a consequential reduction in negative charge at the benzylic carbon. (The $CH_2^{\delta-}$–$Sn^{\delta+}$ bond would be polarised as indicated in the ground state). The observation that the benzylic carbon is far more susceptible to attack by SO_2 than the methyl carbon is in line with some negative character at carbon in the transition state. This contrasts with the situations for HgX_2 and CF_3COOH cleavage of benzylstannanes, where CH_3–Sn and benzyl–Sn cleavages proceed at comparable rates[10]. The ^{13}C spectra of the benzylstannanes were examined[7] to probe possible ground state energy differences but no definite conclusion was possible. The chemical shift of the benzylic carbon (at ca. 172–173 ppm from CS_2) was poorly responsive to ring substituent. In addition differing degrees of solvation of ground and transition states may influence rates in a significant but unpredictable manner.

The small spread in rate constants made analysis involving "σ" constants very difficult, but no acceptable correlation with σ, σ^+, σ_I or σ_N was realised. The acceleration caused by both electron-withdrawing (*e.g.* CF_3) and -donating groups (*e.g.* CH_3) suggests the mechanism is changing with substituent, and no free-energy relation is operating*. This type of behaviour appears to be rather common at centers α to an aromatic nucleus[11], and in particular Russian workers have noted[12] that in the iodine/cadmium iodide cleavage of substituted benzylmercuric halides both electron donors and the *p*-NO_2 group (too rapid to measure) caused rate enhancements.

Rate constants for insertion of the parent compound, benzyltrimethylstannane, were obtained at 30, 40, 50 and 60°, and yielded thermodynamic parameters of activation as $\Delta H^{\ddagger} = 9.6$ kcal·mole^{-1} and $\Delta S^{\ddagger} = -40$ kcal·deg^{-1}·mole^{-1} (at 30°). The large negative entropy of activation is consistent with a substantial loss in freedom of vibrational and translational modes, and in view of the poor response to substituents, the most meaningful description of the transition state is one where bond formation and rupture are near to synchronous.

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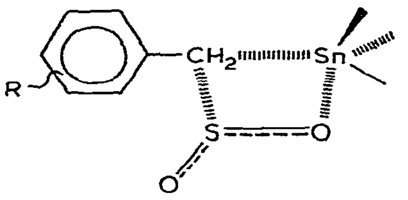
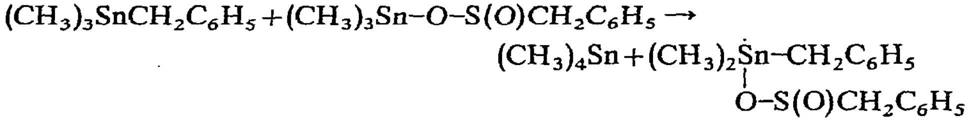
* It is not suggested that the change in mechanism is abrupt or gross, but simply that the charge distribution, and the degree of concertedness of bond rupture and formation, are responding to the nature of the substituent, leading to a gradual mechanistic change. See ref. 11 for a full discussion.



One further aspect of the reaction is to be noted. Towards the end of each kinetic run a very small peak was resolved on the low field edge of the $(CH_3)_3Sn$ resonance of the substrate and a second peak, of half the intensity of the first appeared slightly to higher field of the $(CH_3)_3Sn{-}O{-}S(O)$ resonance. The phenomenon was most noticeable in reaction mixtures containing an excess of tetraorganotin, and could be duplicated by mixing equal amounts of benzyltrimethylstannane and its insertion product. The emergent peaks were identified as tetramethyltin and the monoinsertion product of dibenzyldimethyltin by preparation and examination of authentic samples. Hence a redistribution reaction



$$\mathrm{(CH_3)_3SnCH_2C_6H_5 + (CH_3)_3Sn{-}O{-}S(O)CH_2C_6H_5 \rightarrow (CH_3)_4Sn + (CH_3)_2\underset{\substack{|\\ O-S(O)CH_2C_6H_5}}{Sn}{-}CH_2C_6H_5}$$

was occurring (a similar reaction at the $Sn{-}CH_2C_6H_5$ bond would be trivial), but was slow enough for it not to interfere in the kinetics.

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