

PREPARATION AND CHARACTERISATION OF TRIMETHYLTIN DERIVATIVES OF SOME 4-SUBSTITUTED PHENYL SULFIDES

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SUMMARY

The preparation of trimethyltin-sulfur compounds of the type $\text{Me}_3\text{SnSC}_6\text{H}_4\text{-4-X}$, where $\text{X} = \text{F, Cl, Br, CH}_3, \text{NH}_2, \text{and NO}_2$ is reported and the nature of the bonding between tin and sulfur is discussed on the basis of IR, UV, PMR, and Raman data. The mass spectrum of each compound is tabulated.

INTRODUCTION

π -Bonding between Group IV elements and attached groups has been well studied¹, especially in the case of amino², alkoxy³, aryl⁴ and vinyl⁵ Group IV derivatives. All the data points to a decrease in π -bonding upon descending the series from silicon to lead. Paralleling this decrease in π -bonding with increase in atomic weight, is an increased tendency towards intermolecular bonding and polymerisation.

The series of compounds described in this paper were prepared in order to study the tin-sulfur bond and to ascertain whether any $d_{\pi}\text{-}p_{\pi}$ bonding exists.

EXPERIMENTAL

Mass spectra were taken using a Perkin-Elmer Hitachi RMU-6D double focusing spectrometer at 70 eV ionising energy with perfluorotributylamine as internal mass marker. Samples were introduced into the ion source using the "sub-oven" inlet system, with the temperature of the main oven being maintained at 200°. IR spectra were recorded on a Perkin-Elmer 621 grating spectrophotometer. Raman spectra were obtained with a Spex Ramalogue with 4880 Å argon ion excitation. PMR spectra were taken using a Varian Associates DB-60 spectrometer at 60 MHz. UV spectra were measured with a Cary Model 14 spectrophotometer.

Analyses were carried out by Schwarzkopf Microanalytical Laboratories, Woodside, N.Y.

The substituted thiophenols were obtained from Aldrich Chemical Company, Inc. and trimethyltin chloride from Alfa Inorganics, Inc. All were used without further purification with the exception of 4-aminothiophenol which was distilled prior to use.

The trimethyltin derivatives were prepared by the procedure of Abel and Brady⁵. The analytical, m.p., b.p., and molecular weight data and yields of pure product are

given in Table 1. Liquid products and $\text{Me}_3\text{SnSC}_6\text{H}_4\text{-4-Br}$ were purified by distillation and the solids by recrystallisation or sublimation. The preparation of $\text{Me}_3\text{SnSC}_6\text{H}_4\text{-4-NH}_2$ and $\text{Me}_3\text{SnSC}_6\text{H}_4\text{-4-NO}_2$ are described since their work-up differs from the reported procedure.

Preparation of trimethyltin 4-aminophenyl sulphide

To a solution of trimethyltin chloride (8.0 g, 0.04 mole) in deoxygenated water (200 ml) was added freshly distilled 4-aminothiophenol (5.5 g, 0.044 mole). To the suspension was added dropwise sufficient sodium hydroxide (ca. 2 g) in deoxygenated

TABLE 1

ANALYTICAL DATA

Compound	Color	B.p. (°C/mm)	M.p. ^a (°C)	Elemental analysis, found			Yield (%)
				(calcd.) (%)			
				C	H	Mol. wt. ^b	
$\text{Me}_3\text{SnSC}_6\text{H}_4\text{-4-Me}$		66-68/0.01		41.81 (41.85)	5.58 (5.62)	288 (288)	50
$\text{Me}_3\text{SnSC}_6\text{H}_4\text{-4-F}$		60-62/0.01		36.88 (37.15)	4.49 (4.50)	292 (292)	52
$\text{Me}_3\text{SnSC}_6\text{H}_4\text{-4-Cl}$		80-81/0.005		35.28 (35.16)	4.22 (4.26)	310 (310)	48
$\text{Me}_3\text{SnSC}_6\text{H}_4\text{-4-Br}$	Colorless	75/0.02	46.5-47.5	30.83 (30.72)	3.67 (3.72)	354 (354)	59
$\text{Me}_3\text{SnSC}_6\text{H}_4\text{-4-NH}_2$	White		96	37.93 (37.52)	5.19 (5.25)	289 (289)	45
$\text{Me}_3\text{SnSC}_6\text{H}_4\text{-4-NO}_2$	Yellow		53	34.43 (33.99)	4.19 (4.15)	319 (319)	37

^a Uncorrected. ^b Mass spectrometry.

water (125 ml) to just make the resulting solution basic. Stirring was maintained for 12 h and then the product was filtered off, washed with water, and dried in vacuo over P_2O_5 . The product could be purified either by recrystallisation from hot hexane or by sublimation (90°/0.01 mm).

Preparation of trimethyltin 4-nitrophenyl sulphide

The actual preparation was the same as above except an orange solid was present at all times and the solution was red. After filtering off the orange solid the mother-liquor was carefully neutralised with 0.5 M hydrochloric acid and the resulting yellow solid filtered off. Both solids were dried in vacuo over P_2O_5 . The first solid was mainly unreacted 4-nitrothiophenol. Upon recrystallising the second solid from hexane/methylene chloride, the first fraction obtained was bis(4-nitrophenyl)-disulphide (m.p. 175°, lit.⁷ 182°). The second fraction was twice recrystallised from hot hexane to give pure product. Attempted sublimation caused some decomposition although PMR of the sublimate indicated a substantial amount of product had sublimed (75°/0.01 mm).

TABLE 2

PMR^a OF Me₃SnSC₆H₄-4-X

X	τ^b (relative area)		
	Sn-CH ₃ ^c	C ₆ H ₄ ^d	
NH ₂	9.67(9)	3.56(2), 2.88(2)	6.37 ^e (2) C-NH ₂
CH ₃	9.65(9)	2.87(4)	6.09 ^e (3) C-CH ₃
H	9.64(9)		2.76 ^d (5) C ₆ H ₅
F	9.64(9)	2.94(4)	
Cl	9.63(9)	2.79(4)	
Br	9.62(9)	2.72(4)	
NO ₂	9.51(9)	2.39(2), 1.82(2)	

^a CH₂Cl₂ solution. ^b Relative to Me₄Si (ppm). ^c Singlet; $J(^{119}\text{Sn}-\text{C}-\text{H})$ 56.7 Hz $J(^{117}\text{Sn}-\text{C}-\text{H})$ 54.2 Hz^d Multiplet. ^e Broad singlet.

DISCUSSION

The PMR for the series of trimethyltin sulfides were recorded (Table 2).

The nature of the interaction between the aromatic ring and the sulfur atom in substituted thiophenols is believed to involve sulfur 3*p*-orbital participation⁸, creating a sulfur-aromatic π -bond together with the σ -bond. Involvement of sulfur 3*d*-orbitals has been suggested⁹ but seems unlikely. Substituent effects can therefore be transmitted to sulfur via an inductive and a mesomeric effect. This has been observed (*e.g.* pK_a^{10} and IR¹¹).

The chemical shifts (Sn-CH₃) for the series Me₃SnSC₆H₄-4-X do not shed much light on the nature of the Sn-S bond. The compounds Me₃SnSC₆H₄-4-NH₂ and Me₃SnSC₆H₄-4-NO₂ represent the two extremes in substituent effect in this series; SC₆H₄-4-NH₂ being the least electronegative and therefore deshielding the Sn-CH₃ protons to the least extent and SC₆H₄-4-NO₂ being the most electronegative. The chemical shifts observed [τ 9.51 (NO₂) and τ 9.67 (NH₂)] support this.

The close similarity of the chemical shifts of all the derivatives except the nitro compound, which is significantly different, is important in conjunction with the IR and UV data discussed later.

A solution IR spectrum was run for all derivatives in the range 600–200 cm⁻¹ to observe the $\nu(\text{Sn}-\text{C})$ and $\nu(\text{Sn}-\text{S})$ stretching vibrations. It was not possible to assign the $\nu(\text{Sn}-\text{S})$ vibration in all cases, with certainty, because of the presence of other absorptions in the 400–300 cm⁻¹ region. However, by running the Raman spectra between 600 and 200 cm⁻¹ it was possible to assign unambiguously the $\nu(\text{Sn}-\text{S})$ vibration for all the compounds. The selected IR and Raman data are presented in Table 3.

Changes in the S-H stretching vibration of some 4-substituted thiophenols have been studied¹¹ and show predicted variations; electron withdrawing groups (*e.g.* NO₂, Cl, Br, I) decrease the $\nu(\text{S}-\text{H})$ vibration while electron donating groups (*e.g.* NH₂, CH₃, *t*-Bu) increase the $\nu(\text{S}-\text{H})$ vibration. However, the Sn-S stretching vibration increases with all 4-substituents (compared with Me₃SnSC₆H₅) except for the nitro derivative, which shows a decrease. These results are consistent with the mesomeric

TABLE 3
SELECTED IR^a AND RAMAN^b DATA OF Me₃SnSC₆H₄-4-X (cm⁻¹)

X	ν(Sn-C)		ν(Sn-S)
	Antisymmetric	Symmetric	
NH ₂	530 vs (528)	509 s (509)	^c (384)
F	530 vs (534)	509 s (509)	359 m (371)
Cl	529 vs (541)	508 s (509)	357 m (358)
CH ₃	530 vs (534)	509 s (509)	354 m (355)
Br	531 vs (534)	508 s (509)	355 m (354)
H	530 vs (535)	509 s (509)	^c (341)
NO ₂	530 vs (528)	509 s (509)	341 m (326)

^a CCl₂CCl₂ solution in 0.5 mm polyethylene cells. ^b Data in brackets, benzene solution. ^c Not possible to assign.

TABLE 4
UV DATA^a OF Me₃SnSC₆H₄-4-X AND HSC₆H₄-4-X

X	λ _{max} (nm), (ε)	
	Me ₃ SnSC ₆ H ₄ -4-X	HSC ₆ H ₄ -4-X
F	231(15800), 258(4960)	233(6500), 283(860), 289(860), 297(660)
H	232(17300), 258(7100)	238(8400), 273(660), 281(640), 290(440)
CH ₃	236(14800), 260(5500)	239(11130), 278(710), 288(700), 295(480)
Cl	240(16000), 263(6800)	246(10300), 281(720), 290(660), 299(400)
Br	240(17100), 263(8500)	247(11000), 281(910), 290(760), 300(440)
NH ₂	263(14200), 300(2900)	^b
NO ₂	317(9200)	304(13000)

^a Hexane solution. ^b Not measured.

release of electron density being more important than inductive withdrawal in the ground state configuration. This observed order of increase of the ν(Sn-S) vibration, NH₂ > F > Cl > Br ≈ CH₃, is the order expected if electron release is more important than electron withdrawal. This surprising observation can be rationalised by assuming a partial positive charge developing on the sulfur atom as a result of d_π(Sn)-p_π(S) interaction in which the tin atom draws electron density from the thiophenyl group. However, molecular spectra studies of Ph₃SnSPh and (Ph₃Sn)₂S and their comparison with similar compounds suggest no appreciable d_π-p_π bonding between tin and sulfur^{1,2}.

The presence of d_π(Sn)-p_π(S) interaction is supported by the electronic spectra (Table 4). The electronic spectra of the parent thiophenols exhibit a broad multi-shouldered absorption due to π-π* transitions and low intensity absorptions due to

$p_{\pi}(\text{S})-p_{\pi}(\text{C})$ transitions⁸. 4-Nitrothiophenol, however, shows a very broad absorption that masks the $p_{\pi}(\text{S})-p_{\pi}(\text{C})$ transitions. The electronic spectra of the trimethyltin 4-substituted phenyl sulfides show little change in the position of the $\pi-\pi^*$ transition compared with the thiophenols except that the extinction coefficients are significantly larger. The complete absence of any absorptions due $p_{\pi}(\text{S})-p_{\pi}(\text{C})$ is very significant and can be interpreted if it is assumed that a partial positive charge develops on sulfur as a result of $d_{\pi}(\text{Sn})-p_{\pi}(\text{S})$ interaction. This charge would either move the $p_{\pi}(\text{S})-p_{\pi}(\text{C})$ transition to significantly higher energy that would be masked by the $\pi-\pi^*$ transition or eliminate this transition completely. The increase in intensity of the $\pi-\pi^*$ absorptions supports an increase in electron density on the phenyl group as a result of mesomeric release from the *para*-substituent. $\text{Me}_3\text{SnSC}_6\text{H}_4-4-\text{NO}_2$ present an exception. The absorption at 317 $m\mu$ prevents any decision concerning $p_{\pi}(\text{S})-p_{\pi}(\text{C})$ interaction.

TABLE 5

TIN-CONTAINING IONS IN THE MASS SPECTRA OF $\text{Me}_3\text{SnSC}_6\text{H}_4-4-\text{X}$ (70 eV)

Ion	m/e^a (relative intensity) for X =						
	H	CH ₃	NH ₂	F	Cl	Br ^c	NO ₂ ^d
$\text{Me}_3\text{SnSC}_6\text{H}_4\text{X}^{+b}$	274(28)	288(73)	289(73)	292(50)	308(33)	352(26)	319(13)
$\text{Me}_2\text{SnSC}_6\text{H}_4\text{X}^+$	259(88)	273(78)	274(76)	277(83)	293(62)	337(50)	304(30)
$\text{MeSnSC}_6\text{H}_4\text{X}^+$	244(2)	258(3)	259(5)	262(2)	278(1)	332(1)	289(1)
$\text{SnSC}_6\text{H}_4\text{X}^+$	229(69)	243(50)	244(100)	247(68)	263(42)	307(29)	274(18)
$\text{SnSC}_6\text{H}_3^+$				227(6)	227(6)	227(6)	
$\text{SnC}_6\text{H}_4\text{X}^+$	197(4)	211(4)	212(4)	215(3)	231(4)	275(2)	258(6)
Me_3Sn^+	165(42)	165(39)	165(65)	165(100)	165(100)	165(100)	165(100)
Me_2Sn^+	150(10)	150(8)	150(12)	150(13)	150(13)	150(10)	150(10)
SnX^+				139(4)	155(35)	199(25)	
MeSn^+	135(42)	135(35)	135(46)	135(64)	135(42)	135(37)	135(21)
Sn^+	120(12)	120(11)	120(9)	120(12)	120(12)	120(13)	120(12)

^a The m/e values were calculated for ¹²⁰Sn, ³⁵Cl, and ⁷⁹Br, where appropriate. ^b Parent ion. ^c Also observed; $\text{Me}_2\text{SnSC}_6\text{H}_4^+$ 258(6), $\text{MeSnSC}_6\text{H}_4^+$ 243(2), $\text{SnSC}_6\text{H}_4^+$ 228(10). ^d Also observed; $\text{SnSC}_6\text{H}_4\text{O}^+$ 244(5), $\text{SnSC}_6\text{H}_4^+$ 228(14), $\text{SnSC}_5\text{H}_4^+$ 216(1).

These conclusions agree well with the results obtained by Mössbauer spectra¹³ which also indicated a decrease in $p_{\pi}(\text{S})-p_{\pi}(\text{C})$ interaction due to a $d_{\pi}(\text{Sn})-p_{\pi}(\text{S})$ perturbation.

The mass spectrum of each compound was studied and the observed fragments and their assignments are presented in Table 5.

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