

SYNTHESES AND CHARACTERIZATION OF ARYL TRIORGANOTIN(IV) SULPHITES

Yash Sharda

Department of Chemistry, M.R.P.D. Govt. College, Talwara, Punjab, India.

Abstract:- Aryl tri-n-butyltin(IV) sulphites have been synthesized by the reaction of μ -oxo-bis[tri-n-butyltin(IV)] with aryl chlorosulphites in 1:1 molar ratio at reflux temperature. The compounds so obtained $Bu_3SnOS(O)OR$ where $R=C_6H_5, p-CH_3C_6H_4$ have been characterized with the help of IR, ¹H, ¹³C, ¹¹⁹Sn and mass (low/high resolution) spectral studies & elemental analyses. On the basis of these studies it was observed that Aryl triorganotin(IV)sulphites can be assigned tetrahedral structure in non-coordinating solvents & Trans-trigonalbipyramidal in coordinating solvents.

1. INTRODUCTION

Organotin compounds occupy a unique place among the organometallics because of their use in organic synthesis, in range of technical processes as well as their favorable environmental & toxicological properties.

Generally Organotin esters are derived from inorganic and organic acids and contain Sn-O-X (where X=S, P, C, N etc.) groups. These compounds have been synthesized either by insertion of sulphur dioxide/ sulphur trioxide into Sn-C [1, 2, 3] bond or by reacting organotin (IV) oxides, chloride or hydroxides with corresponding acids. X-ray crystal data revealed that to be five-coordinating tin polymers having common trigonalbipyramidal environment. The difference in their structure related only to disposition of the bonded group in space keeping the basic geometry of the molecule same.

Attempt has been made to synthesize alkyl organotin (IV) sulphites by convenient method by reacting - μ - oxobis[tri-n- butyl tin(IV)] with aryl chlorosulphite. The compound isolated are characterized through molecular spectroscopy.

2. EXPERIMENTAL

Preparation of aryl chlorosulphites.

These chlorosulphites have been prepared by reacting thionyl chloride with, phenol and p-CH₃C₆H₅ in 1:1 molar ratio. Syntheses of aryl tri -n- butyl tin (IV) sulphites

Phenyl chlorosulphite(4.41g,25mmole)and P- methylchlorosulphite(4.76g,25mmol) was taken in a two necked round bottom flask fitted with pressure equalizing dropping funnel,reflux condenser and silica gel guard tube. μ - oxobis[tri-n- butyl tin(IV)](14.95,25 mmol) was added into the flask maintained at 0-5o C with constant stirring and then refluxed for about 5-6 hours. A viscous oils obtained, were distilled on long fractionating column.The relevant physical and analytical data are given below

Anal. Calc. for C₁₈H₃₂O₃SSn; Sn 26.6; S 7.1

Found Sn 26.0; S 7.3 b.pt 173^oC

Anal. Calc. for C₁₉H₃₄O₃SSn; Sn 25.8; S 6.9

Found Sn 25.5; S 6.4 b.pt 174^oC

• SPECTROSCOPY

IR spectra were recorded on KBr pelletson model Hitachi 270-250 double beam grating infrared spectrophotometer.¹H NMR spectra in CDCl₃Were recorded on the spectrophotometer varian EM-390-90 MHz.¹¹⁹Sn NMR were recorded on 33-37 MHz JEOLFX90 Q .The ¹³C chemical shifts were determined by reference tothe signal from the solvent (CDCl₃, δ 77 .00 ppm).The ¹H, ¹¹⁹Sn chemical shifts are quoted relative to Me₄Si, Me₄Sn respectively. Mass spectral measurements were recorded on VG analytical mass spectrometer model 70-swith 11-250 -J data system.

3. RESULTS AND DISCUSSION

The titlecompounds were obtained by the reaction of Phenyl chlorosulphite, P-methylchlorosulphite with μ - oxobis[tri-n-butyl tin(IV)] in 1:1 molar ratio. The elemental anlysis given aboveshow them to have compositionBu₃SnOS(O)OR

In IRspectra the band due to ν S=O [4] [2] absorptions at 1220-1210cm⁻¹ in aryl chlorosulphite shifts to alower frequencyat 1185-1170cm⁻¹. This negative spectral shift may be due to the mass effect of tri-n- butyltin (IV) moiety .Other characteristic absorptions due to ν S=O, ν S=O₂, ν S=O₃appear at 1182-1170cm⁻¹,1 1077-1080 cm⁻¹,873-870 cm⁻¹respectively as shown in table 1.

Table 1: Major infrared absorption

$C_6H_5OSO_2Sn(C_4H_9)_3$	$p-CH_3C_6H_4OSO_2Sn(C_4H_9)_3$	Assignments
3040	3022	ν CH(aromatic)
2956	2920	ν CH(aliphatic)
2840	2728	
1590	1599	C=C(skeletal)
1485	1464	
1377	1377	δ CH(aromatic)
1341	1290	
1290		
1233		
1182	1170	ν S=O
1149	1110	
1071	1080	ν SO ₂ .
1023	1010	
906	970	ν asSO ₂ .
873	870	ν SO ₃ .
831		
768	770	
684	680	δ CH bending
603		ν SnC
507	510	

¹H NMR show a multiplet centered at 7.1 and 6.9 ppm due to ring proton of phenyl and p-methyl phenyl-tri-n butyltin (IV) sulphite respectively. The resonance peak due to methyl group of the latter compound appear at 2.4 ppm. The ring proton undergo an upfield shift of 0.5 to 0.4 ppm from the corresponding aryl chlorosulphites. This upfield shift indicates the replacement of chlorine of aryl chlorosulphites by OSnBu₃ moiety. These compounds show a signal at 0.9 (multiplet), 1.3 (multiplet), and 1.6 ppm (triplet) due to CH₃, CH₂, and -CH₂ (Sn) protons respectively.

Table 2: Proton NMR

¹H NMR spectral data of aryl tri-n-butyltin(IV) sulphites

Compound	Chemical shift (δ) in ppm.				
	CH ₃	CH ₂	SnCH ₂	Ring-O	Ring-CH ₃
C ₆ H ₅ OSO ₂ Sn(C ₄ H ₉) ₃	0.9 (9H, t)	1.3 (12H, m)	1.6 (6H, t)	7.1 (5H, m)	-
p-CH ₃ C ₆ H ₄ OSO ₂ Sn(C ₄ H ₉) ₃	0.9 (9H, t)	1.3 (12H, m)	1.6 (6H, t)	6.9 (5H, m)	2.4 (3H, s)

¹³CNMR and ¹¹⁹Sn spectra of these compounds have been recorded in inert (CDCl₃) and donor (DMSO & PY) solvents.

¹³CNMR spectral studies show that in (CH₃CH₂CH₂CH₂)SnOS(O)R show $\delta^{13}C(1)$ of n-butyl tin(IV) group undergo downfield shift in coordinating solvents as compared to that in CDCl₃ solutions. The downfield shift is found to be 3.37 ppm in phenyl and 3.24 ppm in p-methyl tri-n-butyl tin (IV) sulphites in DMSO and 1.10 & 0.7 ppm in Py respectively. $\delta^{13}C(1)$ NMR data throws light on the configuration of tin atom. Nadvornik et al [5] have suggested that the formation of trans-trigonalbipyramidal triorganotin (IV) complex is associated with downfield shift of $\delta^{13}C(1)$. Another important change is the downfield shift of $\delta^{13}C(ipso)$ in coordinating solvents. This upfield shift was 9.5 and 1.83 ppm in phenyl and in p-methyl tri-n-butyl tin (IV) sulphites respectively.

¹¹⁹Sn spectra of these compounds in CDCl₃ exhibit, $\delta^{119}Sn$ NMR values in the range 153.60-158.43 ppm which are characteristic of four coordinate tin atom [8]. However, in coordinating solvents such as DMSO and Py these values move upfield in range 7.46-29.18 ppm. These upfield shifts are in conformity with change in coordination number from four to five around central tin atom [7,8]. These results are also indicative of the following equilibrium



The values of ¹J(¹¹⁹Sn-¹³C) coupling constant in the range 338.13-338.74 Hz (CDCl₃) and 457.77-413.80 Hz (DMSO, Py) are also indicative of tetrahedral and trigonalbipyramidal geometry of these compounds respectively.

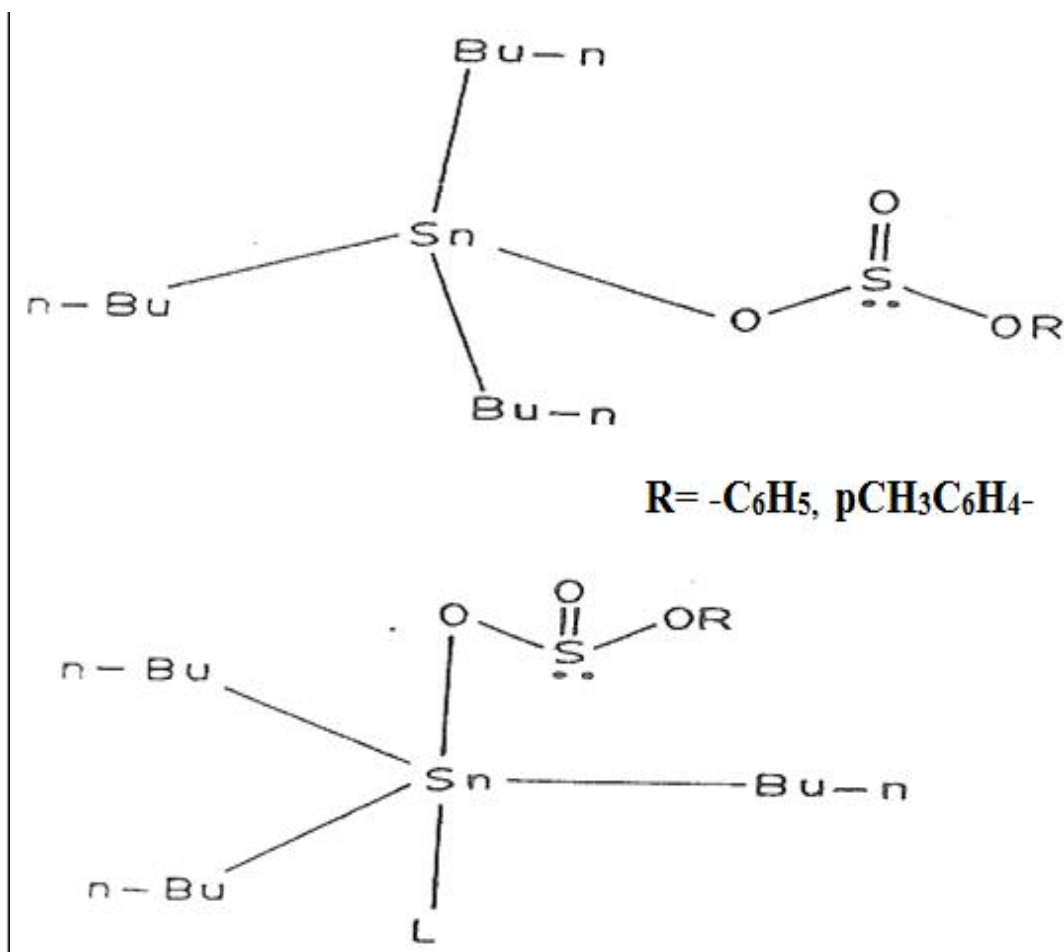
From above studies aryl tri-n-butyl tin (IV) sulphites can tentatively be assigned a tetrahedral structure in non-coordinating solvents and trigonalbipyramidal geometry in coordinating solvents [4].

The above structures are also indicated through theoretical calculations of C-Sn-C angle using of ¹J(¹¹⁹Sn-¹³C) coupling constant values [1]. These angles occur in the range 109-110.50 in CDCl₃ which correspond to nearly tetrahedral geometry. In DMSO and Py these values are between 117.5-121.60. These values point to and trans-trigonalbipyramidal geometry.

Mass spectra of these compounds show the absence of molecular ion peak, yet the fragmentation pattern remains the same. From the high resolution mass spectra there was a good agreement between the calculated and observed isotopic ions.

4. CONCLUSION

From ¹³C, ¹¹⁹Sn NMR, ¹J(¹¹⁹Sn-¹³C), of C-Sn-C angle and mass spectral values, these compounds can be assigned tetrahedral structure in non-coordinating solvents and trigonalbipyramidal geometry in coordinating solvents as given below



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