SYNTHESIS AND SPECTROSCOPIC (IR, ^{1}H, ^{13}C, AND ^{119}Sn NMR) CHARACTERIZATION OF MONO- AND DIORGANOTIN(IV) COMPLEXES CONTAINING STERICALLY HINDERED N-ARYLSALICYLALDIMINATE GROUPS

Shashank Mishra, Manju Goyal and Anirudh Singh*

Department of Chemistry, University of Rajasthan, Jaipur-302 004, India
<kudiwal@datainfosys.net>

ABSTRACT

Derivatives of the types $Me_2SnX_{2-n}(OC_6H_4CH{=}NAr)_n$ (Ar = $C_6H_3Me_2$-2,6, $C_6H_2Me_3$-2,4,6, $C_6H_3Et_2$-2,6, $C_6H_3Pr^i_2$-2,6; X = Cl, OPr^i; n = 1 or 2) and $BuSn(OPr^i)_{3-n}(OC_6H_4CH{=}NAr)_n$ (n = 1,2 or 3) have been prepared either by the salt elimination or alkoxy-ligand exchange reactions. The reactions of $Me_2Sn(OPr^i)(OC_6H_4CH{=}NC_6H_3Et_2$-2,6) with an excess of MeOH or Bu^tOH have also been investigated. All these derivatives have been characterized by elemental (C, H, N and Sn) analyses, spectroscopic [IR, NMR (^{1}H, ^{13}C, and ^{119}Sn)] studies and molecular weight measurements.

INTRODUCTION

The chemistry of organotin compounds with Schiff bases has been investigated in considerable details during the past few decades [1-3]. Structural features of organotin chelates and molecular adducts with Schiff bases are markedly influenced [3-10] by the number and nature of alkyl/aryl groups attached to tin as well as to azomethine nitrogen atom. In order to investigate the role of steric demand of the group attached to the donor nitrogen atom in influencing the stereochemical aspects of organotin(IV) complexes, we have carried out reactions of dimethyltin diisopropoxide/dimethyltin dichloride and butyltin triisopropoxide with a number of sterically hindered N-arylsalicylaldimines such as $HOC_6H_4CH{=}NC_6H_3Me_2$-2,6, $HOC_6H_4CH{=}NC_6H_2Me_3$-2,4,6, $HOC_6H_4CH{=}NC_6H_3Et_2$-2,6, and $HOC_6H_4CH{=}NC_6H_3Pr^i_2$-2,6. In addition, the effect of the steric demand of the group X (X = Cl, OMe, OPr^i, OBu^t) in derivative of the type $Me_2SnX(C_6H_4CH{=}NAr)$ has also been investigated. The structural elucidation of these new derivatives have been carried out by IR and NMR (^{1}H, ^{13}C, and ^{119}Sn) spectroscopic studies.

MATERIALS AND METHODS

All synthesis and manipulations were carried out under strictly anhydrous conditions. The (BDH) solvents : benzene, toluene, *n*-hexane, methyl alcohol, *tert*-butyl alcohol and carbon tetrachloride were dried and purified by the literature methods [11]. Dimethyltin diisopropoxide [12] and butyltin triisopropoxide [13] were prepared as described in the literature. $Me_2Sn(OPr^i)_2$ was sublimed (112°C/0.2 mm, 85% yield) whereas $BuSn(OPr^i)_3$ distilled (110°C/0.5 mm, 90% yield) prior to use. Me_2SnCl_2 (Aldrich) was recrystallized by *n*-hexane before use. The sterically hindered N-arylsalicylaldimines (**HL^1-HL^7**) were prepared according to the procedure described in our recent publication [14]. Isopropyl alcohol in the azeotrope was determined by oxidimetric method [15] using 1N $K_2Cr_2O_7$ solution in 12.5% H_2SO_4. Chlorine was determined by Volhard's method [16]. Tin was determined gravimetrically as SnO_2.

The ^{1}H (89.55 MHz, $CDCl_3$) and ^{13}C (22.49 MHz, CCl_4) NMR were recorded on a JEOL FX-90O FT NMR spectrometer using TMS as an internal reference. ^{119}Sn (33.35 MHz) NMR spectra were recorded in CCl_4 or C_6H_6 solutions using tetramethyltin as an external reference. IR (4000-200 cm^{-1}) spectra were recorded as Nujol mulls on a Nicolet Magna 550 spectrophotometer using CsI optics. Microanalyses (C, H, N) were performed using Perkin Elmer 2400 CNS/O analyzer. Molecular weights were determined ebullioscopically in benzene using a Gallenkamp ebulliometer.

Synthesis of $Me_2SnCl(OC_6H_4CH{=}NC_6H_2Me_3$-2,4,6) (1)

A solution of $NaOC_6H_4CH{=}NC_6H_2Me_3$-2,4,6 [freshly prepared by the interaction of Na (0.31 g, 13.56 mmol) with HL^c (3.22 g, 13.47 mmol) in THF] was added dropwise to a pre-stirred solution of Me_2SnCl_2 (2.96 g, 13.47 mmol) in benzene (~ 20 ml). The reaction mixture was then allowed to stir at room temperature for ~10 h. The precipitated NaCl (0.75 g, 12.83 mmol) was separated by filtration. Volatiles from the filtrate were removed under reduced pressure to afford the title compound (**1**) (4.72 g, 82%) as a yellow solid. The product was further purified by recrystallization from a 1:3 mixture of *n*-hexane and toluene at –20°C in 54% yield.

In a similar procedure, the interaction of Me_2SnCl_2 (1.16 g, 5.31 mmol) with two equivalents of $NaOC_6H_4CH{=}NC_6H_2Me_3$-2,4,6 [freshly prepared from Na(0.24 g, 10.63 mmol) and the HL^2 (2.54 g, 10.61 mmol)] afforded yellow solid of composition $Me_2Sn(OC_6H_4CH{=}NC_6H_2Me_3$-2,4,6)$_2$ (**5**) (2.98 g, 89%). The compound (**5**) was purified by recrystallization from a 3:1 mixture of toluene and *n*-hexane at –20°C in 60% yield.

Synthesis of $Me_2Sn(OPr^i)(OC_6H_4CH{=}NC_6H_3Et_2\text{-}2,6)$ (2)

The reaction mixture containing benzene (70 ml) solution of $Me_2Sn(OPr^i)_2$ (1.29 g, 4.86 mmol) and HL^3 (1.22 g, 4.85 mmol) was refluxed for 10 h, during which time the liberated isopropyl alcohol was fractionated out azeotropically and estimated (0.24 g, 4.80 mmol). After completion of the reaction, the volatile components from the reaction mixture were removed under reduced pressure to yield yellow sticky product, which was recrystallized from a 4:1 mixture of toluene and n-hexane at –20°C as yellow solid. Yield, 1.68 g (75%).

Adopting a similar procedure, derivatives (**3**), (**4**), (**6**) and (9)-(**12**) were also prepared from appropriate reactants in required amounts shown in parentheses below :

(**3**) : from $Me_2Sn(OPr^i)_2$ (1.22 g, 4.59 mmol) and HL^4(1.29 g, 4.60 mmol); (**4**) : from $Me_2Sn(OPr^i)_2$ (1.37 g, 5.15 mmol) and HL^1(2.31 g, 10.25 mmol); (6) : from $Me_2Sn(OPr^i)_2$ (1.39 g, 5.22 mmol) and HL^2(2.64 g, 10.43 mmol); (9) : from $BuSn(OPr^i)_3$ (1.09 g, 10.08 mmol) and HL^3(1.04 g, 10.35 mmol); (**10**) : from $BuSn(OPr^i)_3$ (1.11 g, 3.15 mmol) and HL^3(1.60 g, 6.31 mmol); (**11**) : from $BuSn(OPr^i)_3$ (0.51 g, 1.45 mmol) and HL^3(0.09 g, 4.32 mmol); and (**12**) : from $BuSn(OPr^i)_3$ (1.24 g, 3.50 mmol) and HL^4(2.95 g, 10.50 mmol).

Reactions of (2) with an excess of alcohols

(a) With methyl alcohol

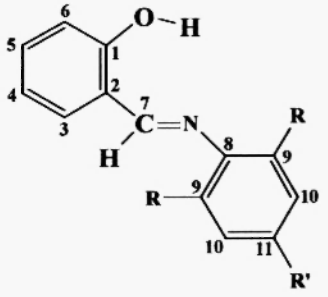
To a benzene (40 ml) solution of (**2**) (2.15 g, 4.68 mmol) was added an excess of methyl alcohol (~ 35 ml) and the resulting solution was refluxed for ~ 7 h with continuous removal of the volatile components. Removal of the remaining volatiles under reduced pressure afforded yellow solid $Me_2Sn(OMe)(OC_6H_4CH{=}NC_6H_3Et_2\text{-}2,6)$ (7), which was recrystallized from a 4:1 mixture of toluene and *n*-hexane at –20°C. Yield, 1.47 g (73%).

(b) With *tert*-butyl aclohol

To a benzene (80 ml) solution of (**2**) (2.09 g, 4.55 mmol) was added an excess of *tert*-butyl alcohol (~ 35 ml) and the resulting solution was refluxed for 14 h, during which time the liberated isopropyl alcohol was fractionated out and estimated (0.27 g, 4.53 mmol) to monitor the progress and completion of the reaction. When azeotrope showed no evidence for the presence of an oxidizable material, refluxing was stopped. Removal of the volatiles from reaction mixture under reduced pressure yielded yellow powdery solid of composition $Me_2Sn(OBu^t)(OC_6H_4CH{=}NC_6H_3Et_2\text{-}2,6)$ (**8**). Yield, 2.11 g (98%). Recrystalization from a 4:1 mixture of toluene and *n*-hexane at –20°C afforded analytically pure (**8**) in ~ 70 % yield.

RESULTS AND DISCUSSION

N-Arylsalicylaldimines (HL^1-HL^4) of the type shown below,



(HL^1) : R = Me, R' = H

(HL^2) : R, R' = Me

(HL^3) : R = Et, R' = H

(HL^4) : R = Pr^i, R' = H

and their sodium derivatives react with $Me_2Sn(OPr^i)_2$ and Me_2SnCl_2, respectively to afford yellow solid products (eq. i).

(i) $Me_2SnX_2 + n\ EOC_6H_4CH{=}NAr \xrightarrow{C_6H_6} Me_2SnX_{2-n}(OC_6H_4CH{=}NAr)_n + n\ EX$

(**1**): Ar = $C_6H_2Me_3$-2,4,6, X = Cl, E = Na, *n* = 1; (**2**): Ar = $C_6H_3Et_2$-2,6, X = OPr^i, E = H, *n* = 1;
(**3**): Ar = $C_6H_3Pr^i_2$-2,6, X = OPr^i, E = H, *n* = 1; (**4**): Ar = $C_6H_3Me_2$-2,6, X = OPr^i, E = H, *n* = 2 ;
(**5**): Ar = $C_6H_2Me_3$-2,4,6, X = Cl, E = Na, *n* = 2; (6): Ar = $C_6H_3Et_2$-2,6, X = OPr^i, E = H, *n* = 2

Reactions of (**2**) with an excess of methyl alcohol or *tert*- butyl alcohol in benzene afford (7) and (**8**), respectively (eq.ii).

(ii) (**2**) + ROH $\xrightarrow{C_6H_6}$ $Me_2Sn(OR)(OC_6H_4CH{=}NC_6H_3Et_2\text{-}2,6) + Pr^iOH$
(7) : R = CH_3 ; (**8**) : R = $C(CH_3)_3$

Interestingly, the similar reaction with a more sterically demanding 2,6-di-*tert*-butyl-4-methylphenol failed to occur to an observable extent even after refluxing over a period of more than 36 h, possibly due to steric factors.

Butyltin complexes, $BuSn(OPr^i)_{3-n}(OC_6H_4CH{=}NAr)_n$ (*n* = 1,2 or 3 ; Ar = $C_6H_3Et_2$-2,6 ; $C_6H_3Pr^i_2$-2,6) have been prepared according to the reaction (eq. iii) shown below :

(iii) $BuSn(OPr^i)_3 + n\ HOC_6H_4CH{=}NAr \xrightarrow{C_6H_6} BuSn(OPr^i)_{3-n}(OC_6H_4CH{=}NAr)_n + n\ Pr^iOH$

(9) : Ar = $C_6H_3Et_2$-2,6 (n = 1) ;(10) : Ar = $C_6H_3Et_2$-2,6 (n = 2)
(11) : Ar = $C_6H_3Et_2$-2,6 (n = 3) ; (12) : Ar = $C_6H_3Pr^i_2$-2,6 (n = 3)

Derivatives (1)-(12) (Table 1) are yellow solids, soluble in common organic solvents such as benzene, toluene, carbon tetrachloride, dichloromethane but sparingly soluble in *n*-hexane (except for butyltin complexes (9)-(12), which are freely soluble in *n*-hexane) and depict (ebullioscopically) monomeric behaviour in benzene.

Infrared spectra

As expected, the broad absorption band characteristic of hydrogen bonded -OH of the N-arylsalicylaldimines in the region 2800-3250 cm^{-1} disappeared in the IR spectra of (1)-(12) (Table I). The C=N stretching vibrations, which appeared at 1620-1626 cm^{-1}, are almost unchanged compared to those observed in free N-arylsalicylaldimines. A similar observation has been reported by Mehrotra and co-workers for dialkyltin derivatives of salicylaldimines [4]. The ν(C-O), observed in the region 1288-1300 cm^{-1}, exhibited a higher frequency shift of 15 ± 5 cm^{-1} [17]. The chelating nature of N-arylsalicylaldiminate ligands in (1)-(12) is evident by the appearance of medium intensity bands in the regions 558-573 and 410-426 cm^{-1}, which are assigned to ν(Sn-O) [18] and ν(Sn←N) [19], respectively. The bands at 520 ± 10 and 585 ± 15 cm^{-1} may be assigned to ν_s(Sn-C) and ν_{as}(Sn-C), respectively [20].

^{1}H NMR spectra

The ^{1}H NMR spectra (Table II) of (1)-(12) exhibit absence of singlet due to the hydrogen bonded phenolic OH group in the region δ 13.52-14.18 ppm. The singlet for the azomethine proton, observed in the region δ 8.58-8.71 ppm, exhibits a small (0.04-0.17 ppm) downfield shift compared to those observed in parent N-arylsalicylaldimines [21]. The aromatic ring protons appear as multiplets in the regions δ 6.90-7.86 ppm. The substituents (Me, Et, Pr^i) on aniline moiety appears in the region δ 3.68-1.77 ppm with expected multiplicity and integrated intensity ratio.

^{1}H NMR spectra of (1), (2), (3), (7), and (8) exhibit two singlets for protons of Me_2Sn(IV) at δ 0.32-0.68 ppm. In addition, (2), (3), and (9) show two distinct septets also in the region δ 3.25-4.21 ppm for $OCHMe_2$ protons. These observations indicate the existence of two isomers in the solution [22] for (1), (2), (3), (7), (8), and (9). The observed tin-proton coupling constants, 72 Hz [$^2J(^{119}Sn\text{-}H)$] and 71.2 Hz [$^2J(^{117}Sn\text{-}H)$] for (1), are consistent with pentacoordination around tin atom [4]. The C-Sn-C angle has been calculated as 121.8° using the equation $\theta(C\text{-}Sn\text{-}C) = 0.0161\ [^2J(Sn\text{-}H)]^2 - 1.32[^2J(Sn\text{-}H)] + 133.4$ [23,24], which is consistent with the two methyl groups being in equatorial positions. Derivatives (4)-(6) show a singlet at δ 0.40-0.58 ppm for Me_2Sn(IV) protons. The observed $^2J(^{119}Sn\text{-}H)$ and $^2J(^{117}Sn\text{-}H)$ for (5) and (6) are 79.7 and 77.0 Hz, consistent with hexacoordinated tin atom [25]. Similar trend for increase in coupling constant values with increase in coordination number has been reported in other dimethyl derivatives [25]. The θ(C-Sn-C angle) values calculated [23,24] from ^2J is found to be 130.4° for (5) and (6), indicating distorted octahedral geometry around tin atom. In butyltin derivatives (9)-(12), protons of butyl group appear as triplet at δ 0.94-0.98 ppm and two multiplets at δ 1.52-1.57 and 2.09-2.14 ppm, due to CH_3 and CH_2 groups, respectively. The ^2J(Sn-H) coupling constant values in butyltin derivatives could not be observed as signals due to methylene group attached to the tin atom at ~ δ 2.50 ppm are merged with the signals due to CH_2CH_3 groups present on aniline moiety of the ligand.

^{13}C NMR Spectra

^{13}C NMR spectra (Table III) of (1)-(12) show signals due to C-O and CH=N carbons in the regions δ 166.47-168.40 and 163.32-165.17 ppm, which exhibit a downfield shift of 1.5 ± 0.8 and 3 ± 0.8 ppm for C-O and CH=N groups, respectively [26]. Signals due to other aromatic carbons appear in the region δ 149.08-115.76 ppm. Me_2Sn(IV) carbons in (1), (2), (3), (7), and (8) are observed at δ 1.94-6.19 ppm as two peaks whereas a single peak at δ 1.09-5.03 ppm has been observed for the same group in (4)-(6). The $^1J(^{119}Sn\text{-}^{13}C)$ values, 505 ± 3 Hz for (1), (2), (3), (7), and (8) are consistent with five coordinate tin atom [27]. The θ(C-Sn-C angle) values in these derivatives have been estimated as ~ 125° (Table III) using the equation $^1J(^{119}Sn\text{-}^{13}C) = 9.99\ \theta - 746$ [28], which is very near to the values (~ 122°) calculated from ^2J(Sn-H) coupling constants. The signals at ~ δ 13.4, 23.8, 26.3 and 27.5 ppm in (9)-(12) are assigned to **Bu**Sn(IV) carbons. In these butyltin derivatives (9)-(12), however, the ^1J(Sn-C) coupling constant values could not be observed due to the low intensity of **Bu**-Sn carbon resonances which resulted in a poor signal / noise ratio [29].

Table I. Physical, Analytical and IR Spectral Data for Organotin(IV) N-arylsalicylaldiminate Derivatives (1)-(12)

Compound Emperical formula Yield[a] (g %)	Pr^iOH/ NaCl (g) Found (Calcd.)	Colour & State m.p (°C)	Analysis (%) Found (Calcd.) C	H	N	Sn	Cl	M. wt. Found (Calcd.)	IR (cm^{-1})
(1) $C_{18}H_{22}ClNOSn$ (3.10,54)	0.75 (0.75)	Yellow solid 115	51.08 (51.17)	5.28 (5.24)	3.27 (3.31)	27.69 (28.09)	8.35 (8.39)	430 (423)	1626 s ν(C=N), 1288 m ν(C–O), 562 m ν(Sn–O), 419 m ν(Sn←N), 580 m ν_{as}(Sn–C), 519w ν_s(Sn–C), 280w ν(Sn-Cl)
(2) $C_{22}H_{31}NO_2Sn$ (1.47,73)	0.29 (0.29)	Yellow solid 220 (dec.)	56.81 (57.42)	6.74 (6.79)	2.98 (3.04)	25.51 (25.79)	-	477 (460)	1625 s ν(C=N), 1294 m ν(C–O), 559 m ν(Sn–O), 420 w ν(Sn←N), 585 w ν_{as}(Sn–C), 522 w ν_s(Sn–C)
(3) $C_{24}H_{35}NO_2Sn$ (1.66,74)	0.27 (0.27)	Yellow solid 230 (dec.)	58.47 (59.07)	6.99 (7.22)	2.79 (2.87)	24.50 (24.31)	-	480 (488)	1627 s ν(C=N), 1294 m ν(C–O), 558 m ν(Sn–O), 415 w (Sn←N), 588 m ν_{as}(Sn–C), 520 m ν_s(Sn–C)
(4) $C_{32}H_{34}N_2O_2Sn$ (2.42,79)	0.61 (0.61)	Yellow solid 121	64.60 (64.32)	5.60 (5.74)	4.60 (4.69)	19.80 (19.86)	-	590 (597)	1624 s ν(C=N), 1288 m ν(C–O), 558 m ν(Sn–O), 422 m ν(Sn←N), 573 w ν_{as}(Sn–C), 530 w ν_s(Sn–C)
(5) $C_{34}H_{38}N_2O_2Sn$ (2.00,60)	0.60 (0.61)	Yellow solid 125	65.21 (65.30)	6.17 (6.12)	4.53 (4.47)	18.87 (18.98)	-	637 (625)	1626 s ν(C=N), 1269 m ν(C–O), 565 m ν(Sn–O), 419 m ν(Sn←N), 580 m ν_{as}(Sn–C), 519 w ν_s(Sn–C)
(6) $C_{36}H_{42}N_2O_2Sn$ (2.88,84)	0.62 (0.62)	Yellow solid 137	66.38 (66.21)	6.29 (6.48)	4.23 (4.29)	18.24 (18.16)	-	665 (6.53)	1625 s ν(C=N), 1290 m ν(C–O), 567 m ν(Sn–O), 415 m ν(Sn←N), 577 m ν_{as}(Sn–C), 529 m ν_s(Sn–C)
(7) $C_{20}H_{27}NO_3Sn$ (1.47,73)	-	Yellow solid 260 (dec.)	55.10 (55.58)	6.13 (6.29)	3.20 (3.24)	27.33 (27.40)	-	448 (433)	1626 s ν(C=N), 1294 m ν(C–O), 559 m ν(Sn–O), 426 w ν(Sn←N), 585 m ν_{as}(Sn–C), 530 w ν_s(Sn–C)
(8) $C_{22}H_{31}NO_2Sn$ (1.50,70)	0.27 (0.27)	Yellow solid 265 (dec.)	58.09 (58.26)	6.89 (7.01)	2.89 (2.95)	24.79 (25.03)	-	488 (474)	1624 s ν(C=N), 1288 s ν(C–O), 573 s ν(Sn–O), 415 w ν(Sn←N), 573 m ν_{as}(Sn–C), 536 m ν_s(Sn–C)
(9) $C_{27}H_{41}NO_3Sn$ (1.49, 82)	0.19 (0.19)	Yellow sticky solid -	58.91 (59.36)	6.70 (7.56)	2.47 (2.56)	21.39 (21.79)	-	528 (546)	1625 s ν(C=N), 1300 s ν(C–O), 560 s ν(Sn–O), 415 m ν(Sn←N), 600 s ν_{as}(Sn–C), 520 m ν_s(Sn–C)
(10) $C_{41}H_{52}N_2O_2Sn$ (1.77,76)	0.37 (0.37)	Yellow sticky solid -	66.70 (66.63)	6.89 (7.09)	3.68 (3.78)	15.81 (16.04)	-	732 (739)	1625 s ν(C=N), 1288 m ν(C–O), 559 m ν(Sn–O), 420 w ν(Sn←N), 600 w ν_{as}(Sn–C), 514 w ν_s(Sn–C)
(11) $C_{55}H_{63}N_3O_3Sn$ (1.15,85)	0.25 (0.26)	Yellow sticky solid -	70.84 (70.88)	6.70 (6.81)	4.37 (4.50)	12.59 (12.74)	-	920 (933)	1625 s ν(C=N), 1288 m ν(C–O), 558 m ν(Sn–O), 422 w ν(Sn←N), 600 m ν_{as}(Sn–C), 522 m ν_s(Sn–C)
(12) $C_{61}H_{75}N_3O_3Sn$ (2.74,77)	0.62 (0.63)	Yellow solid -	70.68 (72.06)	7.28 (7.43)	4.37 (4.13)	11.58 (11.67)	-	1020 (1017)	1626 s ν(C=N), 1294 m ν(C–O), 558 m ν(Sn–O), 420 m ν(Sn←N), 588 m ν_{as}(Sn–C), 520 m ν_s(Sn–C)

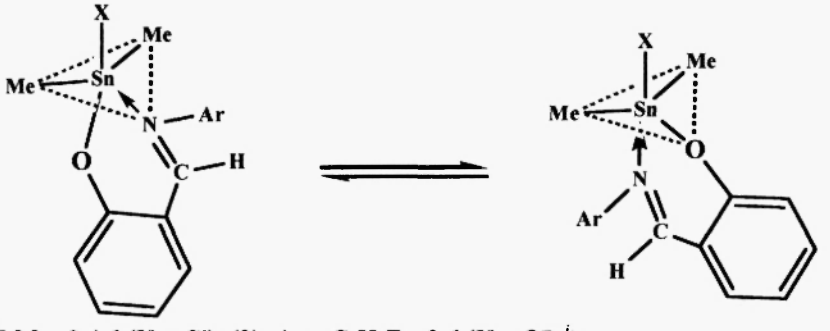
[a]Corresponds to recrystallized product.

Table II. ^{1}H and ^{119}Sn NMR Data (δ, ppm) for Organotin(IV) N-arylsalicylaldiminate Derivatives.

Compound	-CH=N-	Ar-H	Me/Et/Pr^{i} / Me_2Sn/ Bu-Sn	^{119}Sn NMR
(1)	8.58 (s, 1H)	6.94-7.57 (m,6H)	2.31(s, 3H, Me-4), 2.19(s, 6H, Me-2,6), 0.58, 0.67(s, 6H, **Me_2**Sn)	-
(2)	8.58 (s,1H)	7.75-6.90 (m,7H)	4.22, 3.65(sept, J = 6.2 Hz, 1H, OC**H**Me_2), 2.60 (q, J = 6.2 Hz, 4H, CH_2CH_3), 1.17 (t, J = 6.2 Hz, 12H, CH_2**CH_3** + OCH**Me_2**), 0.64,0.58(s, 6**H**, **Me_2**Sn)	-139.4, -170.2
(3)	8.67 (s,1H)	7.80-7.10 (m,7H)	4.20, 3.60 (sept, J = 6.2 Hz, 1H, OC**H**Me_2), 2.94 (sept, J = 6.2 Hz, 2H, C**H**Me_2), 1.21 (d, J = 6.2 Hz, 18H, OCH**Me_2** + CH**Me_2**), 0.67, 0.56(s,6H, **Me_2**Sn)	-138.8, -168.3
(4)	8.59 (s,2H)	7.72-6.96 (m,14H)	2.28(s,12H,CH_3), 0.40(s,6H, **Me_2**Sn)	-340.5
(5)	8.59 (s,2H)	6.84-7.69 (m,12H)	2.31(s,6H,Me-4), 2.18(s,12H,Me-2,6), 0.51(s,6H, **Me_2**Sn)	-342.9
(6)	8.64 (s,2H)	7.83-7.08 (m,14H)	2.65(q, J = 6.2 Hz, 8H,CH_2CH_3), 1.20 (t, J = 6.2 Hz, 12H, CH_2**CH_3**), 0.58(s,6H, **Me_2**Sn)	-356.8
(7)	8.64 (s,1H)	7.86-7.08 (m,7H)	2.68 (q, J = 6.2 Hz, 4H,CH_2CH_3), 1.23 (t, J = 6.2 Hz, 6H, CH_2CH_3+ O**CH_3**), 0.52,0.32(s,6H, **Me_2**Sn)	-131.5, -170.8
(8)	8.58 (s,1H)	7.80-7.02 (m,7H)	2.56 (q, J = 6.2 Hz, 4H, CH_2CH_3), 1.17 (t, J = 6.2 Hz, 15H, CH_2CH_3+ O**Me_3**), 0.61,0.48(s,6H, **Me_2**Sn)	-142.5, -171.1
(9)	8.71 (s,1H)	7.73-7.24 (m,7H)	4.19,3.25 (sept, J = 6.2 Hz, 2H, OCH**Me_2**), 2.50 (q, J = 6.2 Hz, 6H, CH_2CH_3 + -CH_2Sn), 2.09(m, 2H,CH_3CH_2 CH_2CH_2-), 1.57(m, 2H, $CH_3CH_2CH_2CH_2$-), 1.26(t, J = 6.2 Hz, 18H,CH_2CH_3+ OCH**Me_2**), 0.94(t, J = 6.2 Hz, 3H, $CH_3CH_2CH_2CH_2$-)	-436.3, -446.6
(10)	8.64 (s,2H)	7.80-6.95 (m,14H)	4.12 (sept, J = 6.2 Hz, 1H, OCH**Me_2**), 2.65 (q, J = 6.2 Hz, 10H, CH_2CH_3 + -CH_2Sn), 2.11(m, 2H, $CH_3CH_2CH_2CH_2$-), 1.57(m, 2H, $CH_3CH_2CH_2CH_2$-), 1.20(t, J = 6.2 Hz, 18H, CH_2 CH_3 + OCH**Me_2**), 0.96(t, J = 6.2 Hz, 3H, $CH_3CH_2CH_2CH_2$-)	-577.3
(11)	8.67 (s,3H)	7.86-7.11 (m,21H)	2.63 (q, J = 6.2 Hz, 14H, CH_2CH_3 + -CH_2Sn), 2.13(m,2H, $CH_3CH_2CH_2CH_2$-), 1.57(m, 2H, $CH_3CH_2CH_2CH_2$-), 1.20(t, J = 6.2 Hz, 18H,CH_2CH_3+ OCH**Me_2**), 0.97(t, J = 6.2 Hz, 3H, $CH_3CH_2CH_2CH_2$-)	-726.3
(12)	8.67 (s,3H)	7.80-6.98 (m,21H)	2.94 (sept, J = 6.2 Hz, 8H, C**H**Me_2 + -CH_2Sn), 2.13(m, 2H, $CH_3CH_2CH_2CH_2$-), 1.57(m, 2H, $CH_3CH_2CH_2CH_2$-), 1.21(d, J = 6.2 Hz, 36H,CH**Me_2**), 0.98(t, J = 6.2 Hz, 3H, $CH_3CH_2CH_2CH_2$-)	-757.3

^{119}Sn NMR spectra

^{119}Sn NMR spectra (Table II) of (**2**), (**3**), (**7**) and (**8**) show two distinct signals at δ -137 ± 6 and -170 ± 2 ppm in 3:2 relative intensity ratios, consistent with penta coordinated tin atom [30] in two isomeric forms as shown below.

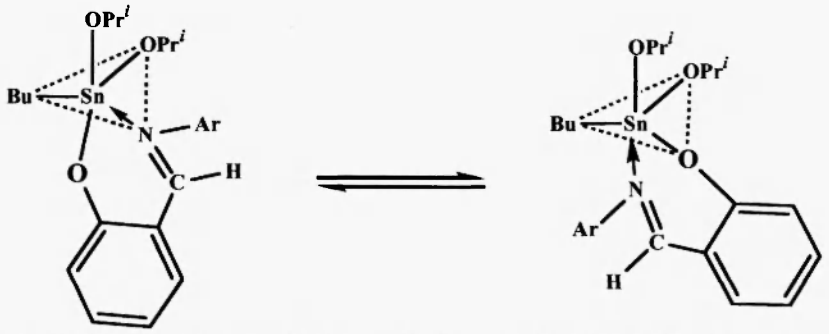


(**1**): Ar = $C_6H_2Me_3$-2,4,6 (X = Cl); (**2**): Ar = $C_6H_3Et_2$-2,6 (X = OPr^{i});
(**3**): Ar = $C_6H_3Pr^{i}_2$-2,6 (X = OPr^{i}); (**7**): Ar = $C_6H_3Et_2$-2,6 (X = OMe);
(**8**): Ar = $C_6H_3Et_2$-2,6 (X = OBu^{t})

Table III. ^{13}C NMR Data (δ, ppm) for Organotin (IV) N-arylsalicylaldiminate Derivatives.

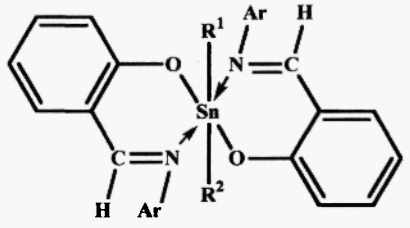
Compound	^{13}C NMR
(1)	166.68 (C-1), 163.45 (C-7), 145.84 (C-8), 133.62 (C-11), 132.71 (C-5), 131.67 (C-3), 128.87 (C-9), 127.64 (C-10), 118.60 (C-4), 118.34 (C-6), 117.43 (C-2), 20.79 (**Me**-4), 18.45 (**Me**-2,6), 6.15, 4.10 (**Me**$_2$Sn, $^1J(^{119}Sn\text{-}^{13}C)$ = 501.7 Hz, 0(C-Sn-C) = 124.9).
(2)	166.85 (C-1), 165.17 (C-7), 149.88 (C-8), 134.61 (C-9), 133.85 (C-5), 132.18 (C-3), 26.16 (C-10), 125.08 (C-11), 122.26 (C-4 and C-6), 117.11 (C-2), 65.50 (O**C**HMe$_2$), 26.54 OCH**Me**$_2$), 24.59(**C**H$_2$CH$_3$), 15.05 (CH$_2$**C**H$_3$), 6.08, 4.81 (**Me**$_2$Sn, $^1J(^{119}Sn\text{-}^{13}C)$ = 501.7 Hz, θ(C-Sn-C) = 124.9).
(3)	167.01 (C-1), 165.10 (C-7), 147.80 (C-8), 139.38 (C-9), 133.85 (C-5), 132.23(C-3), 125.40 (C-11), 123.18 (C-10), 122.32 (C-4), 121.29 (C-6), 117.33 (C-2), 65.38 (O**C**HMe$_2$), 27.84 (**C**HMe$_2$), 26.80 (OCH**Me**$_2$), 23.88 (**C**H**Me**$_2$), 6.19, 5.20 (**Me**$_2$Sn, $^1J(^{119}Sn\text{-}^{13}C)$ = 507.7 Hz, θ(C-Sn-C) = 125.4).
(4)	166.63 (C-1), 163.32 (C-7), 148.16 (C-8), 132.84 (C-5), 131.85 (C-3), 128.94 (C-9), 128.16 (C-10), 124.71 (C-11), 118.47 (C-4 and C-6), 117.30 (C-2), 18.45 (**Me**-2,6), 1.04 (**Me**$_2$-Sn)
(5)	166.60 (C-1), 163.50 (C-7), 145.89 (C-8), 133.60 (C-11), 132.71 (C-5), 131.56 (C-3), 128.69 (C-9), 127.71 (C-10), 118.57 (C-4), 118.17 (C-6), 117.37 (C-2), 20.90 (**Me**-4), 18.49 (**Me**-2,6), 4.97 (**Me**$_2$Sn)
(6)	167.96 (C-1), 164.15 (C-7), 147.62 (C-8), 134.23 (C-9), 133.96 (C-5), 131.90 (C-3), 126.87 (C-10), 125.51 (C-11), 118.74 (C-4), 118.44 (C-6), 117.48 (C-2), 24.75 (**C**H$_2$CH$_3$), 14.89 (CH$_2$**C**H$_3$), 5.03 (**Me**$_2$Sn).
(7)	166.47 (C-1), 163.65 (C-7), 148.90 (C-8), 134.18 (C-9), 133.37 (C-5), 131.90 (C-3), 126.22 (C-10), 125.82 (C-11), 119.01 (C-4), 117.71 (C-6), 116.79 (C-2), 48.69 (O**C**H$_3$), 24.75 (**C**H$_2$CH$_3$), 14.89 (CH$_2$**C**H$_3$), 4.00, 1.94 (**Me**$_2$Sn, $^1J(^{119}Sn\text{-}^{13}C)$ = 501.7 Hz, θ(C-Sn-C) = 124.9).
(8)	166.60 (C-1), 163.60 (C-7), 148.93 (C-8), 134.11 (C-9), 133.23 (C-5), 131.87 (C-3), 126.41 (C-10), 125.70 (C-11), 118.69 (C-4), 117.57 (C-6), 116.59 (C-2), 68.57 (O**C**Me$_3$), 31.31 (OC**Me**$_3$), 24.75 (**C**H$_2$CH$_3$), 14.87 (CH$_2$**C**H$_3$), 6.15, 4.90 (**Me**$_2$Sn, $^1J(^{119}Sn\text{-}^{13}C)$ = 501.7 Hz, 0(C-Sn-C) = 124.9).
(9)	168.36 (C-1), 163.51 (C-7), 148.09 (C-8), 135.37 (C-9), 134.83 (C-5), 132.39 (C-3), 126.05 (C-10), 125.30 (C-11), 122.15 (C-4), 116.19 (C-6), 115.76 (C-2), 65.97 (O**C**HMe$_2$), 27.51 (C-α, Bu-Sn), 26.81 (OCH**Me**$_2$), 26.32 (C-β, Bu-Sn), 24.64 (**C**H$_2$CH$_3$), 24.15 (C-γ, Bu-Sn), 14.89 (CH$_2$**C**H$_3$), 13.81 (C-δ, Bu-Sn).
(10)	168.40 (C-1), 163.50 (C-7), 147.80 (C-8), 135.75 (C-9), 134.91 (C-5), 132.69 (C-3), 126.11 (C-10), 125.35 (C-11), 118.41 (C-4), 118.05 (C-6), 116.34 (C-2), 64.95 (O**C**HMe$_2$), 27.51 (C-α, Bu-Sn), 26.81 (OCH**Me**$_2$), 26.32 (C-β, Bu-Sn), 24.64 (**C**H$_2$CH$_3$), 23.83 (C-γ, Bu-Sn), 14.89 (CH$_2$**C**H$_3$), 13.81 (C-δ, Bu-Sn).
(11)	167.61 (C-1), 163.41 (C-7), 148.10 (C-8), 135.81 (C-9), 134.80 (C-5), 132.68 (C-3), 126.70 (C-10), 125.63 (C-11), 118.17 (C-4), 117.94 (C-6), 116.17 (C-2), 27.30 (C-α, Bu-Sn), 26.41 (C-β, Bu-Sn), 24.60 (**C**H$_2$CH$_3$), 22.80 (C-γ, Bu-Sn), 14.80 (CH$_2$**C**H$_3$), 13.47 (C-δ, Bu-Sn).
(12)	167.12 (C-1), 162.08 (C-7), 146.37 (C-8), 138.19 (C-9), 132.88 (C-5), 131.74 (C-3), 125.19 (C-11), 122.97 (C-10), 118.47 (C-4), 118.36 (C-6), 117.49 (C-2), 28.00 (**C**HMe$_2$), 27.35 (C-α, Bu-Sn), 26.48 (C-β, Bu-Sn), 23.56 (CH**Me**$_2$), 22.69 (C-γ, Bu-Sn), 13.43 (C-δ, Bu-Sn).

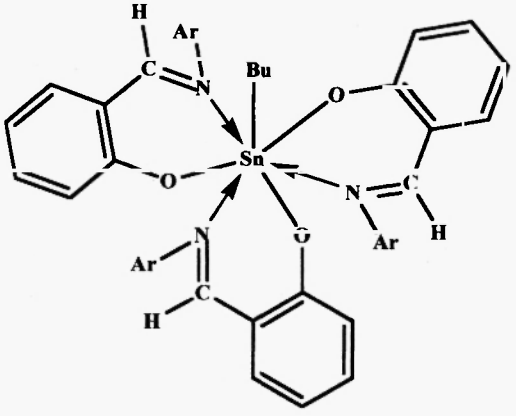
The butyltin derivative (**9**) shows two ^{117}Sn NMR peaks in 1 : 2 relative intensities at δ -436.3 and -446.6 ppm, respectively, indicating five-coordinate tin atom [31-33] and presence of two isomers as shown below in which butyl group is in equatorial position, consistent with the earlier observations [29, 34].



An octahedral environment [35] around tin atom in dimethyltin derivatives (**4**)-(**6**) and butyltin derivative (**10**) is supported by the appearance of single ^{119}Sn NMR peak at δ -348 ± 8 and – 577.3 ppm,

respectively. Seven coordinated tin atom in derivatives **(11)** and **(12)** is supported by the single ^{119}Sn NMR peak at δ –726.3 and – 757.3 ppm, respectively. These ^{119}Sn NMR values are consistent with the earlier observations [36,37] of upfield shifts with increasing coordination number of tin.





(4): Ar = $C_6H_3Me_2$-2,6 (R^1, R^2 = Me)
(5): Ar = $C_6H_2Me_3$-2,4,6 (R^1, R^2 = Me)
(6): Ar = $C_6H_3Et_2$-2,6 (R^1, R^2 = Me)
(10): Ar = $C_6H_3Et_2$-2,6 (R^1 = Bu, R^2 = OPr^i)
(11): Ar = $C_6H_3Et_2$-2,6
(12): Ar = $C_6H_3Pr^i_2$-2,6

ACKNOWLEDGEMENTS

A.S. thanks the University Grants Commission (UGC), New Delhi for the Emeritus Scientist Award. **S.M.** is grateful to the State Government of Rajasthan and the Department of Chemistry, University of Rajasthan for the followship under Special Assistance Programme.

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Received: November 15, 2001 - Accepted: November 26, 2001 - Accepted in publishable format: March 20, 2002