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Some New Salicyldeneimine Complexes of Diorganotin(IV)

RASHMI TIWARI, G. SRIVASTAVA, R. C. MEHROTRA

Department of Chemistry, University of Rajasthan, Jaipur, India

and A. J. CROWE

International Tin Research Institute, Greenford, U.K.

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Abstract

Sixteen new dialkyltin derivatives of the type $R_2\overline{SnOC_6H_4C(R')=NR''O}$ (R = Me, Et, Bu and Ph; R' = H and Me and R'' = $-CH_2CH_2-$ and $-CH_2CH_2CH_2-$) have been synthesised by the reactions of dialkyltin diisopropoxides with the corresponding Schiff bases in refluxing benzene, followed by removal of isopropanol azeotropically. Pentacoordination of tin in these compounds has been proposed on the basis of elemental analyses, molecular weight determinations, IR, PMR and Mössbauer spectral studies.

Introduction

The Schiff base complexes of organotin(IV) moieties have been widely investigated [1–4] and the subject has been recently reviewed [5]. Interest in these compounds may be ascribed to their novel structural features, which are possibly caused by the multidenticity of Schiff base ligands.

The bifunctional tridentate Schiff bases, in particular ketamines and aldimines show a remarkable tendency to complexation with different metals [6–9]. Therefore, we have employed some of these ligands in the syntheses of some new Schiff base complexes of diorganotin moieties.

Experimental

Special precautions were taken to exclude moisture throughout the experimental manipulations. Benzene and isopropanol were dried by standard methods. Schiff bases [10] and dialkyltin diisopropoxides [11] were prepared by the methods reported in the literature.

Nitrogen was estimated by Kjeldahl's method [12] and tin was estimated as SnO_2.

Molecular weights were determined cryoscopically in benzene. IR spectra were recorded on a Perkin-Elmer 577 spectrophotometer in the range 4000–200 cm^{-1} as nujol mulls using CsI plates. PMR spectra were obtained in CCl_4 and $CDCl_3$ using TMS as an internal standard on a Varian XL 100A spectrophotometer.

The ^{119m}Sn Mössbauer spectra were obtained from the International Tin Research Institute, Greenford using a constant acceleration microprocessor spectrometer with a 512 channel data store. A 15 mCi Ba $^{119m}SnO_3$ source was used at room temperature and the samples were packed in a perspex disc. Spectra were recorded at 80 K using a liquid nitrogen crystal and fitted with Lorentzian functions by a least-squares fitting programme.

In addition to the values reported for the complex, values (QS = 1.25 mm s^{-1}; I.S. = 0.60 mm s^{-1}) were also observed in the Mössbauer spectrum of the derivative. These arose, obviously, from the hydrolysis of the derivative during transit, etc.

Reaction of Dimethyltin Diisopropoxide with N-2-Hydroxyethyl Salicyldeneimine in 1:1 Molar Ratio

A mixture of dimethyltin diisopropoxide (0.82 g, 3.08 mmol) and N-2-hydroxyethyl salicyldeneimine (0.51 g, 3.09 mmol) was refluxed in anhydrous benzene (~70 ml) and the isopropanol liberated in the reaction was removed azeotropically in 4 h and estimated by the usual method. Excess of the solvent was removed under reduced pressure and a yellow, powdery solid was obtained.

Similarly, other complexes were obtained adopting the above procedure. The pertinent data of these complexes have been compiled in Table I.

Results and Discussion

Reactions of dialkyltin diisopropoxides with bifunctional tridentate ketamines and aldimines (derived from the condensation of salicyldehyde and 2-hydroxy acetophenone with amino alcohols) in 1:1 molar ratio in refluxing benzene led to the liberation of 2 mol of isopropanol.

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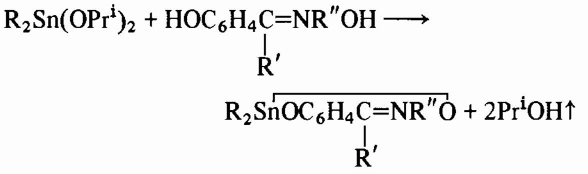
TABLE I. Analytical Data of Dialkyltin Derivatives of Ketamines and Aldimines

Reactants (g)			Product (% Yield)	Pr^iOH (g), Found (Calcd.)	Physical state, m.p. (°C)	% Analysis, Found (Calcd.)		Molecular weight Found (Calcd.)
$R_2Sn(OPr^i)_2$ (R)	$HOC_6H_4C(R')=NR''OH$							
	(R')	(R'')				Sn	N	
Me (0.82)	H	$-CH_2CH_2-$ (0.51)	$Me_2\overline{SnOC_6H_4CH{=}NCH_2CH_2O}$ 97	0.3403 (0.3692)	Yellow powdery solid, 147	38.25 (38.10)	4.25 (4.50)	295 (311)
Et (1.37)	H	$-CH_2CH_2-$ (0.77)	$Et_2\overline{SnOC_6H_4CH{=}NCH_2CH_2O}$ 99	0.5161 (0.5574)	Yellow powdery solid, 84–85	34.84 (34.94)	4.12 (4.12)	368 (340)
Bu (0.89)	H	$-CH_2CH_2$ (0.42)	$Bu_2\overline{SnOC_6H_4CH{=}NCH_2CH_2O}$ 99	0.2988 (0.3018)	Deep yellow sticky solid	29.92 (29.99)	3.42 (3.54)	
Ph (1.22)	H	$-CH_2CH_2$ (0.52)	$Ph_2\overline{SnOC_6H_4CH{=}NCH_2CH_2O}$ 91	0.3782 (0.3754)	Light-yellow powdery solid, 177	27.38 (27.24)	3.10 (3.20)	392 (435)
Me (1.24)	CH_3	$-CH_2CH_2$ (0.85)	$Me_2\overline{SnOC_6H_4CCH_3{=}NCH_2CH_2O}$ 80	0.5338 (0.5601)	Light yellow powdery solid, 172–174	36.35 (36.44)	4.28 (4.30)	
Et (1.18)	CH_3	$-CH_2CH_2$ (0.72)	$Et_2\overline{SnOC_6H_4CCH_3{=}NCH_2CH_2O}$ 97	0.5124 (0.4802)	Yellow powdery solid, 127	33.91 (33.56)	3.91 (3.96)	
Bu (1.33)	CH_3	$-CH_2CH_2-$ (0.68)	$Bu_2\overline{SnOC_6H_4CCH_3{=}NCH_2CH_2O}$ 94	0.3752 (0.4543)	Yellow solid	28.40 (28.97)	3.48 (3.42)	
Ph (1.35)	CH_3	$-CH_2CH_2-$ (0.64)	$Ph_2\overline{SnOC_6H_4CCH_3{=}NCH_2CH_2O}$	0.4082 (0.4164)	Light yellow powdery solid, 147–149	26.31 (26.39)	2.77 (3.10)	
Me (1.47)	H	$-CH_2CH_2CH_2-$ (0.99)	$Me_2\overline{SnOC_6H_4CH{=}NCH_2CH_2CH_2O}$ 97	0.6011 (0.6615)	Yellow sticky solid	36.40 (36.44)	3.80 (4.30)	
Et (1.12)	H	$-CH_2CH_2CH_2-$ (0.68)	$Et_2\overline{SnOC_6H_4CH{=}NCH_2CH_2CH_2O}$ 97	0.4946 (0.4557)	Yellow sticky solid	33.24 (33.56)	3.86 (3.96)	
Bu (1.54)	H	$-CH_2CH_2CH_2-$ (0.81)	$Bu_2\overline{SnOC_6H_4CH{=}NCH_2CH_2CH_2O}$ 98	0.4757 (0.5271)	Yellow sticky solid	28.73 (28.97)	3.48 (3.42)	
Ph (1.13)	H	$-CH_2CH_2CH_2-$ (0.53)	$Ph_2\overline{SnOC_6H_4CH{=}NCH_2CH_2CH_2O}$ 97	0.2771 (0.3484)	Yellow powdery solid, 223–225, dec.	26.36 (26.40)	2.78 (3.10)	
Me (1.06)	CH_3	$-CH_2CH_2CH_2-$ (0.77)	$Me_2\overline{SnOC_6H_4CCH_3{=}NCH_2CH_2CH_2O}$ 92	0.4894 (0.4777)	Yellow crystalline solid, 240–243	34.84 (34.94)	3.91 (4.12)	
Et (1.47)	CH_3	$-CH_2CH_2CH_2-$ (0.97)	$Et_2\overline{SnOC_6H_4CCH_3{=}NCH_2CH_2CH_2O}$ 98	0.6058 (0.5972)	Yellow powdery solid	32.20 (32.28)	3.63 (3.81)	
Bu (1.20)	CH_3	$-CH_2CH_2CH_2-$ (0.66)	$Bu_2\overline{SnOC_6H_4CCH_3{=}NCH_2CH_2CH_2O}$ 97	0.4435 (0.4113)	Yellow viscous liquid	27.96 (28.01)	3.14 (3.30)	
Ph (1.50)	CH_3	$-CH_2CH_2CH_2-$ (0.66)	$Ph_2\overline{SnOC_6H_4CCH_3{=}NCH_2CH_2CH_2O}$ 97	0.4049 (0.4615)	Yellow crystalline solid, 215	25.45 (25.60)	3.17 (3.02)	



$$R_2Sn(OPr^i)_2 + HOC_6H_4\underset{R'}{C}{=}NR''OH \longrightarrow R_2Sn\overline{OC_6H_4\underset{R'}{C}{=}NR''O} + 2Pr^iOH\uparrow$$

(R = Me, Et, Bu and Ph: R' = H and Me and R'' = $-CH_2-CH_2-$ and $-CH_2CH_2CH_2-$)

The reactions were pushed to completion in 4–6 h by fractionating out the liberated isopropanol azeotropically with benzene. The completion of the reaction was checked by determining the amount of isopropanol in the azeotrope, estimated by an oxidimetric method [13].

All these compounds (Table I) are yellow powders (a few are of a sticky nature) which are all soluble in C_6H_6, $CHCl_3$ and CCl_4. These tend to hydrolyse in air and are sensitive even to atmospheric moisture. These derivatives have been shown to be monomeric in freezing benzene.

The broad absorption bands of strong to medium intensities in the region 3325–3515 cm^{-1}, due to intramolecularly hydrogen bonded –OH [14] in the IR spectra of the free ligands, disappear in the IR spectra of these organotin complexes indicating the reactivity of both the –OH groups.

The C=N stretching vibrations observed in the region 1615–1625 cm^{-1} in the IR spectra of the free ligands [1, 14] occur almost at same position in the spectra of these complexes. It has been reported that on chelation, the C=N stretching vibration of the Schiff base is only very slightly changed [15].

The ν_{as} (Sn–C) and ν_s (Sn–C) bands have been found to appear at 510 ± 10 cm^{-1} and 485 ± 10 cm^{-1}, respectively [16, 17]. ν (Sn–O) has been empirically estimated by Poller [18] to occur at 570 cm^{-1} and the range 550–570 cm^{-1} has already been suggested by us [19]. Pertinent IR spectral data are given in Table II.

In the PMR spectra the multiplets due to phenyl and butyl protons attached to tin appear in the range δ 6.60–8.08 and δ 0.9–1.84, respectively, while a singlet due to methyl protons appears at δ 0.66.

In the case of butyltin complexes, a clear triplet for terminal methyl protons occurs in the range δ 0.76–1.04 (Table III).

The CH=N signal generally occurs at δ 8.44, which is slightly downfield compared to the signal in the PMR spectra of the free ligand, thus confirming the coordination of azomethine nitrogen with the tin atom.

The coupling constant $J(^{119/117}Sn-^1H)$ is found about 72 cps., which, again, conforms with pentacoordination for tin [20] in these complexes, in solution.

The Mössbauer spectrum of only one compound *i.e.* $Ph_2Sn\overline{OC_6H_4C{\cdot}CH_3{=}NCH_2CH_2CH_2O}$ has been recorded and the values of quadrupole splitting (1.92 mm s^{-1}) and isomer shift (0.94 mm s^{-1}) again prompt to pentacoordination of tin [21–23] in this complex. Similar to other derivatives [5, 17] of the same type, a trigonal bipyramidal geometry has been proposed for these complexes on the basis of the above evidence.

TABLE II. IR Spectral Data (cm^{-1}) of Dialkyltin Derivatives of Ketamines and Aldimines

Compound	ν (C=N)	ν (C–O)	ν_{as} (Sn–C) ν_s (Sn–C)	ν (Sn–O)
$Me_2Sn\overline{OC_6H_4CH{=}NCH_2CH_2O}$	1615s	1275m	520m 490m	570m
$Et_2Sn\overline{OC_6H_4CH{=}NCH_2CH_2O}$	1625s	1240w	530s 500s	580w
$Bu_2Sn\overline{OC_6H_4CH{=}NCH_2CH_2O}$	1610s	1268w	515m 485m	570m
$Ph_2Sn\overline{OC_6H_4CH{=}NCH_2CH_2O}$	1615s	1250w	530s 500m	595s
$Me_2Sn\overline{OC_6H_4C{\cdot}CH_3{=}NCH_2CH_2O}$	1605m	1200s	520m 470m	570s
$Et_2Sn\overline{OC_6H_4C{\cdot}CH_3{=}NCH_2CH_2O}$	1605s	1205s	535s 480m	585s
$Bu_2Sn\overline{OC_6H_4C{\cdot}CH_3{=}NCH_2CH_2O}$	1600s	1265s	530s 485w	570s
$Me_2Sn\overline{OC_6H_4C{\cdot}CH_3{=}NCH_2CH_2CH_2O}$	1615s	1270w	520m 490s	580s

TABLE III. ^{1}H NMR Spectral Data of Dialkyltin Derivatives of Ketamines and Aldimines

Compound	δ (ppm)
$Me_2\overline{SnOC_6H_4CH{=}NCH_2CH_2O}$	8.44, s, 1H (–CH), 7.40–7.04, m, 2H(3, 6H of Ph ring); 6.88–6.54, m, 2H(4, 5H of Ph ring), 4.08, t, 2H(–OCH_2); 3.68, t, 2H(–NCH_2), 0.66, s, 6H(–SnMe)
$Et_2\overline{SnOC_6H_4CH{=}NCH_2CH_2O}$	8.46, s, 1H(–CH), 7.48–7.00, m, 2H(3, 6H of Ph ring); 6.84–6.54, m, 2H (4, 5H of Ph ring), 4.14, t, 2H(–OCH_2); 3.66, t, 2H(–NCH_2), 1.24–1.20,s, 10H(–SnEt)
$Bu_2\overline{SnOC_6H_4CH{=}NCH_2CH_2O}$	8.44, s, 1H(–CH), 7.44–7.0, m, 2H(3, 6H of Ph ring); 6.84–6.54, m, 2H(4,5H of Ph ring), 4.10, t, 2H(–OCH_2); 3.66, t, 2H(–NCH_2), 1.84–1.14, m, 12H-(–$CH_2CH_2CH_2$), 0.9, t, 6H(–CH_3)
$Ph_2\overline{SnOC_6H_4CH{=}NCH_2CH_2O}$	8.44, s, 1H(–CH), 8.08–6.60, m, 14(Ph + 2Ph), 4.27, t, 2H(–OCH_2); 3.34, t, 2H(–NCH_2)
$Me_2\overline{SnOC_6H_4CCH_3{=}NCH_2CH_2O}$	7.50–7.04, m, 2H(3, 6H of Ph ring); 6.86–6.32, m, 2H(4, 5H of Ph ring), 3.86, t, 2H(–OCH_2); 3.64, t, 2H(–NCH_2), 2.26, s, 3H(C–Me), 1.105, s, 10(–SnMe)
$Ph_2\overline{SnOC_6H_4CCH_3{=}NCH_2CH_2O}$	7.96–7.86, m, 4H(–Ph ring); 7.50–7.28, m, 10H(–SnPh), 4.24, t, 2H(–OCH_2) 3.66, t, 2H(–NCH_2), 2.56, s, 3H(C–Me)
$Me_2\overline{SnOC_6H_4CCH_3{=}NCH_2CH_2CH_2O}$	7.44–7.20, m, 2H(3, 6H of Ph ring); 6.92–6.60, m, 2H(4, 5H of Ph ring), 3.54–3.785, m, 4H(–OCH_2 + –NCH_2), 2.185, s, 3H(C–Me), 2.12–1.78, m, 2H(–CH_2)
$Et_2\overline{SnOC_6H_4CCH_3{=}NCH_2CH_2CH_2O}$	7.48–7.08, m, 2H(3, 6H of Ph ring); 6.90–6.54, m, 2H(4, 5H of Ph ring), 3.88–3.56, m, 4H(–OCH_2 + –NCH_2), 2.28, s, 3H(C–Me), 2.08–1.84, m, 2H(–CH_2)
$Ph_2\overline{SnOC_6H_4CCH_3{=}NCH_2CH_2CH_2O}$	7.58–7.10, m, 2H(3, 6H of Ph ring); 6.94–6.52, m, 2H(4, 5H of Ph ring), 3.52–3.92 m, 4H(–OCH_2 + –NCH_2), 2.31, s, 3H(C–Me); 1.76–2.14, m, 2H(–CH_2)

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