Synthesis and Ligand Exchange Reaction of Some Organotin(IV) Bis(N-arylsulphonyl-N-arylhydroxylaminates)

Mrinal K. Das*, Matilal Nath, and Somnath De

Department of Chemistry, Jadavpur University, Calcutta 700032, India
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Organotin(IV), N-Arylsulphonyl-N-arylhydroxylamines, Synthesis, Ligand Exchange Reaction

Several diorganotin(IV)-bis(N-arylsulphonyl-N-arylhydroxylamines) of the general formula \( R_2 Sn[(ON(R')SO_2)R'_2]_2 \) have been synthesized and characterized by elemental analyses and by IR and \(^1\)H NMR spectra. A representative ligand exchange reaction with N-benzoyl-N-phenylhydroxylamine has been carried out.

Introduction

Organotin(IV) complexes of substituted hydroxylamines (or hydroxamic acids) have received considerable attention [1–5], because of their potential biological properties arising out of the combined effects of pharmaceutical and biocidal properties of the hydroxamic acids [6–9] and organotin moieties [10–13], respectively. A very similar group of substituted hydroxylamines, viz. N-arylsulphonyl hydroxylamines [14], have attracted little attention [4] in this respect. We, therefore, report here the synthesis of a few organotin(IV) compounds derived from them, and a ligand exchange reaction.

Experimental

Dibutyltin dichloride (Alfa, U.S.A.) and diphenyltin dichloride (Merck, F.R.G.) were used as received. All solvents and chemicals were of reagent grade quality, and the solvents were dried by usual methods.

Infrared spectra were recorded (in the range 4000–300 cm\(^{-1}\)) as KBr pellets on a Beckman 20A or a Perkin-Elmer 597 or 883 spectrophotometer, and \(^1\)H NMR spectra were recorded on a Varian T-60A or a Hitachi R-600 or a Jeol JNM FX 100 spectrometer in CDCl\(_3\) using TMS as internal reference.

Preparation of ligands

The following ligands have been prepared by condensing arylhydroxylamines with arylsulphonyl chlorides in the presence of pyridine in absolute methanol based on a literature method [14]:

\[
\begin{align*}
C_6H_5SO_2N(C_6H_5)OH (Ps-PHAH) \\
4-CH_3C_6H_4SO_2N(C_6H_5)OH (Ts-PHAH) \\
4-CH_3C_6H_4SO_2N(4-CH_3C_6H_4)OH (Ts-4MePHAH)
\end{align*}
\]

Preparation of the diorganotin(IV) bis(N-arylsulphonyl-N-arylhydroxylamines)

Diorganotin(IV) dichloride, \( R_2SnCl_2 \) (\( R = C_6H_5, n-C_4H_9 \)) (3.44 g for \( R = C_6H_5 \); 3.04 g for \( R = n-C_4H_9 \); 10 mmol), and the appropriate hydroxylamine (\( Ps-PHAH \), 4.98 g; \( Ts-PHAH \), 5.26 g; \( Ts-4MePHAH \), 5.54 g; 20 mmol) were taken in dry benzene (100 ml) in a two-neck flask (250 cm\(^3\)), fitted with a reflux condenser having a fused CaCl\(_2\) drying tube on the top of it. To this, anhydrous triethylamine (2.22 g, 22 mmol) diluted with benzene (10 ml) was added dropwise with constant stirring from a pressure equalizing dropping funnel. The mixture was refluxed on a water bath for 4 h in order to ensure complete reaction. After cooling to room temperature, the precipitated silky-white triethylamine hydrochloride was separated by suction filtration. On removal of the solvent on a rotary evaporator, the compounds in their crude form were obtained as pasty masses. The pasty mass was then triturated several times with petroleum ether (40–60 °C) and then refrigerated for several days while keeping it under petroleum ether to obtain a solid mass. The solid masses were then recrystallized from a suitable solvent (Table I).

Reaction of diphenyltin(IV) bis(N-p-toluene-sulphonyl-N-phenylhydroxylamine) with N-benzoyl-N-phenylhydroxylamine

A solution of diphenyltin(IV) bis(N-p-toluene-sulphonyl-N-phenylhydroxylamine) (3.99 g, 5 mmol) and N-benzoyl-N-phenylhydroxylamine

* Reprint requests to Prof. M. K. Das.

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Table I. Physical and analytical data of \( R_2 \text{Sn}[\text{ON}(R')\text{SO}_2 R_2]_2 \).

<table>
<thead>
<tr>
<th>Compound No.</th>
<th>M.P. (°C)</th>
<th>Solvent of recrystallization</th>
<th>Colour</th>
<th>Analytical data Found (%) (Calcd)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>126–128</td>
<td>benzene-petroleum ether</td>
<td>colourless</td>
<td>16.39 (16.27) 4.02 (3.84)</td>
</tr>
<tr>
<td>2</td>
<td>112–113</td>
<td>benzene-acetone</td>
<td>pale brown</td>
<td>15.4 (15.67) 3.65 (3.7)</td>
</tr>
<tr>
<td>3</td>
<td>80–82</td>
<td>benzene-petroleum ether</td>
<td>pale brown</td>
<td>14.87 (15.11) 3.83 (3.57)</td>
</tr>
<tr>
<td>4</td>
<td>146–148</td>
<td>benzene-petroleum ether</td>
<td>colourless</td>
<td>15.23 (14.88) 3.61 (3.51)</td>
</tr>
<tr>
<td>5</td>
<td>95–96</td>
<td>ethanol</td>
<td>light brown</td>
<td>14.10 (14.38) 3.52 (3.39)</td>
</tr>
</tbody>
</table>

(2.13 g, 10 mmol) in dry benzene (80 ml) was refluxed for 5 h on a water bath. When the reaction was over, the reaction mixture was concentrated to ca. 15 ml, to which about the equal volume of ethanol was added, and the mixture was refrigerated for a week, when a solid was precipitated (yield 70%). This was filtered and recrystallized from methanol to yield a colourless crystalline substance (yield 50%), melting at 155–156 °C (lit. [3] 153–155 °C).

Results and Discussion

Five diorganotin(IV) bis(N-arylsulphonyl-N-arylhydroxylaminates) have been prepared from diorganotin(IV) halides and the ligands according to eq. (1).

\[
R_2 \text{SnCl}_2 + 2 \text{HON}(R')\text{SO}_2 R_2 + 2(C_2 H_5)_3 \text{N} \xrightarrow{\text{benzene, reflux}} R_2 \text{Sn}[\text{ON}(R')\text{SO}_2 R_2]_2 + 2(C_2 H_5)_3 \text{N} \cdot \text{HCl}
\] (1)

Analytical data, physical properties and other pertinent information of the compounds prepared are given in Table I. During the reactions, diorganotin(IV) dichlorides, ligands and triethylamine were taken in the mole ratio of 1 : 2 : 2. The HCl liberated in the reaction was removed as triethylamine hydrochloride (insoluble in benzene at room temperature), the formation of which was the driving force for the completion of the reaction. The diphenyltin derivatives are quite stable towards air and moisture, whereas the dibutyltin analogues undergo slow hydrolysis on exposure to the atmosphere for a long time. They are also unstable towards alcohol, undergoing solvolysis. Thus, attempts to purify the dibutyltin compounds from hot methanol produced dibutyltin(IV) dimethoxide as evident from elemental analysis and physical properties.

Infrared spectra of the diorganotin(IV) derivatives do not show any band due to \( v(O - H) \), which occur in the range 3425–3275 cm\(^{-1}\) in the parent ligands, thus indicating that the reactions had taken place through the replacement of the N–OH hydrogen by the organotin moiety. Relevant group frequencies are shown in Table II. The \( v_{as}(\text{SO}_2) \) and \( v_s(\text{SO}_2) \) bands have been assigned in the ranges 1352–1345 and 1180–1179 cm\(^{-1}\), respectively, for \( R_2 \text{SO}_2 \text{N}(R')\text{OH} \) \((R_2' = \text{CH}_3, \text{C}_6 \text{H}_5; R_1' = \text{H}, \text{CH}_3) \) [15] and at 1345–1320 and 1172–1160 cm\(^{-1}\) for \( R_2 \text{SO}_2 \text{N}(R')\text{OH} \) \((R_2' = \text{CH}_3, \text{C}_6 \text{H}_5; R_1' = \text{H}, \text{CH}_3) \) [14]. Thus the \( v_{as}(\text{SO}_2) \) and \( v_s(\text{SO}_2) \) modes in the organotin(IV) derivatives are assigned to the bands at 1380–1330 and 1170–1150 cm\(^{-1}\), respectively (Table II), which do not differ much from those found in the ligands. The results indicate that the \( v(\text{SO}_2) \) modes in the ligands have undergone very little shifts on complexation, indicating a rather weak coordination through \( \text{SO}_2 \). The \( v(\text{NO}) \) modes found at 968–900 cm\(^{-1}\) for the complexes have undergone slight shifts from 960–896 cm\(^{-1}\), in consonance with the values found in the literature for such compounds.
Table II. Infrared group frequencies (cm$^{-1}$) and chemical shifts (δ in ppm) of R$_2$Sn[ON(R')SO$_2$R]$^2_2$.

<table>
<thead>
<tr>
<th>Compound No.</th>
<th>IR data (cm$^{-1}$)</th>
<th>$^1$H NMR chemical shifts (δ in ppm)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$v_\text{a}(\text{SO}_2)$</td>
<td>$v_\text{s}(\text{SO}_2)$</td>
</tr>
<tr>
<td>1</td>
<td>1344 s</td>
<td>1170 s</td>
</tr>
<tr>
<td>2</td>
<td>1335 s</td>
<td>1150 s</td>
</tr>
<tr>
<td>3</td>
<td>1330 s</td>
<td>1157 s</td>
</tr>
<tr>
<td>4</td>
<td>1380 m</td>
<td>1165 s</td>
</tr>
<tr>
<td>5</td>
<td>1335 s</td>
<td>1160 s</td>
</tr>
</tbody>
</table>

$^a$ Unresolved triplet; $^b$ s = singlet, t = triplet, m = multiplet.

[15]. The $v$(Sn–C) (butyl) and $v$(Sn–C) (phenyl) modes in the diorganotin(IV) derivatives were found at 590–585 and 400–395 cm$^{-1}$ and are in conformity with the values reported in the literature for various organotin complexes [3, 16, 17]. An analogous compound, (CH$_3$)$_3$Sn(TsPSHA), has been reported [4], but no infrared data. The $v$(Sn–O) modes occur at 475–440 cm$^{-1}$ (Table II), in analogy with those of the diorganotin derivatives of N-acyl-N-arylhydroxylamines [2, 3] and organotin acetylacetonates [18]. The diorganotin(IV) bis(N-arylsulphonylhydroxylaminates) can exist in cis-octahedral (A) or trans-octahedral (B) configurations through SO$_2$ and NO bonding. On the basis of group theoretical predictions, a trans-octahedral (B) structure may be suggested for the complexes, since only one Sn–C and one Sn–O stretching mode could be identified, although distorted trans-octahedral or even cis-octahedral structures may not be ruled out, similar to those found for the diorganotin(IV) bis(N-acyl-N-organilylhydroxylaminates) [2, 3, 19, 20] and diphenyltin(IV) bis(acetylacetonates) and -bis(oximates) [21].

The $^1$H NMR spectra present no unusual features. The butyl groups absorb at δ0.92–0.93 as triplets for the methyl protons, and δ1.20–1.86 as multiplets for the methylene protons. The aryl protons absorb over the range δ7.0–7.73 as complex signals.

**Ligand Exchange Reaction**

Transformation reactions involving organotin moieties in which dibutyltin(IV)(salicylate) may be converted to dibutyltin(IV)(catecholate) by ligand exchange are known [22]. The intermolecular ligand exchange reaction between R$_2$Sn(acac)$_2$ (R = CH$_3$, C$_6$H$_5$) and free acetylacetone has been studied [23, 24]. Ligand exchange reactions involving the replacement of a hydroxylamine group by a halogen or a pseudohalogen have also been reported [5]. In the ligand exchange reaction studied here, a representative compound (C$_6$H$_5$)$_2$Sn[ON(C$_6$H$_5$)SO$_2$C$_6$H$_4$–CH$_3$–4]$^2_2$ has been
reacted with $\text{C}_6\text{H}_5\text{CON(C}_6\text{H}_5\text{)}\text{OH}$ in the 1:2 mole ratio in refluxing benzene (eq. (2)).

$$
(\text{C}_6\text{H}_5\text{)}_2\text{Sn}[\text{ON(\text{C}_6\text{H}_5\text{)}\text{SO}_{\text{C}_6\text{H}_4\text{CH}_3\text{}}}]_4] + 2\text{C}_6\text{H}_5\text{CON(\text{C}_6\text{H}_5\text{)}OH} \overset{\text{reflux benzene}}{\longrightarrow} (\text{C}_6\text{H}_5\text{)}_2\text{Sn}[\text{ON(\text{C}_6\text{H}_5\text{)}\text{COC}_6\text{H}_4\text{H}_3\text{}}]_2 + \text{Ts-PHAH} \quad (2)
$$

The reaction product diphenyltin(IV) bis(N-benzoylphenylhydroxylaminate) has been fully characterized by melting point, infrared and $^1\text{H}$ NMR spectra, and by comparing the data with those of an authentic sample prepared from diphenyltin(IV) dichloride and N-benzoylphenylhydroxylamine [1–3]. The results of this typical experiment indicate that the N-acyl-N-arylhydroxylamines are stronger ligands than the N-arylsulphonyl-N-arylhydroxylamines towards organotin moieties. An intermolecular mechanism involving the breakage of a Sn–OS bond to yield a five-coordinate intermediate, which reacts with the incoming N-benzoylphenyl hydroxylamine with the simultaneous replacement of a TsPHAH ligand may be proposed on the basis of a mechanism of ligand exchange proposed for Sn(IV) and diorganotin(IV) acetylacetonates with free acetylacetone [23, 24].