Structural studies on 5- and 6-coordinated unsymmetrical diorganotin(IV) complexes

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Five- and six-coordinated unsymmetrical diorganotin(IV) complexes of the type BuMeSnCl (L) and BuMeSn(L)₂ [where L = anion of acetylacetone (Hacac), benzyloacetone (Hbzac), 2,2,6,6-tetramethylheptanedi-one (Htmhd), 3-methyl-2,4-pentanedione (Hmpd), dibenzoylmethane (Hdbm), 2-thenoyl-l,1,1-trifluoroacetone (Htfa), 1,1,1,5,5,5-hexafluoropentanedione (Hhfpd)] have been synthesized and characterized on the basis of elemental analyses, IR, ¹H NMR, ¹³C NMR and ¹¹⁹Sn NMR spectral studies.

Due to their biocidal properties, organotin compounds of the type R₂SnX₄⁻ (where R = Me, Et, Pr, Bu, Ph, etc. and X is chloride, phosphate, hydroxide, benzoate, acetate, naphthenate, etc.) have been used for pest control, preservation of cellulosic materials and in medicine¹-⁴. A literature survey revealed that no attempt has been made to prepare unsymmetrical diorganotin β-diketonates. Hence we decided to take up the title study.

Experimental

All manipulations were carried out in an inert atmosphere on a vacuum line using Schlenk equilibrium. Trimethyltin chloride (Aldrich) and butyltin trichloride (Aldrich) were used as such. Butylmethyltin dichloride was prepared by literature method⁵ and distilled over a modified fractionating column† at 220°/0.01 mm. Sodium β-diketonates were prepared by the reaction of sodium hydride and β-diketone in ether. Tin and chloride were estimated by standard methods⁶. All the solvents were dried and distilled by reported methods. IR spectra were recorded in the range 4000-200 cm⁻¹ using Perkin-Elmer 842 grating spectrophotometer and Perkin-Elmer 631 spectrophotometer. ¹H NMR spectra were recorded on a Perkin-Elmer R-32 90 MHz spectrometer. ¹³C NMR and ¹¹⁹Sn NMR spectra were recorded on Bruker 300 MHz instrument using TMS and Me₄Sn as standards.

Reaction of butylmethyltin dichloride with sodium salt of acetylacetone in 1:1 molar ratio

To a solution of butylmethyltin dichloride (0.76 g, 2.89 mmol) in ~ 5 ml of dried ethanol was added a solution of sodium acetylacetone (0.35 g, 2.89 mmol) in ~ 5 ml of dried ethanol. The solution was stirred for ~ 1 hr and filtered. The filtrate was evaporated under reduced pressure. The pale yellow product was dissolved in benzene and filtered. The solvent from the filtrate was removed in vacuo to obtain a pale-yellow viscous liquid. The product could not be distilled under reduced pressure due to decomposition (200°/0.01 mm).

Similar procedure was used for other reactions of butylmethyltin dichloride with sodium salts of β-diketones in 1:1 and 1:2 molar ratios, which for the sake of brevity are given in Table 1 along with the analytical data.

Results and discussion

The reaction of trimethyltin chloride with butyltin trichloride in 1:1 molar ratio can be represented as follows:

\[
\begin{align*}
\text{Me}_3\text{SnCl} + \text{BuSnCl}_3 & \quad \rightarrow \quad \text{Me}_2\text{SnCl} + \text{BuMeSnCl}_2 \\
\text{Me}_2\text{SnCl} + \text{BuMeSnCl}_2 & \quad \rightarrow \quad \text{BuMeSnCl}_3 \\
\end{align*}
\]

(1) (II) (III)

(90°/0.01 mm) (120°/0.01 mm) (220°/0.01 mm)

The reactions of compound III with sodium salts of β-diketones can be represented as follows:

\[
\text{BuMeSnCl}_2 + n\text{NaL} \rightarrow \text{BuMeSnCl}_2\cdot\text{L}_n + n\text{NaCl}
\]

(where n = 1 or 2; L = acac, bzac, dbm, tmhd, hfpd and mpd)

All these derivatives are pale yellow viscous liquids, susceptible to hydrolysis and soluble in benzene, chloroform and carbon tetrachloride.

The IR spectrum of III shows characteristic bands at ~ 2950, ~ 2920 and ~ 2850 cm⁻¹ due to ν(C-H) of alkyl group. The band observed at ~ 320 cm⁻¹ has been assigned to ν(Sn-Cl) vibration. The IR spectra of sodium β-diketonates display strong bands in the region 1600-1580 and
Table 1 - Analytical data

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Compound (g mmol)</th>
<th>Ligand (g mmol)</th>
<th>Molar ratio</th>
<th>Product</th>
<th>Found (calc.), %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>BuMeSnCl₂</td>
<td>Naacct</td>
<td>1:1</td>
<td>BuMeSn(acac)₃</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0.76(2.89)</td>
<td>0.55(2.89)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0.54(2.06)</td>
<td>0.50(2.06)</td>
<td>1:2</td>
<td>BuMeSn(acac)₃</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.66(2.49)</td>
<td>0.45(2.49)</td>
<td>1:1</td>
<td>BuMeSn(bzac)₂</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0.63(2.46)</td>
<td>0.60(4.92)</td>
<td>1:2</td>
<td>BuMeSn(bzac)₂</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>0.67(2.59)</td>
<td>0.53(2.59)</td>
<td>1:1</td>
<td>BuMeSn(tmhd)₃</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>0.84(3.22)</td>
<td>1.32(6.44)</td>
<td>1:2</td>
<td>BuMeSn(tmhd)₂</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>0.77(2.94)</td>
<td>0.40(2.94)</td>
<td>1:1</td>
<td>BuMeSn(mpdl)₃</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>0.52(2.00)</td>
<td>0.54(4.00)</td>
<td>1:2</td>
<td>BuMeSn(mpdl)₂</td>
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<tr>
<td>9</td>
<td>0.96(3.68)</td>
<td>0.90(3.68)</td>
<td>1:1</td>
<td>BuMeSn(dbm)₃</td>
<td></td>
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<tr>
<td>10</td>
<td>0.48(1.84)</td>
<td>0.92(3.68)</td>
<td>1:2</td>
<td>BuMeSn(dbm)₂</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>0.48(1.82)</td>
<td>0.44(1.82)</td>
<td>1:1</td>
<td>BuMeSn(tfa)₂</td>
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</tr>
<tr>
<td>12</td>
<td>0.51(1.92)</td>
<td>0.93(3.87)</td>
<td>1:2</td>
<td>BuMeSn(tfa)₂</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>0.88(3.32)</td>
<td>0.76(3.32)</td>
<td>1:1</td>
<td>BuMeSn(hfpd)₃</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>0.74(2.84)</td>
<td>1.30(5.68)</td>
<td>1:2</td>
<td>BuMeSn(hfpd)₂</td>
<td></td>
</tr>
</tbody>
</table>

1520-1500 cm⁻¹ due to νₚₛₘₚᵢ (C=O) and νₚₛₘₚᵢ (C=C) respectively. However, in case of hfpd, these bands are observed at 1650 and 1530 cm⁻¹. The upward shift may be due to high electronegativity of the fluorine atom. The band in the region 1200-1145 cm⁻¹ is due to ν(C=Σ) in case of tfa. The band at 1100-1070 cm⁻¹ is due to ν(C-X). The IR spectra of β-diketonates of III show a downfield shift of 10-40 cm⁻¹ in the carbonyl frequency, thus suggesting bonding through both the terminal oxygens of the carbonyl group. Further, two bands appearing in the region 1075-1020 cm⁻¹ have been assigned to νₚₛₘₚᵢ (C-O)Sn and νₚₛₘₚᵢ (C-O)Sn vibrations thus indicating bonding between central metal atom and oxygens of carbonyl groups. ν(M-O) appears at 430-410 cm⁻¹. The ν(Sn-Cl) band in case of 1:1 derivatives shows a slight upward shift of ~10-20 cm⁻¹ and is observed in the region 340-330 cm⁻¹ indicating the coordination of ligand. The bands due to phenyl group are observed at their usual positions.

¹H NMR spectra of III and its β-diketonates show peaks between δ 0.9 and 1.9 ppm which are due to intermixing of the signal due to −CH₂ and −CH₃ protons of the butyl group with those of the protons of the methyl group. A singlet observed at δ 5.8-6.8 ppm is due to methine protons of the ligand moiety of the β-diketonates. A multiplet observed in the region δ 7.0-8.1 ppm is due to thenoyl protons of tfa and phenyl protons of bzac, dbm, etc. A sharp singlet observed at δ 2.1 ppm is due to methyl protons of acac, bzac, etc. In the case of tmhd, the signal of methyl protons got mixed with those of butyl and methyl

*The detailed spectral data can be obtained from the authors on request.
protons of III. The proton integration area was consistent with the molecular formula.

The $^{13}$C NMR spectra of III show peaks at $\delta$ 26.77, $\delta$ 26.58, $\delta$ 26.10 and $\delta$ 13.46 ppm assignable to C-1, C-2, C-3 and C-4 carbons ($\text{Sn} \bullet \text{Sn; (CH}_3 \text{-CH}_2 \text{-CH}_2 \text{-CH}_2 \text{-CH}_3$) of the butyl group and a peak observed at $\delta$ 6.68 ppm has been assigned to C-5 carbon. $^{13}$C NMR spectra of p-diketonates of III show a slight downfield shift indicating coordination. A signal observed in the range $\delta$ 203.1-177.8 ppm is due to carbon of the carbonyl group. In the case of hfpd, $\text{-CF}_3$ peak is observed at $\delta$ 117.03 and $\text{IJ}(^{13}\text{C}-^{19}\text{F})=283.86$ Hz and $\text{IJ}(^{13}\text{C}-^{19}\text{F})=35.18$ Hz. A sharp singlet observed in the range $\delta$ 96.1-90.2 ppm is due to methine protons of the ligand moiety. The complexes of tmhd show a signal at $\delta$ 29.66 ppm due to tert. carbon C(CH$_3$)$_3$. In the case of acac and bzac derivatives, the signals due to methyl group got mixed with signals of the butyl group. The thenoyl and phenyl carbons are observed at their usual positions.

$^{119}$Sn NMR spectrum of III shows a sharp singlet at $\delta$ 132.1 ppm that can be attributed to tetra-coordinated Sn atom. In 1:1 and 1:2 $\beta$-diketonate of III, singlets are observed at $\delta \sim -76$ and $\delta \sim -346$ ppm indicating 5- and 6-coordinated structures respectively. This large upfield shift observed for 1:1 and 1:2 complexes from $\delta$ 132.1 ppm for 4 coordinate to $\delta \sim -76$ (5-coordinate) to $\delta \sim -346$ (6-coordinate) is ascribed to interaction of the donor atoms (Bu and Me) with the valence 5s orbitals of Sn atom during the formation of 5- and 6-coordinate complexes, which results in an increase in the electron density on Sn atom reinforced by the two oxygen donors of $\beta$-diketone.

The observation of coupling constants $\text{nIJ}^{119}\text{Sn} - ^{13}\text{C}_\text{meotyl}$ at 391.24 Hz (n=1) and 102.43 Hz (n=3) for III, 555.0-673.0 Hz (n=1) and 850-970.0 Hz (n=3) for 1:1 derivatives, 795.8-940.0 Hz (n=1) and 126-159 Hz (n=3) for 1:2 derivatives also confirms the formation of 4-, 5- and 6-coordinated compounds respectively. The parameters of $^{13}$C and $^{119}$Sn NMR spectra [values of chemical shift ($\delta$ $^{13}$C and $\delta$ $^{119}$Sn) and the coupling constants $\text{nIJ}^{119}\text{Sn} - ^{13}\text{C}$] confirm the five- and six-coordination of $\beta$-diketonates of III.

The following structures (A and B) can, therefore, be tentatively assigned to 1:1 and 1:2 derivatives, respectively:

In these structures, a trans configuration has been predicted for BuMeSnCl$_2$ and its $\beta$-diketonates. This has been ascribed to the $\sigma$-donor ability of methyl and butyl groups which tend to maximize the tin 5s character in the Sn-C bond, resulting in a nearly linear C-Sn-C structure.

References