Electrophilic cleavage of tin-alcyclic and tin-aryl bonds involving the synthesis of cyclohexyl-tin, -tellurium and -antimony compounds—Part I

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Cyclohexyl-tin, -tellurium and -antimony halides have been obtained in good yields by the electrophilic cleavage of Sn–C bond(s) from symmetrical and unsymmetrical cyclohexyl tins, Cy_nSnPh_{4-n} (n=1,2,4) employing Br_2, I_2, ICl, IBr, TeCl_4 and SbCl_5 in CCl_4 under mild conditions.

In sharp contrast to well documented cleavage reactions of Sn-alkyl and Sn-aryl bonds from tetraorganotins, those involving alcyclic tin derivatives have not been reported so far. The present note reports the facile preparation of cyclohexyl-tin, -tellurium and -antimony compounds through cleavage of Sn–C bond(s) from tetraorganotins using halogens, interhalogens and metallic salts which are expected to be biologically active in view of the reported observations.

Experimental

Cyclohexyltins of the type Cy_nSnPh_{4-n} where (n=1,2,4) were prepared by reported methods. Iodine monochloride (Fluka), Antimony pentachloride (Fluka) and tellurium tetrachloride (E. Merck) were used as such. IBr was prepared by a known method. All manipulations were carried out in a nitrogen atmosphere.

The IR spectra were recorded in the range 4000-200 cm^{-1} by using KBr/CsI pellets on a Perkin-Elmer 577 spectrophotometer.

Two typical experiments are given below and the detailed data are presented in Table 1.

**Reaction of (C_{6}H_{11})_{3}Sn with ICl (1:1)**

A solution of iodine monochloride (1.62 g, 0.01 mol) in carbon tetrachloride (30 ml) was added to a stirred solution of tetracyclohexyltin in CCl_4 (200 ml). The reactants were further stirred for 2 h. The removal of volatiles afforded a solid residue which was crystallized from pet ether (40-60°C) and identified as (C_{6}H_{11})_{3}SnCl (yield 2.81 g, 69.5%, m.p. 128°C (lit. 129-130°C)

**Reaction of Ph_{3}SnCy with TeCl_{4}**

A solution of triphenylcyclohexyltin (1.08 g, 0.0025 ml) and tellurium tetrachloride (0.68 g, 0.0025 ml) in toluene (60 ml) was stirred at room temperature to afford an off white solid, characterised as PhTeCl_3, m.p. 213-214°C, lit. 214-216°C yield 56 g, 72%. The filtrate on concentration yielded Ph_{2}CySnCl,m.p. 148-150°C.

**Results and discussion**

Though both bromine and iodine monochloride are strong electrophiles yet they cleave only one Sn – C bond from Cy_{4}Sn at room temperature (Eqn 1)

\[ \text{CyBr} + \text{Cy}_{3}\text{SnBr} \xrightarrow{\text{Br}_2, \text{r.t.}} \text{Cy}_{4}\text{Sn} \xrightarrow{\text{ICl}} \text{Cy}_{3}\text{SnCl} + \text{Cy} \]

\( \text{... (1)} \)

However, in refluxing CCl_4, two Sn – C bonds are cleaved as given by Eqn (2)

\[ 2\text{ICl} + \text{Cy}_{2}\text{SnCl}_{2} \xrightarrow{2\text{Br}_2, \text{r.t.}} \text{Cy}_{4}\text{Sn} \]

\( \text{... (2)} \)

On the other hand, iodine monobromide and iodine are weak electrophiles and cleave only one tin-cyclohexyl bond even with an excess of electrophile in refluxing CCl_4 as shown by Eqn (3),

\[ \text{CyI} + \text{Cy}_{3}\text{SnI} \xrightarrow{1/2 \text{I}_2, 77°C} \text{Cy}_{4}\text{Sn} \xrightarrow{\text{IBr}, 77°C} \text{Cy}_{3}\text{SnBr} + \text{Cy} \]

\( \text{... (3)} \)

**Reactions with metallic halides**

\( \text{TeCl}_4 \) is a mild electrophile and cleave only one Sn – P bond from Cy_{3}Sn even in mild conditions as given by Eqn (4),

\[ \text{Cy}_{3}\text{Sn} + \text{TeCl}_4 \rightarrow \text{Cy}_{3}\text{SnCl} + \text{CyTeCl}_3 \]

\( \text{... (4)} \)

However, from Cy_{2}SnPh_{2} successive cleavage of Sn – Ph bond could be achieved under varying conditions in toluene as shown by Eqn (5),
Table 1—Reactions of cyclohexyltin derivatives with halogens (Br₂, I₂), interhalogens (ICl & IBr) and metallic halides (SbCl₅, TeCl₄)

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Reactants (Molar ratio)</th>
<th>Reaction time (h) and temperature (°C)</th>
<th>Product*</th>
<th>M.P. (lit. m.p.) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>(C₆H₁₁)₄Sn + Br₂ (1:1)</td>
<td>3h (30)</td>
<td>(C₆H₁₁)₄SnBr</td>
<td>75-76 (77)¹⁰</td>
</tr>
<tr>
<td>2.</td>
<td>(C₆H₁₁)₄Sn + Br₂ (1:2)</td>
<td>3h (77)</td>
<td>(C₆H₁₁)₂SnBr₂</td>
<td>56-57 (58)¹⁰</td>
</tr>
<tr>
<td>3.</td>
<td>(C₆H₁₁)₄Sn + ICl (1:1)</td>
<td>3h (30)</td>
<td>(C₆H₁₁)₂SnCl</td>
<td>128 (129-130)¹⁰</td>
</tr>
<tr>
<td>4.</td>
<td>(C₆H₁₁)₄Sn + ICl (1:2)</td>
<td>3h (77)</td>
<td>(C₆H₁₁)₄SnCl₄</td>
<td>87-89 (88-89)¹⁰</td>
</tr>
<tr>
<td>5.</td>
<td>(C₆H₁₁)₄Sn + I₂ (1:1)</td>
<td>5 (30)</td>
<td>(C₆H₁₁)₂SnI</td>
<td>64 (65)¹⁰</td>
</tr>
<tr>
<td>6.</td>
<td>(C₆H₁₁)₄Sn + IBr (1:1)</td>
<td>6 (77)</td>
<td>(C₆H₁₁)₂SnBr</td>
<td>76 (77)¹⁰</td>
</tr>
<tr>
<td>7.</td>
<td>(C₆H₁₁)₄Sn + IBr (1:2)</td>
<td>12 (77)</td>
<td>(C₆H₁₁)₄SnBr</td>
<td>75-77 (77)¹⁰</td>
</tr>
<tr>
<td>8.</td>
<td>(C₆H₁₁)₄Sn + SbCl₅ (1:1)</td>
<td>2 (0)</td>
<td>(C₆H₁₁)₂SnCl₂</td>
<td>87 (88-89)¹⁰</td>
</tr>
<tr>
<td>9.</td>
<td>(C₆H₁₁)₂(C₆H₁₃)Sn + SbCl₅ (1:1)</td>
<td>1 (0)</td>
<td>(C₆H₁₁)₂SnCl₅</td>
<td>168-170 (171-172)¹⁴</td>
</tr>
<tr>
<td>10.</td>
<td>(C₆H₁₁)₂(C₆H₁₃)Sn + SbCl₅ (1:1)</td>
<td>1 (0)</td>
<td>(C₆H₁₁)₂SnCl₅</td>
<td>98-99 (98-100)¹²</td>
</tr>
<tr>
<td>11.</td>
<td>(C₆H₁₁)₂(C₆H₁₃)Sn + TeCl₄ (1:1)</td>
<td>3 (30)</td>
<td>(C₆H₁₁)₂SnCl₅</td>
<td>169-171 (171-172)¹⁴</td>
</tr>
<tr>
<td>12.</td>
<td>(C₆H₁₁)₂(C₆H₁₃)Sn + TeCl₄ (1:1)</td>
<td>3 (110)</td>
<td>(C₆H₁₁)₂SnCl₅</td>
<td>88 (88-89)¹⁰</td>
</tr>
<tr>
<td>13.</td>
<td>(C₆H₁₁)₂Sn + TeCl₄ (1:1)</td>
<td>3 (110)</td>
<td>(C₆H₁₁)₂SnCl₅</td>
<td>88-89 (89)¹⁰</td>
</tr>
<tr>
<td>14.</td>
<td>(C₆H₁₁)₂Sn(C₆H₁₃)₂ + TeCl₄ (1:1)</td>
<td>3 (30)</td>
<td>(C₆H₁₁)₂SnCl₅</td>
<td>168-170</td>
</tr>
<tr>
<td>15.</td>
<td>(C₆H₁₁)₂Sn(C₆H₁₃)₂ + TeCl₄ (1:1)</td>
<td>3 (110)</td>
<td>(C₆H₁₁)₂SnCl₅</td>
<td>87-88 (88-89)¹⁰</td>
</tr>
</tbody>
</table>

*The products were obtained in 65-75% yield. Corresponding Cy Br and Cyl were removed as volatiles at reduced pressure. Found: C, 35.68; H, 5.67; Sb, 30.08% Reqd. for C₆H₁₁SnBr₂: C, 36.59; H, 5.59; Sb, 30.74%; Found: C, 39.04; H, 5.98; Te, 33.98%. Reqd. for C₆H₁₁SbCl₃: C, 39.56; H, 6.04; Te, 34.89% Found: C, 54.14; H, 6.70; Sn, 29.50%. Reqd. for C₆H₁₁SnCl: C, 54.54; H, 6.81; Sn, 29.79.

Ph₂TeCl₂ + Cy₂SnCl₂ \(\xrightarrow{\text{TeCl}_4, \text{r.t.}}\) Cy₂SnPh₂ \(\xrightarrow{\text{TeCl}_4, \text{r.t.}}\)

The reaction of Ph₃SnCy proceeded in a similar fashion by Eqn (6),

PhCySnCl₂ + Ph₃TeCl₄ \(\xrightarrow{\text{reflux, TeCl}_4, 4\text{t.}}\) Ph₂CySnCl + Ph₅TeCl₃ \(\xrightarrow{\text{reflux}}\)

As compared to TeCl₄, antimony pentachloride is a strong electrophile and cleave two Sn – C bond(s) from organotins as presented by Eqns (7-9),

\(\text{(C₆H₁₁)Sn + SbCl₅} \rightarrow \text{(C₆H₁₁)₂SnCl₂} + \text{(C₆H₁₁)₂SbCl₃}\)

\(\text{Ph₂SnC₆H₁₃ + SbCl₅} \rightarrow \text{Ph₂SbCl₃} + \text{Ph(C₆H₁₃)SnCl₃}\)

The mechanism of cleavage reactions may possibly involve a four centered transition state as has been suggested earlier for M – C, M – P and M – As (where M = Si, Sn, Pb) bond cleavage with halogens and interhalogens¹³-¹⁴.

The infrared absorptions at 540, 520 and 580 cm are assigned to Sb-Cyclohexyl¹⁵, Te-cyclohexyl¹⁶ and Sn-cyclohexyl¹⁷ stretching vibrations respectively. The absorptions at 340, 290 and 385 cm are assigned to Sb – C¹⁵, Te – C¹⁶ and Sn – C¹⁷ stretching frequencies respectively.
Acknowledgement
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