Electrophilic tin-carbon bond cleavage reactions employing iodine halides \( Y \) (\( Y = \text{Cl} \) and \( \text{Br} \)) and bromine have been used to synthesize mixed diaryltin dihalides (\( \text{Ar}_2\text{SnXY} \); \( \text{Ar} = \) phenyl and \( p\)-tolyl; \( XY = \text{ClBr} \)). Reactions of \( \text{Ph}_3\text{SnI} \) with iodine halides to prepare \( \text{Ph}_3\text{SnCl} \) or \( \text{Ph}_3\text{SnBrI} \) are also discussed. The mixed halides also form 1:2 dimethyl sulphoxide addition complexes similar to other organotin halides.

As compared to extensively reported diorgano-tin dihalides \( R_2\text{SnX}_2 \) (ref. 1), compounds containing two different halogens \( X \) and \( Y \) attached to tin, e.g. \( R_2\text{SnXY} \), are rare. Aronheim\(^8\) reported two such compounds \( \text{Ph}_2\text{SnClBr} \) and \( \text{Ph}_2\text{SnClI} \). Redistribution or exchange methods have been employed to synthesize \( R_2\text{SnClBr} \) (ref. 3, 4) or \( R_2\text{SnFCl} \) (ref. 5, 6) (\( R = \text{Me}, \text{i-Bu} \)). A recent note\(^7\) on mixed dialkytin dihalides (\( R_2\text{SnXY} \); \( R = \text{Me}, \text{Et} \) or \( \text{n-Bu} \); \( XY = \text{ClBr} \), \( \text{ClI} \) or \( \text{BrI} \)) prompted us to present our results on the preparation of diaryltin dihalides through electrophilic cleavage of tin-aryl bond with halogen and iodine monohalides.

Iodine monohalide (\( \text{ICl} \)) has also been previously\(^8\) used to prepare \( \text{PhBiClBr} \) from \( \text{Ph}_3\text{BiBr} \). The conditions for the cleavage reactions described in this paper are uniform and mild and thus are advantageous over redistribution reactions which need varying specific conditions.\(^3, 4\) The newly synthesized compounds were converted into their 1:2 dimethyl sulphoxide addition complexes (\( \text{Ar}_2\text{SnXY} : 2\text{DMSO} \)) and a tentative structure assigned.

Materials and Methods

Triaryltin chlorides and bromides were synthesized by the redistribution reaction of tetraaryltins and the corresponding stannic halides.\(^4\) Triphenyltin iodide was prepared by the previously reported method.\(^6\)

Iodine monochloride (Fluka grade) was distilled before use. Iodine monobromide was prepared by dissolving iodine in an excess of bromine and purified by the published method.\(^9\)

Anhydrous \( \text{CCl}_4 \) was used as a solvent and moisture was excluded during the reactions and their work up.

Reactions of \( \text{Ar}_2\text{SnX} \) compounds with \( \text{IY} \) and \( \text{Br}_2 \) -- Typical experiments are given here. Further details are given in Table 1.

Reactions of \( \text{Ph}_3\text{SnCl} \) and \( I_2 \) (1:1) -- The reaction did not take place at room temperature. Even refluxing a mixture containing equimolar solution of the reactants in \( \text{CCl}_4 \) for 7 hr gave the starting \( \text{Ph}_3\text{SnCl} \) after evaporation of the solvent. No trace of iodobenzene could be detected.

Reaction of \( \text{Ph}_3\text{SnI} \) with \( \text{ICl} \) (1:1) -- Gradual addition of \( \text{ICl} \) (0.81 g, 0.005 mole) in \( \text{CCl}_4 \) (20 ml) to a solution of triphenyltin iodide (2.35 g, 0.005 mole) in \( \text{CCl}_4 \) (100 ml) at room temperature produced a violet colour which persisted even after (10 hr) refluxing. The solvent was distilled off (which removed partially the violet colour) and the distillate gave test for free iodine. The residue was dissolved in pet. ether (4 ml) which on cooling afforded

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**Table 1 — Reactions of \( \text{Ar}_2\text{SnX} \) (\( X = \text{Cl}, \text{Br}, \text{I} \)) with \( \text{ICl}, \text{IBr} \) and \( \text{Br}_2 \)**

<table>
<thead>
<tr>
<th>( \text{Ar}_2\text{SnX} )</th>
<th>Mole ratio</th>
<th>Reaction time (hr)</th>
<th>Product(s) ((a,b))</th>
<th>m.p. ( \degree \text{C} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Ph}_3\text{SnI} )</td>
<td>1 : 2</td>
<td>2 (30)</td>
<td>( \text{Ph}_3\text{SnCl}_2 )</td>
<td>41-42</td>
</tr>
<tr>
<td>( \text{Ph}_3\text{SnI} )</td>
<td>1 : 1</td>
<td>6 (30)</td>
<td>( \text{Ph}_3\text{SnBr} )</td>
<td>120</td>
</tr>
<tr>
<td>( \text{Ph}_3\text{SnCl} )</td>
<td>1 : 2</td>
<td>4 (77)</td>
<td>( \text{Ph}_3\text{SnBr}_2 )</td>
<td>38</td>
</tr>
<tr>
<td>( \text{Ph}_3\text{SnCl} )</td>
<td>1 : 2</td>
<td>4 (77)</td>
<td>( \text{Ph}_3\text{SnCIBr} )</td>
<td>38</td>
</tr>
<tr>
<td>( (p\text{-Tol})_3\text{SnCl} )</td>
<td>1 : 1</td>
<td>4 (77)</td>
<td>( (p\text{-Tol})_3\text{SnClBr} )</td>
<td>59</td>
</tr>
</tbody>
</table>

**Reaction with ICl**

| \( (p\text{-Tol})_3\text{SnCl} \) | 1 : 1 | 1 (30) | \( (p\text{-Tol})_3\text{SnClBr} \) | 59 |

**Reaction with \( \text{Br}_2 \)**

| \( \text{Ph}_3\text{SnCl} \) | 1 : 1 | 1 (10) | \( \text{Ph}_3\text{SnCIBr} \) | 38-39 |
| \( (p\text{-Tol})_3\text{SnCl} \) | 1 : 1 | 1 (10) | \( (p\text{-Tol})_3\text{SnClBr} \) | 58-59 |

(a) Corresponding amounts of aryl halides are also obtained.
(b) Products are obtained in 60-75% yields.
(c) Literature melting points (ref. 1) are given in parentheses.

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unreacted triphenyltin iodide (1·10 g, 46%), m.p. 120° (lit. m.p. 121°). After adding ether (10 ml) to the filtrate, it was treated with water, ethanol and petroleum ether. The white solid thus separated was filtered, washed with water, ethanol and petroleum ether. It was characterized (superimposable IR) as dihexyltin oxide (0·6 g, 83%) (Found: C, 49·28; H, 3·50; Sn, 40·08. Calc. for C12H10Sn: C, 49·79; H, 3·46; Sn, 41·09%).

The organic layer on concentration afforded phenyl iodide (0·4 g, 78·4%), b.p. 182° (lit. b.p. 180-84°). After adding ether (10 ml), it recrystallized with pet. ether (40-60°), m.p. 38° (Found: C, 37·0; H, 2·48; Sn, 30·44. Calc. for C16H22BrC102S2:Sn requires C, 35·26; H, 3·35; Sn, 28·57%).

Similarly tri-p-tolyltin bromide and iodine monocarbide gave di-p-tolyltin chloride bromide, m.p. 38° (lit. m.p. 39°); yield 1·5 g (70%), mol. wt 568 (calc. 388-5).

Reaction of PhaSnBr with ICl (1:1): Formation of diphenyltin chloride bromide — ICl (0·81 g, 0·005 mole) in CCl4 (20 ml) was slowly added to a constant-stirred solution of triphenyltin bromide (2·15 g, 0·005 mole) in the same solvent (100 ml) at room temperature. The contents were stirred for 30 min and then worked up. Phenyl iodide (0·7 g, 69%) was distilled off at 63·65°/10 mm to afford crystals of diphenyltin chloride bromide (Found: C, 35·30; H, 2·48; Sn, 40·08. Calc. for C12H10SnBrC1: C, 37·06; H, 2·57; Sn, 30·65%). It recrystallized with pet. ether (40-60°), m.p. 38° (lit. m.p. 39°); yield 1·5 g (70%), mol. wt 568 (calc. 388-5).

Reaction of PhaSnCl2 and PhaSnI2 — Heating an equimolar mixture of the reactants for 2 hr at 120° did not give any product except that diphenyltin dichloride (blood red) is immediately turned violet in nucleophilic character of tin-aryl bonds in Ar-aSnCl.

Results and Discussion

Iodination of tetraaryltin compounds (ArSn) by I2 have been reported to cleave up to two tin-aryl bonds successively yielding the corresponding diaryl tin diiodides (Ar2SnI2), through an isolable intermediate Ar2SnI. Attempts were made under identical conditions to synthesize diaryl tin chloride iodide (Ar2SnClI) by the reaction of I2 and PhaSnCl. No reaction was observed and the reactants were recovered unchanged probably due to the reduced nucleophilic character of tin-aryl bonds in Ar2SnCl as compared to that in ArSn or in Ar2SnI.

In an earlier investigation on the reaction of tetraorganometallics with ICl and IBr we have observed that both mono and di-tin-carbon bond cleavages occur. This prompted us to try this reaction on PhaSnI (for PhaSnClI or PhaSnBrI) with these electrophiles. Unexpectedly, cleavage of both tin-phenyl and tin-iodine bonds were observed. Thus, the reaction of equimolar quantities of ICl and PhaSnI gave 0·5 mole of PhaSnCl4 along with 0·5 mole of unreacted PhaSnI, on doubling the molar ratio of electrophiles (ICl and IBr) only the diphenyltin dichlorides or dibromides were obtained (Eqs. 1 and 2).

IBr which is a weaker electrophile than ICl (ref. 10) when reacts with PhaSnI preferentially cleaves the tin-iodine bond only giving PhaSnBr and I2.

\[ \text{PhaSnI} + \text{ICl} \rightarrow \text{PhaSnCl}_2 + \frac{1}{2} \text{I}_2 + \frac{1}{2} \text{PhI} + \frac{1}{2} \text{PhaSnI} \]  \hspace{1cm} (1)

\[ \text{PhaSnI} + 2 \text{IBr} (\text{Cl or Br}) \rightarrow \text{PhaSnCl}_2 (\text{or Br}) + \text{PhI} + \text{I}_2 \]  \hspace{1cm} (2)

Cleavage of Sn-Ph and Sn-I bonds by ICl may be due to the similar electronegativity and electron withdrawing capacity of the iodide and phenyl groups. In this reaction the Sn-I bond presumably is cleaved first as the colour due to iodine monochloride (blood red) is immediately turned violet indicating the formation of molecular iodine. The reactions of Ar2SnBr with ICl or of Ar2SnCl with IBr successively yielded the mixed diaryltin dihalides Ar2SnClBr and aryl iodide.

The mixed diaryltin dichlorides (Ar2SnClBr) were also obtained through the reaction of Br2 with Ar2SnCl. The other product obtained was aryl bromide.

It is thus evident that the replacement of I in Ar2Sn with Cl or Br stabilizes the Sn-halogen bond towards cleavage by ICl or IBr due to the greater electronegativity of Cl and Br and at the same time decreases the nucleophilicity of the tin-aryl bond through their electron withdrawing power and only the Ar-Sn bond is cleaved. Similar reactions of Ar2SnF in which there is a further decrease in nucleophilicity of Ar-Sn bonds and the effect of change in the metal, e.g. with Ar2GeX and Ar2PbX are currently being studied.

In some preliminary experiments attempts were made to synthesize diphenyltin chloride iodide by
disproportionation of the corresponding dihalides. The reactants were recovered unchanged after heating for 2 hr at 120°, suggesting for more drastic conditions.

All the mixed dihalides prepared were converted into their corresponding 1:2 DMSO complexes (R₂SnXY·2DMSO) which showed the characteristic shift in νS=O from 1045 cm⁻¹ in DMSO to 945 ± 5 cm⁻¹ in the tin complexes, indicating coordination through oxygen of the DMSO molecule to tin. The structures of R₂SnX₂·2DMSO have been exhaustively studied earlier¹⁵⁻¹⁷ and an octahedral arrangement around the tin atom has been suggested. The presence of different halides are expected to deform the regular octahedron geometry, in the complexes of mixed dihalides.

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References