

## Cleavage of Triaryltin Halides with Iodine Halides & Halogens: A Novel Route to Mixed Diaryltin Dihalides

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Electrophilic tin-carbon bond cleavage reactions employing iodine halides IY (Y = Cl and Br) and bromine have been used to synthesize mixed diaryltin dihalides ( $Ar_2SnXY$ ; Ar = phenyl and *p*-tolyl; XY = ClBr). Reactions of  $Ph_3SnI$  with iodine halides to prepare  $Ph_2SnClI$  or  $Ph_2SnBrI$  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  $R_2SnX_2$  (ref. 1), compounds containing two different halogens X and Y attached to tin, e.g.  $R_2SnXY$ , are rare. Aronheim<sup>2</sup> reported two such compounds  $Ph_2SnClBr$  and  $Ph_2SnClI$ . Redistribution or exchange methods have been employed to synthesize  $Bu_2SnClBr$  (ref. 3, 4) or  $R_2SnFCl$  (ref. 5, 6) (R = Me, *t*-Bu). A recent note<sup>7</sup> on mixed dialkyltin dihalides ( $R_2SnXY$ ; R = Me, Et or *n*-Bu; XY = ClBr, ClI or 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 (ICl) has also been previously<sup>8</sup> used to prepare  $PhBiClBr$  from  $Ph_2BiBr$ . 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<sup>1,4</sup>. The newly synthesized compounds were converted into their 1:2 DMSO adducts ( $Ar_2SnXY \cdot 2DMSO$ ) 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<sup>1</sup>. Triphenyltin iodide was prepared by the previously reported method<sup>9</sup>.

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<sup>10</sup>.

Anhydrous  $CCl_4$  was used as a solvent and moisture was excluded during the reactions and their work up.

*Reactions of  $Ar_3SnX$  compounds with IY and  $Br_2$* —Typical experiments are given here. Further details are given in Table 1.

*Reaction of  $Ph_3SnCl$  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  $CCl_4$  for 7 hr gave the

TABLE 1 — REACTIONS OF  $Ar_3SnX$  (X = Cl, Br, I) WITH ICl, IBr AND  $Br_2$

$Ar_3SnX$	Mole ratio	Re-action time (hr) and temp. (°C)	Products(a,b)	m.p. °C(c)
REACTION WITH ICl				
$Ph_3SnI$	1 : 2	2 (30)	$Ph_2SnCl_2$	41-42 (42-44)
REACTION WITH IBr				
$Ph_3SnI$	1 : 1	6 (30)	$Ph_3SnBr$	120 (120-21)
do	1 : 2	4 (77)	$Ph_2SnBr_2$	37-38 (38)
$Ph_3SnCl$	1 : 1	4 (77)	$Ph_2SnClBr$	38 (39)
$(p-Tol)_3SnCl$	1 : 1	4 (77)	$(p-Tol)_2SnClBr$	59
REACTION WITH ICl				
$(p-Tol)_3SnCl$	1 : 1	1 (30)	$(p-Tol)_2SnClBr$	59
REACTION WITH $Br_2$				
$Ph_3SnCl$	1 : 1	1 (-5)	$Ph_2SnClBr$	38-39 (39)
$(p-Tol)_3SnCl$	1 : 1	1 (-5)	$(p-Tol)_2SnClBr$	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.

starting  $Ph_3SnCl$  after evaporation of the solvent. No trace of iodobenzene could be detected.

*Reaction of  $Ph_3SnI$  with ICl (1:1)*—Gradual addition of ICl (0.81 g, 0.005 mole) in  $CCl_4$  (20 ml) to a solution of triphenyltin iodide (2.35 g, 0.005 mole) in  $CCl_4$  (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

unreacted triphenyltin iodide (1.10 g, 46%), m.p. 120° (lit.<sup>9</sup> m.p. 121°). After adding ether (10 ml) the filtrate was treated with 0.1M KOH. The white solid thus separated was filtered, washed with water, ethanol and petroleum ether. It was characterized (superimposable IR) as diphenyltin oxide (0.6 g, 83%) (Found: C, 49.28; H, 3.50; Sn, 40.08. Calc. for C<sub>12</sub>H<sub>10</sub>OSn: 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.<sup>11</sup> b.p. 180-84°).

**Reaction of Ph<sub>3</sub>SnBr with ICl (1:1): Formation of diphenyltin chloride bromide** — ICl (0.81 g, 0.005 mole) in CCl<sub>4</sub> (20 ml) was slowly added to a constantly 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, 37.0; H, 2.48; Sn, 30.44. Calc. for C<sub>12</sub>H<sub>10</sub>SnBrCl: C, 37.06; H, 2.57; Sn, 30.63%). It recrystallized with pet. ether (40-60°), m.p. 38° (lit.<sup>1</sup> m.p. 39°); yield 1.5 g (70%); mol. wt 368 (calc. 388.5).

Similarly tri-*p*-tolyltin bromide and iodine monochloride gave di-*p*-tolyltin chloride bromide, m.p. 59° (Found: C, 40.40; H, 3.27; Sn, 28.52. C<sub>14</sub>H<sub>14</sub>BrClSn requires C, 40.33; H, 3.35; Sn, 28.57%); mol. wt 403 (calc. 416.5).

**Reaction of Ph<sub>2</sub>SnCl<sub>2</sub> and Ph<sub>2</sub>SnI<sub>2</sub>** — Heating an equimolar mixture of the reactants for 2 hr at 120° did not give any product except that diphenyltin diiodide was recovered quantitatively.

**Complexes (1:2) of Ar<sub>2</sub>SnXY with DMSO** — A representative experiment is given below. Further details are given in Table 2.

Diphenyltin chloride bromide (1.94 g, 0.005 mole) in pet. ether (60-80°, 40 ml) was refluxed with (0.78 g, 0.011 mole) dimethyl sulphoxide for 1 hr. Excess solvent was distilled off, chloroform added and cooled to give a crystalline compound. This was finally washed with ether and dried *in vacuo*

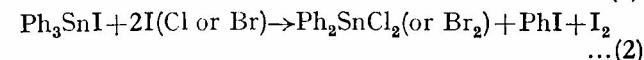
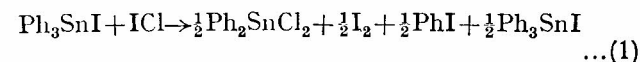
(2.3 g, 74%), m.p. 144° (Found: C, 35.30; H, 4.04; Sn, 21.90. C<sub>16</sub>H<sub>22</sub>BrClO<sub>2</sub>S<sub>2</sub>Sn requires C, 35.26; H, 4.04; Sn, 21.85%).

## Results and Discussion

Iodination of tetraaryltin compounds (Ar<sub>4</sub>Sn) by I<sub>2</sub> have been reported<sup>12</sup> to cleave up to two tin-aryl bonds successively yielding the corresponding diaryltin diiodides (Ar<sub>2</sub>SnI<sub>2</sub>), through an isolable intermediate Ar<sub>3</sub>SnI. Attempts were made under identical conditions to synthesize diaryltin chloride iodide (Ar<sub>2</sub>SnClI) by the reaction of I<sub>2</sub> and Ph<sub>3</sub>SnCl. No reaction was observed and the reactants were recovered unchanged probably due to the reduced nucleophilic character of tin-aryl bonds in Ar<sub>3</sub>SnCl as compared to that in Ar<sub>4</sub>Sn or in Ar<sub>3</sub>SnI.

In an earlier investigation<sup>13</sup> on the reaction of tetraorganometallics by ICl and IBr we have observed that both mono and di-tin-carbon bond cleavages occur. This prompted us to try this reaction on Ph<sub>3</sub>SnI (for Ph<sub>2</sub>SnClI or Ph<sub>2</sub>SnBrI) with these electrophiles. Unexpectedly, cleavage of both tin-phenyl and tin-iodine bonds were observed. Thus, the reaction of equimolar quantities of ICl and Ph<sub>3</sub>SnI gave 0.5 mole of Ph<sub>2</sub>SnCl<sub>2</sub> along with 0.5 mole of unreacted Ph<sub>3</sub>SnI, 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 Ph<sub>3</sub>SnI preferentially cleaves the tin-iodine bond only giving Ph<sub>3</sub>SnBr and I<sub>2</sub>.



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<sup>14</sup>. 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 Ar<sub>3</sub>SnBr with ICl or of Ar<sub>3</sub>SnCl with IBr successfully yielded the mixed diaryltin dihalides Ar<sub>2</sub>SnClBr and aryl iodide.

The mixed diaryltin dihalides (Ar<sub>2</sub>SnClBr) were also obtained through the reaction of Br<sub>2</sub> with Ar<sub>3</sub>-SnCl. The other product obtained was aryl bromide.

It is thus evident that the replacement of I in Ar<sub>3</sub>SnI 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 Ar<sub>3</sub>SnF in which there is a further decrease in nucleophilicity of Ar-Sn bonds and the effect of change in the metal, e.g. with Ar<sub>3</sub>GeX and Ar<sub>3</sub>PbX are currently being studied.

In some preliminary experiments attempts were made to synthesize diphenyltin chloride iodide by

TABLE 2 — ADDUCTS OF Ar<sub>2</sub>SnXY WITH DIMETHYL SULPHOXIDE

Adducts(a,b)	m.p. (°C)	Found (%) (Calc.)		
		C	H	Sn
Ph <sub>2</sub> SnClBr.2L	144	35.30 (35.26)	4.04 (4.04)	21.90 (21.85)
Ph <sub>2</sub> SnClBr.2L	143-44	35.24 (35.26)	4.00 (4.04)	21.88 (21.85)
Ph <sub>2</sub> SnClBr.2L	144	35.42 (35.26)	3.96 (4.04)	21.94 (21.85)
( <i>p</i> -Tol) <sub>2</sub> SnClBr.2L	164-65	37.42 (37.72)	4.44 (4.54)	20.72 (20.78)
( <i>p</i> -Tol) <sub>2</sub> SnClBr.2L	165	37.64 (37.72)	4.38 (4.54)	20.70 (20.78)
( <i>p</i> -Tol) <sub>2</sub> SnClBr.2L	165	37.68 (37.72)	4.50 (4.54)	20.74 (20.78)

(a) L = dimethyl sulphoxide.

(b) Products are obtained in 80-90% yields.

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 ( $R_2SnXY_2 \cdot 2DMSO$ ) which showed the characteristic shift in  $\nu_{S=O}$  from 1045  $cm^{-1}$  in DMSO to  $945 \pm 5$   $cm^{-1}$  in the tin complexes, indicating coordination through oxygen of the DMSO molecule to tin. The structures of  $R_2SnX_2 \cdot 2DMSO$  have been exhaustively studied earlier<sup>15-17</sup> 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

1. INGHAM, R. K., ROSENBERG, S. K. & GILMAN, H., *Chem. Rev.*, **60** (1960), 459.
2. ARONHEIM, B., *Ann. Chem.*, **194** (1878), 145.
3. HUGEL, G., *Kolloid Z.*, **4** (1953), 131.
4. ALLESTON, D. L. & DAVIES, A. G., *J. chem. Soc.*, (1962), 2050.
5. KANDIL, S. A. & ALLRED, A. L., *J. chem. Soc.*, (A), (1970), 2987.
6. LEVCHUK, L. E., SAMS, J. R. & AUBKE, F., *Inorg. Chem.*, **11** (1972), 43.
7. ARMITAGE, D. A. & TARASSOLI, A., *Inorg. Chem.*, **14** (1975), 1210.
8. CHALLENGER, F. & ALLPRESS, C. F., *Proc. chem. Soc.*, **30** (1914), 292.
9. SRIVASTAVA, T. N. & BHATTACHARYA, S. N., *J. inorg. nucl. Chem.*, **28** (1966), 2445.
10. FOLARANMI, A., MCLEAN, R. A. N. & WADIBIA, N., *J. organometal. Chem.*, **73** (1974), 59.
11. VOGEL, A. I., *Practical organic chemistry* (Longmans, Green, London), 1971, 538.
12. SRIVASTAVA, T. N. & BHATTACHARYA, S. N., *Z. anorg. allg. Chem.*, **344** (1966), 102.
13. BHATTACHARYA, S. N., PREM RAJ & SRIVASTAVA, R. C., *J. organometal. Chem.*, **105** (1976), 45.
14. FERGUSON, L. N., *The modern structural theory of organic chemistry* (Prentice-Hall, Englewood, New York), 1963, 172.
15. LANGER, H. G. & BLUT, A. H., *J. organometal. Chem.*, **5** (1966), 288.
16. TANAKA, T., *Inorg. chim. Acta*, **1** (1967), 217.
17. KHURANA, M., *Studies on arylltin and aryllead complexes with some nitrogen and oxygen donors*, Ph.D. Thesis, Lucknow University, 1976.