



## HALO AND PSEUDOHALO-DEMETALLATION IN TETRA AND PENTA-ORGANOMETAL AND METALLOIDS

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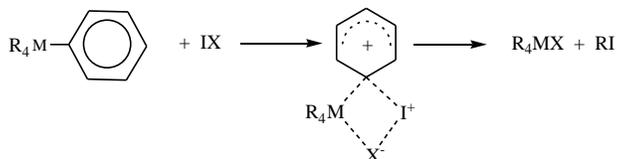
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### ABSTRACT

Halo and pseudohalo demetallation reactions of higher valent pentaphenyl -arsenic and antimony and tetrapolyfluorophenyl tin have been carried out employing halogens  $X_2$  ( $X = \text{Br}, \text{I}$ ) interhalogens  $\text{IX}$  ( $X = \text{Cl}, \text{Br}$ ),  $\text{ICl}_3$ , pseudohalogen  $(\text{SCN})_2$ , halo-pseudohalogens  $\text{XSCN}$  ( $X = \text{Cl}, \text{Br}$ )  $\text{IN}_3$ ,  $\text{INCO}$  and, metallic halides  $\text{TeCl}_4$  and  $(\text{NH}_4)_2\text{PbCl}_6$ . Reaction of  $(\text{C}_6\text{H}_5)_5\text{M}$  ( $\text{M} = \text{As}, \text{Sb}$ ) with these electrophiles afforded corresponding arsonium and stibonium derivatives  $(\text{C}_6\text{H}_5)_4\text{MX}$  while reactions of tetrafluorophenyl tin  $(\text{C}_6\text{F}_5)_4\text{Sn}$  with halogens and interhalogens yielded corresponding  $(\text{C}_6\text{F}_5)_n\text{SnX}_{4-n}$  ( $X = \text{Cl}, \text{Br}$   $n = 2, 3$ ) derivatives depending upon the molar ratio of reactants and the reaction conditions. The products have been identified by m.p. elemental analysis and spectroscopic data.

**Keywords:** Pentaphenyl -arsenic and -antimony, tetrahalophenyltins, halogens, pseudohalogens, halo-pseudohalogens, metallic halides.

**Graphical abstract:** Halogens, interhalogens, pseudohalogens and metallic halides cleave metal-carbon bond(s) from  $\text{R}_5\text{M}$  ( $\text{M} = \text{As}, \text{Sb}$ ) under varying conditions.



**Keywords:** Pentaphenyl -arsenic and -antimony, tetrahalophenyltins, halogens, pseudohalogens, halo-pseudohalogens, metallic halides.

## INTRODUCTION

Despite a considerable interest in the electrophilic cleavage and oxidative addition reactions of symmetrical tetra and hexa-organometallics of group 14 and symmetrical trivalent group 15 organometallic derivatives involving metal-carbon and metal-metal bonds based on hydrocarbon ligands with halogens  $X_2$  ( $X = Cl, Br, I$ ), interhalogens  $IX$  ( $X = Cl, Br$ ),  $ICl_3$ , pseudohalogens  $(SCN)_2$ , halo-pseudohalogens ( $IN_3, INCO$ ), metallic halides ( $HgCl_2, TeCl_4, SbCl_5$ ), positive halogen containing heterocyclic derivatives viz. N-bromosuccinimide, N-halophthalimide and N-chlorobenzotriazole, reactions of pentaphenylarsenic, -antimony and -bismuth ( $R_5M, M = As, Sb$ ) and tetra(pentafluorophenyl)tin and -lead have been reported to a limited extent.<sup>[1-11]</sup> Apart from this, reactions of less common electrophiles viz.  $ClSCN, BrSCN, (NH_4)_2PbCl_6$ , with pentaaryl arsenic, -antimony and -bismuth are yet to be investigated. Sowerby et al.<sup>[10]</sup> have partially examined the oxidative addition reactions of  $R_3Sb$  ( $R = Ph, Me$ ) with  $BrSCN$  and  $ClSCN$ . Reactions of diammonium hexachloro plumbate  $(NH_4)_2PbCl_6$  and diselenocyanogen  $(SeCN)_2$  have been reported to limited extent.<sup>[1]</sup> However, oxidative addition reactions of such electrophiles with tris(pentafluorophenyl)antimony have been investigated by Singhal et al. <sup>[4-7]</sup> Reactions of pentaphenyl arsenic, -antimony and -bismuth in higher valent with these electrophiles have not been reported so far. The lack of published data coupled with our interest on the oxidative addition and electrophilic cleavage reactions of group 14 and 15 metal-carbon bond(s) we now wish to report.

- ❖ Reactions of  $Ph_5M$  ( $M = As, Sb$ ) with halogens ( $Cl, Br, I$ ) interhalogens  $ICl, IBr$  and  $ICl_3$ , and less common electrophiles such as  $IN_3, INCO, (SCN)_2, ClSCN, BrSCN$ , and metallic halides  $(NH_4)_2PbCl_6, TeCl_4$  and  $HgCl_2$  which have not been reported to date.
- ❖ Reactions of tetra (pentafluorophenyl)tin with halogens and interhalogens.

Apart from synthetic utility to provide newer organometallic derivatives which are otherwise difficult to obtain, these reactions provide an insight to the relative ease of cleavage of an organic group from the metal. Reactions of less common electrophiles  $INCO, IN_3$  have earlier been used for regio and stereo specific addition in synthetic organic chemistry.

**EXPERIMENTAL**

Pentaaryl –arsenic and –antimony and tetra is (polyfluorophenyl) tin were prepared by the reported methods <sup>[1-3]</sup> ICl, ICl<sub>3</sub>, TeCl<sub>4</sub> (Sigma Aldrich) were used without further purification. (NH<sub>4</sub>)<sub>2</sub>PbCl, (NH<sub>4</sub>)<sub>2</sub>PbCl<sub>6</sub> was prepared by the reported procedure. (SCN)<sub>2</sub>, IN<sub>3</sub>, INCO, XSCN(X = Cl, Br) were freshly generated in solution before use. A few experiments are given below. Further details are given in Tables-1 to 4.

Reactants	Molar ratio	Products	Melting point °C	Temp. & solvent
Ph <sub>5</sub> Sb+ (NH <sub>4</sub> ) <sub>2</sub> PbCl <sub>6</sub>	1:1	Ph <sub>4</sub> SbCl	205°C	Room temp. CCl <sub>4</sub>
Ph <sub>5</sub> Sb + TeCl <sub>4</sub>	1:1	Ph <sub>4</sub> SbCl PhTeCl <sub>3</sub>	205°C	Room temp. Toluene
Ph <sub>5</sub> Sb + TeCl <sub>4</sub>	1:1	Ph <sub>3</sub> SbCl <sub>2</sub> Ph <sub>2</sub> TeCl <sub>2</sub>	142°C	Reflux temp. Toluene
Ph <sub>5</sub> As+ (NH <sub>4</sub> ) <sub>2</sub> PbCl <sub>6</sub>	1:1	Ph <sub>4</sub> AsCl	256°C	Room temp. CCl <sub>4</sub>
Ph <sub>5</sub> As + TeCl <sub>4</sub>	1:1	Ph <sub>4</sub> AsCl PhTeCl <sub>3</sub>	256°C	Room temp. Toluene
Ph <sub>5</sub> As + TeCl <sub>4</sub>	1:1	Ph <sub>3</sub> AsCl <sub>2</sub> Ph <sub>2</sub> TeCl <sub>4</sub>	205°C	Reflux temp. Toluene

**Table 1:** Reaction with metallic halides

Reactants	Molar ratio	Products	Melting point (0°C)	Temp. & solvent
Ph <sub>5</sub> Sb + 2ICl	1:2	Ph <sub>3</sub> SbCl <sub>2</sub>	142	0°C Acetonitrile
Ph <sub>5</sub> As + 2ICl	1:2	Ph <sub>3</sub> AsCl <sub>2</sub>	205	0°C Acetonitrile
Ph <sub>5</sub> Sb + ICl <sub>3</sub>	1:1	Ph <sub>3</sub> SbCl <sub>2</sub>	142	0°C Acetonitrile
Ph <sub>5</sub> As + Br <sub>2</sub>	1:1	Ph <sub>3</sub> AsBr <sub>2</sub>	213	-5°C CCl <sub>4</sub>
Ph <sub>5</sub> Sb + (SCN) <sub>2</sub>	1:1	Ph <sub>4</sub> Sb(SCN) PhSCN	226	-5°C CCl <sub>4</sub>
Ph <sub>5</sub> As + (SCN) <sub>2</sub>	1:1	Ph <sub>4</sub> As(SCN) PhSCN	130	-5°C CCl <sub>4</sub>
Ph <sub>5</sub> Sb + BrSCN	1:1	Ph <sub>4</sub> SbBr PhSCN	210	0°C Acetonitrile
Ph <sub>5</sub> Sb + ClSCN	1:1	Ph <sub>4</sub> SbCl PhSCN	205	0°C Acetonitrile
Ph <sub>5</sub> As + BrSCN	1:1	Ph <sub>4</sub> AsBr PhSCN	314	0°C Acetonitrile
Ph <sub>5</sub> Sb + IN <sub>3</sub>	1:1	Ph <sub>4</sub> SbN <sub>3</sub> PhI	190	-10°C Acetonitrile
Ph <sub>5</sub> Sb + INCO	1:1	Ph <sub>4</sub> SbNCO PhI	140	0°C Acetonitrile
Ph <sub>5</sub> As + I <sub>2</sub>	1:1	Ph <sub>4</sub> AsI PhI	315	Room Temp. Methyl Cyanide
Ph <sub>5</sub> Sb + I <sub>2</sub>	1:1	Ph <sub>4</sub> SbI PhI	200	Room Temp. Methyl Cyanide
Ph <sub>5</sub> As + 2IBr	1:2	Ph <sub>3</sub> AsBr <sub>2</sub> PhI	213	Room Temp. CCl <sub>4</sub>
Ph <sub>5</sub> Sb + 2IBr	1:2	Ph <sub>3</sub> SbBr <sub>2</sub> PhI	214	Room Temp. CCl <sub>4</sub>

**Table 2:** Reaction with Halogens, interhalogens and pseudohalogens

Compound	Molecular formula	M.P. (Lit) °C	Yield (%)	Ref.
Ph <sub>4</sub> Sb(SCN)	C <sub>25</sub> H <sub>20</sub> NSSb	226 (226-228)	70	14
Ph <sub>4</sub> As(SCN)	C <sub>25</sub> H <sub>20</sub> AsNS	130 (131)	60	13
Ph <sub>4</sub> SbN <sub>3</sub>	C <sub>24</sub> H <sub>20</sub> N <sub>3</sub> Sb	190 (191)	65	14
Ph <sub>4</sub> SbNCO	C <sub>25</sub> H <sub>20</sub> NOSb	140 (141)	67	14
Ph <sub>4</sub> SbBr	C <sub>24</sub> H <sub>20</sub> BrSb	210 (210-212)	63	14
Ph <sub>4</sub> SbCl	C <sub>24</sub> H <sub>20</sub> ClSb	205 (204-205)	58	14
Ph <sub>4</sub> AsCl	C <sub>24</sub> H <sub>20</sub> AsCl	256 (257)	72	15
Ph <sub>4</sub> AsBr	C <sub>24</sub> H <sub>20</sub> AsBr	314 (319)	57	15
Ph <sub>4</sub> AsI	C <sub>24</sub> H <sub>20</sub> AsI	315 (314-319)	62	12,13
Ph <sub>3</sub> SbCl <sub>2</sub>	C <sub>18</sub> H <sub>15</sub> SbCl <sub>2</sub>	142 (143.5)	56	13
Ph <sub>3</sub> AsCl <sub>2</sub>	C <sub>18</sub> H <sub>15</sub> AsCl <sub>2</sub>	205 (205)	70	12
Ph <sub>4</sub> SbI	C <sub>24</sub> H <sub>20</sub> SbI	200 (200)	67	14
Ph <sub>3</sub> SbBr <sub>2</sub>	C <sub>18</sub> H <sub>15</sub> SbBr <sub>2</sub>	214 (216)	72	15
Ph <sub>4</sub> As(SCN)	C <sub>25</sub> H <sub>20</sub> AsNS	130 (131)	60	13
Ph <sub>3</sub> AsBr <sub>2</sub>	C <sub>18</sub> H <sub>15</sub> AsBr <sub>2</sub>	213 (213-214)	56	15

**Table 3:** Analytical data of tri and tetraaryl antimony (V) derivatives

Compound	Empirical Formula	Molecular Weight	Found (Calcd.)	Found (Calcd.)	Found (Calcd.)
			% - C	% - H	% - N
Ph <sub>4</sub> Sb(SCN)	C <sub>25</sub> H <sub>20</sub> NSSb	488.26	61.50 (61.22)	4.13 (4.56)	2.87 (2.98)
Ph <sub>4</sub> As(SCN)	C <sub>25</sub> H <sub>20</sub> AsNS	441.42	68.02 (68.23)	4.57 (4.14)	3.17 (3.19)
Ph <sub>4</sub> SbN <sub>3</sub>	C <sub>24</sub> H <sub>20</sub> N <sub>3</sub> Sb	472.22	61.05 (61.12)	4.27 (4.78)	8.90 (8.81)
Ph <sub>4</sub> SbNCS	C <sub>25</sub> H <sub>20</sub> NSSb	488.26	61.50 (62.34)	4.13 (4.34)	2.87 (2.03)
Ph <sub>4</sub> SbNCO	C <sub>25</sub> H <sub>20</sub> NOSb	472.19	63.23 (64.12)	4.56 (4.01)	2.88 (2.07)
Ph <sub>4</sub> SbBr	C <sub>24</sub> H <sub>20</sub> BrSb	510.08	56.51 (56.12)	3.95 (3.45)	-
Ph <sub>4</sub> SbCl	C <sub>24</sub> H <sub>20</sub> ClSb	465.63	61.91 (61.12)	4.33 (4.10)	-
Ph <sub>4</sub> AsCl	C <sub>24</sub> H <sub>20</sub> AsCl	418.79	68.83 (68.34)	4.81 (4.48)	-
Ph <sub>4</sub> AsBr	C <sub>24</sub> H <sub>20</sub> AsBr	463.24	62.23 (62.14)	4.35 (4.01)	-
Ph <sub>4</sub> AsI	C <sub>24</sub> H <sub>20</sub> AsI	510.24	56.49 (56.34)	3.95 (3.67)	-
Ph <sub>3</sub> SbCl <sub>2</sub>	C <sub>18</sub> H <sub>15</sub> SbCl <sub>2</sub>	423.98	50.99 (50.45)	3.57 (3.41)	-
Ph <sub>3</sub> AsCl <sub>2</sub>	C <sub>18</sub> H <sub>15</sub> AsCl <sub>2</sub>	377.14	57.32 (57.56)	4.01 (4.90)	-
Ph <sub>4</sub> SbI	C <sub>24</sub> H <sub>20</sub> SbI	557.08	51.74 (51.39)	3.62 (3.09)	-

**Table 4:** Elemental Analysis of Metal and Organometal -Halides/-pseudohalides

**Reaction of Pentaphenylarsenic with ICl (1:2):**

Iodine monochloride (3.4g, 0.02 mol) in acetonitrile was slowly added to a well stirred and chilled cold (0°C) suspension of pentaphenylarsenic (4.6g, 0.01 mol) in the same solvent. The initial blood-red colour of ICl solution disappeared immediately after each addition. The mixture was further stirred for 30 min to ensure complete reaction and then worked up. The residue (after distilling off PhI) was recrystallised from pet. Ether and identified as triphenylarsinic dichloride.

M.P.: - 205°C

Lit.: - 205°C<sup>[12]</sup>**Reaction of Pentaphenylantimony with ICl (1:2):**

Ph<sub>3</sub>SbCl<sub>2</sub> was prepared same by method as described above from Iodine monochloride (3.4g 0.02 mol) and pentaphenylantimony (5.02g 0.0099mol) in acetonitrile.

M.P.: - 142°C

Lit.: 143.5°C<sup>[13]</sup>**Reaction of Pentaphenylantimony with ICl<sub>3</sub>:**

Iodine trichloride (2.33g 0.01mol) in acetonitrile was slowly added to a well stirred and chilled cold (0°C) suspension of pentaphenylantimony (5.07g 0.01mol) in same solvent. The mixture was further stirred for 30 min. to ensure complete reaction and worked up. The residue (after distilling PhI) was recrystallised from pet. Ether and identified as triphenylantimony dichloride.

M.P.: - 142°C

Lit. : 143.5°C<sup>[13]</sup>**Reaction of Pentaphenylantimony with I<sub>2</sub> (1:1):**

A solution of I<sub>2</sub> (2.53g, 0.01 mol) in methyl cyanide was added dropwise for 30 min to a well stirred solution of pentaphenylantimony (5.07g 0.01 mol) in CH<sub>3</sub>CN at room temperature. The violet colour of I<sub>2</sub> disappeared after each addition. Towards the end of the reaction the solution changed its colour to pink. Subsequently, the solution was stirred for 1h. It was freed from solvent and phenyl iodide distilled off. The residue was recrystallised from pet. Ether to give Ph<sub>4</sub>SbI.

M.P.: - 200°C

Lit.: 200°C<sup>[14]</sup>**Reaction of Pentaphenylarsenic with Bromine (1:2):**

A solution of bromine (3.2g 0.02 mol) in CCl<sub>4</sub> was added dropwise over a period of half an hour to a well stirred cold (-5°C) suspension of pentaphenylarsenic (4.6g 0.01 mol) in CCl<sub>4</sub>. The initial red colour of bromine immediately disappeared after each addition. At the end of the reaction the solution was further stirred for half an hour. It was then free from the solvent and the residue was distilled at reduced pressure to give triphenylarsenic dibromide.

M.P.: -213°C

Lit.: - 213-214°C<sup>[15]</sup>**Reaction of Pentaphenylantimony with (SCN)<sub>2</sub>:**

A freshly prepared solution of thiocyanogen in CCl<sub>4</sub> (30ml) was added with stirring to pentaphenylantimony (5.07g 0.01mol) in CCl<sub>4</sub> (50ml) subsequently stirred for 1h and warmed to room temperature. The removal of the solvent under reduced pressure afforded a crystalline solid. After recrystallization from ethanol it was characterised as tetraphenylantimony thiocyanate.

M.P.: - 226°C

Lit.: - 226-228°C<sup>[14]</sup>

Similarly reaction of pentaphenylarsenic and thiocyanogen yielded tetraphenylarsenic thiocyanate.

M.P.: - 130°C

Lit.: - 131°C<sup>[13]</sup>**Reaction of Pentaphenylantimony with IN<sub>3</sub>:**

A freshly generated solution of Iodine azide (1.68g 0.01mol) in acetonitrile (50ml) at -10°C was added to stirring solution of pentaphenylantimony (5.07g 0.01mol) in the same solvent (50ml) during 15min under nitrogen atmosphere. The reactant were stirred for 1h at initial temp. and then allowed to come at room temp. The solution was evaporated under reduced pressure and cooled overnight, after adding pet. ether crystalline solid was obtained characterised as tetraphenylantimony azide.

M.P.: - 190°C

Lit.: 191°C<sup>[14]</sup>**Reaction of Pentaphenylantimony with BrSCN:**

In a typical experiment a freshly generated red brown colour solution of BrSCN was added dropwise to Ph<sub>5</sub>Sb (5.07g 0.01mol) over a period of 30min. at 0°C temp. and contents were stirred for 2h more. After usual work-up tetraphenylantimony bromide was obtained.

M.P.: - 210°C

Lit.: 210-212°C<sup>[14]</sup>

Similarly, the reaction of thiocyanate bromide and Ph<sub>5</sub>As yielded Ph<sub>4</sub>AsBr

M.P.: - 314°C

Lit.: 319°C<sup>[15]</sup>**Reaction of Pentaphenylantimony with ClSCN:**

Freshly generated golden yellow solution of ClSCN was added to Ph<sub>5</sub>Sb (5.07g 0.01mol) in 100ml CCl<sub>4</sub> over a period of 30 min. in ice cold temp. The reactants were stirred at the same temp. After work-up in usual fashion, tetraphenylantimony chloride was obtained.

M.P. :- 205°C

Lit.:204-205°C<sup>[14]</sup>

**Reaction of Pentaphenylantimony with  $(\text{NH}_4)_2\text{PbCl}_6$  (1:1):**

Pentaphenylantimony (5.07g 0.01mol) and ammonium hexachloroplumbate (4.56g 0.01mol) were stirred in pet. ether for 1h at room temperature. The initial bright-yellow colour of  $(\text{NH}_4)_2\text{PbCl}_6$  changed to creamish white. After the completion of the reaction, the inorganic halides was filtered and washed twice with acetonitrile. Evaporation of the solvent yielded tetraphenylantimony chloride.

M.P.: - 205°C

Lit.: - 204-205°C<sup>[14]</sup>

Similarly the reaction of pentaphenylarsenic and ammonium hexachloroplumbate at room temp. yielded  $\text{Ph}_4\text{AsCl}$

M.P.: - 256°C

Lit.: - 257°C<sup>[15]</sup>**Reaction of Pentaphenylantimony with  $\text{TeCl}_4$  (1:1 Room Temperature):**

A mixture of pentaphenylantimony (5.07g 0.01mol) and  $\text{TeCl}_4$  (2.69g 0.01mol) in toluene were stirred at room temperature for 1h and filtered. The filtrate on concentration yielded tetraphenylantimony chloride. Phenyltellurium trichloride being insoluble was separated as off white solid.

 $\text{Ph}_4\text{SbCl}$  M.P.: - 205°CLit.: - 204-205°C<sup>[15]</sup> $\text{PhTeCl}_3$  M.P.: -214°CLit.: - 214-216°C<sup>[15]</sup>**Reaction of Pentaphenylantimony with  $\text{TeCl}_4$  (Reflux Temperature):**

Pentaphenyl antimony (5.07g 0.01mol) in 100ml toluene and  $\text{TeCl}_4$  (2.69g 0.01mol) in the same solvent (40ml) were refluxed together for 3hrs. diphenyltellurium dichloride obtained as insoluble off white solid was filtered out.

M.P.: - 158°C

Lit. :-160°C<sup>[15]</sup>The filtrate on concentration yielded  $\text{Ph}_3\text{SbCl}_2$ 

M.P.: -142°C

Lit. :-143.5°C<sup>[13]</sup>**Reactions of  $(\text{C}_6\text{F}_5)_4\text{Sn}$  with  $\text{ICl}$ :**

A solution of iodine monochloride 3.24g(0.02mol) in carbon tetrachloride was added dropwise to a solution of tetrakis(pentafluorophenyl)tin 7.86g(0.01mol) in the same solvent over a period of 30 minutes. After each addition colour of  $\text{ICl}$  faded away. The reaction mixture was stirred for a period of one hrs to ensure completion of the reaction. The solvent was distilled off at reduced pressure to leave behind a viscous mass which could not be crystallised. It was isolated as DMSO complex and characterized as  $(\text{C}_6\text{F}_5)_2\text{SnCl}_2 \cdot 2\text{DMSO}$ .

M.P.: - 129°C

Lit.: - 130°C<sup>[16]</sup>

## RESULTS AND DISCUSSION

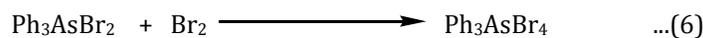
In earlier communications reported from our laboratory cleavage of metal-carbon bond from tetraorganometallics both symmetrical and unsymmetrical (M= Si, Ge, Sn, Pb) employing halogens, interhalogens and pseudohalogens has been reported.<sup>[2-10]</sup> Similarly, the oxidative addition reactions of triaryl-arsenic and -antimony with such electrophiles has been substantially reported. Contrasting behaviour of triarylbismuth compounds where cleavage of bismuth-carbon bond rather than addition to bismuth oxidatively has been observed. In view of the limited data available for the cleavage reactions of pentaphenyl-arsenic and -antimony with less common electrophiles we undertook a systematic study on higher valent arsenic and antimony compounds reported herein together with other systems.

### Cleavage Reactions of Pentaphenyl-Arsenic and -Antimony:

Both ICl and ICl<sub>3</sub> are strong electrophiles and cleave two M-C bonds from Ph<sub>5</sub>M (M= As, Sb) irrespective of the molar ratio of the electrophile used.



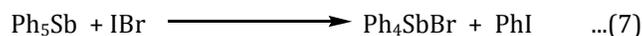
Even with an excess of ICl further cleavage of As-C or Sb-C bond was not observed. It is surprising since bromine which is an equally strong electrophile like ICl has been reported to produce Ph<sub>3</sub>AsBr<sub>4</sub> in the sense of equations shown below (Eqs.5 & 6)



Bromination of pentaphenylantimony produced triphenylantimony dibromide at 0°C irrespective of the molar ratio of bromine used. However, iodine cleavage of Ph<sub>5</sub>Sb yielded tetraphenylantimony iodide with 1 mole of I<sub>2</sub> and triphenylantimony diiodide with 2 moles of I<sub>2</sub>, respectively. Addition of three moles of bromine and iodine was not successful in producing triphenylantimony tetrahalides presumably due to the reduced nucleophilic character of antimony-phenyl bonds in triphenylantimony dihalides as compared to that in pentaphenylantimony. Reactions of iodine monochloride with pentaphenylantimony invariably produced Ph<sub>3</sub>SbCl<sub>2</sub> at a lower temperature, irrespective of the molar ratio of the electrophiles used. However, 1:1 and 1:2 molar reactions of IBr with Ph<sub>5</sub>Sb gave Ph<sub>4</sub>SbBr and Ph<sub>3</sub>SbBr<sub>2</sub> at room temperature and 70° respectively.

The extent of cleavage is confined only to the removal of two phenyl groups from pentaphenylarsenic or -

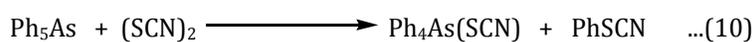
antimony compounds with iodine monochloride and iodine trichloride which was confirmed by treating the pentaphenylarsenic or -antimony compounds with an excess amount (>2mole) of the iodine halides. Formation of diphenyl-metal (V) trihalides did not take place on prolong stirring. This observation is also supported by the fact that iodine monochloride did not decolourise in refluxing CH<sub>3</sub>CN when treated against Ph<sub>3</sub>MCl<sub>2</sub> and unreacted starting material was recovered quantitatively. An argument in favour of cleavage of two phenyl groups from pentaphenylarsenic is also based on the observation that a similar reagent Br<sub>2</sub> reacts with Ph<sub>3</sub>AsBr<sub>2</sub> to produce Ph<sub>3</sub>AsBr<sub>4</sub>. No further cleavage was observed. Reaction of IBr and I<sub>2</sub> with pentaaryl-arsenic and -antimony proceeded in the sense shown below.



The observation made with IBr and I<sub>2</sub> are in line with the fact that the Sb-C bond is more reactive than As-C. Also the fission of second As-C in these reactions proceeds less readily due to reduced nucleophilic character of As-C bond coupled with the less polar nature of IBr and I<sub>2</sub>. However, there seems to be no kinetic study so far which have been carried out on this second fission reactions in pentaphenylarsenic.

From the results reported above and from our earlier investigations, the reactivity was found to be in the orders, Br<sub>2</sub> ≈ ICl > IBr > I<sub>2</sub> and As-C < Sb-C > Bi-C which is also the decreasing order of their bond polarity.

The formation of Ph<sub>3</sub>AsCl<sub>4</sub> was not observed with either of the electrophile. Both I<sub>2</sub> and IBr are weak electrophils and have been reported to cleave one metal-carbon bond both from Ph<sub>4</sub>E (E= Sn, Pb) and Ph<sub>5</sub>M (M= As, Sb).<sup>[17]</sup> Pseudohalogen like (SCN)<sub>2</sub> and pseudohalogens BrSCN and ClSCN are still weaker electrophiles but were found to cleave one As-C and Sb-C bond from Ph<sub>5</sub>M at 0° in acetonitrile.



Even with an excess of freshly generated solution of (SCN)<sub>2</sub>, BrSCN and ClSCN no further cleavage was observed. On raising the temperature above 0°C polymerisation of (SCN)<sub>2</sub> and XSCN (X= Cl, Br) preceded the cleavage. The study also provide an insight into the relative reactivity of X<sub>2</sub> (X= Cl, Br) with respect to (SCN)<sub>2</sub>. Both Cl<sub>2</sub> and Br<sub>2</sub> being more electronegative get attached to arsenic and antimony. It may be noted that both BrSCN and ClSCN are oxidatively added to Ph<sub>3</sub>M (M= As, Sb) to give oxidative addition products Ph<sub>3</sub>MXSCN (X= Cl, Br) and cleave metal-carbon bond from Ph<sub>4</sub>E (E= Sn, Pb) to a limited extent<sup>[5-8]</sup>. Further cleavage from Ph<sub>5</sub>E is possible to give dithiocyanate

or dihalide products and even more halogenated products in presence of  $\text{AlCl}_3$  as catalyst as has been reported for group 14 organometallics.<sup>[1]</sup> However, such reactions were not attempted as the organometallic products formed after the reactions are not expected to survive the drastic condition of hydrolysis.

$\text{IN}_3$  and  $\text{INCO}$ , which are still weaker electrophiles and were found to cleave one As-C bond from  $\text{Ph}_5\text{As}$  and one Sb-C bond from  $\text{Ph}_5\text{Sb}$  but to a limited extent and the yield of the product is low. This suggests that (i) both  $\text{IN}_3$  and  $\text{INCO}$  are also weaker electrophile as compared to  $\text{XSCN}$  ( $\text{X} = \text{Cl}, \text{Br}$ ) and  $(\text{SCN})_2$  and (ii) Sb-C bond is much more reactive as compared to As-C bond as indicated by the yield of the products. We have earlier reported that  $\text{IN}_3$  and  $\text{INCO}$  cleaved metal-carbon (Sn) bond only in presence of  $\text{AlCl}_3$  while the reaction of tetraorganolead with  $(\text{SCN})_2$ ,  $\text{BrSCN}$  and  $\text{ClSCN}$  proceed at  $0^\circ\text{C}$  in absence of  $\text{AlCl}_3$ .<sup>[2-8]</sup>



Reactions of  $\text{Ph}_5\text{Sb}$  and  $\text{Ph}_5\text{As}$  were also carried out with diammonium hexachloroplumbate which has been used in past as chlorinating agent especially, in the cleavage reactions of tetraaryl leads. While the cleavage of Pb-C bond in tetraarylleads employing chlorine is uncontrolled and more than three lead-carbon bonds are cleaved. Reactions with  $(\text{NH}_4)_2\text{PbCl}_6$  is limited to the cleavage of two lead-carbon bonds due to the slow release of chlorine. In the present investigation reaction of pentaphenyl antimony and pentaphenylarsenic proceeded with the cleavage of only one Sb-C and As-C bond respectively.

### Reaction of Ammonium Hexachloroplumbate $(\text{NH}_4)_2\text{PbCl}_6$ with $\text{Ph}_5\text{M}$ ( $\text{M} = \text{As}, \text{Sb}$ ):

$(\text{NH}_4)_2\text{PbCl}_6$  is a slow chlorinating agent which dissociate in the sense of equation show below

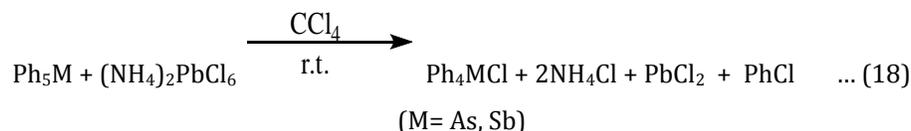


The slow release of  $\text{Cl}_2$  in solution such as acetonitrile has been used in the past for the controlled cleavage of tetraarylleads to give diaryllead dihalides. Direct chlorination of tetraaryllead is quite devastating and cleave two Pb-C bonds to give ultimate product  $\text{PbCl}_2$ . However with the slow release of  $\text{Cl}_2$  in solution exclude the cleavage beyond more than two lead-carbon bonds

In case of  $\text{Ph}_5\text{M}$ , cleavage of both As-C and Sb-C bond was observed. It is interesting to note in both the case only cleavage of one metal-carbon bond was observed.



Both  $\text{Ph}_4\text{SbCl}$  and  $\text{Ph}_4\text{AsCl}$  were separated from the mixture being soluble in organic solvents while  $\text{NH}_4\text{Cl}$  and  $\text{PbCl}_2$  being insoluble in the solvent are easily separated out.

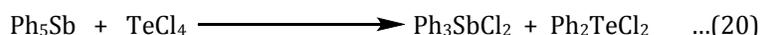


Tetraphenylstibonium and -arsenium being soluble in organic solvent are easily separated out from the solution.

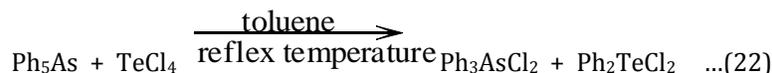
Similarly, the reaction of tellurium tetrachloride at room temperature proceeded with the cleavage of one Sb-C from pentaphenylantimony.



However, at reflux temperature of toluene two Sb-C carbon bonds are cleaved.



Similar course of reaction was observed with Ph<sub>5</sub>As



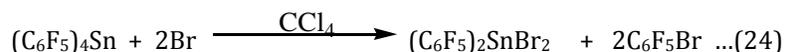
The mechanism of such reactions may possibly involve a four centered transition state in which nucleophilic attack on metal atom (facilitated by the availability of vacant d-orbitals) by incipient chloride or bromide ion is synchronous with electrophilic attack by incipient iodide ion on carbon atom of the aromatic rings. Similar mechanism has earlier been suggested for the cleavage of group 14 compounds with halogens and interhalogens.<sup>[1-11, 16]</sup>

### Cleavage Reactions with Tetrakis(pentafluorophenyl)tin:

Both ICl and Br<sub>2</sub> are strong electrophile and have been reported to cleave two tin-aryl bonds from symmetrical and unsymmetrical tetraaryltins. Reaction of tetrakis(polyfluorophenyl)tin were expected to proceed in the same fashion but the extent of cleavage has not been studied so far. In the present study the author has found cleavage reaction to proceed in the sense of equation shown below.



Similarly bromine which is equally strong electrophile cleave to yielded bis(pentafluorophenyl)tin dibromide.



Both ICl and Br<sub>2</sub> are strong electrophile and cleave two Sn-C<sub>6</sub>F<sub>5</sub> bond to yield corresponding dihalides which is parallel to the reactions observed with tetraphenyltin. However (C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>SnCl<sub>2</sub> are obtained as a viscous mass and

the attempts to recrystallize it could not be successful. Alternatively it was characterized as its DMSO complex  $(C_6F_5)_2SnCl_2 \cdot 2DMSO$  which is white solid having satisfactory elemental analysis and IR.

Thus the cleavage pattern of partially or fully substituted phenyl group is same as for tetraphenyltin. In all the case at least two Sn-C bond are cleaved and that too at room temperature.

### Infrared spectra:

The title compounds were also identified on the basis of their infrared spectra in the range ( $4000\text{cm}^{-1}$ – $200\text{cm}^{-1}$ ). Absorption frequencies associated with phenyl groups bound to the metal atom, do not show any significant change. The thiocyanato group is capable of bonding through N or S of NCS group. Absorptions associated with various modes of vibrations of the pseudohalide group have been identified and indicate the nature of bonding to the antimony atom. The chalcogen group NCS gives rise to three fundamental modes of vibration due to  $\nu(C \equiv N)$ ,  $\nu(C-S)$  and  $\delta(NCS)$ . The  $\nu_{asy}$  NCS mode appears as a broad band of strong intensity at  $2060\text{ cm}^{-1}$  and is fully consistent with a N-bonded NCS group, in consonance with the usual isostructure reported for tetraphenylantimony isothiocyanates<sup>[18-22]</sup>

Further it has been reported that the intensity of  $\nu_{asy}$  NCS mode is 50-100 times stronger than that of  $\nu_{asy}$  SCN and the shape is broad for the former and sharp in the latter case. The position intensity and the shape of  $\nu NCS$  thus suggest an isostructure.<sup>[22]</sup>

The  $\delta$  NCS mode which is virtually  $\nu C-S$  mode, according to established views, lies at distinctly higher frequency in the isothiocyanates ( $760\text{-}880\text{cm}^{-1}$ ) and is a deciding factor about the nature of pseudohalide in these compounds. Thus, the appearance of a medium intensity band at  $860\text{ cm}^{-1}$  in all the derivatives suggests an isostructure. Further, the appearance of a band at  $472 \pm 2$  is suggestive of the presence of M-N bonding.

As for mass sensitive frequencies a medium strong band appearing in the region  $450\text{-}488\text{cm}^{-1}$  can be assigned to Sb stretching frequencies corresponding to  $\gamma$  mode. Absorption frequencies corresponding to the  $t$  mode appear in the region  $240\text{-}220\text{ cm}^{-1}$ . The values are good agreement with the reported frequencies of the Sb-C bond in  $Ar_4SbX$  derivatives ( $X = \text{halo or pseudohalo group}$ ).<sup>[18,19]</sup>

## CONCLUSION

The noteworthy features of cleavage reactions reported herein are

- ❖  $Br_2$ ,  $ICl$  and  $ICl_3$  act as strong electrophiles towards M-C bond(s) ( $M = As, Sb$ )
- ❖ Not more than two metal-carbon bond(s) are cleaved employing  $Br_2$  and further addition of  $Br_2$  leads to the formation of heptavalent compounds particularly in case of arsenic viz.,  $Ph_3AsBr_4$ .
- ❖ Pseudohalogen  $(SCN)_2$ , interhalopseudohalogens  $IN_3$ ,  $INCO$  and  $XSCN$  ( $X = Cl, Br$ ) are capable of cleaving only one metal-carbon bond from  $Ph_5M$  but the reactions are sluggish. On the basis of yield the reactivity of these

electrophiles can be arranged in the order  $\text{ClSCN} > \text{BrSCN} > (\text{SCN})_2 > \text{IN}_3 > \text{INCO}$ .

- ❖ On the basis of nature of products the polarity of XSCN appear to be  $\text{Cl}^{\delta-}\text{-SCN}^{\delta+}$  and  $\text{Br}^{\delta-}\text{-SCN}^{\delta+}$ . Thus Cl and Br are more electro negative than (SCN).
- ❖ Diammonium hexachloroplumbate  $(\text{NH}_4)_2\text{PbCl}_6$  can be used as chlorinating agent. Due to slow release of chlorine, the formation of heptavalent compound does not take place.
- ❖ Reactions with  $\text{TeCl}_4$  in varying conditions provide  $\text{PhTeCl}_3$  and  $\text{Ph}_2\text{TeCl}_2$  derivatives in high yield and high purity together with onium salts  $\text{Ph}_4\text{MCl}$  (M= As, Sb) which otherwise involve tedious quarterization reaction involving triarylmets  $\text{Ar}_3\text{M}$  and arylhalides in presens of Lewis acid catalylst at higher temperature.
- ❖ The reactivity of M-C bond (M= As, Sb, Bi) can be arranged in the order  $\text{As-C} > \text{Sb-C} > \text{Bi-C}$ .
- ❖ Both IBr and  $\text{I}_2$  are weak electrophiles as compared to ICl and  $\text{Br}_2$ .

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