

On The Synthesis and Reactivity of Electrophillic Cleavage Reactions of Tin-Carbon Bond(s)

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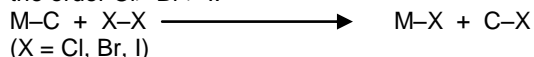
Abstract

Cleavage of Tetraphenyl-Tin and Tetrabutyl-Tin with Iodine monochloride (ICl) and Iodine monobromide (IBr) and Pentafluorophenyl tin $(C_6F_5)_nSn(C_6H_5)_{4-n}$ were treated with an telluriumtetrachloride ($TeCl_4$), Antimonypentachloride ($SbCl_5$), Iodineazide (IN_3), Thiocynozen (SCN)₂, DMSO, INCO etc. IN_3 and INCO thereby increasing their electrophilic character so that their positive end attacks the electron of their aromatic ring. The presence of tin- phenyl has been established by the interaction of organotin with tellurium tetrachloride ($TeCl_4$), Iodine monochloride (ICl), Iodine monobromide (IBr), IN_3 , INCO in high yield and high purity. In case of Tetraphenyl-Tin products ware characterized by converting them into corresponding oxide. The products have been characterized by elemental analysis and spectroscopic data (IR, 1H and ^{19}F NMR spectra).

Keywords: Organotin; IBr; ICl; Isothiocynate; INCO; IR; 1H ; ^{19}F ; ^{13}C ; NMR Spectra.

Introduction

Cleavage of group 14 metal-carbon bond(s) under the action of halogens is one of the most studied reactions of these compounds. It gives a potential route for the preparation of organometallic halides, together with a clear understanding of the reaction mechanism involved. They form an excellent example of electrophillic substitution, since the attack of an electrophillic reagent is wholly localized at metal-carbon bond and the reactions are generally not complicated by additional factors such as orientation and formation of polysubstituted products as the reaction conditions are usually very mild. In the case of the tetraorganometallics, (M=Si, Ge, Sn, Pb) halodemetalation has been studied fairly thoroughly for elucidating the mechanism of substitution at an aromatic carbon atom [1,2]. The ease with which the metal-carbon bond is cleaved depend both on the halogen used and on the nature of the metal-carbon bond to be attacked. Although the four halogens have been found to be active cleaving agents bromine and iodine are more commonly employed. Cleavage with fluorine has never been practiced and rarely applied with chlorine, because of their gaseous state, corrosive nature and excessive reactivity. Reactions in general may be represented as below with the reactivity decreasing in the order $Cl > Br > I$.



Halodestannylation

The first two organic groups in a tetraorganotin can be cleaved by halogens gradually under the appropriate reaction condition. In a very few cases, cleavage of three aryl group (e.g. phenyl) by bromine can be achieved [3]. One group is readily split off by bromine in carbon tetrachlorides or chloroform or in the absence of a solvent for tetraalkyltin compounds at -40° to $-30^\circ C$ [4], whereas two groups are readily removed at room temperature. In case of diethyltin bromide third group is cleaved with one equivalent of bromine at $70-80^\circ C$, to yield ethylotinnitramide [5]. From tetraaryltins two groups are simultaneously split off by bromine, even at low temperature. If, however, a solution of bromine in pyridine is used, triaryltin bromide can be prepared in good yield [6]. Not unexpectedly, cleavage by iodine proceeds less readily. In boiling ether or xylene [7] only one organic group is cleaved from tetraorganotins by iodine. Triphenyltin iodide is formed when tetraphenyltin is treated with iodine in refluxing chloroform [8]. Instances are known, however, where excess iodine in

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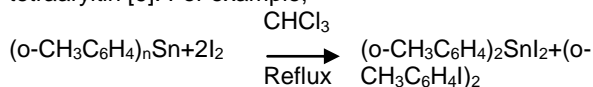
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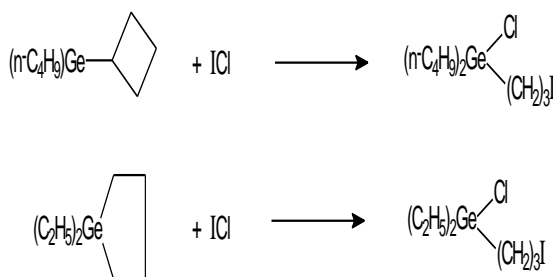
boiling chloroform will cleave two aryl groups from a tetraaryltin [9]. For example,



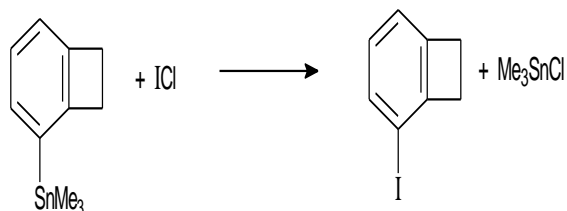
Iodohalodemetalation with Iodine Monochloride and Iodine Monobromide

Despite the great amount of work reported both on the preparative and mechanistic aspects of the reaction of tetraorganometallic compounds $\text{R}_n\text{MR}'_{4-n}$ (M= Ge, Sn and Pb) with halogen, the reactions of interhalogen such as XY (ICl, IBr and BrCl) and XY_3 (ICl_3) have only been the subjects of brief study.

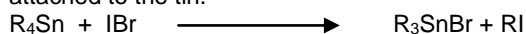
In case of organogermanium compounds iodine monochlorides has been effectively used to cleave the germmacyclobutane and germanocyclopentanes by Mazerolles *et al.* [10].



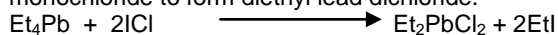
Eaborn *et al.* [11] reported the formation of 3-iodo-1,2-dihydrocyclobutane and presumably a triorganotin chloride from the cleavage of the corresponding 3-trimethyltin derivative with iodine monochloride.



Earlier a kinetic study [12] of iodine monobromide with tetramethyl and tetrapropyl-tin showed that in a non-polar solvent the polar mechanism involving two molecules of the interhalogen in the rate determining step was much more important than with the halogens. In all the cases products were determined by bond polarities and not by prediction based on hard or soft properties *i.e.* the mono electronegative atom (Br) being attached to the tin.

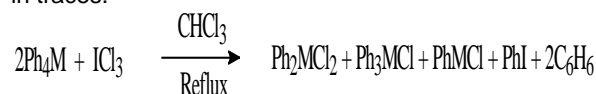


In 1950 Jahn [13] reported that tetraethyl lead undergo facile cleavage with iodine monochloride to form diethyl lead dichloride.



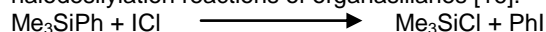
This reaction has been employed as a means of determining tetraethyl lead in air [14]. Cleavage of tetraphenyltin and lead with iodine trichloride has also been reported [15]. The products were dependent on stoichiometry and reaction

conditions. In refluxing chloroform, diphenyl and triphenyl lead and tin chlorides were obtained as the major products along with iodobenzene and benzene in traces.



(M = Pb, Sn)

Iodine monochloride has also been used in halodesilylation reactions of organosilanes [16].



Shaw and Allred reported the cleavage reactions of hexamethyldimetal compounds containing unsymmetrical metal-metal (M=C, Si, Ge and Sn) bond with ICl and critically examined the hypothesis that product of similar reactions are determined by polarity of the reacting bonds [17]. Cleavage of tin-arsenic and silicon-arsenic [18] and silicon-phosphorous [19] bonds with iodine monochloride and monobromide with a tetra-alkyltin (butyl) and a tetraoxytin (Phenyl) were also reported. In case of tetraphenyl tin products were characterized by converting them into corresponding oxides. Reactions of tetrabutyltin were also examined by ^1H NMR spectroscopy [20]. From the experiments of synthetic utility carried out in the present investigation it is not possible to predict the exact nature of the reaction mechanism involved. The kinetics of the reaction of tetramethyl and tetrapropyl tin with IBr indicate the presence of concurrent second and third order reaction with the third order mechanism dominating [21]. The ICl reactions because of the more polar nature of ICl are likely to be even more dominated by the third order mechanism involving complex formation between ICl and tetraaryl metal compound. Thus, the third order mechanism involved a π complex function between the iodine halide and aromatic ring as proposed by Eaborn [22]

Experimental

A few typical experiments are described here, further details are listed in Table-1 and Table-2

Reaction of $(\text{C}_6\text{H}_5)_3\text{Sn}(\text{C}_6\text{F}_5)$ with TeCl_4 (1:1 ratio)

A suspension of TeCl_4 (0.270 g, 1mmol) in toluene (20 ml) was added dropwise to a well stirred solution of $(\text{C}_6\text{H}_5)_3\text{SnC}_6\text{F}_5$ (0.366 g, 1 mmol) in the same solvent (50 ml) at room temperature in a span of 30 minutes. This mixture was stirred for about 20 hr to ensure the completion of the reaction. PhTeCl_3 thus formed was filtered off leaving behind diphenylpentafluorophenyl tin monochloride $(\text{C}_6\text{H}_5)_2\text{SnC}_6\text{F}_5\text{Cl}$ which was obtained after reducing the solvent and subsequent refrigeration.

M.P. Insoluble (PhTeCl_3) = 215° Lit. 218° (24)

Soluble [$(\text{C}_6\text{H}_5)_2\text{SnC}_6\text{F}_5\text{Cl}$] – 145°C

Reaction of $(\text{C}_6\text{H}_5)_3\text{Sn}(\text{C}_6\text{F}_5)$ with SbCl_5 (1:1 ratio)

A solution of SbCl_5 (0.30 g, 1 mmol) in CCl_4 (20 ml) was added dropwise to a well stirred solution of $(\text{C}_6\text{H}_5)_3\text{SnC}_6\text{F}_5$ (0.366 g, 1 mmol) in the same solvent (60 ml) at -5°C . This reaction mixture was stirred further an hour to ensure the completion of reaction. The excess solvent was distilled off. Diphenylantimony(V)trichloride was obtained as a white solid, m.p. 170°C (Lit.(25) $171\text{-}172^\circ\text{C}$) pentafluorophenyl (phenyl) tin dichloride could not be

solidified. Attempts to distill it could not succeed as $(C_6F_5)_3SnCl_2$ is decomposed. It was identified as its DMSO complex, prepared as follows:

Preparation of DMSO Complex

To a solution of $(C_6H_5)_3SnCl_2$ in pet ether (60-80°), dimethyl sulphoxide (1.56 g, 0.02 mol) in the same solvent (20 ml) was added. The contents were stirred for one hour more. The white solid formed was identified as:

$(C_6H_5)_3Sn \cdot 2DMSO$ M.P. 148°C

Found C, 35.90 H 1.00, Calcd. for C-36.18, H-1.27

Reaction of $(C_6H_5)_3Sn(C_6F_5)$ with $TeCl_4$ (1:1 molar ratio)

A suspension of $TeCl_4$ (0.270 g, 1 mmol) in toluene (20 ml) was added dropwise to a well stirred solution of $(C_6H_5)_3SnC_6F_5$ (0.366, 1 mmol) in the same solvent (50 ml). The contents were stirred for 4 h at reflux temperature (110° C). Diphenyl tellurium dichloride (m.p. 158°, Lit. (26): 160°) formed as white solid was filtered off. $(C_6H_5)_3SnCl_2$ could not be solidified. It was isolated as its DMSO complex.

M.P.: 147°C

Reaction of $(C_6H_5)_3SnC_6F_5$ with $PhTeCl_3$ (1:1 molar ratio)

A solution of $PhTeCl_3$ (0.310 g, 1 mmol) in toluene (20 ml) was added dropwise to a well stirred solution of $(C_6H_5)_3SnC_6F_5$ (0.366 g, 1 mmol) in the same solvent (50 ml). The contents were stirred for 2 h at reflux temperature (110°C). Diphenyl tellurium dichloride (m.p. 158°; Lit.(26): 160°) was filtered off. On reducing the solvent and subsequent refrigeration it afforded $(C_6H_5)_2C_6H_5SnCl$.

M.P. 170°C.

Reaction of $(C_6H_5)_3SnC_6F_5$ with ICl (1:1 molar ratio)

A solution of ICl (0.12 ml, 1 mmol) in CCl_4 (5 ml) was added dropwise to a well stirred solution of $(C_6H_5)_3SnC_6F_5$ (0.366 g, 1 mmol) in the same solvent (150 ml) at -5°C in a span of 30 minutes. After each addition, the colour of ICl disappeared. This mixture was stirred for about 2 h to ensure the completion of the reaction. The pink colour of ICl persisted at the end of the reaction. The excess of solvent was distilled off to give a colourless liquid (PhI) while the residue (found after distilling off PhI) was recrystallized from pet ether 60-80°C and was identified as $(C_6H_5)_2C_6F_5SnCl_2$ (phenyl pentafluorotin dichloride) (IV).

M.P. 150°C

Reaction of $(C_6H_5)_3Sn(C_6F_5)$ with IBr (1:1 molar ratio)

A solution of IBr (0.200, 1 mmol) in CCl_4 (5 ml) was added dropwise to a well stirred solution of $(C_6H_5)_3SnC_6F_5$ (0.366 g, 1 mmol) in the same solvent (150 ml) at -5°C for 5 hours. On removal of the solvent and recrystallization from cold pet ether diphenylpentafluoro phenyl tin (IV) monobromide [$(C_6H_5)_2C_6F_5SnBr$] M.P. 180°C were obtained along with corresponding yield of phenyl iodide.

Reaction of $(C_6H_5)_3Sn(C_6F_5)$ with IBr (1:1 molar ratio)

A solution of IBr (0.200, 1 mmol) in CCl_4 (151 ml) was added dropwise to a well stirred solution of $(C_6H_5)_3Sn(C_6F_5)$. The reactants were stirred reflux

temperature (-80°C) for 5 h. On removal of the solvent and recrystallization from cold pet ether phenyl pentafluorotin (IV) dibromide $(C_6H_5)_2(C_6F_5)SnBr_2$ were obtained along with corresponding yield of phenyl iodide (PhI).

M.P. 156°C.

Attempted Reaction of $(C_6H_5)_3Sn(C_6F_5)$ with INCO (1:1 molar ratio)

A freshly generated solution of iodine isocyanate (0.170 g, 1 mmol) in acetonitrile (20 ml) at -5°C was added to a precooled (-5°C) stirring solution of triphenylpentafluorophenyl tin (0.366 g, 1 mmol) in the same solvent (100 ml) during 15 minutes under nitrogen atmosphere. The reactants were stirred at -5°C and for 2 h at room temperature. On working up the reactants $(C_6H_5)_3C_6F_5Sn$ was obtained unchanged. INCO which polymerized was separated as a yellow solid from the solution.

Attempted Reaction of $(C_6H_5)_3Sn(C_6F_5)$ with IN_3 (1:1 molar ratio)

A freshly generated solution of Iodine azide (0.338 g, 1 mmol) in acetonitrile (-50 ml) at -5°C was added to a precooled (-5°C) stirring solution of phenyl pentafluorophenyl tin (0.366 g, 1 mmol) in the same solvent (100 ml) during 15 minutes under nitrogen atmosphere. The reactants were stirred for 4 h at room temperature. The solution was evaporated under reduced pressure and cooled overnight to give $(C_6H_5)_3SnC_6F_5$ unchanged. IN_3 is polymerized as a yellow reddish solid which was filtered off.

Reaction of $(C_6H_5)_3Sn(C_6F_5)$ with $(SCN)_2$ (1:1 molar ratio)

A freshly prepared solution of thiocyanogen (0.116 g, 1 mmol) in CCl_4 (20 ml) was added with stirring to $(C_6H_5)_3SnC_6F_5$ (0.366 g, 1mmol) in CCl_4 (100 ml) at room temperature. The reaction mixture was subsequently stirred for 2 h and the yellowish white solid, containing a polymerized $(SCN)_2$, which separated was filtered off. The solvent on fractional crystallization yielded $(C_6H_5)_2C_6F_5(NCS)$ and unchanged $(C_6H_5)_3SnC_6F_5$.

M.P. = 140°C; yield=0.482 mg (10%).

Reaction of $(C_6H_5)_3Sn(C_6H_4OCH_3)$ with $TeCl_4$ (1:1 molar ratio)

A suspension of $TeCl_4$ (0.270 g, 1 mmol) in toluene (20 ml) was added dropwise to a well stirred solution of $(C_6H_5)_3SnC_6H_4OCH_3$ (0.456 g, 1mmol) in the same solvent (100 ml). The contents were stirred for 4 h at room temperature (25°C). On removal of the solvent and recrystallization from cold pet ether *p*-methoxy phenyl tellurium trichloride were obtained (m.p. 117°C). On concentration and refrigeration, Ph_3SnCl was obtained (m.p. 103°, Lit. 105°)[25].

Reaction of $(C_6H_5)_3Sn(C_6H_4OCH_3)$ with $TeCl_4$ (1:1 molar ratio)

A solution of $TeCl_4$ (0.270 g, 1 mmol) in toluene (20 ml) was added dropwise to a well stirred solution of $(C_6H_5)_3SnC_6H_{11}$ (0.432 g, 1mmol) in the same solvent at room temperature (25°C) for 4 h. Phenyl tellurium trichloride thus formed was filtered off (m.p. 216°; Lit.(24) - 218°). The solvent on concentration and refrigeration yielded $(C_6H_5)_2(C_6H_{11})SnCl$ (m.p. 110°C).

Reaction of $(C_6H_5)_3Sn(C_6H_4OCH_3)$ with $TeCl_4$ (1:1 molar ratio)

A suspension of $TeCl_4$ (0.270 g, 1 mmol) in toluene (20 ml) was added dropwise to a well stirred solution of $(C_6H_5)_3SnC_6H_4OCH_3$ (0.460, 1 mmol) ($110^\circ C$) for 2 h. The contents were refluxed for 2 h at reflux. On removal of the solvent and recrystallization from cold pet ether yielded phenyl *p*-methoxy phenyl tin dichloride $(C_6H_5)_2Sn(C_6H_4OCH_3)Cl_2$ (m.p. $125^\circ C$) were obtained along with corresponding diphenyl tellurium dichloride (m.p. $158^\circ C$; Lit. $160^\circ C$)[26].

Reaction of $(C_6H_5)_3Sn(C_6Cl_5)$ with $TeCl_4$ (1:1 molar ratio)

A suspension of $TeCl_4$ (0.270 g, 1mmol) in toluene (20 ml) was added dropwise to a well stirred solution of $(C_6H_5)_3Sn(C_6Cl_5)$ (0.598 g, 1 mmol) in the same solvent at room temperature for 3 h. Phenyl tellurium trichloride (m.p. $216^\circ C$; Lit. $218^\circ C$) [24] was filtered off. On concentration and refrigeration a white solid characterised as $(C_6H_5)_2Sn(C_6Cl_5)Cl$ was separated.

M.P. = $150^\circ C$

Found C, 38.10 H 1.70 Sn - 21.00

Calcd. for C 38.77 H 1.81 Sn - 21.30

TABLE-1: Cleavage Reaction of Different Compound With Interhalogen Pseudohalogen, Pseudointerhalogen $(C_6H_5)_3Sn(C_6F_5)$, $(C_6H_5)_3Sn(C_6H_5)$ and Metallic Halide

S. No.	Reagents	Molar ratio	Reaction temperature ($^\circ C$)	Reaction Time (h)	Solvent	Organometallic halides obtained	Melting point ($^\circ C$)
1.	$(C_6H_5)_3SnC_6F_5$	(1:1) $TeCl_4$	Room Temp. ($25^\circ C$)	2	Toluene	$(C_6H_5)_2SnC_6F_5Cl$ $(C_6H_5)_2TeCl_3$	145
2.	$(C_6H_5)_3SnC_6F_5$	1:1 $SbCl_5$	Room Temp. ($25^\circ C$)	1	Toluene	$(C_6H_5)_2C_6F_5SnCl_2 \cdot 2DMSO$ Ph_2SbCl_3	148
3.	$(C_6H_5)_3SnC_6F_5$	1:1 $TeCl_4$	Reflux Temp. ($\approx 110^\circ C$)	4	Toluene	$(C_6H_5)_2(C_6F_5)SnCl_2 \cdot 2DMSO$ Ph_2TeCl_2	147
4.	$(C_6H_5)_3SnC_6F_5$	1:1 $PhTeCl_3$	Reflux Temp. ($\approx 110^\circ C$)	2	Toluene	$(C_6H_5)_2(C_6F_5)SnCl$ Ph_2TeCl_2	170
5.	$(C_6H_5)_3SnC_6F_5$	1:1 ICl	$-5^\circ C$	2	(CCl_4)	$(C_6H_5)_2C_6F_5SnCl_2$ $C_6F_5I + C_6H_5I$	150
6.	$(C_6H_5)_3SnC_6F_5$	1:1 I_2	$-5^\circ C$	2	CCl_4	$(C_6H_5)_2C_6F_5SnBr$ C_6H_5I	180
7.	$(C_6H_5)_3SnC_6F_5$	1:2 I_2	Reflux Temp. ($\approx 110^\circ C$)	2	CCl_4	$(C_6H_5)_2C_6F_5SnBr_2$ $2C_6H_5I$	156
8.	$(C_6H_5)_3SnC_6F_5$	1:1 $INCO$	Room Temp. ($25^\circ C$)	4	CCl_4 $AlCl_3$	$(C_6H_5)_3C_6F_5Sn$ $INCO$	130
9.	$(C_6H_5)_3SnC_6F_5$	1:1 IN_3	Room Temp. ($25^\circ C$)	4	CCl_4 $AlCl_3$	$(C_6H_5)_3C_6F_5Sn$ IN_3	130
10.	$(C_6H_5)_3SnC_6F_5$	1:1 $(SCN)_2$	Room Temp. ($25^\circ C$)	2	CCl_4 $AlCl_3$	$(C_6H_5)_2C_6F_5Sn \cdot NCS$ $C_6H_5 \cdot NCS$	140
11.	$(C_6H_5)_3SnC_6H_4OCH_3$	1:1 $TeCl_4$	Room Temp. ($25^\circ C$)	4	Toluene	$(C_6H_5)_3OCH_3 \cdot TeCl_3$ Ph_3SnCl	117
12.	$(C_6H_5)_3SnC_6H_{11}$	1:1 $TeCl_4$	Room Temp. ($25^\circ C$)	4	Toluene	$(C_6H_5)_2SnC_6H_{11}Cl$ $C_6H_5TeCl_3$	110
13.	$(C_6H_5)_3SnC_6H_4OCH_3$	1:1 $TeCl_4$	Reflux Temp. ($\approx 110^\circ C$)	2	Toluene	$C_6H_5SnC_6H_4OCH_3Cl_2$ $(C_6H_5)_2TeCl_2$	125
14.	$(C_6H_5)_3SnC_6Cl_5$	1:1 $TeCl_4$	Room Temp. ($25^\circ C$)	3	Toluene	$(C_6H_5)_2Sn(C_6Cl_5)Cl$ $C_6H_5TeCl_3$	150

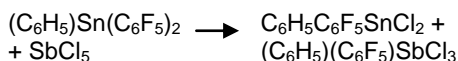
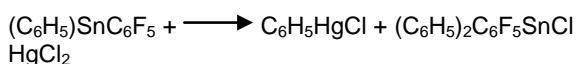
Table-2: Elemental Analysis of Different Compound with Interhalogen Pseudohalogen, Pseudointerhalogen $(C_6H_5)_3Sn(C_6F_5)$, $(C_6H_5)_3Sn(C_6H_5)$ and Metallic Halide

S.N.	Molecular formula	Molecular weight	Found (Calculate)%	
			Carbon	Hydrogen
1.	$C_{18}H_{10}F_5SnCl$	465.32	46.00 (46.42)	2.00 (2.14)
2.	$C_{12}H_5F_5SnCl_2$	398.32	435.90 (36.18)	1.00 (1.27)
3.	$C_{12}H_5F_5SnCl_2$	443.86	32.20 (32.47)	2.90 (3.14)
4.	$C_{12}H_5F_5SnCl$	398.32	36.00 (36.18)	1.00 (1.27)
5.	$C_{12}H_5F_5SnCl_2$	433.78	33.00 (33.33)	1.00 (1.16)
6.	$C_{18}H_{10}F_5SnBr$	519.88	42.20 (41.59)	1.70 (1.94)
7.	$C_{12}H_5F_5SnBr_2$	522.68	27.57 (28.25)	0.80 (0.96)
8.	$C_{12}H_5F_5Sn$	362.69	39.00 (39.70)	1.00 (1.37)
9.	$C_{18}H_{10}F_5SnN_3$	481.99	44.70 (44.85)	2.06 (2.09)
10.	$C_{12}H_{10}F_5SnNCS$	425.99	36.40 (36.70)	2.10 (2.40)
11.	$C_7H_7OTeCl_3$	341.09	24.20 (24.65)	2.0 (2.07)
12.	$C_{18}H_{21}SnCl$	391.52	54.90 (55.22)	5.37 (5.41)

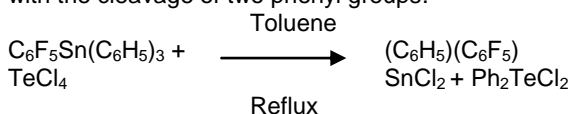
S.N.	Molecular formula	Molecular weight	Found (Calculate)%	
			Carbon	Hydrogen
13.	C ₁₃ H ₁₂ SnOCl ₂	373.85	41.20 (41.77)	3.21 (3.50)
14.	C ₁₈ H ₁₀ SnCl ₆	557.70	38.10 (38.77)	1.70 (1.81)

Result and Discussion

Relative ease of cleavage of phenyl group *vis-a-vis* pentafluoro phenyl group has been reported for unsymmetrical phenyl pentafluorophenyltins (C₆F₅)_nSn(C₆H₅)_{4-n} towards BCl₃ and HCl. The comparative reactivity of methyl and C₆F₅ in MeHg C₆F₅ against HCl has been reported as early as in 1960. The reactivity pattern has been following these cleavage reaction has been found in order Ph > C₆H₅ > Me. We have earlier established the pattern of cleavage of an aryl group from organotins by antimony pentachloride. The organic group included in this study were sterically congested group, alkyl and aryl groups and the reactivity pattern has been investigated. In the present study antimony pentachloride reaction with Ph_n(C₆F₅)_{4-n}Sn in an organic solvent has been found to cleave both pentafluorophenyl and phenyl group simultaneously. It is not surprising since in the reaction of (C₆F₅)₂SnPh₂ and (C₆H₅)₃SnC₆F₅ with HCl has also been reported to cleave phenyl and pentafluorophenyl group simultaneously. It may be noted that in the reaction of C₆H₅Sn(C₆F₅)₃ it is the phenyl group which is cleaved first with the less reactive electrophiles, such as HgCl₂. (C₆H₅)₃SnC₆F₅ + \longrightarrow (C₆H₅)₂SbCl₃ + C₆H₅C₆F₅SnCl₂ SbCl₅

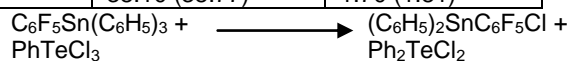


Since HgCl₂ is less reactive it is not capable of breaking more than one organic group even in drastic condition but SbCl₅ being a strong electrophile can easily cleave to organic group and in the mixed organotin reaction both phenyl and C₆F₅ groups are cleaved simultaneously. Reaction of TeCl₄ with C₆F₅(C₆H₅)₃Sn in toluene at reflux temperature proceeded with the cleavage of two phenyl groups.



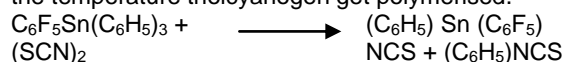
The isolation of product does not pose any difficulty as the diphenyl tellurium is highly insoluble and separated from the mixture readily. While mixed organotin chloride was obtained as oily mass which could not be crystallised and the on distillation it decomposed. It may also be concluded from above reaction that simultaneous cleavage of phenyl and pentafluoro phenyl group is possible and when there is more than one C₆F₅ groups attached to tin along with phenyl group(s). Similarly, the reaction of PhTeCl₃ which also act as an electrophile was found to cleave one phenyl group from (C₆H₅)₃SnC₆F₅ in the sense of equation shown below.

Toluene



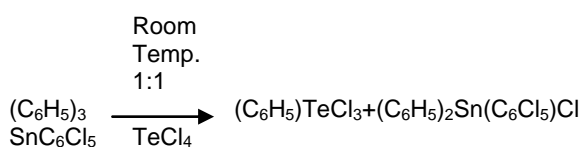
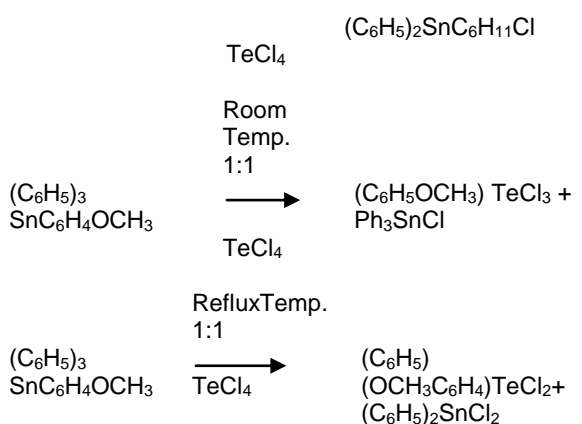
Again, diphenyltelluriumchloride being insoluble organic solvent is easily digested but (C₆H₅)₂SnC₆F₅Cl remain in the solvent and was separated after concentrating and cooling the solution. Diphenyltelluriumdichloride was identified by mixed melting point and super imposable IR spectra. Reactions of iodine halides have been earlier studied with both symmetrical and unsymmetrical organotins and the pattern of cleavage has been established. These reactions were also found useful for stereospecific addition of a halide ion to organic molecules which otherwise are difficult to obtain. However ease of pattern of C₆F₅ group in the complex of phenyl group has not been investigated to date. In the present work reaction of ICl with (C₆H₅)₃SnC₆F₅ was carried out on -5°C in CCl₄ and found to cleave both pentafluorophenyl group and phenyl group simultaneously. It is surprising since in the reactions metallic halides pentafluorophenyl is not removed, if there are less than two C₆F₅ groups. IBr being a weak electrophile as compared to ICl does not cleave two organic group(s), from the unsymmetrical tetraorganotins and thus it could be used decisively to establish the relative activity of pentafluorophenyl and phenyl group. Thus the reaction of IBr in 1:1 molar ratio proceeded with the cleavage of one phenyl group only. However under drastic conditions iodine monochloride in 1:2 molar ratio cleaved two phenyl group pentafluoro phenyl group remain intact.

Thiocyanogen (SCN)₂ also cleaved one phenyl group from (C₆H₅)₃SnC₆F₅ but to a limited extent. Thiocyanogen is weak electrophile and on increasing the temperature thiocyanogen get polymerised.

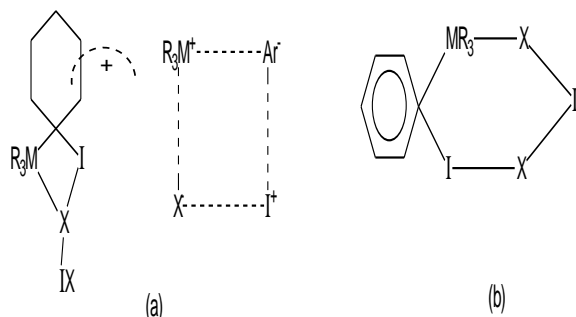


Further, IN₃ and INCO are still weak electrophiles and cleave tin-phenyl only in presence of AlCl₃. However during the process of hydrolysis, organotin moiety could not survive the drastic conditions of hydrolysis and thus is not isolable. These reactions are of only academic interest and only phenyl iodide was distilled off. In addition to above some related reactions of unsymmetrical tetraorganotin bearing other than phenyl group(s) were also carried out with tellurium tetrachloride just for the sake of comparison. These could be represented as below:





The mechanism of such reactions may possibly involve a four centered (a) or six centered state (b) as shown below:

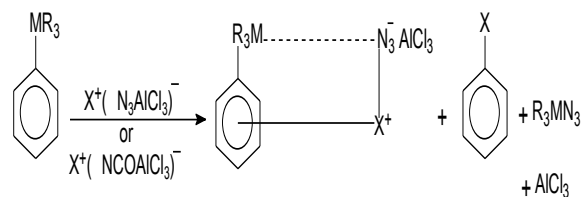


(X = Cl, Br)

An argument in favour of a four-centered transition state such as (a) has been based on the observation that ICl reacts with phenyltrimethylsilane (to give iodobenzene) in acetic acid some 8 times as fast as does chlorine, where as in ordinary halogenation of aromatic compound chlorine is much more reactive [23]. This could imply a substantial difference between the transition states in halogenation and incleavage and would be consistent with a four centered, mechanism, for the cleavage in which nucleophilic attack on metal by incipient chloride ion is synchronous with electrophilic attack by the greater reactivity of ICl as compared to IBr due to the increased polarity through the Cl atom and the better electrophilic through I atom similar mechanism has been suggested for the cleavage of M-P and M-As in organotin and silicon, phosphine and arsines with ICl.

The presence of aluminiumtrichloride in the reaction induces some degree of polarisation in IN_3 and INCO thereby increasing their electrophilic character so that their positive end attacks the electron of the aromatic ring. After the fission of IN_3 and I-NCO bond in forming σ -complex with aromatic ring, the anionic complex, $(\text{AlCl}_3.\text{N}_3)^-$ or $(\text{AlCl}_3.\text{NCO})^-$

so obtained, then removes the MR_3 group to yield arylhalide. Thus in these reactions, both IN_3 and INCO act as nucleophile through N_3^- & NCO^- atom and as electrophile through halide (I^-).



(X = I, Br)

Conclusions

Synthesized compounds produced moderate yields, in addition low cost and less hazardous methods. Compounds 1,2,3,4,5 were screened for the antibacterial activity against *aspergilluscoli* all the compounds exhibited moderate activity. Compounds 4,5 exhibited good activity against *E.Coli* compounds 7&8 were screened for in vitro activity. It is concluded that the compounds substituted with Central Drugs Research Institute Lucknow.

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