SUMMARY

Investigations embodied in this thesis entitled 'PREPARATION AND REACTIONS OF SOME ORGANOTIN COMPOUNDS: APPLICATIONS TO ORGANIC SYNTHESIS' are primarily concerned with studies on organotin compounds in the arena of their applications in organic synthesis alongwith their effectiveness as biocides as an extension. The thesis has been divided into two parts: **PART-I** and **PART-II**. PART-I deals with the studies directed towards utilisation of triorganotin carboxylates in organic synthesis and as fungicides and comprises three sections.

SECTION-A : **Preparation and characterisation(spectral and elemental) of a series of α,β-unsaturated(olefinic and acetylenic) triorganostannyl carboxylates and their regioselective reaction with mercury(II) salts.**

In the **Introduction**, the chemistry of organotins has been briefly reviewed with special emphasis to the preparation, structure and reactivity of triorganotin carboxylates.

In order to investigate the relative reactivity of stannyl ester and C—C multiple bond towards mercury(II) salts, a series of α,β-unsaturated(olefinic and acetylenic) tri-n-butyl- and triphenyl- stannyl esters(1-13) have been prepared from their corresponding acids. The structural compositions for these esters have been assigned from their spectral (IR, UV, ^{1}H-, ^{13}C- and ^{119}Sn-NMR) and elemental analyses data. From the IR spectra, the chemical shifts

$R^1\text{-}CH{=}CH\text{-}COOSnR_3$

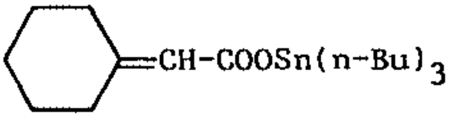
(1); R^1 = H, R = n-Bu (2); R^1 = Me, R = n-Bu

(3); R^1 = Me, R = Ph (4); R^1 = Ph, R = n-Bu

(5); R^1 = $p\text{-}NO_2C_6H_4\text{-}$, R=n-Bu (6); R^1 = $p\text{-}NO_2C_6H_4\text{-}$, R = Ph

(7); R^1 = $CH_3CH{=}CH\text{-}$, R=n-Bu (8); R^1 = $CH_3CH{=}CH\text{-}$, R = Ph

(9);



(10); $CH_3C{\equiv}C\text{-}COOSn(n\text{-}Bu)_3$ (11); $CH_3C{\equiv}C\text{-}COOSnPh_3$

(12); $Ph\text{-}C{\equiv}C\text{-}COOSn(n\text{-}Bu)_3$ (13); $Ph\text{-}C{\equiv}C\text{-}COOSnPh_3$

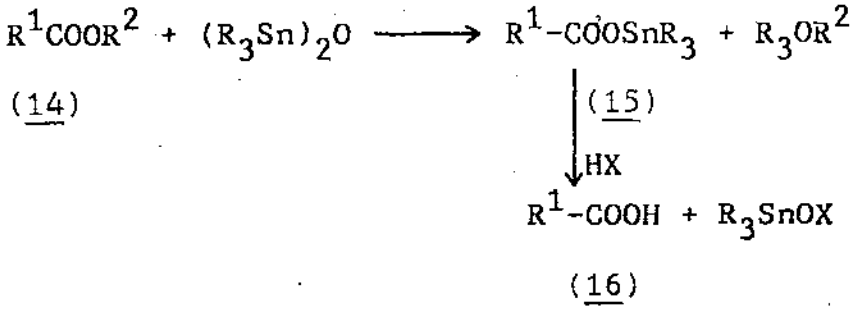
values in ^1H-, ^{13}C- and ^{119}Sn-NMR spectra and the $^nJ(^{119}Sn\text{-}^{13}C)$ values (n = 1, 2, 3; the carbon atoms attached to tin), the structural features relating to coordination number of tin atom and the possible geometry of the molecule have been discussed. Although most of these esters have been assigned as possessing tetrahedral arrangement with four-coordinate tin, the triphenyltin-but-2-ynoate(11) has the spectral data compatible with having trans trigonal bipyramidal geometry and five-coordinate tin atom.

Finally, the reaction of these unsaturated stannyl esters with HgX_2 (X = Cl; OAc) has been studied in different solvents ranging from protic/aprotic polar to aprotic nonpolar. From the results, it has been revealed that the unsaturated stannyl esters undergo demetallation reactions resulting in the formation of the corresponding acids and no mercuration of the olefinic/acetylenic multiple bond has been detected. While the alkyl esters of α,β-unsaturated acids, upon treatment with mercury(II) salts, undergo solvomercuration of C-C multiple bonds, the corresponding stannyl esters, upon similar treatment, react preferentially at the ester function keeping the olefin/acetylene unreacted. The present study, therefore, develops a useful approach for protection of C-C multiple bonds with the preferential and regioselective reactions of different functionalities in α,β-unsaturated esters towards mercury(II) salts.

SECTION-B : Transesterification of alkyl/aryl esters to triorganostannyl esters under neutral condition and their hydrolysis into carboxylic acids using dilute acids at room temperature.

In this section, development of a new mild and facile method for the hydrolysis of alkyl (primary, tertiary) and aromatic esters through their corresponding triorganostannyl esters has been described. As a prelude to this section, the previous methods for masking and demasking a carboxyl function have been briefly reviewed.

The present method consists of two steps. In the first step, the alkyl/aryl carboxylates are transesterified to the triorganostannyl esters under completely neutral conditions, such as (i) by azeotropic distillation of esters(14) with bis tri-n-butyl- or triphenyl- tin oxide in carbon tetrachloride or toluene or (ii) by heating their neat mixture. The corresponding triorganostannyl carboxylates(15) so formed undergo easy hydrolysis to acids(16) by treatment with dilute acids (5N HCl or glacial AcOH) at room temperature.



$$R^1COOR^2 + (R_3Sn)_2O \longrightarrow R^1\text{-}COOSnR_3 + R_3OR^2$$

(14) (15)

$$\xrightarrow{HX} R^1\text{-}COOH + R_3SnOX$$

(16)

R^1=alkyl (primary, tertiary), aryl, α,β-unsaturated functions,
R^2=alkyl, phenyl and benzyl groups,
R= n-butyl, phenyl groups,
X=Cl, OAc.

In all the cases, facile formation of stannyl esters and their facile hydrolysis have been observed in overall excellent yields.

SECTION-C : **Toxicity (fungucidal and phyto-)** of a series of α,β-unsaturated triorganostannyl carboxylates against some phytopathogenic fungi.

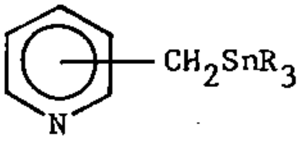
As a prelude to this section, a concise account of applications and biological effects of triorganotin carboxylates has been outlined. As an extension, the present study comprises the fungicidal- and phyto- toxicity *in vitro* of a series of α,β-unsaturated triorganotin carboxylates against two fungi, *Alterneria solani* and *Piricularia oryzae* and the results have been discussed. The compounds screened here have been prepared in connection with studies described in **SECTION-A.** The ED_{95} values (fungicidal effectiveness) for each compounds at different times (24 hr., 48hr. and 72 hr.) have been obtained from the % of growth inhibition of the fungi at different concentrations. From the results, all the compounds tested are found to be active against *A. solani* and *P. oryzae*. Tri-n-butylstannyl crotonate

(2) and tri-n-butylstannyl p-nitro cinnamate(5) have exhibited highest fungitoxicity against A. solani. In contrast, triphenylstannyl but-2-ynoate(11) is the most toxic against P. oryzae after 24 hours incubation though its corresponding tri-n-butylstannyl ester(10) is more toxic after 48 hours and 72 hours of incubation. The compound(9), tri-n-butylstannyl cyclohexylidene acetate inhibits the growth of fungi(P. oryzae) within a range of average activity. With regard to phytotoxicity, most of these esters exhibit little or no toxicity against the germination of rice seed.

[The present study (**SECTION-A**) on the selectivity of mercury(II) salts in reactions with α,β-unsaturated(olefinic) stannyl esters has been published in J. **ORGANOMET.** CHEM. and a reprint has been attached. The extension of this work with acetylenic and triphenyltin esters alongwith detail spectral findings has been submitted to J. **ORGANOMET.** CHEM. The works described in SECTION-B have been published in **IND.** J. CHEM.(B) and a reprint has been attached. A part of this work has been presented in the **27th. Annual Convention of Chemists (1990).** A part of the experimental findings presented in SECTION-C has been submitted to **SYNTH. REACT.** INORG. MET. -ORG. CHEM.]

PART-II : **Preparation of Picolyltrialkylstannanes and on the mechanism involving ambident nucleophilicity of picolyl anion.**

This part of the thesis describes studies with unsymmetrical tetraorganotin compounds of the type R^1SnR_3, where R^1 stands for a $C_5H_5N\text{-}CH_2$ (2-,4-), picolyl group, and R stands for alkyl group. In the **Introduction**, these systems have been compared with allyl-(18) and benzyl-(19) trialkylstannanes and their methods of preparation and reactions are briefly discussed. During the present work, several attempts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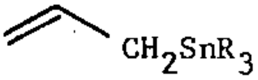
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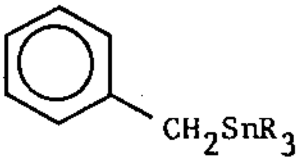
(19)

R = Me or R = n-Bu

have been made to prepare the compounds(17) through the generation of picolyl anion. Based on chemical/spectral evidence, involvement of ambident nucleophilicity of the picolyl anion has been suggested. The competition between N-stannylation versus C-stannylation has been considered in terms of role of solvents. A poor yield of the picolyltrialkyl stannane(17) has been realised during the present study. Further works to improve the yields are being undertaken in this laboratory for substantiating the suggested mechanism and for studying their proposed reactions.