

PREFACE

The present dissertation is divided into the following eight chapters:

Chapter 1:

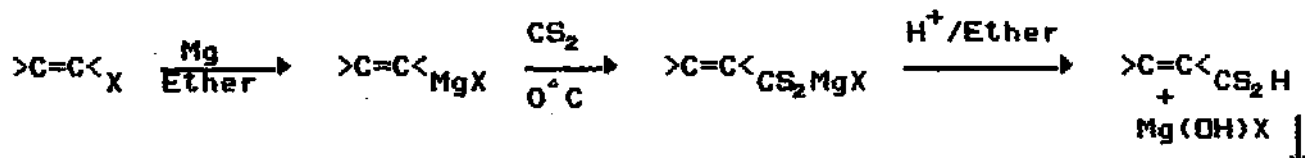
This chapter deals with a brief overall literature survey relating organotin compounds in general, specially highlighting the wide variety of developments in the field of organotin chemistry.

Chapter 2:

This chapter deals more specifically with the literature survey relevant to the organotin(IV) dithiocarboxylates and the related ligands, namely, organotin(IV) aryloxyacetates. The literature related to the organotin(IV) esters of (4-pyridylthio) acetic acid and (2-pyrimidylthio) acetic acid is absent. Literatures on available organotin(IV) carboxylates were studied for comparative purposes with the newly synthesised thio-acetates, viz., organotin(IV) (4-pyridylthio) acetates and organotin(IV) (2-pyrimidylthio) acetates. The literature relating the dithiocarboxylic acid of the general formulae RCS_2H ; [where R \equiv an alkenyl group $\begin{matrix} R' \\ >C=C< \\ R' \end{matrix}$, $R' = H$, or alkyl group] are also rare. Survey shows absences of any literature on alkenyltin(IV) dithiocarboxylates.

Chapter 3:

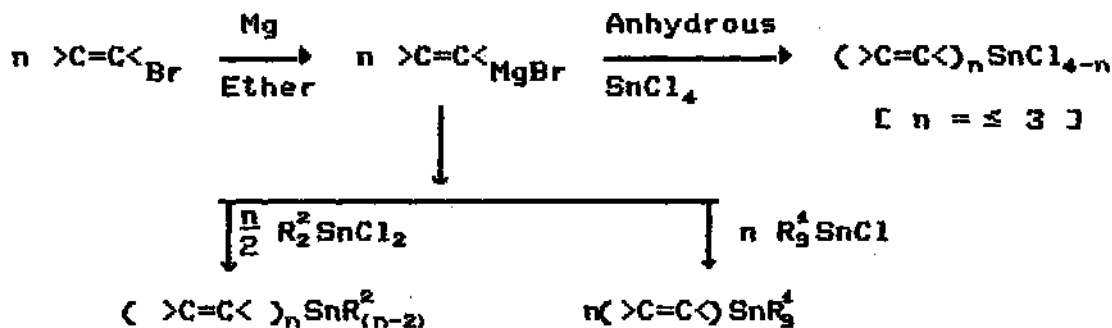
This chapter deals with the syntheses of alkenyldithiocarboxylic acids. The reactions were carried out by Grignard method of reaction following the route given below:



By this way, three new alkenyl dithiocarboxylic acids were synthesised and characterised. In case where Grignard reagent formation was not possible, with a particular alkenyl bromide, the same reaction was carried out by lithiating the alkenyl halide followed by the addition of carbon disulfide to the lithiated salt under cold condition. There has been scattered studies on the organotin alkenyls. The partial aim, therefore, was to synthesise more new organotin(IV) alkenyls together with their reactions to prepare the dithiocarboxylates.

Chapter 4:

Here the syntheses of a number of (8) new alkenyltin(IV) compounds were synthesised, by the following route:



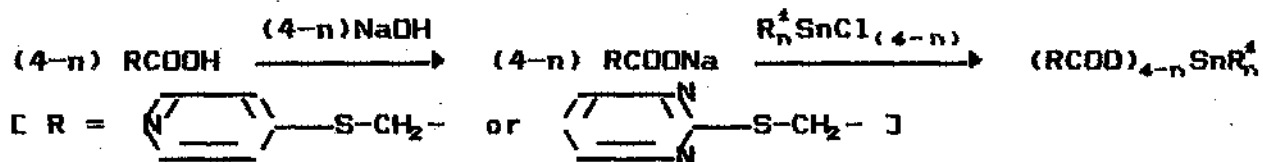
Chapter 5:


This chapter deals with the reactions of the piperidinium salts of dithiobenzoic acids and the newly synthesised dithiocarboxylic acids with a number of organotin(IV) halides. These reactions were also carried out with the newly synthesised alkenyltin(IV) halides. It is interesting to note that

these reactions gave unusual results with the isolation of organotin(IV) dithiocarbamates instead of the desired organotin(IV) dithiocarboxylates. In the course of our study we have done X-ray diffraction study of a reaction product from piperidinium salt of dithiobenzoic acid and triphenyltin chloride and it was established to be triphenyl piperidinium dithiocarbamate $\text{C}_6\text{H}_{11}\text{N}-\text{C}(=\text{S})_2-\text{S}-\text{SnPh}_3$. We have attempted to draw the plausible mechanism of the unusual observation, though it needs further study to say the final words.

Chapter 6:

This chapter deals with the syntheses of organotin(IV) esters of two ligands related to the dithiocarboxylic acids. In addition to the $-\text{COO}-$ group, ligands contain 'N' atom as well as 'S' atom as donors. The ligands used were (4-pyridylthio) acetic acid and (2-pyrimidylthio) acetic acid. The reactions were carried out using the following route:



The reactions were carried out in dry methanol, in appropriate ratios, as detailed in relevant sections. All the 15 new compounds were characterised and found to be air stable. One of the compounds, viz.,  -S-CH₂-COO-SnPh₃ was analysed by single

crystal diffraction study, which revealed a trigonal bipyramidal, trans-D₂SnR₃ environment of tin in the compound, as discussed in the relevant part. It is also interesting to note the difference

in the ligating behaviours of the two carboxylic acids studied. The acyloxy coordination to tin in the (4-pyridylthio) acetate is weaker indicating the acid to be a stronger than the other [(2-pyrimidylthio) acetic acid]. The IR and ^1H NMR support these observations.

Chapter 7:

This chapter deals with the reaction of sodio- salt of dithiocarbazic acid with triphenyltin chloride. The desired product, $\text{Ph}_3\text{SnS}_2\text{CNHNH}_2$ was isolated as an air sensitive product in nonpolar solvent. In polar solvent, however, the product always converted to the $(\text{Ph}_3\text{Sn})_2\text{S}$. Plausible mechanism for such behaviour is suggested.

Chapter 8:

This chapter deals with the study of biocidal properties of a number of the newly synthesised compounds of the types: a) Alkenyltin(IV) chloride b) Dithiocarbamate c) Organotin(IV) (4-pyridylthio) and (2-pyrimidylthio) acetates. The study were carried out with Helmenthesporium group of fungi which causes damages to the crops like rice, maize etc. The study show all of these compounds studied to be active against these fungi. Encouragingly, the phytotoxicity values of these compounds are within the level of tolerance.