

CHAPTER I

INTRODUCTION



The industrial use of triorganotin compounds was first evaluated as biocides in 1954 [1]. They are suitable for use in various purposes, such as, disinfectants, agricultural fungicides, textile preservatives, wood preservatives and marine anti-fouling compositions. [2] Even though the exact mechanism for biocidal activity is not well understood, it is postulated that their biocidal behavior was due to their ability to inhibit mitochondrial oxidative phosphorylation of organism.[3]

1.1 The Use of Organotin Compounds.

Trialkyltin compounds were first proposed for use in the field of wood preservation in 1954 by van der Kerk and Luijten,[1] carrying out systematic investigations into the preparation and biocidal properties of organotin compounds. In the report, the fungitoxicities of various compounds towards four different mould species were determined by the agar dilution method. As a result of the high activity, two selected compounds -triethyltin hydroxide and acetate were tested against wood rotting fungi. They also showed that, in a series of triethyltin compounds, Et_3SnX , the nature of the group X did not influence their fungitoxicity in agar tests. In contrast, the fungicidal activity of the compounds of the type R_3SnX (X = acetate) was

shown to vary markedly with the R group, optimal activity being found with the tributyltin compounds. In a later, Bis(tributyltin) oxide (T.B.T.O.) had achieved commercialisation as a fungicide in organic solvent based wood preservatives and other tributyltins have been introduced for this purpose.[4]

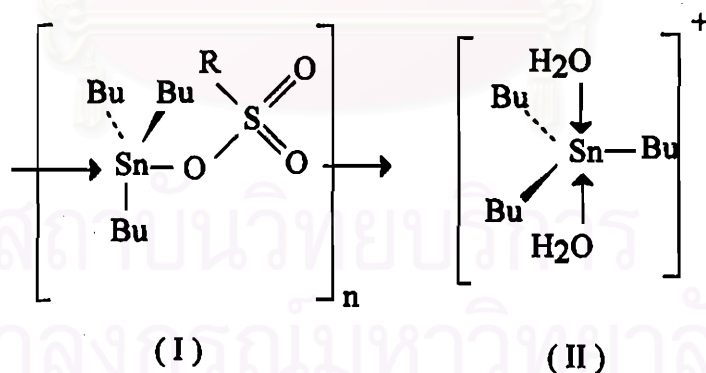
Although the biological activity against most types of fungi of tributyltin compounds is excellent, but the compounds are very low soluble in water (e.g. 0.001% w/v for T.B.T.O. at 25 °C). This precludes their use for biocidal application which requires an aqueous carrier, where a concentration of 0.5-1.0% of the organotin compound would normally be required.[5]

One way to overcome this problem has been to emulsify the tributyltin biocide such as T.B.T.O., with a suitable quaternary ammonium salt to produce a water-dispersible concentrate. Formulations of this type are used extensively for the eradication of moss, algae and lichens on stonework and are currently under development as wood preservatives. [6]

A second, more desirable approach to the problem is to synthesize a discrete, water soluble tributyltin fungicide. A number of novel anionic tributyltin salts of general formula $(R_4P)^+(Bu_3SnCl_2)^-$ and their cationic analogues, $(Bu_3SnL_2)^+BPh_4^-$, where $L = DMSO, Ph_3PO, Ph_3AsO$ etc., were subsequently prepared but were found to be substantially insoluble in water. Similar tributylthiotin biocides, such as $Bu_3SnSCH_2CO_2^-Na^+$ where the tributyltin moiety is also part of an anionic residue have been reported to be water soluble, but no quantitative data were given. [6,7]

In 1976, Suzuki and his co-workers [6] claimed that tributyltin methane- and ethane-sulphonate are soluble in water to the extent of 3 - 10 % and a systematic study of compounds of the type $\text{RSO}_3\text{SnBu}_3$ has therefore been carried out to determine the effect of the R group on the solubility.

The results showed that, in general, the water solubility of the $\text{RSO}_3\text{SnBu}_3$ compounds increases with the electron-releasing power of the R group and that a maximum is attained when $\text{R} = \text{Et}$. A further increase in chain length of the n-alkyl group causes a drop in solubility. The solubilities of most of the compounds were found to rise to a maximum value on standing for a period of time and this was attributed to the ease with which the water molecules are able to break up the self-associated polymeric structure (I), which exists in most of the pure compounds, to produce the hydrated pentacoordinate tributyltin cation (II)



The tributyltin alkanesulphonates are prepared in the laboratory by azeotropically dehydrating a mixture of the appropriate alkanesulphonic acid and bis(tributyltin) oxide in boiling toluene for 2-4 hr., using a Dean and Stark trap : $2\text{RSO}_2\text{OH} + \text{Bu}_3\text{SnOSnBu}_3 \rightarrow 2\text{Bu}_3\text{SnOSO}_2\text{R} + \text{H}_2\text{O}$ (R=Me or Et)

The compounds are obtained by removal of solvent, using prolonged pumping at reduced pressure and room temperature.

In 1991 Surat Prachyakul [8] could synthesize tributyltin alkyl sulfate esters by the reaction of bis(tributyltin) oxide and appropriate alkyl hydrogen sulfates. The resulting tributyltin alkyl sulfate esters were found to exhibit fungicidal activity on *Penicillium*, *Aspergillus* and *Syncephalustrum* species, but they were found to be substantially insoluble in water.

1.2 The Objective of this Research

The objective of this research can be summarized as follow:

1. To investigate the methods for the synthesis of water soluble organotin fungicides.

2. To study the solubility in water, fungicidal activity and other properties of synthesized organotin compounds.

In this study, the triorganotin compounds were synthesized by reacting TBTO with various alkanolamines and glycols. Water from reaction was removed from the reaction by means of Dean-Stark trap.



[R= alkyl group, X= hydroxy group (for glycols) or amino group (for alkanolamines)]



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