

ORGANOTIN CHEMISTRY

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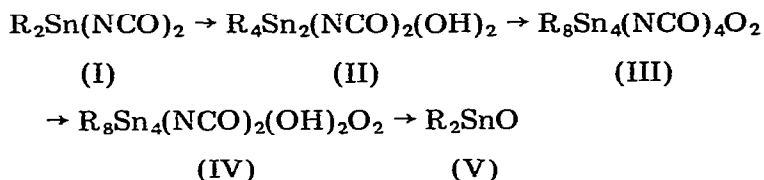
It is a pleasure to contribute this brief chapter to a volume honouring Professor R.C. Mehrotra on his sixtieth birthday.

Early in Professor Mehrotra's distinguished career he studied at Birkbeck College. It was after spending a year doing post-doctoral work at that institution that I moved to Queen Elizabeth College and began to get interested in the chemistry of organotin compounds. At that time, nearly twenty years ago, they seemed to be an exotic group of compounds with an arcane chemistry which was ripe for exposure and exploitation.

I soon began to question the then current dogma that the coordination number at tin would only exceed four in very exceptional circumstances. I tried to show the real situation, i.e. that organotin chemistry was dominated by compounds and transient intermediates containing 5- and 6-coordinate tin atoms, in a short review article entitled "Coordination in Organotin chemistry" published in 1965 [1]. Some of our work on this subject is discussed below as are certain other areas which became of particular interest to us. These include compounds containing tin-sulphur bonds, preparative methods particularly of compounds containing functional substituents and the application of fundamental chemistry to solve problems thrown up by the large-scale application of organotin compounds.

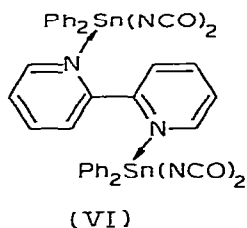
Coordination Chemistry

Having made the generalization that, for organotin compounds of formulae $R_xSnX_{(4-x)}$ ($x = 1, 2$ or 3), structures containing 5- and 6-coordinate tin were the norm, it became clear that this had special significance for structures then being proposed for products obtained by the partial hydrolysis of organotin dihalides. We found that the corresponding diisocyanates (I) had the property of ready hydrolysis in the atmosphere.



For R = Bu, compounds III and IV were isolated in sequence from I while the diphenyl compounds were so reactive that I (R = Ph) could not be isolated. However, II (R = Ph) was obtained which, on crystallisation, was first converted to III (R = Ph) followed by IV before giving the oxide V (R = Ph) [2]. Thus, the sequential formation of these intermediates was demonstrated showing that they are necessary stages in the hydrolysis.

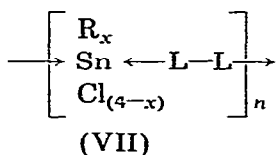
Attempting to stabilize I against hydrolysis by complex formation with 2,2'-bipyridyl we found that the unusual structure VI containing the bridging ligand was obtained [3].



(At about the same time structures containing bridging 2,2'-bipyridyl groups were proposed for other tin compounds [4,5] as well as rhodium [6] and zirconium [7] complexes).

I had shown in 1963 that when the organic groups attached to tin were large and bulky, as in the *o*-phenoxyphenyltin compounds, steric hindrance caused interesting modifications to the chemistry. Hydrolysis of bis(*o*-phenoxyphenyl)tin dichloride gave (*o*-C₆H₅OC₆H₄)₄Sn₂(OH)₂O and (impure) (*o*-C₆H₅OC₆H₄)₂Sn(OH)₂ and no (*o*-C₆H₅OC₆H₄)₂SnO was obtained [8].

About this time there was much interest in polymeric organometallic compounds and we prepared various coordination polymers (VII) where L-L is



a non-chelating bidentate ligand such as 4,4'-bipyridyl [9] and *trans*-dithian disulphoxide [10]. The tetradentate ligand bis(8-hydroxy-5-quinolyl)methane formed 1 : 1 dialkyltin complexes which also appeared to be polymeric [11].

With the advent of Mössbauer spectroscopy, one of several fruitful projects carried out in collaboration with Bill McWhinnie was to acquire the necessary parts and build an instrument which we first used to study a problem in iron chemistry [12]. I was then joined by John Ruddick, a very enthusiastic cham-

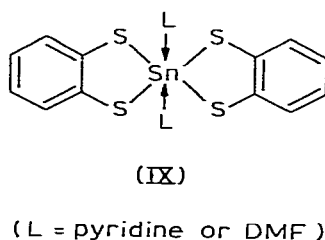
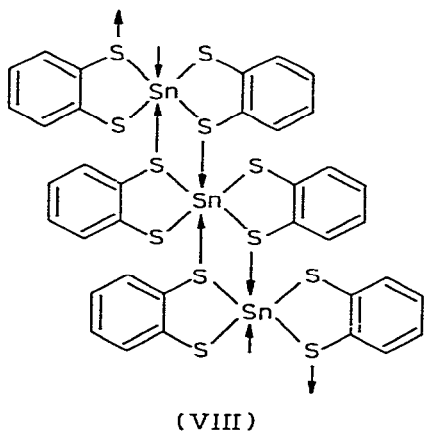
pion of the technique and we used Mössbauer spectroscopy to assign structures and configurations to organotin oxinates [13] as well as to complexes of organotin dihalides with 2,2'-bipyridyl, di-2-pyridylamine and tri-2-pyridylamine [14].

As we had accumulated a sufficient number of polymeric organotin compounds we were interested to test the empirical observation [15] that compounds showing a Mössbauer effect at room temperature are polymeric. Out of 26 compounds examined 14 gave Mössbauer signals at room temperature. These included all of the 13 compounds known to possess polymeric structures [16]. Today the relationship between intermolecular force constant and the temperature dependence of the Mössbauer fraction is much better understood [17], but wherever the existence of an effect at room temperature can be demonstrated this readily accessible piece of information can be regarded as strong evidence for a polymeric structure.

Looking back on our own and other people's work of that period it is striking that IR, Mössbauer and NMR spectra were so successful in establishing the general principles for organotin structure and stereochemistry. The large number of X-ray crystal structure determination which have subsequently been reported have placed these principles on a firmer, but essentially the same, footing.

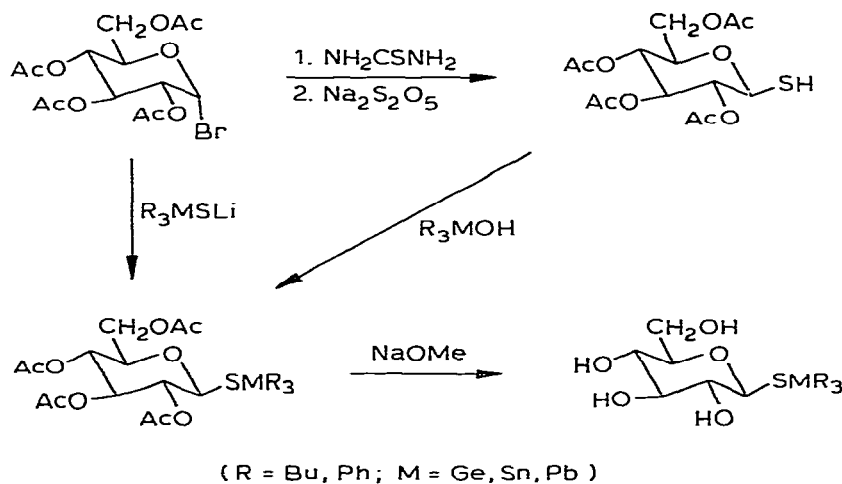
Organotin sulphur compounds

The tin-sulphur bond is generally less reactive than tin-oxygen and, for example, thiolates are much more readily handled than alkoxides. My own interest in sulphur compounds began early when I puzzled over why bis(ethane-1,2-dithiolato)tin is a colourless low melting soluble compound whereas bis(toluene-3,4-dithiolato)tin is a high melting insoluble red compound. I suggested [18] that the latter had structure VIII. Presumably delocalisation of the π -electrons over the sulphur atoms to give an *o*-quinonoid (and hence coloured) component to the structure is stabilized by $S \rightarrow Sn$ coordination. The IR [19] and Mössbauer [20] spectra are quite consistent with this structure and further evidence came from the fact that the compound dissolved in donor solvents with loss of colour and pale yellow 2:1 adducts (IX) could be isolated. The adducts on storage in air, or more rapidly on heating, lost the ligand and reverted to VIII.



Although falling outside the usual definition of organotin compounds these tetrathiolatotins derived from thiols and dithiols together with the adducts obtained on addition of Lewis bases proved to be a rewarding field. Mössbauer spectroscopy was used to assign structures to the adducts since it was known [21] that for SnX_4Y_2 compounds the magnitude of the quadrupole splitting for a *trans* isomer is approximately twice that of the corresponding *cis* compound. It had also been predicted that the sign of the quadrupole splitting should be different in *cis* and *trans* isomers but measurements on adducts of organotin compounds where $\text{Y} = \text{C}$ had failed to demonstrate this dependence of sign of Δ on configuration due to distorted geometries [22]. For the tetrathiolatotin adducts $\text{X} = \text{S}$, $\text{Y} = \text{N}$ or O we were able to observe the reversal in sign of the quadrupole splitting for *cis*-bis(ethane-1,2-dithiolato)tin-2,2-bipyridyl $\Delta = +1.17 \text{ mm s}^{-1}$ and *trans*-bis(ethane-1,2-dithiolato)tin(Et_2SO) $_2$ $\Delta = -1.9 \text{ mm s}^{-1}$ [23].

The Lewis acidity of organotin thiolates such as $\text{R}_2\text{Sn}(\text{SR}')_2$ is so reduced compared with tetrathiolatotin compounds that stable adducts cannot be isolated. The $\text{Sn}-\text{S}$ bond in thiolatotins is sensitive to reagents such as aqueous alkali, mercury(II) chloride and acetate, tin(IV) chloride and iodine [24]. Nevertheless, compared with the corresponding alkoxide and phenoxides the lower reactivity of the sulphur compounds, particularly to protic reagents, is significant. Advantage was taken of this to obtain organometallic derivatives of glucose where stability to water was ensured by using sulphur to link tin to the sugar [25].



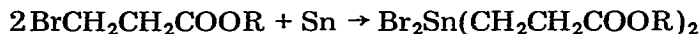
Synthesis of organotin compounds

There are a large number of ways of forming tin-carbon bonds but the most commonly used methods employ organometallic reagents so they cannot be used to attach functionally substituted organic groups to tin. One and sometimes two functionally substituted groups can be introduced onto the metal atom via hydride addition:

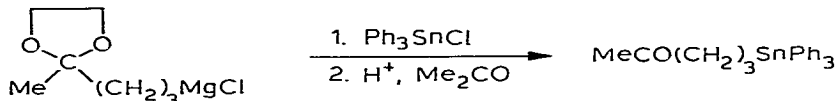


(X = COR', COOR'C, CN, etc.)

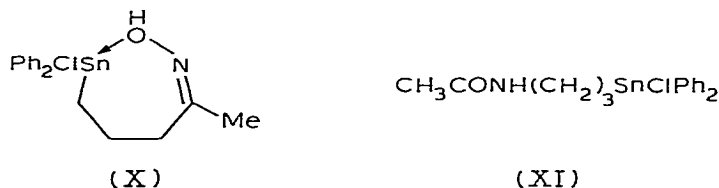
In a few cases the direct reaction [26] between tin metal and a functionally substituted alkyl halide can be used, for example:



When we wanted to prepare some 4-oxopentyltin compounds to test some ideas on PVC stabilization (see below) routine protecting groups were used so that alkylation could be carried out with a Grignard reagent:

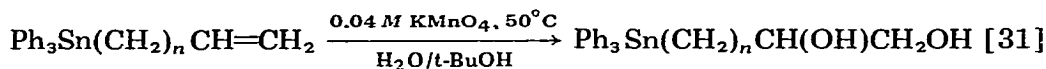
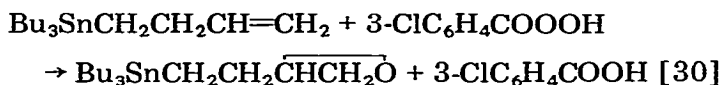
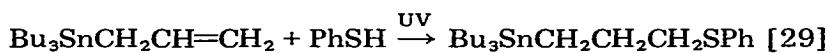


Provided reaction conditions were mild enough to prevent Sn—C bond scission it was possible to transform the carbonyl into other functional groups. It was interesting to observe that 4-oximinopentylidiphenyltin chloride existed both in the solid state and in solution as the single stereoisomer (X) due to intramolecular coordination of oxygen to tin.

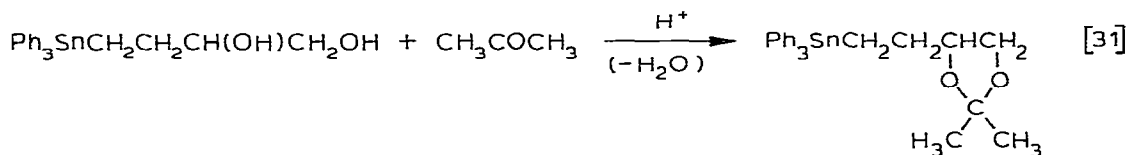
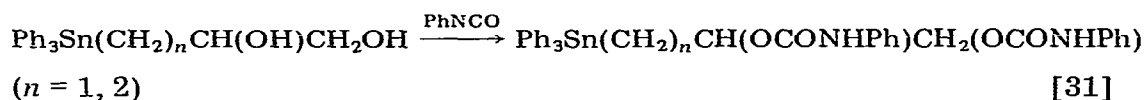
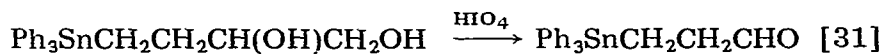


Beckmann rearrangement of X should have given the tin-substituted *N*-methylbutyramide from the usual *trans* exchange. Instead the sole product was *N*-[3-(chlorodiphenylstannyl)propyl]acetamide (XI) a rare example of rearrangement in which the groups which are *cis* to each other exchange [28]. The most likely explanation is that the actual species undergoing rearrangement contains the N—O—P grouping and has the opposite configuration to that in X.

A more sustained approach to the preparation of functionally substituted compounds has been to exploit the reactivity of double bonds in alkenyltin compounds, accepting the limitations imposed by the lability of carbon—tin bonds. The method has proved quite successful and the following equations illustrate its scope:



($n = 1, 2$)



Radical developments in chemistry often stem from new synthetic methods and products. Certainly synthesis is the key to commercial exploitation and we can expect continuing development of methods of preparing both simple and complex organotin compounds.

Industrial use of organotin compounds

The principal uses are as stabilizers to delay thermal (and to a less extent photochemical) degradation of PVC and as catalysts for a variety of reactions. We discovered fortuitously an example of the remarkable ability of some organotin derivatives to catalyse transesterification reactions [32], but have been primarily concerned with their use as PVC stabilizers. In almost all of our studies on PVC stabilization I have had the good fortune of working in collaboration with Geoff Ayrey (also of Queen Elizabeth College).

Our approach in this field, where most of the methodology has been empirical, has been to examine under carefully controlled conditions reactions of the pure stabilizers firstly with model compounds and subsequently with PVC itself. Much work in industry has been aimed at trying to recreate in the laboratory conditions which approximate closely to those in the plant, whereas we have been concerned to isolate and evaluate the parameters which most influence reactions occurring between stabilizer and polymer.

We began in 1967 with some work on organotin maleates. When dibutyltin oxide was treated with maleic acid (or anhydride), monomeric, trimeric and tetrameric but no polymeric forms of dibutyltin maleate were obtained [33]. It was shown that alkyltin maleates readily undergo Diels-Alder reactions with suitable dienes [34].

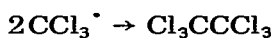
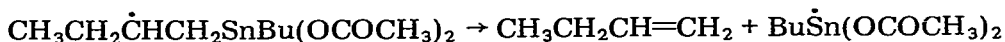
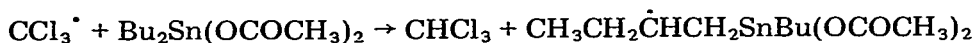
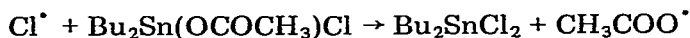
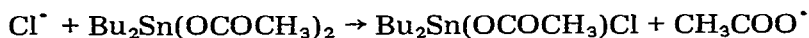
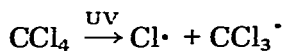
To test current ideas, we next examined reactions between a range of stabilizers and model secondary, tertiary and allylic chlorohydrocarbons [35]. While this work was in progress Klemchuk published the results of similar studies [36]. These were in broad agreement with our own results, namely that the relative rates at which stabilizers, R_2SnX_2 ($\text{X} = \text{SCH}_2\text{COOC}_8\text{H}_{17}$), OCOR' , etc.), exchanged X groups with chlorine atoms in chlorohydrocarbons depended on the environment of the chlorine in the sense allylic $>$ tertiary \gg secondary and that these exchanges were catalysed by dialkyltin dichlorides. In addition, our work showed that the relative reactivity of a range of tin compounds to allylic chlorine paralleled exactly the relative stabilizing ability. This suggested that exchange with allylic chlorine atoms was significant in the stabilization

process. Also our results indicated that exchange was accompanied by allylic rearrangement, a factor which could be important in interrupting conjugated polyene sequences in degrading polymer [37].

Given the increasingly low levels at which dialkyltin compounds, R_2SnX_2 , are added to PVC there is little doubt that they are converted to the dichlorides, R_2SnCl_2 , by reaction with hydrogen chloride as well as by exchange reactions. The role of the dichloride is paradoxical in that although traces catalyse the stabilizing exchange reactions discussed in the previous paragraph, larger amounts of these undoubtedly Lewis acidic compounds would be expected to catalyse the dehydrochlorination reaction. By using bis(4-oxopentyl)tin di(isooctyl thioglycolate), $(CH_3COCH_2CH_2CH_2)_2Sn(SCH_2COOC_8H_{17})_2$, we demonstrated that the stabilizing effect had been enhanced by a factor of about 2.5 compared with the corresponding dibutyltin compound. The reason for the increased stabilization activity was considered to be that the Lewis acidity and hence the prodegradant activity in the derived dichloride, $(CH_3COCH_2CH_2CH_2)_2SnCl_2$, was suppressed by internal coordination of the carbonyl groups [27,38].

We then began work which is still continuing on reactions between PVC and stabilizers carrying radioactive labels. When di(butyl[^{35}S]thiolato)dibutyltin was heated with PVC at $180^\circ C$ there was a dominant reaction leading to incorporation of ^{35}S into the polymer as a steady rate which continued for more than 8 hours. The amount of incorporation was greatly in excess of what would be expected from exchange reactions between reactive chlorine atoms and ^{35}SBu groups and was shown to be due to addition of $Bu^{35}SH$ to double bonds in the degrading polymer [39,40]. This addition of thiol liberated by hydrogen chloride from the organotin mercaptides is very important in the canon of stabilizing reactions and the predominance of isooctyl thioglycolate stabilizers is due to the greater facility for addition to double bonds of thioglycolates compared with simple alkane or arene thiols [41].

The arguments that once raged as to whether the thermal degradation of PVC is a radical or an ionic process have now largely subsided and there is tacit agreement that, generally, both processes occur. The free radical version of events requires chain-carrying chlorine atoms and it was of interest to determine whether organotin stabilizers could scavenge free chlorine atoms. The products obtained when carbon tetrachloride was photolysed in the presence of dibutyltin diacetate were consistent with the following scheme [42].

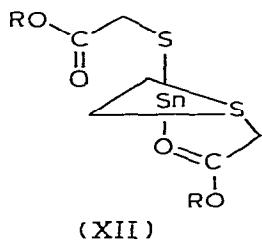


Thus it was concluded that scavenging of chlorine atoms is another reaction

leading to stabilization, though its relative importance has yet to be established. The displacement of a carboxylate radical from tin by a chlorine atom is interesting since *t*-butoxy radical displaces an alkyl radical from alkyltin carboxylates [43].

Little has been published on how the relative stabilizing effect of organotin bis(isooctyl thioglycolates), $R_2Sn(SCH_2COOC_8H_{17})_2$, varied with the nature of the organic group *R*. Using the time taken for colour development as a measure of effectiveness, about twenty compounds were compared with some surprising results. Where *R* = alkyl there were no great differences except that the di-*t*-butyl compound was a very poor stabilizer. The aryl compounds were generally less effective than the alkyltins but both electron-donating and electron-withdrawing substituents in phenyltin compounds reduced the stabilizing activity. The major features of these results were explained in terms of increasing ease of fission of Sn—C bonds by hydrochloric acid on going from *R* = alkyl → C_6H_5 → *p*-MeOC₆H₄. In separate experiments we showed that the least effective stabilizers readily underwent Sn—C bond scission with hydrogen chloride giving the strongly prodegradant tin(IV) chloride, whereas the alkyltin compounds resisted Sn—C bond protolysis [44].

Continuing this approach, now in collaboration with Dr. M. Lequan (École Nationale Supérieure de Chimie de Paris) mixed dialkyltin bis(isooctyl thioglycolates), $RR'Sn(SCH_2COOC_8H_{17})_2$, were examined and the following stabilizing sequence was obtained. *R*, *R'* = Me, *i*-Pr > Me, *t*-Bu ≈ Me, Et > di-*i*-Pr ≈ Me, C_8H_{17} > di-*n*-Bu ≈ Me, C_6H_{13} ; Me, *n*-Bu; di- C_8H_{17} > di-*t*-Bu [45]. The contrast between the ineffective compound where *R* = *R'* = *t*-Bu and the efficient stabilizer where *R* = *t*-Bu and *R'* = Me is striking. From IR and Mössbauer spectra it was shown that the most effective stabilizers have one ester group coordinated to tin as in XII, a fact which had been noted earlier [46]. How this 5-coordinate structure promotes stabilization is not clear. The coordinated carbonyl group may just weaken the Sn—S bond sufficiently to facilitate exchange with allylic chlorine. It is tempting to suggest that exchange of allylic chlorine might be promoted by some kind of interaction between the allylic double bond and the



tin atom. While it is clear that there is no π -bonding to tin in the ground state [47], this does not rule out favourable interactions in a transition state.

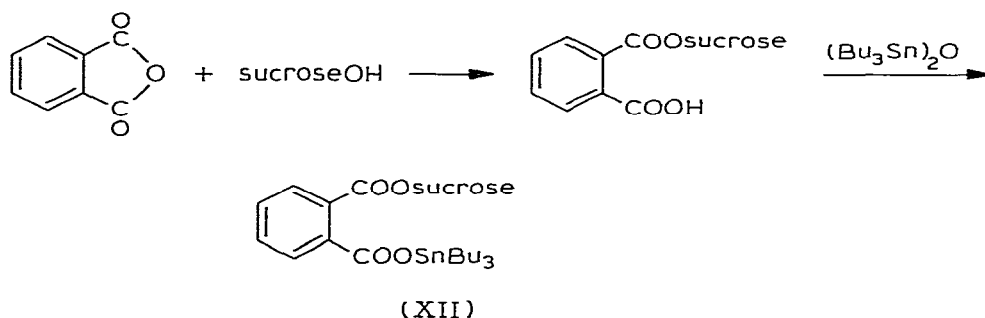
Use of organotins as biocides

Biological activity is usually at a maximum in compounds with three Sn—C bonds, i.e. R_3SnX (*R* = alkyl or aryl), and is often independent of the nature of the group *X*. In some early work it was shown that triphenyltin compounds,

Ph_3SnX , had no contact insecticidal properties to *Sitophilus oryzae* (L). Towards larvae of the common clothes-moth *Tineola bisselliella* (Humm.), however, the triphenyltin compounds functioned as stomach poisons and mortality varied from 75% to 0% depending upon the nature of X [48].

Biological activity in tin compounds is exceptional in that it is mainly confined to the organic derivatives, inorganic tin compounds being much less active. Thus organotin pesticides are attractive environmentally if it can be demonstrated that they are broken down to the relatively harmless inorganic compounds. Using triphenyltin compounds carrying ^{14}C labels on the phenyl groups we showed that microbiological degradation occurred in soil and the compounds had a half-life of about 150 days [49].

A major limitation to the more widespread use of organotin biocides is lack of specificity and frequently the plant host is affected as well as the pest. In an attempt to alter the specificity it was decided to effect a major increase in solubility by attaching the biocidal organotin residue to a sugar. In a first approach sucrose was converted to sucrose hydrogen phthalate by direct reaction with phthalic anhydride. This product was then treated with, for example, tributyltin oxide to give tributyltin sucrose phthalate (XIII) [50,51].



Although these products were mixtures which contained a considerable quantity of free sucrose [52] they were found to have a higher biological activity against fungi and algae than tributyltin oxide. This increased activity was both qualitative in that the sucrose derivatives attacked fungi which are impervious to tributyltin oxide and quantitative even when equal weights of compound are compared, but the increase in activity is even more striking when the basis of comparison is equal weight of tin [51].

Currently, we are still studying interactions between tin compounds and PVC as well as pursuing the goal of biocides with higher specificities. In our work on organotin compounds over the last 18 years or so, of which a somewhat random selection has been surveyed above, I have had the pleasure of cooperating with several coworkers. To those named in the text and all those whose names appear in the reference list, I am most grateful.

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