

# THE CHEMISTRY OF ORGANOTIN COMPOUNDS

R. C. Poller

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## PREFACE

In writing this book the aim has been to produce a balanced and up-to-date account of organotin chemistry intended primarily for those concerned with pure and applied research in this field. It is hoped that the book will also serve as an introduction to a fascinating area of organometallic chemistry for research workers in allied subjects and for advanced undergraduates.

The various classes of organotin compounds are systematically presented in the first two-thirds of the book, the remaining space being devoted to topics which are more satisfactorily treated in a unified manner. In a work of this size it would be inappropriate to give exhaustive lists of compounds, particularly as these are available elsewhere (the most useful source, which contains references to the end of 1964, is *Organometallic Compounds, Part II*, Second Edition, edited by R. W. Weiss, Springer-Verlag, New York, 1967). The descriptions of the various classes of compounds are, therefore, illustrated by concise tables showing the physical properties of typical members of each class.

Although it is not possible, or desirable, to suppress entirely one's own interests the choice of material has been largely determined by the content of the current chemical literature. Systematic coverage of the literature extends to the end of 1968 and several references for 1969 have been included. Since the process of publication always takes a finite time, readers who wish to bring themselves comprehensively up-to-date with the literature on organotin chemistry should begin searching with the first issue of *Chemical Abstracts* for 1969 (Volume 70).

It is a pleasure to record thanks to Miss Alison Anderson of Logos Press for her valuable help and advice.

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## SOME PRELIMINARY CONSIDERATIONS

### 1.1 NOMENCLATURE

Current practice in the naming of organotin compounds is based on the use of 'tin' as a suffix so that  $\text{Me}_4\text{Sn}$  is tetramethyltin and  $(\text{Me}_3\text{Sn})_2\text{O}$  is *bis*(trimethyltin) oxide<sup>6, 28</sup>. In the older system compounds are regarded as derivatives of the (sometimes hypothetical) stannanes  $\text{Sn}_n\text{H}_{2n+2}$  and the above compounds are called tetramethylstannane and hexamethyldistannoxane respectively. Both systems have advantages and both are used in this book. The modern system is logically based but reluctance to regard an organotin group as a substituent can result in cumbersome or inappropriate names; for example, the most felicitous name for  $(\text{Bu}_3\text{Sn})_2\text{NEt}$  is *bis*(tributylstannyl)ethylamine. The principal objection to the stannane system is that, for catenated compounds with more than two tin atoms, the parent compound does not exist but as this does not apply to the majority of organotin compounds it does not seem to be a serious objection.

### 1.2. REACTIVITY OF ORGANOTIN COMPOUNDS

Before beginning a detailed scrutiny of organotin chemistry it is appropriate to consider the extent to which the general reactivity of organotin compounds can be predicted from fundamental principles. In fact it is difficult to make valid generalisations since many factors will be involved in determining how a particular compound will react in a given set of circumstances<sup>57</sup>. Hence it is most profitable to discuss specific reactions of, for example, the tin-carbon bond in detail (Chapter 3) but it is, nevertheless, instructive to consider in a more general way, the more pertinent factors influencing reactivity. Discussion is mainly confined to reactions of the tin-carbon bond in comparison with corresponding bonds between carbon and other Group IVb elements.

Metal-carbon bond strengths have been reviewed by Skinner<sup>58</sup> who noted that mean bond dissociation energies ( $\bar{D}$ ) fall as a subgroup is descended so that  $\bar{D}(\text{C}-\text{R}) > \bar{D}(\text{Si}-\text{R}) > \bar{D}(\text{Ge}-\text{R}) >$



$\bar{D}(\text{Sn}-\text{R}) > \bar{D}(\text{Pb}-\text{R})$ . Some figures are given in Table I which, although useful for indicating trends, are imperfect guides to reactivity since (a) they are mean values [ $\bar{D}(\text{Sn}-\text{Me})$  is one quarter of the energy required to break the 4 C—Sn bonds in  $\text{Me}_4\text{Sn}$ , this differs from the dissociation energy  $D(\text{Me}_3\text{Sn}-\text{Me})$  i.e. the energy required to break one Sn—C bond in  $\text{Me}_4\text{Sn}$ ] and (b) they refer to homolytic bond fission, whereas the majority of the reactions of these compounds involve heterolysis. By the use of electron-impact studies a number of bond dissociation energies have been investigated for organotin compounds (Table II). These figures, when compared with those

TABLE I

*Mean bond dissociation energies (kcal. mole<sup>-1</sup>)*

Bond	$\bar{D}^a$	Reference
Sn—Me	50–52	53, 54, 55
Sn—Et	46–47	53, 54, 55
Sn—Ph	54	54
Sn—O(Et <sub>3</sub> SnOCOPh)	98	54
Sn—Sn(Ph <sub>3</sub> SnSnPh <sub>3</sub> )	30 ± 15	54
C—Me	83	13
Si—Me	70	13
Ge—Me	59	13
Ge—Et	57	53
Pb—Me	37	13
Pb—Et	31	53

<sup>a</sup> Unless otherwise stated the error is ±1–2 kcal. mole<sup>-1</sup>.

given in Table I emphasise the fact that bonds dissociate in a stepwise fashion with different energies being involved at each step. From measurements of the heats of redistribution reactions it was shown that, while 56 kcal. mole<sup>-1</sup> are required to dissociate the first Sn—C bond in dimethyltin dichloride, only 32 kcal. mole<sup>-1</sup> are required for the second Sn—C bond<sup>41</sup>.

Although progress is being made in the determination of bond energies the problem of predicting reactivity in heterolytic processes remains and it is necessary to consider the relative ionic character of the tin-carbon bond.

TABLE II

*Bond dissociation energies (kcal. mole<sup>-1</sup>) estimated from electron impact studies*

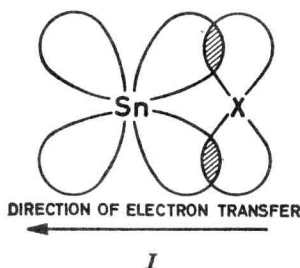
Bond	D <sup>a</sup>	Reference	Bond	D <sup>a</sup>	Reference
Me <sub>3</sub> Sn—Me	73	61	Me <sub>3</sub> Sn—C <sub>2</sub> H <sub>3</sub>	78	61
Me <sub>3</sub> Sn—Me	60	32a	Me <sub>3</sub> Sn—CH <sub>2</sub> Ph	57	61
Me <sub>3</sub> Sn—Me	61	33a	Me <sub>3</sub> Sn—Br	94	61
Me <sub>3</sub> Sn—Et	68	61	Me <sub>3</sub> Sn—I	80	61
Me <sub>3</sub> Sn—Et	55	32a	Me <sub>3</sub> Sn—SnMe <sub>3</sub>	76	61
Me <sub>3</sub> Sn—Pr	68	61	Me <sub>3</sub> Sn—SnMe <sub>3</sub>	63	32a
Me <sub>3</sub> Sn—Pr	55	32a	Me <sub>3</sub> Sn—GeMe <sub>3</sub>	67	33a
Me <sub>3</sub> Sn—Ph	57	61	Me <sub>3</sub> Sn—SiMe <sub>3</sub>	66	33a
			Me <sub>3</sub> Sn—CMe <sub>3</sub>	60	33a

<sup>a</sup> The error is  $\pm 2-6$  kcal. mole<sup>-1</sup>.

Unfortunately the electronegativities of the Group IVb elements is a controversial subject; the results of a number of different approaches to the problem have recently been tabulated<sup>46</sup>. It is implicit in Pauling's definition of electronegativity 'the power of an atom in a molecule to attract electrons to itself'<sup>44</sup> that the electronegativity of an element may vary with its molecular environment and this, together with the fact that it is not possible to make direct electronegativity measurements, accounts for the large number of different values published<sup>8</sup>. The values given by Pauling<sup>44</sup> are unsatisfactory in that they scarcely discriminate between the elements silicon, germanium, tin and lead. Although certain measurements<sup>15, 40</sup> are compatible with the electronegativity sequence which would be predicted from the positions of the elements in the Periodic Table i.e. C > Si > Ge > Sn > Pb, Allred and Rochow<sup>4</sup> have adduced compelling chemical and physical evidence for the sequence C > Pb > Ge > Sn > Si. This order has been criticised<sup>16, 17</sup> but there is some theoretical justification for it and a similar alternation of electronegativity values is observed in Group IIIb<sup>3</sup>. The Allred-Rochow values are: C, 2.60; Si, 1.90; Ge, 2.00; Sn, 1.93; Pb, 2.45 and while these emphasise the polarity of the tin-carbon bond they offer little hope of explaining the very real differences in reactivity between organosilicon and organotin compounds. (For example, hydrogen in the alkyl groups of tetraalkylsilanes can be substituted by chlorine or bromine whereas these reagents give only tin-carbon cleavage products with tetraalkylstannanes.)

The relative inductive effects of trialkylstannyl and analogous groups are more certain. Studies of the relative rates of acid cleavage of the compounds  $p\text{-Me}_3\text{MCH}_2\text{C}_6\text{H}_4\text{SnMe}_3$  ( $\text{M} = \text{Si}, \text{Ge}, \text{Sn}$ )<sup>9</sup> and the rates of alkaline hydrolysis of  $\text{R}_3\text{M}(\text{CH}_2)_n\text{COOEt}$  ( $\text{R} = \text{Me}, \text{Et}$ ;  $n = 1, 2, 3$ ;  $\text{M} = \text{Si}, \text{Ge}, \text{Sn}$ )<sup>60</sup> and of other compounds<sup>18a</sup>, spectroscopic measurements on  $(\text{Me}_3\text{Si})_2\text{N}(\text{MMe}_3)$  ( $\text{M} = \text{Si}, \text{Ge}, \text{Sn}, \text{Pb}$ )<sup>61</sup> and calculations<sup>27</sup> establish that the  $\text{R}_3\text{M}$  groups have a +I effect. The order of electron release is  $\text{Me}_3\text{Pb} > \text{Me}_3\text{Sn} > \text{Me}_3\text{Ge} > \text{Me}_3\text{Si}$ .

One difficulty which often arises in experiments designed to measure relative inductive effects is that there may be some  $\pi$ -character in a bond between tin and an element possessing  $p$  electrons<sup>39, 60</sup>. Thus in a  $\text{Sn}-\text{X}$  bond where  $\text{X}$  is  $sp^2\text{C}$ ,  $\text{N}$ ,  $\text{O}$ ,  $\text{S}$  or halogen it is possible that, opposing the inductive electron drift  $\text{Sn} \rightarrow \text{X}$ , there may be some overlap between a filled  $p$ -orbital on  $\text{X}$  and empty  $5d$  orbitals on  $\text{Sn}$  causing a transfer of electron density in the opposite direction as in *I*.



Despite some controversy<sup>19, 25, 47, 48</sup> it is widely accepted that there are significant  $(p \rightarrow d)\pi$  contributions to the  $\text{Si}-\text{N}$  bonds in compounds such as the planar trisilylamine<sup>45</sup>. Is it reasonable to assume that tin and the other Group IVb elements will show a similar tendency to  $\pi$ -bond formation? Theoretical considerations suggest that the overlap of  $p$  and  $d$  orbitals would not be particularly sensitive to the sizes of the orbitals<sup>14</sup> and there is no marked decrease in  $p\pi-p\pi$  bond strengths in Group III as the atomic numbers increase<sup>45</sup>. Although this suggests that  $\pi$ -bonding should be present in suitably substituted tin compounds, examination of the literature shows disagreement regarding its extent. There is some evidence that, in phenyltin compounds, interaction occurs between the  $\pi$ -electrons of the phenyl groups and the  $5d$  orbitals of tin. This conclusion is based on the interpretation of nmr-<sup>38, 59</sup>, infrared-<sup>33</sup> and

ultraviolet<sup>33</sup>-spectra and dipole moments<sup>26</sup> of phenyltin compounds and on the acid strengths of the substituted benzoic acids  $p\text{-Me}_3\text{MC}_6\text{H}_4\text{COOH}$  ( $\text{M} = \text{C}, \text{Si}, \text{Ge}, \text{Sn}$ )<sup>11</sup>. It cannot be assumed that other aromatic groups behave similarly since the  $pK_a$  values for a series of pyridines having  $\text{Me}_3\text{M}$  ( $\text{M} = \text{C}, \text{Si}, \text{Ge}, \text{Sn}$ ) substituents in the 2-position indicated the absence of  $p\pi\text{-}d\pi$  bonding in the tin-pyridine link<sup>5</sup>. The existence of  $p\pi\text{-}d\pi$  bonding in propenyltin compounds is indicated by lithium cleavage experiments<sup>52</sup> and differences in chemical shifts observed in the nmr spectra of tetraallyl- and tetravinyl-tin compounds suggest double bond character in the tin-vinyl bond<sup>7</sup> but opposite conclusions were reached from the infrared spectra of  $\text{CH}_2=\text{CHMCl}_3$  compounds ( $\text{M} = \text{Si}, \text{Ge}, \text{Sn}$ )<sup>34</sup>. In the course of infrared and Raman studies of compounds  $\text{R}_3\text{SnXSnR}_3$  ( $\text{X} = \text{O}, \text{S}$ ) it was concluded that there was no  $\pi$ -contribution to the  $\text{Sn-O}$  and  $\text{Sn-S}$  bonds<sup>32</sup>, similar conclusions regarding  $\text{Sn-O}$  and  $\text{Sn-S}$  bonds in other compounds were reached by other workers<sup>1, 2, 38a</sup>. Using diverse arguments several authors have concluded that there is no double bond character in the tin-nitrogen bond<sup>24, 25, 30, 47, 48</sup> but nmr measurements on methylstannylamines indicated considerable  $p\pi\text{-}d\pi$  bonding<sup>35</sup>. Calculations based upon nuclear quadrupole resonance measurements indicated  $\pi$ -character in the  $\text{Sn-I}$  bonds of diethyltin diiodide<sup>10</sup> whereas it was concluded from the dipole moments of organotin chlorides that the  $\text{Sn-Cl}$  bond order is close to unity<sup>26</sup>. There is evidence for  $d\pi\text{-}d\pi$  interaction in the bonds formed between tin and certain transition metals<sup>20, 29</sup> and the possibility of drift of  $d$ -electrons from tin into  $\text{C-F}$  antibonding orbitals in trifluoromethyltin compounds has been discussed<sup>12</sup>. To summarise, the extent of  $p\pi\text{-}d\pi$  bonding in tin compounds is uncertain, the balance of evidence suggests that it may not be important except, perhaps, in some  $sp^2\text{C-Sn}$  bonds.

Another factor which can be important in influencing reactivity is the increased tendency to higher coordination numbers on passing from germanium to tin. This general subject is developed in Chapter 11 but we note here that this can lead to changes in reaction mechanisms with striking results<sup>18</sup>.

The foregoing brief discussion indicates the difficulty of evaluating some of the factors which determine reactivity. This, together with the problem of identifying the particular factors which are relevant to a specific reaction point up the challenge and interest involved in a fundamental understanding of organotin reactions.

## 1.3. ISOTOPES OF TIN

Tin (atomic number 50, atomic weight 118.69) has the following isotopic composition<sup>43</sup>:

Isotope:	112	114	115	116	117	118	119	120	122	124
% Abundance:	1	0.68	0.34	14.4	7.54	24.1	8.62	32.5	4.7	5.9

This multiplicity of isotopes is, on the whole, advantageous to the experimentalist in the range and usefulness of the physical techniques which are consequently applicable to organotin compounds (Chapter 13). For studies utilising radioactive tracer techniques the  $^{113}\text{Sn}$  isotope is employed;  $^{113}\text{Sn}$  metal, some inorganic compounds, and a few organotin derivatives containing this isotope are available commercially. Details of the synthesis of  $\text{Bu}_3^{113}\text{SnCl}$ <sup>58</sup>,  $(\text{Bu}_3^{113}\text{Sn})_2\text{O}$ <sup>56</sup> and  $\text{Bu}_3^{113}\text{SnOCOPh}$ <sup>42</sup> have been published.

## 1.4. ANALYSIS OF ORGANOTIN COMPOUNDS

The best routine method for the determination of tin in organotin compounds is based on conversion to stannic oxide which is estimated gravimetrically. The following details are similar to those given by van der Kerk and Luijten<sup>36</sup>.

The organotin compound (~0.1 g) is weighed into a silica test tube (length 130 mm, external diameter 17 mm, internal diameter 15 mm) which has been heated, with a Meker burner, to constant weight. By means of a dropping pipette, 25 drops of a mixture of concentrated nitric acid (3 volumes) and concentrated sulphuric acid (2 volumes) are added cautiously. When the reaction subsides the tube is supported horizontally and the mixture heated with a low flame. As frothing subsides the rate of heating is increased until, finally, the tube is heated strongly with a Meker burner for 2–3 hours.

Titrimetric methods<sup>21, 49</sup> of tin determination are usually based on a final oxidation of tin(II) to tin(IV) and suffer from the following disadvantages: (a) all traces of the oxidising agent used in the initial combustion must be removed and (b) an inert atmosphere must be maintained until the final titration is complete because of the ready oxidation of tin(II) by oxygen. Tin estimation by complexometric titration<sup>22</sup>, polarography<sup>23</sup>, spectrography<sup>31</sup> and X-ray fluorescence<sup>37</sup> has also been described.

Methods for the estimation of specific classes of organotin compounds are given in the appropriate chapters.

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