1 Introduction

1.1 History

The first organotin compound was prepared over 150 years ago. In 1849, in a paper devoted largely to the reaction which occurred when ethyl iodide and zinc were heated together in a sealed tube, Frankland says:1 “In conclusion, I will describe, very briefly, the behaviour of iodide of ethyl in contact with several other metals, at elevated temperatures ... Tin also effected the decomposition of iodide of ethyl at about the same temperature (150 °C to 200 °C); the iodide became gradually replaced by a yellowish oily fluid, which solidified to a crystalline mass on cooling: no gas was evolved either on opening the tube or subsequently treating the residue with water ... It would be interesting to ascertain what combination the radical ethyl enters in the last ... decomposition”. This paper is often held to mark the first systematic study in organometallic chemistry.2,3

\[
\begin{align*}
2 \text{EtI} + \text{Sn} & \rightarrow \text{Et}_2\text{SnI}_2 & \quad (1-1) \\
2 \text{EtI} + 2 \text{Zn} & \rightarrow 2 \text{EtZnI} & \rightarrow \text{Et}_2\text{Zn} + \text{ZnI}_2 & \quad (1-2) \\
2\text{Et}_2\text{Zn} + \text{SnCl}_4 & \rightarrow \text{Et}_2\text{Sn} + 2\text{ZnCl}_2 & \quad (1-3) \\
\text{EtI} + \text{ZnSn} & \rightarrow \text{Et}_4\text{Sn} + \text{Znl}_2 & \quad (1-4) \\
\text{Et}_2\text{Zn} + \text{SnCl}_2 & \rightarrow \text{Et}_2\text{Sn} + \text{ZnCl}_2 & \quad (1-5)
\end{align*}
\]

Frankland subsequently showed that the crystals were diethyltin diiodide (equation 1-1).4,6 In independent work,7 Löwig established that ethyl iodide reacted with a tin/sodium alloy to give what is now recognised to be oligomeric diethyltin, which reacted with air to give diethyltin oxide, and with halogens to give diethyltin dichlorides (though through using incorrect atomic weights, the compositions that he ascribed to these compounds are wrong).

As an alternative to this so-called direct method, an indirect route was devised by Buckton in 1859,8 who obtained tetraethyltin by treating tin tetrachloride with Frankland’s diethylzinc.

Organotin Chemistry, Alwyn G. Davies
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In 1900, Grignard published his synthesis of organomagnesium halides in ether solution. These reagents were much less sensitive to air than Frankland’s solvent-free organozinc compounds, and they rapidly replaced and extended the scope of the zinc reagents as a source of nucleophilic alkyl and aryl groups. In 1903, Pope and Peachey described the preparation of a number of simple and mixed tetraalkylstannanes, and of tetrphenyltin, from Grignard reagents and tin tetrachloride or alkyltin halides,

and reactions of this type soon became the standard route to alkyl- and aryl-tin compounds.

This early work is summarised in Krause and von Grosse’s Organometallische Chemie which was published first in 1937,

and which described examples of tetraalkyl- and tetaaryl-stannanes, and of the organotin halides, hydrides, carboxylates, hydroxides, oxides, alkoxides, phenoxides, R₃Sn(II) compounds (incorrectly), distannanes (R₂SnSnR₃), and oligostannanes (R₂Sn)ₙ.

Tin played a full part in the great increase of activity in organometallic chemistry which began in about 1949, and this was stimulated by the discovery of a variety of applications. Structural studies have always been prominent in organotin chemistry, and particularly the structural changes which occur between the solution and solid states. Mössbauer spectroscopy was extensively used during the 1960s and 1970s for investigating structures in the solid state, but it has now largely given place to X-ray crystallography and high resolution solid state tin NMR spectroscopy.

In 1962, Kuivila showed that the reaction of trialkyltin hydrides with alkyl halides (hydrostannolysis) (equation 1-6) was a radical chain reaction involving short-lived trialkyltin radicals, R₃Sn,

and in 1964, Neumann showed that the reaction with non-polar alkenes and alkynes (hydrostannation) (equation 1-7) followed a similar mechanism,

and these reactions now provide the basis of a number of important organic synthetic methods.

\[
\begin{align*}
R₃SnH + R'X &\rightarrow R₃SnX + R'H \\
R₃SnH + C= &\rightarrow R₃Sn\equiv CH
\end{align*}
\]

\(1-6\)

\(1-7\)

Salts of the free R₃Sn⁻ anion and R₃Sn⁺ cation have been examined by X-ray crystallography. The formation of short-lived stannylene, R₂Sn, has been established, and by building extreme steric hindrance into the organic groups, long-lived stannylene have been isolated, and stable compounds with double bonds to tin, e.g. R₂Sn=CR'₂, R₂Sn=SiR'₂, R₂Sn=SnR'₂, and R₂Sn=NR' have been prepared.

The various species of mononuclear organotin compounds with only carbon-bonded ligands, which are known, are summarised in Table 1-1. The best evidence which is available at the present time for the existence of these species, and the section where they are discussed, are listed in Table 1-1.

It is convenient to denote the number of valence electrons m, and the number of ligands n, by the notation m-Sn-n. For example the radical R₃Sn⁺ would be a 7-Sn-3 compound.

A major development in recent years has been the increasing use of organotin reagents and intermediates in organic synthesis, exploiting both their homolytic and heterolytic reactivity.

In parallel with these developments, organotin compounds have found a variety of applications in industry, agriculture, and medicine, though in recent years these have been circumscribed by environmental considerations. In industry they are used for the stabilisation of poly(vinyl chloride), the catalysis of the formation of the polyurethanes, and the cold vulcanisation of silicone polymers, and also as transesterification catalysts.
Their biological properties are made use of in antifouling paints on ships (though this is now curtailed by legislation; see Chapter 23), in wood preservatives and as agricultural fungicides and insecticides, and in medicine they are showing promise in cancer therapy and in the treatment of fungal infections.16

1.2 Nomenclature

Attempts to reconcile the practices of organic and inorganic chemists in the meeting ground of organometallic chemistry have led to IUPAC sanctioning a number of alternative systems of nomenclature.

(1) Under the extended coordination principle, the names of the attached ligands are given, in alphabetical order, in front of the name of the central metal; anionic ligands are given the -o suffix. Thus Me₂SnCl₂ would be dichlorodimethyltin, and Me₃SnMe₃ would be hexamethylditin.

(2) More commonly, the organic groups plus the metal are cited as one word, and the anionic component(s) as another. Thus Me₂SnCl₂ is usually called dimethyltin dichloride, and the common (Bu₃Sn)₂O (tributyltin oxide or TBTO) is bis(tributyltin) oxide.

(3) Under the substitutive scheme, mononit compounds can be named by citing replacement of hydrogen in the appropriate tin hydride. Stannane is SnH₄, and Me₂SnCl₂ would be called dichlorodimethylstannane. The compounds Bu₃SnSnBu₃ can similarly be called hexabutyldistannane as a derivative of distannane, H₂SnSnH₂, and (Bu₃Sn)₂O is hexabutyl distannoxane.

(4) The organotin group can itself be treated as a substituent, the H₃Sn group being stannyl, and the H₃Sn⁺ group being stanniio. This is useful in compounds with more complicated structures, e.g. Me₂SnCH₂CH₂CO₂H is 3-(trimethylstannyl)propanoic acid, and Et₂Sn(C₆H₄OH-P)₂ is 4,4’-diethylstanniodiphenol.

(5) The suffix ‘a’ can be added to the stem of the substituent (giving stanna) and used to indicate replacement of carbon. This is most useful with cyclic compounds, thus cyclo-(CH₃)₂SnMe₂ is 1,1-dimethylstannacyclopentane. Doubly bonded compounds are similarly named as alkynes with one or two of the doubly-bonded atoms replaced by tin: the compound R₂Sn=CR₂ is a stannene, and R₂Sn=SnR₂ is a distannene.

(6) By analogy with alkyl radicals and carbones (methynes), the species R₃Sn⁺ are stannyl radicals, and the species R₂Sn: are stannylenes or stannylidyls.

### Table 1-1 Organotin species RₙSn

<table>
<thead>
<tr>
<th>Formula</th>
<th>No. of electrons m</th>
<th>No. of ligands n</th>
<th>Evidence</th>
<th>Name</th>
<th>Location</th>
</tr>
</thead>
<tbody>
<tr>
<td>R₃Sn</td>
<td>8</td>
<td>4</td>
<td>X-Ray</td>
<td>stannane</td>
<td>Chaps. 5-10</td>
</tr>
<tr>
<td>R₃Sn⁺</td>
<td>7</td>
<td>4</td>
<td>ESR</td>
<td>stannane radical cation</td>
<td>Section 20.3</td>
</tr>
<tr>
<td>R₃Sn⁻</td>
<td>9</td>
<td>4</td>
<td>ESR</td>
<td>stannane radical anion</td>
<td>Section 20.4</td>
</tr>
<tr>
<td>R₂Sn⁻</td>
<td>10</td>
<td>5</td>
<td>NMR</td>
<td>hypervalent stannate anion</td>
<td>Sections 5.3.5 and 22.1</td>
</tr>
<tr>
<td>R₂Sn=C(R')₂</td>
<td>8</td>
<td>3</td>
<td>X-Ray</td>
<td>stannene</td>
<td>Section 21.4</td>
</tr>
<tr>
<td>R₂Sn⁺</td>
<td>6</td>
<td>3</td>
<td>X-Ray</td>
<td>stannylium ion</td>
<td>Section 7.2</td>
</tr>
<tr>
<td>R₂Sn⁻</td>
<td>7</td>
<td>3</td>
<td>ESR</td>
<td>stannyl radical</td>
<td>Section 20.1</td>
</tr>
<tr>
<td>R₂Sn⁻</td>
<td>8</td>
<td>3</td>
<td>X-Ray</td>
<td>stannate anion</td>
<td>Section 19.1</td>
</tr>
<tr>
<td>R₂Sn⁻</td>
<td>6</td>
<td>2</td>
<td>X-Ray</td>
<td>stannylene</td>
<td>Section 21.1 and 21.5</td>
</tr>
</tbody>
</table>

16 Their biological properties are made use of in antifouling paints on ships (though this is now curtailed by legislation; see Chapter 23), in wood preservatives and as agricultural fungicides and insecticides, and in medicine they are showing promise in cancer therapy and in the treatment of fungal infections.
1 Introduction

Chemical Abstracts indexing practice is summarised in the 1992 Index Guide, page 199, and is as follows.
(1) Acyclic compounds are named as derivatives of the acyclic hydrocarbon parents (see item 3 above), with an “ane” modification to indicate the presence of a chalcogen, for example H₃Sn, stannane; H₃Sn(SnH₂)₁₁SnH₃, tridecastannane; (H₃SnO)₂SnH₂, tristannoxane.
(2) Heterocyclic compounds are named as stanna replacement of carbon (see item 5 above).
(3) As substituent prefixes, H₃Sn- is indicated by stannyl, H₂Sn= by stannylene, and HSn= by stannylidyne.

Some illustrative examples are as follows.
Bu₂SnO stannane, dibutylxido
Bu₂Sn⁺ stannenediylium, dibutyl
Me₃SnCN stannacarbonitrile, trimethyltin cyanide
ClSnMe₂OSnMe₂Cl distannoxane, 1,3-dichloro-1,1,3,3,-tetramethyl
Me₃SnCH=CHCH=CHSnMe₂ stannane, 1,3-butadiene-1,4-diylbis[trimethyl
cyclo-BrPhSn(CH₂)₆SnBrPh(CH₂)₆, 1,8-distannacyclotetradecane, 1,8-dibromo-1,8-di-
phenyl.

If there is doubt, the correct name can usually be found through the formula index.

1.3 Overview of Synthesis

An overview of the principal groups of organotin compounds and their interconversions is given in Scheme 1-1, which deals mainly with tin(IV) compounds, and Schemes 1-2 and 1-3 which cover compounds related to tin(III) and tin(II) species, respectively. It

![Scheme 1-1](image-url)
1.3 Overview of Synthesis

**Scheme 1-2** Organotin synthesis based on reactions of SnH and SnM compounds.

**Scheme 1-3** Routes to lower valence state organotin compounds.

should be emphasised that, particularly with respect to Scheme 1-3, some of the reactions shown are as yet known only for specific organotin compounds, and are not necessarily general reactions.

Products which result from the formation of a new tin-carbon bond are boxed in the Schemes. The four principal ways in which this can be accomplished are the reaction of metallic tin or a tin(II) compound with an organic halide, of an organometallic reagent RM (M = lithium, magnesium, or aluminium) with a tin(II) or tin(IV) halide, of a trialkyltin hydride with an alkene or alkyne, or of a triorganotin-lithium reagent (R₃SnLi) with an alkyl halide.

The reaction which is most commonly used is that of a Grignard reagent with tin tetrachloride; complete reaction usually occurs to give the tetraorganotin compound (Scheme 1-1). This is then heated with tin tetrachloride when redistribution of the groups R and Cl occurs to give the organotin chlorides, R₃SnCl₄₋ₙ (n = 3, 2, or 1) (the Kocheshkov comproportionation). Replacement of the groups Cl with the appropriate nucleophile X (HO⁻, RCO₂⁻, RO⁻ etc.) then occurs readily to give the derivatives R₃SnX₄₋ₙ.
With a metal hydride as the nucleophile, the organotin hydrides, $R_nSnH_{4-n}$, are formed, which, by addition to an alkene or alkyne (hydrostannation), usually by a radical chain mechanism involving stannyl radicals, $R_3Sn^+$, provide the second way of generating the tin-carbon bond (Scheme 1-2).

Under the influence of a base or a platinum catalyst, the triorganotin hydrides and dialkyltin dihydrides eliminate hydrogen to give the distannanes ($R_3SnSnR_3$) and the oligostannanes ($R_2Sn$)$_n$, respectively. The halides, hydrides, or distannanes can be converted into the metallic derivatives $R_3SnM$, where $M$ is an alkali metal, and these act as sources of nucleophilic tin, which, by reaction with alkyl halides, provide a further way of creating a tin-carbon bond.

Recent years have seen important developments in the chemistry of tin(II) compounds and compounds with multiple bonds to tin (Scheme 1-3). The cyclopentadienyltin(II) compounds, which are formed from CpM and SnCl$_2$, are pentahapto monomers. When $R$ is a simple alkyl or aryl group, the stannylene $R_2Sn(II)$ are known only as short-lived reactive intermediates, but when the organic group is bulky [e.g. bis(trimethylsilyl)methyl or 2,4,6-trisubstituted aryl], as indicated by $R^*$ in Scheme 1-3, the monomeric stannylene, $R^*_2Sn^-$, have been isolated, and have provided routes to the stannenes ($R^*_2Sn=CR_2$) and distannenes ($R^*_2Sn=SnR^*_2$), and other compounds with a multiple bond to tin.

### 1.4 Overview of Structures

This description of the various types of organotin compounds must be supplemented by a description of the structures of the compounds, which are seldom as simple as the above formulae might indicate, and which frequently depend on the physical state of the sample.

Simple tetraalkyl- and tetraaryltin(IV) compounds exist under all conditions as tetrahedral monomers, but in derivatives $R_nSnX_{4-n}$ ($n = 1$ to $3$), where $X$ is an electronegative group (halide, carboxylate etc.), the Lewis acid strength of the tin is increased, and Lewis bases form complexes with a higher coordination number. The compounds $R_3SnX$ usually give five-coordinate complexes $R_3SnXL$ which are approximately trigonal bipyramidal, and the compounds $R_2SnX_2$ and $RSnX_3$ usually form six-coordinate complexes $R_2SnX_2L_2$ and $RSnX_3L_2$ which are approximately octahedral. The first such complex to have its structure determined by X-ray crystallography was $Me_3SnCl.py$ (1-1) and some further examples of such complexes are shown in structures 1-2 and 1-3.

![Structures 1-1, 1-2, 1-3](image_url)

The groups $X$, however, usually carry unshared electron pairs, and can themselves act as Lewis bases, resulting in intermolecular self-association to give dimers, oligomers, or polymers. Some examples are shown in formulae 1-4–1-6.
This self-association is governed by the nature of the ligands L and also by the steric demands of R, X, and L, and it is common for the degree of association to increase in the sequence gas < solution < solid.

If R or X carries a functional substituent Y beyond the α-position, the alternative of intramolecular coordination can occur leading to the formation of monomers with 5-, 6-, 7-, or 8-coordinated tin. Some examples are shown in formulae 1-7–1-10.

The structures of these intramolecularly self-associated monomers, oligomers, and polymers are seldom those of regular polyhedra, and the determination of their structures, and the steric and electronic factors which govern them, has been an important feature of organotin chemistry since the early 1960s. Initially the evidence came largely from proton NMR spectra and IR spectra on solutions, and IR and Mössbauer spectra on the solid state, supported by a few X-ray studies of single crystals. More recently, comparison of the high resolution $^{119}$Sn (or $^{117}$Sn) NMR spectra in solution and the solid state has proved to be a very sensitive indicator of changes in structure, and single crystal X-ray studies are now commonplace.

Systematic studies of organotin(II) compounds (Chapter 21) are much less extensive than those of tin(IV) compounds, but already it is apparent that there is a wide variety of structures. In bis(cyclopentadienyl)tin(II), the two rings are pentahapto-bonded, but the lone pair is stereochemically active and the rings are non-parallel. Other cyclopentadienyltin compounds, however, are known in which the rings are parallel, or the hapticity may change, or the CpSn+ ion may be present. The discovery of the σ-bonded stannylene [(Me$_2$Si)$_2$CH)$_2$Sn(II) (Lappert’s stannylene) in 1973 has stimulated a lot of studies. In the vapor phase it is monomeric, but in the solid state a dimer of $C_{2h}$ symmetry is formed. Many further diarylstannlenes, Ar$_2$Sn(II), and their corresponding distannenes, Ar$_2$Sn=SnAr$_2$, with sterically hindering ortho substituents have subsequently been prepared.

No Sn(III) radicals have yet been isolated (Chapter 20), though some are known which are stable in solution, in equilibrium with their dimers. Evidence regarding their structures comes mainly from ESR spectroscopy, which shows that, in contrast to carbon-centred radicals which are planar, tin-centred radicals are pyramidal even when the tin carries aryl ligands.

These topics are dealt with in detail in subsequent chapters.
1.5 Bibliography

This section lists, largely chronologically, the more important general reviews of organo-
tin chemistry, with some comments as to their contents. More specialised reviews are
referred to at the appropriate sections in the text. Extensive bibliographies are also given
in the volume of Houben Weyl, in volumes 1, 5, 8, 9, 11, 14, 16, 17, 18, 19, and 20 of
Gmelin, and in Science of Synthesis, which are referred to below.

The Chemical Review by Ingham, Rosenberg, and Gilman (1960),23 and the three
volumes of Organotin Chemistry edited by Sawyer (1971),24 provide an extensive if not
comprehensive listing of the organotin compounds which were known at those dates.
Reprints of the Chemical Review were widely circulated and did much to stimulate inter-
est in the subject. The various volumes of Gmelin give a thorough coverage of the com-
ounds known at the date the material went to press; thereafter, one is dependent on
Chemical Abstracts.

E. Krause and A. von Grosse, Die Chemie der Metal-organischen Verbindungen,
(1937, reprinted 1965). Pages 311-372 relate to organotin chemistry.11

preparations and physical and chemical properties, compiled from Chemical Abstracts.
Pages 79-253 relate to organotin chemistry. This supplements the data given in Krause
and von Grosse’s book.

W.P. Neumann Die Organische Chemie des Zinns, (1967),26 and its revised and

K.A. Kocheshkov, N.N. Zemlyanskii, N.I. Sheverdina, and E.M. Panov, Metodi Ele-
thorough coverage of organotin chemistry, though in Russian.

R.C. Poller, The Chemistry of Organotin Compounds, 1970.18

coverage in fourteen chapters by a variety of authors, with extensive lists of compounds;
written at a time before organotin compounds were used extensively in organic synthe-
sis.24

P.J. Smith, A Bibliography of X-ray Crystal Structures of Organotin Compounds
(1981).28

B.J. Aylett. Organometallic compounds, 4th. Edn. Vol. 1 The Main Group Ele-
ments, Part 2. Groups IV and V. (1979).20 Pages 177-276 deal with organotin chemis-
try.

Organotin Compounds: New Chemistry and Applications, ed. J.J. Zuckermann
(1976).29 Based on lectures given at the centenary meeting of the ACS.

G. Bähr and S. Pawlenko, in Methoden der Organischen Chemie (Houben Weyl),
vol. 13/6, (1978), pp. 181-251.31 Emphasises preparative methods, with brief experimen-
tal details.


A.G. Davies and P.J. Smith, Tin in Comprehensive Organometallic Chemistry,
(1982); reprints of this were widely circulated.33

only book on this increasingly important aspect of organotin chemistry, though there is
an excellent supplement in the 2nd edition of Chemistry of Tin (1998), which is noted
below.

Organotin Compounds in Organic Synthesis, Tetrahedron Symposia in Print No. 36,
Ed. Y. Yamamoto (1989).34


H. Ali and J.E. van Lier, Synthesis of Radiopharmaceuticals via Organotin Intermediates. Organotin compounds react rapidly and chemo-, regio-, and stereo-selectively with a variety of reagents, and this has been exploited in the synthesis of pharmaceuticals with a radioactive label, particularly when the radioisotope has a short half-life. A second review covering similar ground is included in Patai’s volume, as noted below.


1 Introduction


Chapters by various authors cover the different aspects of the problems associated with the use of tributyltin compounds in marine antifouling paints.


I. Omae, _Applications of Organometallic Compounds_, (1998).51


All these have been collated by Herbert and Ingeborg Schumann. The Gmelin handbooks cover comprehensively the organometallic compounds of tin. They are available in rather few libraries, but the database can be searched by computer.


_Science of Synthesis_, Vol. 5, (2003). See the textfile on the CD. This is the successor to Houben Weyl.
References to Chapter 1

1.4 E. Frankland, *Phil. Trans.*, 1852, 142, 417.
1.8 G. B. Buckton, *Phil. Trans.*, 1859, 149, 417.
1.9 E. A. Letts and J. N. Collie, *Phil. Mag.*, 1886, 22, 41.
1 Introduction