

CHAPTER 1

ORGANOTIN COMPOUNDS – A SHORT REVIEW ON THE NATURE OF BONDING AND OTHER RELATED PROPERTIES

1.1 Introduction

The Chemistry of tin has been the subject of extensive research in the last few decades. Tin in the form of a metal and its alloys were known to the ancient people and have greatly affected the course of human history [1]. Tin (atomic number, 50; relative atomic mass 118.70) is an element of group 14 of the periodic table, together with C, Si, Ge and Pb. Tin exists in three allotropic modifications and it can form a variety of inorganic and organometallic compounds. These two classes of compounds have different chemical and physical properties, which make them suitable for different applications in industry, agriculture and elsewhere. Tin as a metal, either as such, or in the form of its alloys and chemical compounds, has an astonishing amount of usefulness. Characteristically, in majority of its applications, only small amount of tin is needed to see its effect. This is generally true for organotin compounds, which during the past few decades have developed into extremely useful industrial commodities. Tin is unsurpassed by any other metal in the multiplicity of its applications. These involve such widely divergent fields as stabilizers for polyvinyl chlorides, industrial catalysts, industrial and agricultural biocides, wood preservatives and anti-fouling agents to mention only the most important applications.

Organotin compounds are defined as those that contain at least one carbon-tin covalent bond, the carbon atom being part of an organic group. The compounds contain tetravalent tin centres and are classified as mono-, di-, tri- and tetraorganotin(IV)s, depending on the number of alkyl (R) or aryl (Ar) moieties. The anion is usually a chloride, fluoride, oxide, hydroxide, a carboxylate or thiolate [2].

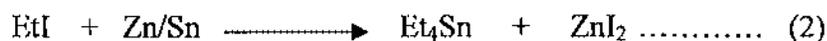
1.2 Literature

The first chemist to report the existence of “organic bodies of tin” as they were then known seems to have been E. Frankland [3]. This paper was devoted largely to the reaction which occurred when ethyl iodide and zinc were heated together in a sealed tube. The behaviour of ethyl iodide in contact with metallic tin, at elevated temperatures (150 to 200°C) was also studied. Frankland later showed that the crystals

obtained by the reaction of EtI with Sn at elevated temperatures (Eq.1) were of diethyltin diiodide [4-6].



In 1852, in an independent work [7], C. Löwig established that ethyl iodide reacted with a tin/sodium alloy to give oligomeric diethyltin. In 1859, Buckton obtained tetraethyltin by treating tin tetrachloride with Frankland's diethylzinc [8]. Letts and Collie showed that tetraethyltin could be prepared (Eq.2) by heating ethyl iodide with a mixture of Zn and Sn powder [9].

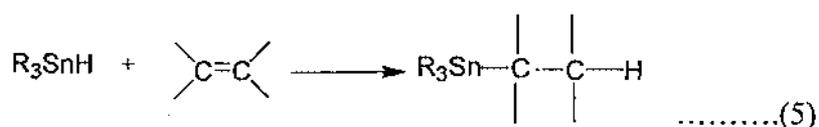
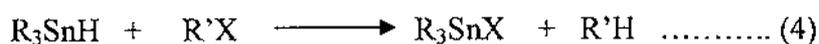


In 1879, Frankland [10] studied the reaction between stannous chloride and diethylzinc, hoping by analogy with results obtained by Buckton [8] simply to displace the chlorides with ethyl groups. The product obtained, however, was Et₄Sn and not Et₂Sn (Eq. 3).



As a route to Et₄Sn, this new reaction proved superior to Buckton's original method [8] and remained the method of choice for preparing tetraalkyltins until the early years of 20th century when Pope and Peachey first made use of the reaction of Grignard reagent on tin tetrachloride or alkyltin halides [11]. These types of reactions soon became the standard route to synthesize alkyl- and aryl- tin compounds. Krause and von Grosse summarized this early work in *Organometallische Chemie* which was first published [12] in 1937.

In 1962, Kuivila and his coworkers showed that the reaction of trialkyltin hydrides with alkyl halides (Eq. 4) was a radical chain reaction involving short-lived trialkyltin radicals R₃Sn· [13]. Subsequently, in 1964, Neumann *et al.* showed that the reaction with non-polar alkenes and alkynes (Eq.5) followed a similar mechanism [14]. These reactions are now the basis of a number of important organic synthetic methods.



The use of organotin hydrides in organic synthesis as selective reducing agents was reviewed in 1964 [15] and 1974 [16]. The uses of organotin compounds in organic synthesis have also been reviewed [17].

The first review of organotin compounds was published in 1937 by Krause and von Grosse [12]. Ingham, Rosenberg and Gilman [18] extended the literature up to 1959. Weiss [19] compiled an exhaustive list of organotin compounds covering the literature from 1937 to 1964. Several monographs by J.J. Zuckerman [20], R.C. Poller [21], W.P. Neumann [22] and a multi-author work edited by A.K. Sawyer [23] were published in 1971-72, and progress during the decade 1970-1980 was reviewed by Davies and Smith [24,25]. The preparation, properties and applications of monoalkyltin compounds have been reviewed by Guo Yushen in 1991 [26].

A review by Gielen and Sprecher [27] includes a discussion of organotin structure in which the coordination number of tin is greater than 4; the same topic was treated in an article by Okawara and Wada [28]. Structural aspects of organotin compounds have been reviewed [29] and a comprehensive bibliography of X-ray diffraction studies is available from the International Tin Research Institute [30]. The structural diversity of organotin compounds have been attracting the attention of a number of researchers and a multitude of structural types have been discovered [31].

Recently, Nath *et al.* have reviewed organotin(IV) complexes of the amino acids and peptides with special reference to their methods of synthesis, structural, thermal properties as well as their solution studies and biological activity [32]. The structures of these complexes were discussed on the basis of IR, electronic, multinuclear (^1H -, ^{13}C - and ^{119}Sn -) NMR, X-ray and ^{119}Sn Mössbauer spectral studies.

Synthesis, reactivity, structural aspects and applications of organotin(IV) complexes with phosphorous-based acids have been reviewed by V.K. Jain [33]. The applications of these complexes as catalysts, corrosion inhibitors and biocides were also discussed in this review.

An excellent critical review by Beckmann *et al.* [34] has appeared on stannasiloxanes in 2001. Chandrasekhar *et al.* have reviewed the recent progress in the area of organotin assemblies that contain Sn-O bonds [35]. Various kinds of tri-, di- and monoorganotin compounds are described in terms of their preparative methods such as hydrolysis of organotin halides, reactions of suitable organotin compounds with various kinds of substrates such as carboxylic acids, sulphonic acids, oxide transfer reagents etc. The structural characterizations of these compounds by the use of ^{119}Sn -NMR, ^{119}Sn Mössbauer and X-ray crystallography have been presented in considerable detail. The amazing structural diversity present in this family of compounds was discussed [35].

A comprehensive review [2] by L. Pellerito and L. Nagy discusses the properties of organotin(IV) complexes formed with biologically active ligands containing {O}, {N}, {S}, or {phosphorous(O)} donor atoms with various composition and stability. The emergence of new experimental techniques (EXAFS, multinuclear ^1H -, ^{13}C -, ^{119}Sn -NMR, ^{119}Sn Mössbauer, etc., spectroscopic techniques) provided useful information about the structure and stability of the complexes formed.

Organotin compounds can be assembled by various synthetic methodologies. Although in most instances, organotin oxide and hydroxides are preferred starting materials for organotin compounds, Sn-C bond cleavage reactions involving organotin compounds also offer a rational route. A very recent review by Chandrasekhar *et al.* [36] deals with the recent progress in this area and examines various reactions, where Sn-C cleavage occurs. A wide range of products are accessible from this approach and these are beautifully presented in the above-mentioned article.

The work on the use of organotins in agriculture was pioneered in the 1950's and early 1960's by van der Kerk and coworkers who discovered high fungicidal activity of tributyl- and triphenyl- tin compounds [37-40].

In 1989, the results obtained in the wide field of bio-organotin(IV) compounds were surveyed by Molloy [41]. Later Tsangaris and Williams [42] published a paper on Sn (including organotin(IV) compounds), compounds in pharmacy and nutrition. A full listing of reports which have evaluated organotin(IV) compounds in agriculture can be found in the two-part review by Crowe [43,44]. Detailed discussions of organotin(IV) compounds as wood preservatives have been published [45, 46].

In 1973, Atsushi *et al.* [47] in a very important piece of work reported the very high affinity of tin for tumours (highest among group 14 elements). This finding was further confirmed by various workers who prepared tin labelled technetium complexes and used them as imaging agents for tumour localization [48]. Two important reviews covering the literature of anticancer activity of organotin compounds have been published recently [49, 50]. Also, Sartaj Tabassum and Claudio Pettinari in their review article in 2006 provided substantial information on the mode of action of organotins in cancer chemotherapy [51].

1.3 Bonding in organotin compounds

Tin has $5s^2, 5p^2$ electronic configuration in its valence shell and therefore, two oxidation states i.e., +2 and +4 (due to 'inert s-pair effect') are possible. The ground state for tin is a 3P state, derived from s^2p^2 configuration [52]. In this state, there are only two unpaired electrons and a covalence of two would be expected. But the tetra-covalent state occurs much more frequently than the divalent state. The four-covalent state is derived from the $sp^3, ^5S$ state of the tin, which is not the ground state but the first excited state.

Essentially, most of the organometallic tin compounds are of the Sn(IV) type [53]. The marked increase in the stability of R_4Sn compounds over R_2Sn compounds demonstrates the effect of increased hybridization. The stability (to heat & oxygen) of

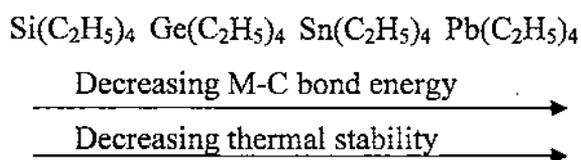
organotin derivatives in tetravalent states is reflected in the vast amount of growing literature about them. By contrast, their bivalent derivatives are much less stable, but these are also beginning to attract attention particularly with sterically demanding ligands {e.g. $\text{CH}(\text{SiMe}_3)_2$ } and π -bonding ligands. These bulky ligands stabilize the compounds in low-coordination geometry, as the congested environment around the metal hinders polymerization due to steric factors [54]. For example, tin(II) cyclopentadienyl, $(\text{C}_5\text{H}_5)_2\text{Sn}$ is a well established compound with tin in the (+2) oxidation state.

1.4 Reactivity of organotin compounds

The tetraalkyl and aryl compounds of main group 14 elements differ from the corresponding derivatives of these elements in neighbouring groups because of their relatively low reactivity. This difference in behaviour is more because of kinetic than thermodynamic factors.

Within group 14, the reactivity of M-C bond in tetra-alkyl and aryl increases progressively from Si to Pb [54] as

- bond energy decreases in the same sequence
- expansion of the coordination number of the metal (M) becomes easier with increasing atomic size and decreasing difference between np and nd orbitals.



The electronegativity of tin change with its oxidation number. Tin(II) compounds are generally more ionic than tin(IV) compounds [55].

The general characteristic pertaining to increase in electropositive character with increase in atomic number in a group is also strikingly pronounced among the metals of group 14. Therefore, the Sn-C bond should be polar since tin is electropositive with

respect to carbon and is represented by $C^{\delta-}-Sn^{\delta+}$. The polarization of $C^{\delta-}-Sn^{\delta+}$ bond makes tin atom more electrophilic and carbon atom attached to tin more nucleophilic. This enhances the reactivity of organotin moieties both towards electrophiles as well as nucleophiles. Reaction of alkyltin chlorides with the appropriate nucleophiles gives the alkyltin alkoxides, amides, thioalkoxides, carboxylates etc. The presence of these electronegative groups on tin renders the metal susceptible to coordination by Lewis bases and simple tetrahedral four-coordination is an exception rather than the rule in such cases [56].

Organotin compounds can undergo Grignard type reactions particularly with carbonyl containing substrates. For instance, allyltin compounds will add across the C=O bond of aldehydes in a manner analogous to that of Grignard reagent [57].



Due to low polarity of C-Sn bond, as in tetraalkyl and aryl derivatives of tin, these are not actually hydrolyzed by water. Hydrolysis however, may be brought about by increasing pressure and temperature and using catalysts such as acid or alkalis which attack 'C' or 'Sn' [58]. A rather unusual feature of the organotin compounds is the ionization of some of the R_3SnX and R_2SnX_2 compounds in water [59]. The extremely ready hydrolysis of a fluorocarbon-tin bond in perfluorophenyl trimethyltin has been partly ascribed to the increased susceptibility of tin to nucleophilic attack [60]. The hydrolysis is catalyzed by halide ion.

There is substantial evidence that the d orbitals of the elements of group 14, other than carbon are used in $d\pi-p\pi$ bonding [59]. A simple example illustrates this phenomenon. With the four acids of the type $p-R_3MC_6H_4COOH$, where M=C, Si, Ge or Sn, C is the most electronegative and should enhance the acid strength to the greatest extent. But, it is found that M=C compound shows the lowest acid strength, indicating that $d\pi-p\pi$ bonding is operative in the other three metal compounds [61, 62]. The tendency to use 'd' orbitals in bonding decreases from Si to Sn, since in $(GeH_3)_2S$ and $(GeH_3)_2O$, the Ge-S-Ge and Ge-O-Ge appear to be highly bent [63] whereas in $(SiH_3)_2O$, the Si-O-Si bond angle is around 150° [64]. However, the possibility of $d\pi-p\pi$ bonding in Sn cannot be completely ignored, atleast with elements of higher atomic numbers,

e.g. Cl, Br, I, etc. This is supported by the higher values of Sn-Cl stretching frequencies in certain tin compounds [65] and Sn-O frequency in $(\text{Ph}_3\text{Sn})_2\text{O}$ [66].

Reactions of the general type:



are of utmost significance in both theoretical and practical studies in organotin chemistry. Although the reactivity of tin-carbon bonds depends on molecular environment, they are susceptible to attack by a wide variety of reagents so that A-B in the above equation may be a halogen, mineral acid, carboxylic acid, thiol, phenol, alcohol, metallic or non-metallic halide, alkali & alkali metal etc. Tin-carbon bond cleavage not only involves electrophilic attack at 'C' but also nucleophilic assistance at the Sn atom [21].

Among organometallic main group compounds, organotin compounds are quite unique in possessing reasonably labile tin-carbon bonds. While compounds containing Sn-allyl bonds are the most labile, those containing Sn-benzyl and Sn-phenyl substituents are sufficiently reactive. The Sn-alkyl bond cleavage is the most difficult to accomplish and occurs under relatively harsh conditions. Even among Sn-alkyl compounds those containing Sn-methyl cleavage are the most documented. In contrast, those involving Sn-butyl cleavage are very few. The current state of knowledge of these Sn-C cleavage reactions allow these compounds to be utilized extensively as synthons. In view of this, it is expected that in addition to organotin halides, oxides and hydroxide compounds containing Sn-alkyl, Sn-benzyl, Sn-phenyl or Sn-allyl bonds will also be very useful as reactants in synthetic procedures for the construction of rings, cages and clusters [36].

1.5 Structure of organotin compounds

Tin(II) compounds are mostly bent, pyramidal or distorted (due to the presence of a stereochemically active lone pair of electrons which does not participate in bonding and occupies a position directed away from the strongly bonded coordination sites). The structural chemistry of tin(IV) compounds reflects the relative simplicity of the electronic configuration in this oxidation state and is dominated by regular bond

arrangements : tetrahedral, trigonal bipyramidal and octahedral depending on the coordination number. Tin(IV) is remarkable in its capacity to expand its coordination number from four (which is found in most simple organotin compounds like the simple tetraalkyls and tetraaryls) to five, six or seven [67-69].

In organotin derivatives of the type R_nSnX_{4-n} ($n = 1$ to 3), where X is an electronegative group (e.g. halide or carboxylate etc.), the Lewis acid strength of tin is increased and subsequently the Lewis bases form complexes with higher coordination number. The compounds R_3SnX usually yield 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 groups X, however, by virtue of the unshared electron pairs which they carry, can themselves act as Lewis bases resulting in intermolecular self-association to give dimers, oligomers, or polymers [70]. Nature of the ligands and the steric demands of R, X and L are the factors influencing the self-association [71].

If R or X carries a functional substituent Y beyond the α -position, intramolecular coordination can occur leading to the formation of monomers with 5-, 6-, 7-, or 8- coordinated tin [70]. In fact, even, coordination number 7 which was once regarded an oddity no longer remains to be so given the appropriate type of ligand to interact with the metal; double-armed bis(semicarbazone) and bis(thiosemicarbazone) ligands derived from pyridine belong to this class [72, 73].

1.6 Applications of organotin compound

1.6.1 Non-biological applications

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 [74-76]. Another important use of organotin compounds is in the stabilization of PVC [77]. Many organotin compounds are used as homogeneous catalysts in industry [78, 79]. Also, several organostannosiloxanes have been shown to be extremely versatile catalysts for transesterification reactions [80, 81]

1.6.2 Biological applications

Organotin compounds have found a variety of applications in agriculture and medicine. The first organotin compounds to reach commercialization in agriculture (in the early 1960s) were triphenyltin acetate (Brestan*, Hoechst A.G.) and triphenyltin hydroxide (Duter*, Philips Duphar, N.V.) both of which are used widely [82]. Aquatic organisms such as algae, crustaceans, fish and mollusks are sensitive to tri-n-butyltin, triphenyl and tricyclohexyltin compounds leading to the incorporation of these triorganotin units in anti-fouling paints for marine transport vessels [77]. Organotin compounds are also used extensively as preservatives of wood [83] and as agricultural fungicides and insecticides, and in medicine they are showing promise in cancer therapy and in the treatment of fungal infections [84].

To summarize, the basic studies in the field of organotin compounds have been developed due to the success of a large number of modern analytical techniques applied to organotin compounds. Investigations can be performed by general techniques such as UV [21], IR [21, 56], $^1\text{H-NMR}$ [85], $^{13}\text{C-NMR}$ [86], mass spectrometry [87] and also by specialized techniques such as ^{119}Sn Mössbauer spectroscopy [21,25] and $^{119}\text{Sn-NMR}$ spectroscopy [88]. ^{119}Sn Mössbauer and $^{119}\text{Sn-NMR}$ Spectroscopy provide complementary information on the structure of the organotin molecules in the solid state and in solution, respectively.

References

1. Encyclopedia Britannica, 15th Ed., Vol.18, 1974, pp.426.
2. L. Pellerito, L. Nagy, *Coord. Chem. Rev.* **224** (2002) 111.
3. E. Frankland, *J. Chem. Soc.* **2** (1849) 263.
4. E. Frankland, *Phil. Trans.* **142** (1852) 417.
5. E. Frankland, *Liebigs Ann. Chem.* **85** (1853) 329.
6. E. Frankland, *J. Chem. Soc.* **6** (1854) 57.
7. C. Löwig, *Liebigs Ann. Chem.* **84** (1852) 308.
8. G.B. Buckton, *Phil. Trans.* **149** (1859) 417.
9. E.A. Letts, J.N. Collie, *Phil. Mag.* **22** (1886) 41.
10. E. Frankland, A. Lawrance, *Trans. Chem. Soc.* (1879) 130.
11. W.J. Pope, S.J. Peachey, *Proc. Chem. Soc.* **19** (1903) 290.
12. E. Krause, A.von Grosse, *Die Chemie der Metal-Organischen Verbindungen*, Borntraeger, Berlin, 1937.
13. H.G. Kuivila, L.W. Menapace, C.R. Warner, *J. Am. Chem. Soc.* **84** (1962) 3584.
14. W.P. Neumann, R. Sommer, *Liebigs Ann. Chem.* **675** (1964) 10.
15. H.G. Kuivila, *Adv. Organomet. Chem.* **1** (1964) 47.
16. *Gmelin Handbuch der Anorganischen Chemie*, Tin, Part 4: Organotin Hydrides, Springer-Verlag, Berlin, 1976.
17. M. Pereyre, J.-C. Pommier, *J. Organomet. Chem. Library*, **1** (1976) 161.
18. R.K. Ingham, S.D. Rosenberg, H. Gilman, *Chem. Rev.* **60** (1960) 459.
19. R.W. Weiss (Ed.), *Organometallic compounds*, 2nd Ed., Vol.2, Springer-Verlag, New York, 1967, pp.158.
20. J.J. Zuckerman (Ed.), *Organotin Compounds: New Chemistry and Applications*, ACS, Washington, D.C. (1976).
21. R.C. Poller, *The Chemistry of Organotin Compounds*, Logos Press, London, 1970.
22. W.P. Neumann, *The Organic Chemistry of Tin*, Wiley, London, 1970.
23. A.K. Sawyer (Ed.), *Organotin Compounds*, Vols.1&2; Vol.3, Marcel Dekker Inc., New York, 1971; 1972.
24. A.G. Davies, P.J. Smith, *Adv. Inorg. Chem. Radio Chem.* **23** (1980) 1.

25. A.G. Davies, P. J. Smith, 'Tin', in: *Comprehensive Organometallic Chemistry*, G. Wilkinson (Ed.), Vol. 2, Pergamon Press, Oxford, 1982, pp. 519.
26. G. Yushen, *Huaxue Shiji* **13** (1991) 43.
27. M. Gielen, N. Sprecher, *Organometallic Chem. Rev.* **1** (1966) 455.
28. R. Okawara, M. Wada, *Advances in Organometallic Chemistry*, Vol. 5, Academic Press, New York and London, 1967, pp. 137.
29. J.A. Zubieta, J.J. Zuckerman, *Prog. Inorg. Chem.* **24** (1978) 251.
30. P.A. Cusack, P.J. Smith, J.D. Donaldson, S.M. Grimes, *A Bibliography of X-ray Crystal Structures Of Tin Compounds*, International Tin Research Institute, London, 1981 (Publication 588).
31. R.R. Holmes, *Acc. Chem. Res.* **22** (1989) 190.
32. M. Nath, S. Pokharia, R. Yadav, *Coord. Chem. Rev.* **215** (2001) 99.
33. V.K. Jain, *Coord. Chem. Rev.* **135/136** (1994) 809.
34. J. Beckman, K. Jurkschat, *Coord. Chem. Rev.* **215** (2001) 267.
35. V. Chandrasekhar, S. Nagendran, V. Baskar, *Coord. Chem. Rev.* **235** (2002) 1.
36. V. Chandrasekhar, K. Gopal, P. Sasikumar, R. Thirumoortii, *Coord. Chem. Rev.* **249** (2005) 1745.
37. G.J.M. van der Kerk, J.G.A. Luijten, *J. Appl. Chem.* **4** (1954) 314.
38. G.J.M. van der Kerk, J.G.A. Luijten, *J. Appl. Chem.* **6** (1956) 56.
39. G.J.M. van der Kerk, J.G.A. Luijten, *J. Appl. Chem.* **11** (1961) 35.
40. J.G. Noltes, J.G.A. Luijten, G.J.M. van der Kerk, *J. Appl. Chem.* **11** (1961) 38.
41. K.C. Molloy, *Bioorganotin Compounds*, in: F.R. Hartley (Ed.), *The Chemistry of Metal-Carbon Bond*, Vol.5, John Wiley and Sons, London, 1989, 465.
42. J.M. Tsangaris, D.R. Williams, *Appl. Organomet. Chem.* **6** (1992) 3.
43. A.J. Crowe, *Appl. Organomet. Chem.* **1** (1987) 143.
44. A.J. Crowe, *Appl. Organomet. Chem.* **1** (1987) 331.
45. S.J. Blunden, P.A. Cusack, R. Hill, *The Industrial Use of Tin Compounds*, Royal Society of Chemistry, London, 1985.
46. A.J. Crowe, R. Hill, P.J. Smith, *Laboratory Evaluation of Tributyltin(IV) Compounds as Wood-Preservatives*, Publication 559, International Tin Research Institute, London, 1979.
47. A. Atsushi, K. Hisada, I. Anda, *Radioisotopes* **22** (1973) 7.
48. M. Yamaguchi, K. Sugii, S. Okada, *J. Toxicol. Sci. Jpn.* **5** (1981) 238.

49. A.K. Saxena, F. Huber, *Coord. Chem. Rev.* **95** (1989) 109.
50. M. Gielen, *Coord. Chem. Rev.* **151** (1996) 41.
51. S. Tabassum, C. Pettinari, *J. Organomet. Chem.* **691** (2006) 1761.
52. C.E. Moore, Atomic energy levels, Circular 467 of the National Bureau of Standards, Vol.1, Government Printing Office, Washington, D.C. (1949).
53. M.J.S. Gynane, M.F. Lappert, S.J. Miles, P.P. Power, *J. Chem. Soc., Chem. Commun.* (1976) 256.
54. R.C. Mehrotra, A. Singh, *Organometallic Chemistry-A unified Approach*, 2nd Ed., New Age International (P) Ltd. Publishers, New Delhi, 2000.
55. M. Veith, O. Recktenwald, M. Gielen, Z.M.C. Rzaev, *Topics in Current Chemistry, Organotin compound*, Springer-Verlag, Berlin, Heidelberg, New York 1982, pp.104.
56. T. Tanaka, *Organomet. Chem. Rev. (A)* **5** (1970) 1.
57. K. Koenig, W.P. Neumann, *Tetrahedron letters*, 1967, 495.
58. A.Roy, Ph.D.Thesis, University of North Bengal, 1978.
59. F.A. Cotton, G. Wilkinson, *Advanced Inorganic Chemistry*, 2nd Ed., Inter Science Publishers, New York, 1967.
60. R.D. Chambers, T. Chivers, *Organometallic Chem. Rev.* **1** (1966) 279.
61. J. Chatt, A.A. Williams, *J.Chem. Soc.*(1954) 4403.
62. F.G.A. Stone, D. Seyferth, *Inorg. and Nuclear Chem.* **1** (1955) 112.
63. T.D. Goldfrab, S. Sujishi, *J. Am. Chem. Soc.* **86** (1964) 1679.
64. R. Verma, A.G. Mac Diarmid, J.G. Miller, *Inorg. Chem.* **3** (1964)1754.
65. W. H. Nelson, D.F. Martin, *J. Inorg. Nucl. Chem.* **27** (1965) 89.
66. R. C. Poller, *J. Inorg. Nucl. Chem.* **24** (1962) 593.
67. G.F. DeSousa, C.A.L. Filgueiras, A. Abras, S.S. Al-Juaid, P.B. Hitchcock, J.F. Nixon, *Inorg. Chim. Acta.* **218** (1994) 139.
68. P.C. Moreno, R.H.P. Francisco, M.T. do P. Gamberdella, G.F. de Sousa, A. Abras, *Acta Cryst. C* **53** (1997) 1411.
69. G. F. De Sousa, C.A.L. Filgueiras, M.Y. Darensbourg, J.H. Reibenspies, *Inorg. Chem.* **31** (1992) 3044.
70. A.G. Davies, *Organotin Chemistry*, Wiley-VCH, Verlag, GmbH & Co., KGaA, Weinheim, 2003.
71. N.W.Alcock, R.E.Timms, *J.Chem. Soc. (A)* 1968, 1873.

72. C. Carini, G. Pelizzi, P. Tarasconi, C. Pelizzi, K.C. Molloy, P.C. Waterfield, J. Chem. Soc. Dalton Trans. **2** (1989) 289.
73. J.S. Casas, A. Castineiras, A. Sanchez, J. Sordo, A. Vazquez-Lopez, M.C. Rodríguez-Arguelles, U. Russo, Inorg. Chim. Acta **61** (1994) 221.
74. M. Pereyre, J.P. Quintard, A. Rahm, Tin in Organic Synthesis, Butterworth, London, 1987.
75. A. Orita, A. Mitsutome, J. Otera, J. Org. Chem. **63** (1998) 2420.
76. Y. Hori, T. Hagiwara, Int. J. Biol. Macromol. **25** (1999) 237.
77. C.J. Evans, in: P.J. Smith (Ed.) Chemistry of Tin, Blackie Academic and Professional, London, 1998, pp. 442.
78. C.S. Parulekar, V.K. Jain, T.K. Das, A.R. Gupta, B.F. Hoskins, E.R.T. Tiekink, J. Organomet. Chem. **372** (1989) 193.
79. T.P. Lockhart, J.C. Calabrese, F. Davidson, Organometallics **6** (1987) 2479.
80. S. Durand, K. Sakamoto, T. Fukuyama, A. Orita, J. Otera, A. Duthie, D. Dakternieks, M. Schulte, K. Jurkschat, Organometallics **19** (2000) 3220.
81. A. Orita, Y. Hamada, T. Nakano, S. Toyoshima, J. Otera, Chem. Eur. J. **7** (2001) 3321.
82. B. Sugavanam, Tin its Uses, **4** (1980) 126.
83. B. Jousseume, V. Guillou, N. Noiret, M. Pereyre, J.M. Frances, J. Organomet. Chem. **450** (1993) 97.
84. C.J. Evans, S. Karpel, Organotin Compounds in Modern Technology, Elsevier, Amsterdam, 1985.
85. M.L. Maddox, S.L. Stafford, H.D. Koesz, Applications of Nuclear Magnetic Resonance to the Study of Organometallic Compounds, in Advances in Organometallic Chemistry, F.G.A. Stone and R. West (Ed.), Vol. 3, Academic Press, London and New York, 1965, pp.1.
86. O.A. Gansow, W.D. Vernon, in: G. C. Levy (Ed.), Topics in Carbon-13 NMR Spectroscopy, Vol. 2, 1970, pp. 270.
87. Y. Limouzin, J.C. Maire, Adv. Chem. Ser. **157** (1976) 227.
88. B. Wrackmeyer, ¹¹⁹Sn NMR Parameters, in: Annu. Rep. NMR Spectrosc., G.A. Webb (Ed.), Vol. 18, Academic Press, London, 1985, pp. 73.