

CHAPTER 1

CHAPTER 1

A SHORT REVIEW OF ORGANOTIN COMPOUNDS

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§ 11. INTRODUCTION :

Any compound containing atleast one tin-carbon σ - linkage may be called organotin compound, the first reported compound of this type being contributed by E. Frankland.¹ Generally the begining of organotin chemistry is considered to start with the work of C. Löwig.² In the next few decades many significant contributions were made in the field, especially in determining the accurate atomic weights of the group IV metals. This area of chemistry is further emboldened with the industrial applications^{3,56,70} of organotin compounds e.g. as stabiliser of polyvinyl chlorides, plastics, as rubber anti-oxidants, Ziegler type catalysts in the polymerisation of olefins, agricultural fungicides, active ingredients in certain veterenary medicines. Trans-esterification reaction mixture containing organotin compounds as catalysts have recently been used in the removal of insoluble organotin compounds.⁶⁴ The same enthusiasm and interest is prevailing still, which started with the renaissance of organotin chemistry starting at about 1949.

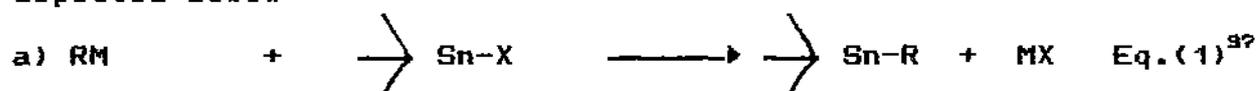
§ 12. PREPARATION OF ORGANOTIN COMPOUNDS — GENERAL PRINCIPLES:

Most of the organotin compounds are the derivatives of tin(IV) and therefore the relevant literatures of tin(IV) compounds are discussed here in a short review form.

R_nSnCl_{4-n} , alkyltin chlorides are prepared by Kocheskov⁶⁶ comproportionation reaction between tetra-alkyl tin and tin tetrachloride mixed in their appropriate proportions at about 200°C. The alkylation of tin tetrachloride with an organometallic reagent results in the formation of it.

A number of benzyltin(IV) compounds $(\text{PhCH}_2)_{4-n}\text{SnMe}_n$ ($n=0-3$), $(\text{PhCH}_2)_{4-n}\text{SnCl}_n$ ($n=0-2$) and complexes $(\text{PhCH}_2)_3\text{SnCl}\cdot\text{DMSO-d}_6$ and $(\text{PhCH}_2)_2\text{SnCl}_2\cdot\text{DMSO-d}_6$ were studied by Holleck *et.al.*⁷⁰

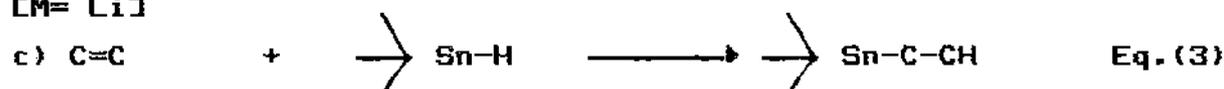
Alkyltin alkoxides, thioalkoxides, carboxylates, thioaryloxy acetates *etc.* are formed from the reaction of alkyltin chlorides with appropriate nucleophiles. The formation and reaction of carbon-tin bond and the tetra-organotin compounds are elaborately reviewed by Van der Kerk and Luijten⁴ in 1968 and then by M. Gielen⁵ in 1981. The three principal ways are schematically depicted below:



(Organometallic) (Tin halide)
[M= Mg, Li, Al, Na, K or Zn]

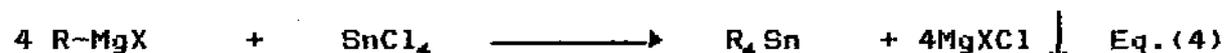


(alkyl halide) (Tin-metal compound)
[M= Li]



(Alkene) (Tin Hydride)

The alkylation of tin tetrachloride with a Grignard reagent is of greater industrial use, though there is a difficulty to stop the reaction at the desired partial stage of substitution. Often the presence of excess amount of Grignard reagent being necessary, when particularly the di-ethyl-ether is used as the solvent. Complete alkylation occurs with THF as solvent if the reaction is carried out at 80°C. The yield of R_4Sn decreases gradually with the increase in the bulkyness of the R- group.



Mixed tetra-alkyltin compounds can similarly be prepared by the reaction between a Grignard reagent and the alkyltin halide. Similarly aryl, vinyl and ethenyl tin compounds can also be prepared. ⁶ Synthesis and mass spectra of tetra n-butenyltin and tri n-butenyltin bromides with both double bonds between C1, C2 and C2, C3 was discussed recently in detail by C. A. Dooley, and J. P. Testa. ⁶⁵

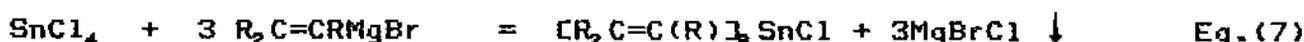
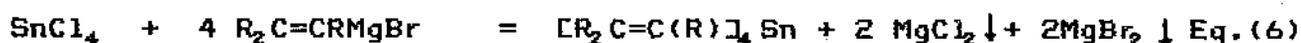
Alkylation of tin halides with organolithium compounds gives a higher yield of the product and the method is especially applicable in the cases of unavailability of the Grignard reagent, ^{4,9} as "alkenyl halides containing a halogen atom adjacent to an ethelnyic bond are very unreactive towards magnesium and give the organo-magnesium derivatives only with greater difficulty, sole known exception being 2-aryl-vinyl bromides e.g. β -bromo-styrene". ^{64,65}

The Wurtz reaction is not readily and widely applied due to its disadvantage with the formation of R-R hydrocarbon when intermediate alkyl-sodium compound react in situ with tin chloride.



Alkylvinyl tins, $R_nSn(CH=CH_2)_{4-n}$, can be synthesised from the corresponding vinyl or substituted ethenyl magnesium bromide with tin tetrachloride in THF. ^{10,11}

The alkenyltin chlorides were prepared by the reaction of anhydrous stannic chloride and Grignard reagent with alkenyl bromide in a required stoichiometric proportions e.g.



The route of syntheses of a number of alkenyltin(IV) dithiocarboxylic acids may be the same as in the case of synthesis of simple dithiocarboxylic acids, using Grignard method except the fact that here R-Br contains R= an alkenyl group. These alkenyltin(IV) chlorides will expectedly give the respective ester on reaction with alkenyl dithiocarboxylic acids of the type RCS_2R' where $R = R' =$ same or different alkenyl group(s).

The preparation and characterisation of some σ -bonded α -unsaturated organic derivatives of tin R_4^1Sn , $R_3^2Sn_2$, R_3^3SnCl , $R_2^4SnMe_2$, R^5SnMe_3 and R^6SnMe_3 [$R^1 = -CPh=CM_2$, $R^2 = -CM_2$ and $R^3 = -CPh=CPh_2$] were reported by Cardin *et.al.*. The interest in syntheses of these arise from the point of view of structural and bonding study as well as from chemical reactivity. The X-ray study of homoleptic alkenyl of tin was also done by the same group of authors where the structure of $(Me_2C=CPh)_4Sn$ were established.

The direct synthesis of triorganotin compounds had been reported recently in 1987 by the reaction of the tin metal with alkyl halides in the presence of a stoichiometric amount of the halide ion in a very good yield. The mechanism of the reactions had also been discussed in detail, where tin halide anions acted as nucleophile. Similar mechanism was used to explain the formation of organomagnesium and organozinc halides.

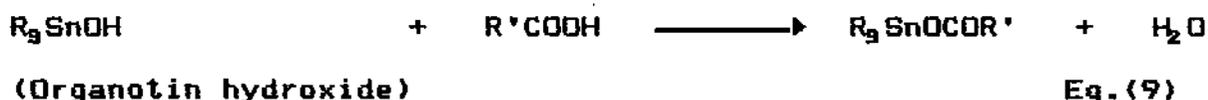
The methods for the preparation of organotin chlorides are also useful as starting material en route to the synthesis of the other organotin halides using a suitable metal halide e.g.,



(X = F, Br, I ; M = K, Na, NH_4 , etc.)

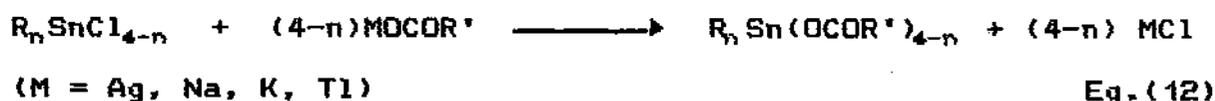
Besides, the organotin halides may be prepared by numerous methods, all of which are not so much mention-worthy and relevant to the present case, and hence not taken for discussion. In brief, organotin hydrides, organotin oxides, hydroxides, and polymeric diorganotins may also act as starting materials.

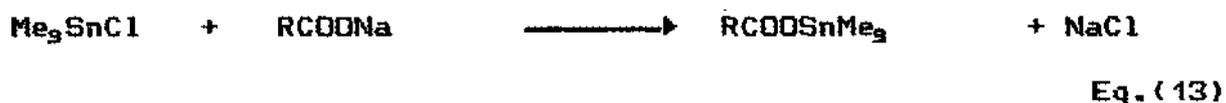
The most important method for the synthesis of organotin carboxylates, and phenoxyacetates is azeotropic dehydration of the reactants in boiling toluene using Dean-Stark separator, usually the reaction becomes complete within 1-2 hours. The thio-aryloxy acetates may also be prepared by the same way.



The triphenyltin carboxylates, Ph_3SnO_2CR ($R = Ph, p-MeO-C_6H_4$, etc.) have been prepared by the reaction of Ph_3SnOH with appropriate polyfluoro carboxylic acid in methanol.

Organotin chlorides react with alkali metal salts of carboxylic acid, thio-aryloxy carboxylic acids as shown below to give the corresponding esters.



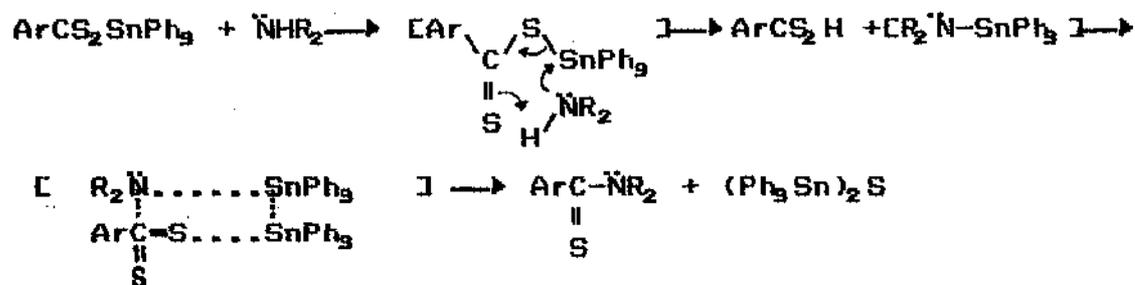


The same esters may also be prepared from tetra-organotin²⁵ and carboxylic acids.



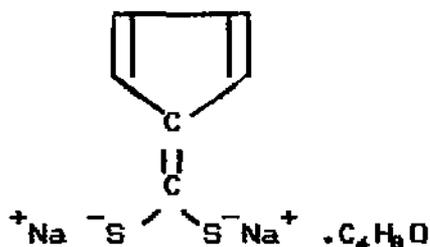
Organotin hydrides react with carboxylic acids to form the esters with the evolution of hydrogen, though this method is seldom used for synthetic purposes.^{16, 17, 26}

The dithiocarboxylic acids date back to the end of the last century. Houben *et.al.* synthesised a number of dithiocarboxylic acids. The piperidinium salts of dithiocarboxylic acids were isolated first by Kato *et.al.*²⁷ and their reactions with organotin(IV) chlorides had also been reported.^{28, 29} Preferential cleavage of Sn-S bond of the dithio ester formed was observed by treating di- and triphenyltin esters of aromatic dithio acids with primary and secondary amines²⁸, in the following way:



Kato. *et.al.* also reported the synthesis and reaction of some unsymmetrical acyl-thioacyl sulfides, $(\text{R-CS}_2\text{-COR}')$ using sodio-salt of the dithio acid RCS_2Na with $\text{R}'\text{COCl}$ or by exchange

reaction between $RC(S)_2CCOR'$ with PPh_3 , 4-Me-C₆H₄CS₂COMe with a variety of nucleophiles. A number of alkali triphenyl stannane dithiocarboxylates and synthesis of their metal carbonyl complexes were also reported. Savino and Bereman reported the synthesis of disodium salt of cyclopentadiene dithiocarboxylic acid from the



reaction between sodium cyclopentadienide and CS₂, the salt being formed in 1:1 complex with recrystallising solvent viz. THF or acetonitrile as bright yellow crystals.

§ 13. BONDING IN ORGANOTIN COMPOUNDS:

Being a member of the group IVA in the periodic table, the fifty electrons of tin atom are arranged in the following way: $1s^2 / 2s^2 2p^6 / 3s^2 3p^6 3d^{10} / 4s^2 4p^6 4d^{10} / 5s^2 5p^2$, the ground state of which is ³P state derived from $s^2 p^2$ configuration. The common tetravalent state is derived from the sp^3 hybridisation by promoting one of the paired 's' electrons to the next higher 'p' level. The tetravalent character occurs most frequently than the divalent one. The stable nature and relative low reactivity of the organotin derivatives of group IV metals may be attributed to the sp^3 hybridisation. Thus, Me₄Sn is unreactive towards air and water but trimethyl indium and trimethyl antimony have a strong affinity towards these reagents. The marked increase in stabilities of R₄Sn compounds over the R₂Sn types are also demonstrative of the effects of increased hybridisation.

Catenation property of tin in organic compounds are also reported by some excellent reviews on tin-tin compounds made in the recent past years. Comparisons of the catenation properties among group IV elements have shown that there is a decrease in the tendencies in catenation in the order: C » Si > Ge ≈ Sn » Pb. This, in general, if not smooth, decreases with the tendency of the catenation properties and may be ascribed to the diminished strength of C-C, Si-Si, Ge-Ge, Sn-Sn, and Pb-Pb bonds, which are approximately 83, 42, 40, 37 K.cal/ mole respectively.

The ionic nature of organotin compounds and the effect of bond polarity upon their reaction are discussed in the following section. The electropositive character increases with atomic number in a group, and is also strikingly pronounced among the metals of group IV. Some properties of the elements are given in table 1 below:

Table 1

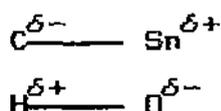
Element	Electronic Structure	I.P. (e.v.)		Electronegativity	Covalent radii (Å)
		1st	2nd		
C	[He]2s ² 2p ²	11.3	24.4	2.50 *	0.77 **
Si	[Ne]3s ² 3p ²	8.1	16.3	1.74	1.17
Ge	[Ar]3d ¹⁰ 4s ² 4p ²	7.9	15.9	2.02	1.22
Sn	[Kr]4d ¹⁰ 5s ² 5p ²	7.3	14.6	1.72	1.40
Pb	[Xe]4f ¹⁴ 5d ¹⁰ 6s ² 6p ²	7.4	15.0	1.55	1.54

* According to Alfred Rochow ** Tetrahedral i.e. sp³ radii

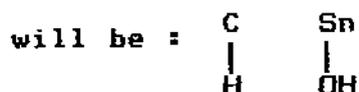
So from table 1, it is evident that due to considerable difference in electronegativities between carbon and other elements of group IV A, the metal carbon bond should be expected to be quite polar. In fact Pauling has calculated the ionic character of C-Si, C-Sn, bonds to be 12% and 15% respectively, which becomes almost

identical to the Alfred Rochow's electronegativity values of 14.2% and 14.6% . As the electronegativity of carbon varies with nature and number of attached groups and atoms, the ionic character of tin carbon bond will also vary.

The physical as well as chemical properties of the compounds depend on the bond polarity. In general the bond partners that carry an appreciable difference of electrical charge relative to each other will serve as an electric dipole that attracts and orients neighbouring reagents. Since tin is positive with respect to carbon, the relative polarity of the tin-carbon bond may formally be represented as $C^{\delta-} - Sn^{\delta+}$. Hence, when an organotin compound is exposed to water, the OH dipole as expected, would be attracted to C-Sn dipole and would orient in the appropriate direction as depicted below:



The approach of dipoles will continue, with corresponding loss in potential energy, until the repulsion of the electron shells is balanced by the attraction. In these circumstances, the formed active intermediate may either break apart into original components or realign these bonds to form new substances. If this change in free energy favours the later possibility, the product



But due to the low polarity of the tin carbon bonds in the tetra alkyl and aryl derivatives of tin, they are not actually hydrolysed by water, which may be brought about in high pressure

and temperature with the use of catalysts such as acids and alkalis, which attacks the carbon or tin. A rather unusual feature of the organotin compounds is the ionisation of some of the R_3SnX and R_2SnX_2 compounds in water. The strength of the single covalent bonds between group IVA and other atoms generally decrease in going down the group, as can be seen from the table 2 below :

Table 2

Elements ^a	Energy of bonds, K cal/mole with						
	H	C	F	Cl	Br	I	O
C	99	83	116	79	66	67	82
Si	70	69	129	86	69	51	88
Ge	74	71	—	85	68	50	—
Sn	71	68	—	82	65	47	—

^a data derived mainly from MX_4 type compounds which are unstable and non-existent when $M = Pb$

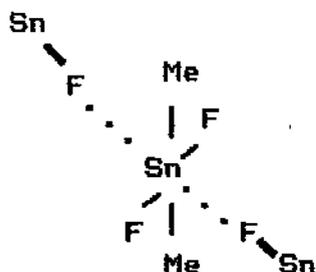
The polarity of the metal carbon bond increases with increasing atomic number within the group and the bond becomes more sensitive to attack by polar reagents. This is also evident from the increase in the polar character of the halogens in compounds such as R_3MX .

§ 14. STRUCTURE OF ORGANOTIN COMPOUNDS - GENERAL FEATURES:

The tetra organotin compounds are usually colourless thermally stable liquids or solids, though degradable to inorganic tin compounds. Numerous X-ray and electron diffraction studies have established tetrahedral structure for them.

The common organotin halides and pseudo-halides are generally soluble in water and most of the organic solvents. In any series of halides R_nSnX_{4-n} (for a given value of X and n), the melting points generally decrease as n-alkyl chain length increases. Their structure was established to be close to tetrahedral in gaseous phase. The most important structural feature of solid organotin halides and pseudo halides are their strong tendency to increase the co-ordination number from 4 to 5 for R_3SnX compounds or 6 for R_2SnX_2 and $RSnX_3$ compounds by intermolecular association. Ph_3SnCl contains discrete monomeric species with four co-ordinated tin. X-ray study of Me_3SnCl shows a halogen bridged structure though tin-chlorine (Sn-Cl) link is rather weak and break on dissolution in organic solvents while tricyclohexyl tin assumes an intermediate structure between tetrahedral monomer and non-linear asymmetric structure, with Sn—X.....Sn bridges. With potentially bidentate ligands, the triorganotin halides still prefer to form penta-coordinated adducts using one of the donor groups and R_3SnCl with octahedral configuration is unknown.

The diorganotin halides have a tendency to form polymeric species through intermolecular association and tin atom prefers to increase the coordination number to 6, due to greater Lewis acidity, e.g. in Me_2SnF_2 each tin is linearly bridged to its four neighbours by one symmetrically disposed fluorine atoms as shown below, the alkyl groups being above and below the planes, making infinite two dimensional sheet of tin and halogen atom.

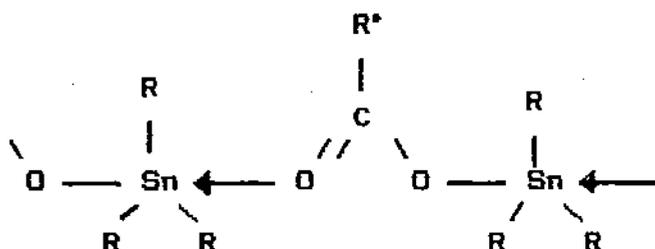


But in Me_2SnCl_2 , Me_2SnBr_2 the association is weaker and consists of chains of molecules. Ph_2SnCl_2 has distorted tetrahedral molecular species in solid state, and any intermolecular association is weak or absent.⁴⁶

RSnX_3 compounds have both bridging and terminal halogen with polymeric structures containing octahedral tin atoms in the solid phase.⁴⁷

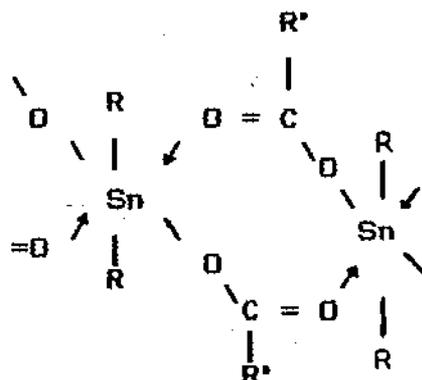
In case of di- and triphenyl stannyl dithio esters (ArCS_2)₂ SnPh_2 , $\text{ArCS}_2\text{SnPh}_3$, the tin atom in di/triorganotin(IV) groups $\text{R}_3\text{Sn-}/\text{R}_2\text{Sn-}$ are co-ordinated by the unidentate carboxylic group.

In the case of organotin carboxylates, the melting points and boiling points are generally variable and have a very low solubility in organic solvents due to the polymeric nature of it in neat or solid state, involving bridging carboxylate groups, as shown below:⁴⁸⁻⁵⁰



and an octahedral trans- R_2SnX_4 , supported by Mössbauer and IR data,^{50,52} though in solution they break to monomeric unit.^{48,52}

Recent X-ray study of a dialkyl chlorotin carboxylate ⁵⁴
 $R_2Sn(OCOR')Cl$ with $R = R' = Me$, confirmed the following structure.



The crystal structure study by X-ray diffraction method of a number of organotin(IV) carboxylates have recently been studied, which have thrown light on the central question in the structural chemistry of triorganotin carboxylates whether the carboxylate group will chelate to form monomers of five coordinate tin or bridge through its carbonyl oxygen to result in five coordinate repeat of $R_3SnDCOR'$ units or instead, will be made up of monomers with four coordinate tin. ⁷²⁻⁷⁸

Multiple bonds involving px orbitals are not known with Si, Ge, Sn or Pb in contrast to carbon. However, there is good evidence that d -orbitals of the elements, other than carbon, are used in $dx-px$ bonding. In fact, $dx-px$ bonding is partly responsible for the higher values of Sn-Cl stretching frequencies in certain tin compounds and Sn-O frequencies in $(Ph_3Sn)_2O$. The study of proton chemical shift and of the spin-spin coupling constants provide informations concerning their structure, degree of 's' character of the 'M' orbital directed towards the carbon atom. The percentage 's' character of the Sn orbital in the tin-carbon bond in Me_2SnX_2 compounds [where $X = PhCS_2, PhC(O)S, BrC_6H_4CS_2, PhCH_2CS_2$] were derived as 0.36. The change in the

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electronic distribution due to different inductive effects in substituted benzene rings, make the o^- , m^- , p^- protons of the phenyl ring different.

There is a linear relationship between long range tin proton coupling constants and the percentage 's' character of the tin metal directed towards carbon. Replacements of the two methyl groups with X leads to an increase of % s character in the tin-carbon bond and in the decrease of the same in the tin-sulfur bond, obviously due to hybridisation change in Sn-C bond.

The examination of ^1H NMR have shown that aromatic protons of the thiocarboxylate ligand are not influenced by alkyl or aryl groups bound to tin, as these groups are separated by at least five ⁶⁰ bonds. In dithio phenyl acetic acid derivatives, aromatic protons are not influenced by the groups directly bonded to tin atom. In all the compounds investigated long range strong tin-proton ⁶⁰ interactions of Fermi contact type are observed. The replacement of two methyl groups in the compound Me_2Sn with two X groups increases the 's' character of Sn-C bond orbital from 0.25 - 0.36 % .

However, from IR and Raman studies of compounds R_3SnXR_3 (X= O, S) it was concluded that there was no π contribution to the Sn-O and Sn-S ⁶⁰ bonds. Similar ideas regarding Sn-O and Sn-S bonds ^{61-69, 71} in the other compounds were reached by other workers.

§ 15 REFERENCES:

1. E. Frankland, *J. Chem. Soc.*, 1850, 2, 267 and Liebigs *Ann. Chem.*, 1849, 71, 171 and 212.
2. C. Löwig, *Liebigs Ann. Chem.*, 1852, 84, 308.
3. R. K. Ingham, S. D. Rosenberg and H. Gilman, *Chem. Rev.*, 1960, 60, 459.
4. G. J. M. Van der Kerk and J. G. A. Luijten, 'Organometallic compounds of Gr. IV elements', Dekker, New York 1968, vol.1, part II, P 91.
5. M. Gielen, *Rev. Silicon, Germanium, Tin, Lead compound*, 1981, 5, 5.
6. G. J. M. Van der Kerk and J. G. Noltes and J. G. A. Luijten, *J. Appl. Chem.*, 1957, 7, 356.
7. A. Bokranz and H. Plum, *Fortschr. Chem. Forsch.*, 1971, 16, 365.
8. L. Killan and B. Wrackmeyer, *J. Organomet. Chem.* 1977, 132 213.
9. E. A. Braude and J. E. Coles, *J. Chem. Soc.*, 1951, 2078.
10. F. Glockling, M. A. Lyle, S. R. Stobart *J. Chem. Soc.*, *Dalton Trans.*, 1974, 2537.
11. J. A. Sonderquist and A. Hassner, *J. Amer. Chem. Soc.*, 1980, 102, 1577.
12. H. G. Kuivila, *Synthesis*, 1970, 499.
13. H. C. Clark and P. J. Puddephatt, in 'Organometallic compounds of Gr. IV elements : The bond to Halogens and Halogenoids' ed. A. G. McDiarmid, Dekker, New York 1972, 2(CII), 71.
14. P. Dunn and D. Oldfield, *J. Organomet. Chem.*, 1970, 23, 459.

15. K. C. Pande, *J. Organomet. Chem.*, 1968, 13, 187.
16. A. K. Sawyer, H. G. Kuivila, *J. Org. Chem.*, 1962, 27, 610.
17. S. Weber and E. I. Becker, *J. Org. Chem.*, 1962, 27, 1258.
18. French Patent, *Chem. Abstr.*, 1965, 62, 16296a
19. P. Dunn and T. Norris, Report no. 269, Australian Defence Scientific Service, Defence Standards Laboratories, 1964.
20. B. F. E. Ford and J. R. Sams, *J. Organomet. Chem.*, 1970, 31, 47.
21. M. Frankel, D. Gertner, D. Wagner and A. Zilkha, *J. Organomet. Chem.*, 1967, 9, 83.
22. B. F. E. Ford, B. V. Liengme and J. R. Sams, *J. Organomet. Chem.*, 1969, 19, 53.
23. T. N. Srivastava and S. K. Tandon, *J. Prakt. Chem.*, 1969, 311(5), 878.
24. C. S. C. Wang and J. M. Shreeve, *J. Organomet. Chem.*, 1972, 38, 287.
25. V. Peruzzo, G. Plazzogna and G. Tagliavini, *J. Organomet. Chem.*, 1972, 40, 121.
26. H. C. Clark, R. J. O' Brien and A. L. Pickard, *J. Organomet. Chem.*, 1965, 4, 43.
27. S. Kato., M. Mizuta., *Bull. Chem. Soc. Japan*, 1972, 45, 3492.
28. S. Kato., T. Kato., T. Yamauchi, Y. Shibahashi, I. Kakuda, M. Mizuta and Y. Ishii, *J. Organomet. Chem.*, 1974, 76, 215.
29. S. Kato., M. Mizuta., Y. Ishii., *J. Organomet. Chem.* 1973, 55, 121.
30. S. Kato, *Liebigs Ann Chem.*, 1981, 10 1798.
31. K. Udo, T. Haettich, *Chem. Ber.* 1982, 115(11), 3663.
32. P. C. Savino and R. D. Beriman, *Inorg. Chem.* 1973, 12(1), 174.

33. Atomic energy levels, circular 467, National Bureau of Standards, Govt. Printing office, Washington D. C. , 1949, vol. 1.
34. K. M. Mackay and R. Watt, Organometal. Chem. Rev. ,1969, A4 137.
35. A. G. McDiarmid, 'Organometallic compounds of Gr.IV elements' Marcel Dekker, New York, 1968.
36. A. K. Sawyer, Organotin compounds, Marcel Dekker, New York, 1972.
37. R. C. Poller, The chemistry of organotin compounds, Logos Press (1970)
38. W. P. Newman, The organic chemistry of tin, John Willey and Sons, London, New York, 1970.
39. F. A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, 1985, 3rd. ed., 8th Wiley Eastern Reprint, Interscience Publishers, New York.
40. R. V. Parish, Prog. Inorg. Chem. , 1972, 15, 101.
41. J. J. Zuckerman, Adv. Organomet. Chem. ,1970, 9 22.
42. J. A. Zubieta and J. J. Zuckerman, Prog. Inorg. Chem. , 1978, 24, 251.
43. N. G. Booki, G. N. Zakharova and Y. T. Struchkov, J. Struct. Chem. , 1970, 11, 828.
44. G. M. Bancroft, R. H. Platt, Adv. Inorg. Chem., Radiochem. , 1972, 15, 59.
45. S. Calgero, P. Ganis, V. Peruzzo, G. Tagliavini, J. Organomet. Chem. , 1979, 179, 145.
46. P. T. Greene and R. F. Bryan, J. Chem. Soc.(A) , 1971, 2549.

47. L. E. Levchuk, J. R. Sams and F. Aubke, *Inorg. Chem.*, 1972, 11, 43.
48. H. Chih and B. R. Penfold, *J. Cryst. Mol. Struct.*, 1973, 3, 285.
49. W. McFarlane and R. J. Wood, *J. Organomet. Chem.*, 1972, 40, C17.
50. R. Okawara and M. Wada, *Organotin Compounds*, ed. A. K. Sawyer, Dekker, New York, 1971, 2, 253.
51. P. B. Simons and W. A. G. Graham, *J. Organomet. Chem.*, 1967, 8, 479.
52. N. W. G. Debye, D. E. Fenton, S. E. Ulrich, and J. J. Zuckerman, *J. Organomet. Chem.*, 1971, 28, 339.
53. Y. Macda and R. Okawara, *J. Organomet. Chem.*, 1967, 10, 247.
54. D. W. Allen, I. W. Nowell, J. S. Brooks and R. W. Carlson, *J. Organomet. Chem.*, 1981, 219, 29.
55. Ng. Seik Weng, V.G. Kumar Das, M. Gielen, E. R. T. Tiekink, *Appl. Organomet. Chem.*, 1992, 6, 19.
56. G. Marcel, M. P. Jasqueline, B. Monique, W. Rudolph and E. K. Abdelaziz. *Appl. Organomet. Chem.*, 1992, 6, 59.
57. T. Sato, J. Otera, N. Hitosi, *J. Org. Chem.*, 1992, 57, 2166.
58. W. H. Nelson and D. F. Martin, *J. Inorg. Nucl. Chem.*, 1965, 27, 89
59. V. Koldea, M. Koldea, I. Haidue, *Rev. Roum. Chem.*, 1981, 26, 1, 71.
60. J. E. Griffiths and K. B. McAfee, *Proc. Chem. Soc.*, 1961, 456.
61. E. W. Abel and D. A. Armitage, *Adv. in Organomet. Chem.*, Academic Press, New York and London, 1967, 5.

62. E. W. Abel, D. A. Armitage and D. B. Brady, *Trans. Faraday Soc.*, 1966, 62, 3459.
63. A. Marchand, J. Mendelsohn, M. Lebedeff and J. Valade, *J. Organomet. Chem.*, 1969, 17, 379.
64. T. Koichi, A. Masayoshi, K. Oka, *Chem. Abstr.*, 1990, 112, 217277n
65. C. A. Dooley, J. P. Testa, *Chem. Abstr.*, 1990, 112, 198614a.
- 66) C. J. Cardin, D. J. Cardin, J. M. Kelly, D. J. H. L. Kirwan, R. J. Norton and A Roy, *Proceedings of the Royal Irish Academy*, 1977, 77(B), 365.
- 67) C. J. Cardin, D. J. Cardin, J. M. Kelly, R. J. Norton, A Roy, B. J. Hathaway, T. J. King, *J. Chem. Soc., Dalton Trans.*, 1983, 671.
- 68) S. F. Holland, *Appl. Organomet. Chem.*, 1987, 1(S), 449.
- 69) K. A. Kocheskov, *Ber.*, 1926, 62, 996.
- 70) X. Quinglam, Z. Jianyu, *Youji Huaxue*, 1991, 11(1), 82; *Chem. Abstr.*, 1991, 114, 207387z.
- 71) A. Marchand, J. Mendelsohn, M. Lebedeff, and H. Valade, *J. Organomet. Chem.*, 1969, 17, 379.
- 72) M. M. Amini, Ng. S. Weng, K. A. Fidelis, H. J. Heeg, C. R. Muchmore, D. V. Helm, and J. J. Zuckerman, *J. Organomet. Chem.*, 1989, 365, 103.
- 73) N. W. Alcock, R. E. Timms, *J. Chem. Soc.(A)*, 1968, 1873.
- 74) Ng. S. Weng, L. C. Kwai, W. Chen, V. G. K. Das, *J. Organomet. Chem.*, 1989, 376, 277.
- 75) K. C. Molloy, K. Guill, I. W. Nowell, *J. Chem. Soc.*, 1987, 101.

- 76) Ng. S. Weng, V. G. K. Das, B. W. Skelton, A. H. White, J. Organomet. Chem., 1989, 377, 221.
- 77) G. K. Sandhu, N. Sharma, E. R. T. Tiekink, J. Organomet. Chem., 1981, 371, C1.
- 78) G. K. Sandhu, S. P. Verma, E. R. T. Tiekink, J. Organomet. Chem., 1990, 393, 195.
- 79) J. Holleck, K. Handlir, M. Nadvornik, A. Lycka, Proc. conf. coord. chem. 1987, 11, 97.