CHAPTER 3

DIPOLE MOMENTS OF ORGANOTIN COMPOUNDS AND VARIATION IN THE TIN-CHLORINE AND TIN-CARBON BOND POLARITY

CHAPTER-3

Introduction:

The electrical dipole moments of organotin compounds, particularly those of organotin halides have been the subject matter of many discussions. Lorberth and Noth[1] measured the dipole moments of a series of organotin halides R_nSnCl_{4-n} ($R = CH_3, C_2H_5, C_4H_9, C_6H_5$) with the aim of studying contributions to the bond strength in the Sn-Cl by back donation of unshaired electron pairs of chlorine to empty d-orbitals of tin. Such a $d_\pi - p_\pi$ double bond contribution would be expected to increase with progressive chlorination of $(CH_3)_4Sn$ because the electronegativity of the group R_nSnCl_{3-n} would increase with increase in halogen substitution. This would tend to decrease the polarity of the Sn-Cl bond. However, to account for the experimental dipole moments, these authors argued in favour of increase in Sn-Cl bond polarity with increase in chlorine substitution. The same conclusion was drawn by Huang et al also, though by a slightly different approach[2]. This conclusion is, however, hard to reconcile with many well known experimental facts[3,4]. Thus, the decrease in the tin-chlorine bond distance, increase in the tin-chlorine stretching frequency and increase in the nuclear quadrupole coupling constant of chlorine atom in R_nSnCl_{4-n} type compounds with increasing number of chlorine atoms definitely indicate that the tin-chlorine bond polarity decreases with progressive chlorine substitution and no really satisfactory explanation was available for this apparent anomaly. The most logical approach to the problem

would be to calculate the bond polarities, hence bond moments, of all the bonds and examine their variations with progressive halogen substitution. The success of the Del Re method in interpreting the heats of atomisation[5] of organotin compounds and the ease with which the desired quantities may be calculated by this method, prompted us to calculate and analyse the variation of bond polarities and dipole moments in organotin compounds with a view to resolving the anomaly just discussed. As in the previous chapter, the $d_{\pi}-p_{\pi}$ bonding has not been considered in the calculations, since almost all the experimental data can be explained without involving any $d_{\pi}-p_{\pi}$ bonding[5-11]. The results of the present calculations not only provide a very satisfactory explanation for the experimental dipole moments of organotin compounds but also account for the observed variation in the nuclear quadrupole coupling constants of the chlorine atom in R_nSnCl_{4-n} compounds. Incidentally, the present results strongly justify the reliability of the partial charges calculated by the Del Re method.

Procedure:

A. Calculation of the σ-moments:

The dipole moment μ is a vector which is a measure of charge displacement and is defined by eqn. (3-1), where e is the charge and $\bar{r}$ is the vector indicating the separation of the positive and the negative charges. Clearly, the bond moment between the two atoms

$$\mu = e.\bar{r} \qquad (3-1)$$

bonded directly is given by the product of the bond polarity and the bond distance as in eqn. (3-2)

$$\mu(\text{bond}) = \text{Bond charge X Bond distance} \qquad (3\text{-}2)$$

Therefore for the σ-bond a-b in a molecule the bond moment, μ^{σ}_{a-b} will be given by eqn. (3-3) where Q_{ab} is the bond polarity, e is the electronic charge and r_{a-b} is the bond length

$$\mu^{\sigma}_{a-b} = e. Q_{ab} . r_{a-b} \qquad (3\text{-}3)$$

The bond polarity (or the Del Re bond charge) Q_{ab} is given by eqn. (3-4) where δ_a and δ_b are the Coulomb integrals of the atoms a and b respectively and ϵ_{ab} is the Del Re resonance integral parameter[12].

$$Q_{ab} = (\delta_b - \delta_a)/2.\epsilon_{ab} \qquad (3\text{-}4)$$

Using a value of 4.802×10^{-10} e.s.u for 'e' and expressing r_{a-b} in A°, eqns. (3-3) and (3-4) give the bond moment in Debye unit as in eqn. (3-5)

$$\mu^{\sigma}_{a-b} = 4.802 (\delta_b - \delta_a)/2.\epsilon_{ab} \qquad (3\text{-}5)$$

In a neutral system, consisting of several charged points, the total or the net dipole moment is the resultant of the component moments. Thus the permanent electric dipole moment of a molecule may be easily calculated by the vectorial addition of bond moments of all the bonds present from a consideration of the geometry of the molecule[13,14]. The electric dipole moment of a molecule having σ-bonds

only, μ^{σ}, is, therefore given by eqn. (3-6)

$$\mu^{\sigma} = \sum_{\text{all bonds}} 4.802 . \bar{r}_{a-b} \, (\delta_b - \delta_a)/2 . \varepsilon_{ab} \qquad (3\text{-}6)$$

The quantities δ_a and δ_b appearing in eqn. (3-6) can be easily computed by the usual Del Re method provided all the necessary Del Re parameters are known.

B. Calculation of the π-moments:

For phenyl and vinyl organotin compounds, having a π-system eqn. (3-6) does no longer give the total dipole moment because the imbalance in the π-charge distribution will lead to an additional moment. For compounds having a π-net work it is convenient to dissect the total dipole moment, μ, into two components, viz., σ-moment, μ^{σ}, and π-moment, μ^{π} as in eqn. (3-7)[13-15]

$$\mu = \mu^{\sigma} + \mu^{\pi} \qquad (3\text{-}7)$$

The σ-moment, μ^{σ}, can be evaluated by the method discussed in the preceding section, while the π-moment can be calculated from the π-charge distribution. The latter may be calculated by the usual Huckel method. As discussed in the previous chapter, substitution of the hydrogen atom of a C-H bond by tin atom primarily alters the coulomb integral of the directly bonded carbon atom only. A general method for evaluating the change in the coulomb integral, h, of the attached carbon atom has been developed there[5] and is given by eqn. (3-8)

$$h = (\alpha - \alpha_0) = \Delta\alpha_r = 0.21 (q_c - q_c^{\circ}) \qquad (3\text{-}8)$$

where q_{C^o} and q_C are the partial σ-charges of the relevant carbon atom in the parent hydrocarbon and in the organotin compound respectively. Using the value of the Coulomb integral thus obtained for the carbon atom bonded to tin and assigning a standard value α_o to the other carbon atoms, the appropriate secular equation necessary for the calculation of the π-energy and π-charges may be obtained. The π-charge distribution in the vinyl group in vinyl tin compound has been calculated directly from the secular equation while the perturbation technique has been employed in the case of phenyl tin compounds because the change in the coulomb integral, h, is very small for all the compounds studied. According to perturbation method the change in the π-charge at the sth atom, Δ_{qs}, of a phenyl group compared to that in benzene, due to a change in the Coulomb integral of the rth atom, $\Delta\alpha$, is given by eqn. (3-10)

$$\Delta q_s = \pi_{s,r} \cdot \Delta\alpha \qquad (3\text{-}10)$$

where $\pi_{s,r}$ is the atom-atom polarisability. Combining eqns. (3-8) and (3-10) we have eqn. (3-11)

$$\Delta q_s = 0.21 (q_C - q_{C^o}) \cdot \pi_{s,r} \qquad (3\text{-}11)$$

which gives the net π-charge at the sth atom of the phenyl group (the π-charge at the benzene carbon atoms being zero due to equal electron density at all the atoms) in terms of σ-charges q_C and q_{C^o}, and polarisability, $\pi_{s,r}$. The σ-charges may be easily calculated by the Del Re method while tabulated data are available for

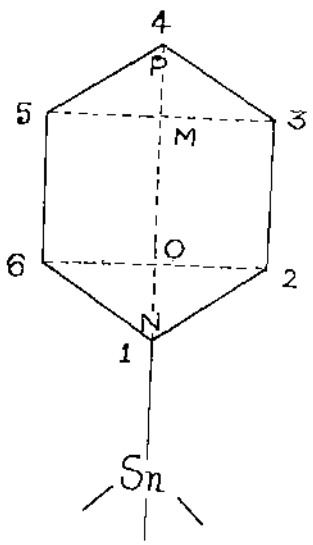

Fig. (3-1) Phenyl ring in phenyltin compounds

the polarisability[16].

If we assume that the phenyl ring present in an organotin compound is a regular hexagon with each side 1.40A° then it can be easily shown that the π-moment, μ^{π}, which lies along the Sn-C bond, is given by eqn. (3-12) [see Fig. (3-1)]

$$\mu^{\pi} = e\left[2q_2 \cdot NO + 2q_3 \cdot NM + q_4 \cdot NP \right] \qquad (3\text{-}12)$$

where q_2, q_3 and q_4 are the π-charges at C_2, C_3 and C_4 respectively. It is easily seen that NO = 0.7A°, NM = 2.1A° and NP = 2.8A°. Substituting these values in eqn. (3-12) and using the value of e, the π-moment due to a phenyl group is given by eqn. (3-13)

$$\mu^{\pi} = 4.802\ (1.4 \times q_2 + 4.2 \times q_3 + 2.8 \times q_4) \qquad (3\text{-}13)$$

Result:

The σ-bond moments in organotin compounds have been computed by eqn. (3-5) using the calculated values of Coulomb integrals. The necessary Del Re parameters are given in Table (1-1), Chapter 1. The net σ-dipole moment, μ^{σ}, has been calculated by vectorial addition of the component bond moments. The π-moment, μ^{π}, for the phenyl group has been calculated from eqn. (3-13) using the π-charges obtained from eqn. (3-11). The π-charge distribution in phenyl and vinyl groups in some organotin compounds are given in Table (3-1)

Table 3-1

Calculated value of the Coulomb parameter 'h' and π-charge distribution in some phenyl and vinyl organotin compounds (C_1 stands

for the carbon atom bonded to the tin atom).

Compound	h	C_1	C_2	C_3	C_4
Vi_3SnCl	-0.014	0.0071	-0.0071		
Vi_2SnCl_2	-0.003	0.0020	-0.0020		
$ViSnCl_3$	0.011	-0.0060	0.0060		
$ViSnMe_3$	-0.027	0.0140	-0.0140		
Ph_3SnCl	-0.014	0.0056	-0.0022	0.0001	-0.0014
Ph_2SnCl_2	-0.003	0.0012	-0.0005	0.0000	-0.0003
$PhSnCl_3$	0.011	-0.0044	0.0017	-0.0001	0.0011
$PhSnMe_3$	-0.027	0.0108	-0.0042	0.0002	-0.0028
$PhSnEt_3$	-0.027	0.0108	-0.0042	0.0002	-0.0028
Ph_3SnEt	-0.025	0.0099	-0.0039	0.0002	-0.0026

In the present calculations, the lengths of Sn-C, C-C, C = C (Vinyl), C = C (phenyl), C-H, Sn-Cl and Sn-H bonds are taken to be 2.18A°, 1.54A°, 1.35A°, 1.40A°, 1.09A°, 2.37A° and 1.70A° respectively[17-19] for all compounds except methyl tin chlorides where the electron diffraction data reported by Skinner[17] have been used. For the tin atom a tetrahedral geometry has been assumed which is consistent with the X-ray and electron diffraction data where these are available[17,20,21].

For compounds such as Me_3SnCl, Me_2SnCl_2, $MeSnCl_3$, Me_3SnH,

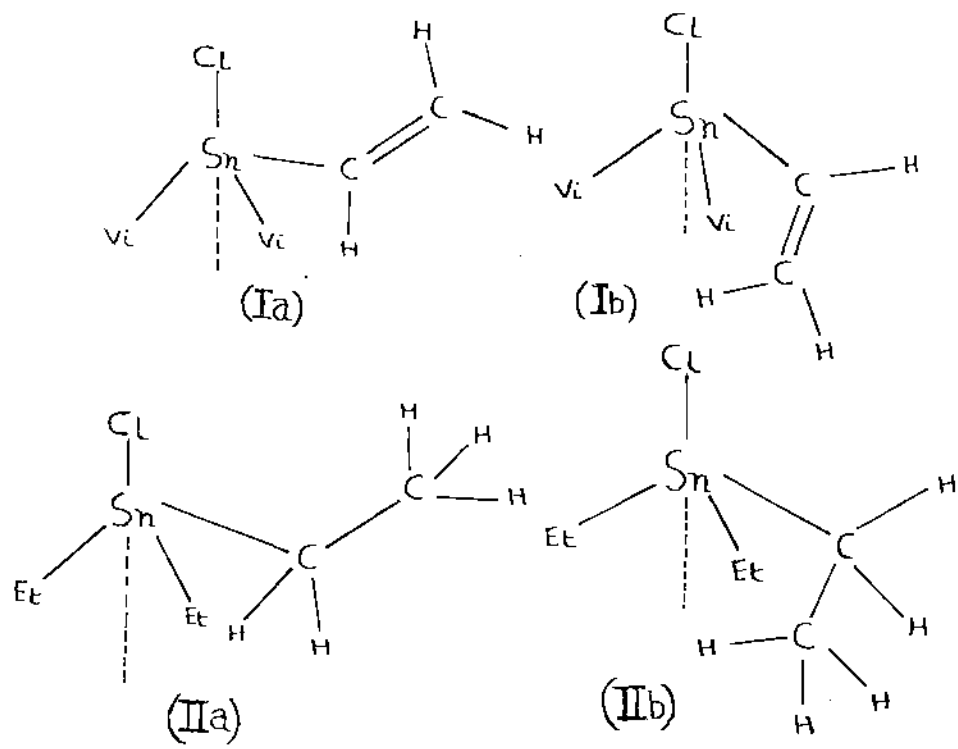

Fig. (3-2) Different orientations of the organic groups about the tin atom

Me_2SnH_2, $MeSnH_3$, ~~$MeSnH_3$~~, Me_3PhSn, Me_3ViSn, t-Bu_2SnCl_2, $ViSnCl_3$, Ph_3SnCl, Ph_2SnCl_2 and $PhSnCl_3$ only one geometry is possible and therefore the calculation of electric dipole moment is not complicated by the possibility of different geometry. However, for organotin compounds having ethyl or vinyl groups different orientations of the organic groups about the tin atom, as shown in Fig. (3-2), are possible. In such cases it is rather difficult to assume any particular conformation[22]. However, the difference in the dipole moments of these enantiomers are expected to be small because of the low values of the bond polarities of C-H and C-C bonds. In order to estimate the magnitude of this difference the dipole moments of Vi_3SnCl and Vi_2SnCl_2 have been calculated for different possible conformations. These values, given in Table (3-2), indicate that the diff-

Table 3-2

Calculated electric dipole moment of Vi_3SnCl and Vi_2SnCl_2 assuming configurations (a) and (b).

Compound	Calcd. dipole moment in Debye (a)	Calcd. dipole moment in Debye (b)	Difference in Debye
Vi_3SnCl	3.053	3.101	0.048
Vi_2SnCl_2	3.645	3.710	0.065

erence in the dipole moments due to a conformational change is of the order of ±0.06D and is much less than the variation in the reported data. For ethyl compounds, this difference is even smaller.

Because of this the sterically most favoured conformation has been assumed whenever there is a possibility of more than one conformation. (For example in the case of Vi_3SnCl and Et_3SnCl configurations Ia and IIa are assumed).

The calculated dipole moments for a number of organotin compounds along with the experimental dipole moments[1,2,23-29] are given in Table (3-3). Considering the large variations in the reported

Table 3-3

Calculated and Experimental dipole moments of organotin compounds in Debye unit.

Compound	Cald. dipole moment	Exper. dipole moment	References
Me_3SnCl	3.46	3.46 - 3.52	1,2,24
Me_2SnCl_2	4.04	4.14 - 4.21	1,2,24
$MeSnCl_3$	3.63	3.62 - 3.77	1,24
Et_3SnCl	3.55	3.44 - 3.80	2,25,26
Et_2SnCl_2	4.14	3.85 - 4.47	2,25,26
$EtSnCl_3$	3.73	4.08	1
Me_3SnH	0.67	--	--
Me_2SnH_2	0.78	--	--
$MeSnH_3$	0.65	0.68	27
Me_3PhSn	0.54	0.51	28
Et_3PhSn	0.50	0.50	27
$EtPh_3Sn$	0.51	0.73	27
Me_3ViSn	0.52	0.45	29
$t\text{-}Bu_2SnCl_2$	4.14	4.34	2

Contd..

Table 3-3 (Contd.)

Compound	Cald. dipole moment	Exper. dipole moment	References
Vi_3SnCl	3.05	3.00	2
Vi_2SnCl_2	3.65	4.06	2
$ViSnCl_3$	3.34	3.77	2
Ph_3SnCl	3.01	3.30 - 3.46	1,2,23,25
Ph_2SnCl_2	3.64	3.59 - 4.31	1,2,23
$PhSnCl_3$	3.39	3.99 - 4.30	1,2,23

dipole moment data the agreement between the calculated and the experimental values is generally very good.

A very significant feature of the present calculation is the change in tin-chlorine bond polarity in going from Me_3SnCl to $SnCl_4$. In order to account for the variations in the dipole moment in the series R_3SnCl, R_2SnCl_2 and $RSnCl_3$ Lorberth and Noth[1] and Huang et al[2] have argued in favour of increase in the tin-chlorine bond polarity with progressive chlorine substitution although the nuclear quadrupole coupling constants[3] and infrared spectra[4] of organotin chlorides indicate a reverse trend. These apparently contradictory conclusions have been reconciled in our calculation. An examination of the variation in the bond polarities of the various bonds of methyltin

chlorides given in Table (3-4) shows that the tin chlorine bond polarity decreases from Me_3SnCl to $MeSnCl_3$ as would be expected from the nuclear quadrupole coupling constant data. However, the

Table 3-4

Polarity (percent) of different bonds in Methyltin Chlorides.

Compound	Sn-Cl	Sn-C	H-C
Me_3SnCl	38.68	10.66	3.30
Me_2SnCl_2	33.79	4.48	3.64
$MeSnCl_3$	28.07	-2.77*	4.05

*Negative sign indicates reversal of polarity.

tin-carbon bond polarity also decreases concurrently and in fact, it is reversed in $MeSnCl_3$. Thus, although the tin-chlorine bond moment decreases in the series, the decrease in the tin-carbon bond moment which acts in the opposite direction leads to an overall higher dipole moment.

That the calculated bond polarities are essentially correct is also reflected from a comparison of the calculated Del Re charges at the chlorine atom in $n\text{-}Bu_2SnCl_2$, $n\text{-}BuSnCl_3$ and $SnCl_4$ and the experimental nuclear quadrupole coupling constants of chlorine in these

compounds[3] given in Table (3-5). A singly occupied p-orbital has a

Table 3-5

Comparison of charge on the chlorine atom with its nuclear quadrupole coupling constant.

Compound	Charge on Cl	Coupling Const. (MHz)
$n\text{-}Bu_2SnCl_2$	-.338	34.6
$n\text{-}BuSnCl_3$	-.281	43.2
$SnCl_4$	-.212	48.2

large gradient at the nucleus and gives rise to a relatively high value of the coupling constant for a chlorine atom, where as that for a chloride ion is zero; a totally filled p-shell has a spherical symmetry and has no interaction with the quadrupole moment[30]. Hence, the nuclear quadrupole coupling constant of chlorine in a series of similar compounds is strongly dependent on the electron density at the chlorine atom and decrease with increasing negative charge on the chlorine atoms. Thus, the calculated charges are in full agreement with the nuclear quadrupole coupling constant data also.

Another point that strongly justifies the validity of the Del Re calculations in the study of organotin compounds is the calculated variation in tin-carbon bond polarity in R_nSnCl_{4-n} type compounds. Because the electronegativity sequence is phenyl> methyl> ethyl> n-butyl> t-butyl[2,31-33], it is expected that the tin-carbon bond polarity would follow the same order. This is clearly demonstrated by the data given in Table (3-6). The tin-carbon bond polar-

Table 3-6

Variation in the tin-carbon bond polarity (percent) of R_nSnCl_{4-n} compounds.

R	R_3SnCl	R_2SnCl_2	$RSnCl_3$
Vi	13.97	7.95	0.82
Ph	13.82	7.70	0.45
Me	10.66	4.48	-2.77*
Et	10.61	4.29	-3.14*
n-Bu	10.58	4.25	-3.19*
t-Bu	10.55	4.05	-3.64*

*Negative sign indicates reversal of polarity.

ity in vinyl tin compounds suggests the vinyl group to be more electronegative than the phenyl group which is consistent with the

results of cleavage of symmetrical organomercury compounds by HCl[34].

Although the present calculations can account for the dipole moments as well as the variation in the bond polarities satisfactorily, in a few cases, viz., $PhSnCl_3$ and $ViSnCl_3$ the calculated moments are some what low. The high dipole moments of these compounds have been attributed to $d_\pi - p_\pi$ bonding between tin and carbon by Huang et al[2]. However, the dipole moments of organotin chlorides, particularly in the case of R_2SnCl_2 and $RSnCl_3$ type compounds, shows a strong solvent dependence. For example the dipole moment of $PhSnCl_3$ varies from 3.99D to 5.81D depending on the solvent[23] indicating a strong solvent solute interaction in this case. Because of such large interactions it is not possible to obtain the dipole moment of the free molecule to which our calculation applies. In any case, the dipole moment of phenyltin chloride in the absence of any interaction would be certainly lower than 3.99D which is the value in hexane since the observed dipole moment increases in solvents like dioxance where the interaction with the solvent is expected to be greater. It may be noted that comparatively large deviation from the calculated values occur only in such cases. Thus, it appears that the discrepancy between the calculated and the observed dipole moments in such cases is more likely to be due to uncertainity in the experimental values rather than due to any $d_\pi - p_\pi$ bonding. This view is supported by the fact that our calculations satisfactorily account for such diverse properties as heat of atomisation, variation in bond polarities, bond distances, nuclear quadrupole coupling constants,

stretching frequencies etc., in organotin compounds[5-11] without invoking any $d_\pi - p_\pi$ bonding.

Summary:

In this chapter the electric dipole moments of 20 organotin compounds containing methyl, ethyl, t-butyl, n-butyl, phenyl and vinyl groups have been calculated using approximate quantum mechanical methods. The σ-moments are computed from the σ-change distributions calculated by the usual Del Re's procedure while the contribution of the π-system to the total moment of a molecule having a π-system is calculated from the π-charge distributions obtained by the Huckel LCAO MO method using perturbation technique. To ascertain the effect of the relative orientation of the organic group R about the central tin atom on the dipole moment, the dipole moments of Vi_3SnCl and Vi_2SnCl_2 have been calculated for two extreme configurations of the vinyl group about the tin atom. The results indicate the change in the dipole moment due to such changes in orientation to be smaller than the variations in the reported values.

Agreement between the calculated and the experimental values is in general very good. The calculated bond polarity of the tin-chlorine bond decreases in the order $R_3SnCl > R_2SnCl_2 > RSnl_3 > SnCl_4$ in accordance with the variation in the nuclear quadrupole coupling constant of chlorine in these molecules. The tin-carbon bond polarity follow the order vinyl > phenyl > methyl > ethyl > n-butyl > t-butyl as would be expected from their relative electronegativities.

References:

1 J.Lorberth and H.Noth, Chem.Ber., 98(1965)969

2 H.H.Huang, K.M.Hui and (in part) K.K.Chiu, J.Organometal. Chem., 11(1968)515

3 E.D.Swiger and J.D.Graybeal, J.Amer.Chem.Soc., 87(1965)1464

4 D.M.Adams, Metal-Ligand and Related vibrations, Arnold, London, 1967, p.51

5 R.Gupta and B.Majee, J.Organometal.Chem., 29(1971)419

6 R.Gupta and B.Majee, J.Organometal.Chem., 36(1972)71

7 R.Gupta and B.Majee, J.Organometal.Chem., 40(1972)97

8 R.Gupta and B.Majee, J.Organometal.Chem., 40(1972)107

9 R.Gupta and B.Majee, J.Organometal.Chem., 49(1973) 191

10 R.Gupta and B.Majee, J.Organometal.Chem., 49(1973)197

11 R.Gupta and B.Majee, J.Organometal.Chem., 49(1973)203

12 G.Del Re, J.Chem.Soc., (1958)4031

13 A.Streitwiesger.Jr., Molecular Orbital Theory for Organic Chemists, Wiley, New York, 1961, Ch.6

14 R.Daudel, R.Lefebvre and C.Moser, Quantum Chemistry Methods and Applications, Interscience, New York, 1965, Ch. IX

15 J.Nagy and P.Hencsei, J.Organometal.Chem., 20(1969)37

16 C.A.Coulson and A.Streitwieser, Dictionary of π-electron Calculation, Pergamon, London, PXII, 35

17 H.A.Skinner and L.E.Sutton, Trans. Faraday Soc., 40 (1944)164

18 G.W.Wheland, Resonance in Organic Chemistry, Wiley, New York, 1955, p.695

19 D.R.Lide, Jr., J.Chem.Phys., 19(1951)1605

20 I.G.Ismailzade and G.S.Zudanov, Zhur.Fiz.Khim., 26(1952)1619 [Chem.Abs. 49(1955) 2811h]

21 I.G.Ismailzade and G.S.Zudanov, Zhur.Fiz.Khim., 27(1953)550 [Chem.Abs. 48 (1954)7969b]

22 W.P.Neumann, The Organic Chemistry of tin, Wiley, New York, 1970, Ch. 2

23 I.P.Goldshtein, E.N.Guryanova, E.D.Delinskaya and K.A.Kocheshkov, Dokl. Akad.Nauk. SSSR, 136(1961)1079 [Chem.Abs. 55(1961)17557g]

24 E.G.Claeys, G.P. ven der Kelen and Z.Eeckhant, Bull.Soc.Chim. Belges., 70(1961)462 [Chem.Abs 56 (1962)6759d]

25 C.P.Smyth, J.Org.Chem., 6(1941)421

26 M.E.Spaght, F.Hein and H.Pauling, Physik.Z., 34(1933)212

27 R.K.Ingham, S.D.Rosenberg and H.Gilman, Chem.Rev.,60(1960)460

28 J.Nagy, J.Reffy, A.Kauszmann-Borbely and K.Palossy-Becker, J.Organometal.Chem., 7(1967)393

29 J.Nagy, S.Ferenczi-Gresz and O.M.Nefedov, Period. Polytech. Chem. (Budapest) 10(1966)319 [Chem.Abs.67(1967) 48245 u]

30 C.H.Townes and B.P.Dailey, J.Chem.Phys., 17(1949)782

31 H.C.Brown, J.Amer.Chem.Soc., 61(1939)1483

32 J.F.J.Dippy, Chem.Rev., 25(1939)151

33 D.Seyferth, J.Amer.Chem.Soc., 79(1957)2133

34 R.E.Dessy, G.F.Reynolds and J.Y.Kim, J.Amer.Chem.Soc., 81(1959)2683