On the Metallo-organic Compounds: Alkyltin Compounds and their Derivatives.*

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Tetralkyltin may be prepared in various ways. The two most important methods heretofore known are those of Grignard and Löwig. The method used by Löwig(1) i.e. treating an Sn-Na alloy with an alkyl iodide, is preferred from the economic point of view if the high cost of the iodide could be replaced by some cheap alkyl halide. A critical study on the preparation of tetraethyltin has been made by treating various Sn-Na alloys containing various percentage of Zn with ethyl bromide under ordinary conditions. The results of the study show that the alloy consisting of 14% Na, 12–22% of Zn and the least amount of Sn gives the highest yield (97%) of tetraethyltin. The compounds represented by R_4Sn (R = Me or Et) are colourless, volatile liquids, and may be distilled without being decomposed. They combine with one molecule of halogen directly giving one molecule of R_3SnX and one molecule of alkyl halide, white with two molecules of halogen they give R_2SnX_2 and two molecules of alkyl halide. With two atoms of sodium they form under certain conditions $NaSnB_3$ and NaR. The compounds of the type R_3Sn exist in free state(2)(3). These free radicals are readily obtained by reducing the compounds of the type R_3SnX with an alkali metal in liquid ammonia. $(CH_3)_3Sn$ and $(C_2H_5)_3Sn$ may be given as examples of this type of products. The reaction is explained by the following equation, where X represents halogen, an electronegative element:

$$R_3SnX + Na = R_3Sn + NaX. \qquad (1)$$

The radicals are also obtained by either of the following reactions in liquid ammonia:

$$R_3SnNa + R_3SnX = R_3SnSnR_3 + NaX \qquad (2),$$

$$NaR_2SnSnR_2Na + 2RX = R_3SnSnR_3 + 2NaX \qquad (3).$$

The group are slowly oxidized to the oxide in air. The oxides are readly decomposed by water into the hydroxides: $[(C_2H_5)_3Sn]_2O$ is representative of the oxides. The interesting properties of the groups are that they combine with the strong electropositive element Na in liquid ammonia, and form the salts of the type represented by the formula R_3SnNa. The sodium compounds of the group R_3Sn are electrolytes for the reason that they ionize into R_3Sn^- and Na^+ in the solution.

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(1) Lowig, *Ann.*, **84** (1852), 309, 313.

(2) Rügheimer, *ibid.*, **364** (1909), 53.

(3) Kraus and Sessions, *J. Am. Chem. Soc.*, **47** (1925), 2629.

The halides of the group $(CH_3)_3Sn$ are non-electrolytes.(4) For example, trimethytln chloride in pure state or in a medium having a relatively high dielectric constant, such as in nitrobenzene or nitromethane, it does not conduct electric current. However, the solutions of the halides in alcohol and pyridine exhibit marked electrolytic properties. It is, therefore worthy of notice that in these solutions the compounds combine with the solvents, alcohol and pyridine, and form the oxonium and ammonium salts respectively. Trimethyltin chloride (m.p. 37°C; b.p. 150–153°C) combines with one molecule of ammonia(5) like hydrogen chloride. The ammonium chloride sublimes without melting when it is heated. In view of these facts the properties of $(CH_3)_3SnCl$ very closely resemble those of HCl.

The groups of the type R_2Sn—e.g., $(C_2H_5)_2Sn$, orange yellow amorphous powder and ignites in air—also are set free, when the compounds R_2SnX_2 are reduced with sodium in liquid ammonia under proper condition. The properties of these groups resemble in many respects those of the groups of the type R_3Sn, i.e., the groups combine directly with electronegative elements, oxygen and halogens, producing the oxide and dihalides, respectively. The groups combine not only with a strong electronegative element halogen, but also with a strong electropositive metal. For example the group $(C_2H_5)_2Sn$ combines with one and two atoms of sodium to form the salts, $Na(C_2H_5)_2SnSn(C_2H_5)_2Na$ and $Na_2(C_2H_5)_2Sn$ respectively.

When the halogens in the molecule of R_3SnX and R_2SnX_2 are replaced by the same number of hydroxyl groups, the corresponding basic compounds of the hydroxide, R_3SnOH, and the oxide, R_2SnO, are formed respectively.

The R_3Sn groups in the hydroxide series show an electropositive character, and this was proved by the fact that the hydrogen in the hydroxyl group can not be replaced by sodium in liquid ammonia. In other words, the sodium compounds R_3SnONa cannot be obtained by the method, but the trialkyltin radical can be obtained. For example, trimethyltin hydroxide reacts readily with one atomic proportion of metallic sodium in liquid ammonia according to the following equation(6):

$$R_3SnOH + Na = R_3Sn + NaOH \qquad (4).$$

Further addition of sodium results in the formation of the sodium stannide by the following reaction:

$$R_3Sn + Na = R_3SnNa \qquad (5).$$

Therefore, the hydroxides are not comparable to alcohols and phenol. The latter substances react with metallic sodium in liquid ammonia according to the following equation, and form the compounds of the type NaOR:

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(4) Kraus and Callis, *J. Am. Chem. Soc.*, **45** (1923), 2624; Kraus and Greer, *ibid.*, **45** (1923), 2446.

(5) Kraus and Greer, *ibid.*, **45** (1923), 3078.

(6) T. Harada, *Bull. Chem. Soc. Japan*, **4** (1929), 266; Kraus and Bullard, *J. Am. Chem. Soc.*, **52** (1930), 4057.

$$ROH + Na = RONa + \tfrac{1}{2}H_2 \qquad (6).$$

The hydroxides of the group R_3Sn are, therefore, comparable to NaOH and KOH. Trialkyltin hydroxides are decomposed easily under certain conditions into the corresponding oxides and water according to the following equation:

$$2R_3SnOH = [R_3Sn]_2O + H_2O \qquad (7).$$

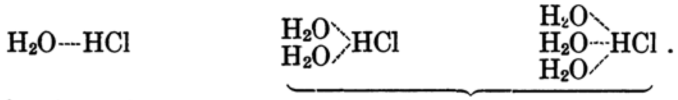
For example, triethyltin hydroxide, heated in the neighbourhood of its boiling point or dried over $CaCl_2$, gives triethyltin oxide and water. However, by prolonged heating at a high temperature, it decomposes into diethyltin oxide and ethane with the following equation:⁽⁷⁾

$$(C_2H_5)_3SnOH = (C_2H_5)_2SnO + C_2H_6 \qquad (8).$$

One of the most interesting properties of the compounds of the types R_3SnX⁽⁸⁾ and R_2SnX_2 is their characteristic affinity for R_3SnOH and R_3SnO respectively with the formation of various complex crystalline compounds in various proportions. Trialkyltin halides combine with one or two molecules of the corresponding hydroxides to form the complex salts having the following formulae:

$$R_3SnOHSnR_3XH_2O\,, \quad [R_3SnOH]_2SnR_3X\,, \quad [R_3SnOH]_2SnR_3XH_2O\,.$$

These compounds resemble the crystalline compounds⁽⁹⁾ formed between hydrogen chloride and water. According to Werner the structural formulae for the hydrates of hydrogen chloride are represented as follows:



$$\underset{\text{Oxonium salt}}{H_2O\text{---}HCl} \qquad \underbrace{\begin{matrix}H_2O\\H_2O\end{matrix}\!\!>\!HCl \qquad \begin{matrix}H_2O\\H_2O\\H_2O\end{matrix}\!\!\text{---}HCl}_{\text{Anomalous oxonium salts}}\,.$$

Dialkyltin dihalides and the diacetates also combine with various molecular proportions of the corresponding oxides and produce various complex compounds, such as $R_2SnOSnR_2X_2$, $[R_2SnO]_2SnR_2X_2$ and $H[R_2SnO]_3OH\cdot SnR_2X_2$, for the former, and $R_2SnOSnR_2(OAc)_2$ and $[R_2SnO]_3SnR_2(OAc)_2$ for the latter under controlled conditions.

Recently Smith and Kipping⁽¹⁰⁾ reported that the formation of di-anhydro-tris-di-benzyl-tin di-hydroxide $HOSnBz_2OSnBz_2OSnBz_2OH$ (di-anhydro-tris-di-benzyl-stannane-diol) takes place by the condensation of three molecules of dibenzyltin dihydroxide $Bz_2Sn(OH)_2$ (di-benzyl-stannane-diol). They also reported that when $HOSnBz_2OSnBz_2OSnBz_2OH$ is heated above 150°C it loses water and gives off Bz_2SnO or a six-membered ring $[Bz_2SnO]_3$ (tri-anhydro-tris-di-benzyl-stannane-diol). Therefore, it may be assumed that the compound of the type $[R_2SnO]_3\cdot$

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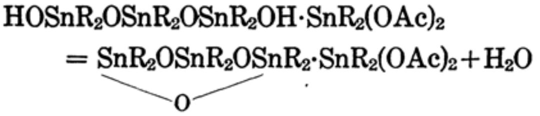
(7) T. Harada, unpublished observations.

(8) Kraus and T. Harada, *J. Am. Chem. Soc.*, **47** (1925), 2568; T. Harada, *Bull. Chem. Soc. Japan*, **6** (1931), 240.

(9) Rupert, *J. Am. Chem. Soc.*, **31** (1909), 851.

(10) Smith and Kipping, *J. Chem. Soc.*, **103** (1913), 2042.

$SnR_2(OAC)_2$ in which $[R_2SnO]_3$ group occurs, should have the following ring formation by splitting off water as follows:



$$HOSnR_2OSnR_2OSnR_2OH \cdot SnR_2(OAc)_2 = \underbrace{SnR_2OSnR_2OSnR_2}_{O} \cdot SnR_2(OAc)_2 + H_2O \qquad (9).$$

Two attempts have been made by the present author on the preparation of di-ethyl-stannane-diol or its condensation product of the type $HOSnR_2OSnR_2OSnR_2OH$ according to the method described by Smith and Kipping for the preparation of di-anhydro-tris-di-benzyl-stannane-diol. However, in the results, di-ethyltinoxide was obtained contrary to the expectation.

The evidence for the formation-tendency of the compound of the type $HOSnR_2OSnR_2OSnR_2OH$ was obtained when dimethyltin oxide was dissolved in phenol and its molecular weight was determined. That is, the value was found to increase parallel with the increase in the concentration. This finding of the increase in values is apparently due to a characteristic phenomenon for the presence of the OH or the OC_6H_5 group, or both in the molecule of the compound. Therefore, the formula for the compounds formed by the combination of three molecules of dialkyltin oxide and one molecule of the corresponding dihalides in the medium of water or alcohol will be represented by $R'[SnR_2O]_3OR'SnR_2X_2$(11) where R′ represents hydrogen or alkyl radical of the respective solvents. R′ representing an alkyl group can be replaced by hydrogen by means of hydrolysis; hence di-anhydro-tris-diethyltin-di-alkoxy-diethyltin dihalide is hydrolysed or decomposed into the corresponding hydroxy-compound by water that may be present as moisture in benzene or in air. The formation of the hydroxy-compound is explained by the following reaction:

$$R'[SnR_2O]_3OR' \cdot SnR_2X_2 + 2H_2O = H[SnR_2O]_3OH \cdot SnR_2X_2 + 2R'OH \qquad (10).$$

The compound of the type $R'[SnR_2O]_3OR' \cdot SnR_2X_2$ is now conveniently called di-anhydro-tris-dialkyltin-dihydroxy-dialkyltin dihalide.

It is evident, therefore, that the dialkyltin dihalides do not link to any other elements of the molecule except to the oxygen by either principal, or auxiliary valencies of the tin. It is consequently conceivable to have various forms, and among which the linkage $>O{::::}SnR_2X_2$ will be highly probable in view of the existence of the compounds of the type $R_2SnOSnR_2X_2$ and $(NH_3)_2SnR_2X_2$.(12) The other type of compounds formed between dialkyltin oxides and dialkytin diacetates or the halides may, therefore, be represented by the following formulae:

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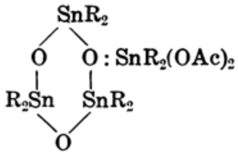
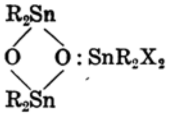
(11) Kraus and T. Harada, *J. Am. Chem. Soc.*, **47** (1925), 2568:— The bromide and the iodide of the type $C_2H_5[Sn(CH_3)_2O]_3OC_2H_5 \cdot Sn(CH_3)_2X_2$ were actually obtained by Kraus and T. Harada in a small quantity by heating trimethyltin hydroxide with trimethyltin bromide and trimethyltin iodide respectively and were recrystallized from alcohol. However they misconcluded and misrepresented the compounds by the formulae $(CH_3)_3SnOHSn(CH_3)_3BrH_2O$ and $(CH_4)_3SnOHSn(CH_3)_3IH_2O$.

(12) Werner and Pfeiffer, *Z. anorg. Chem.*, **17** (1898), 82.



or



Similarly in the constitution of the compounds $R_3SnOHSnR_3XH_2O$, $[R_3SnOH]_2SnR_3X$, and $[R_3SnOH]_2SnR_3XH_2O$ formed between trialkyltin hydroxides and the corresponding halides in the presence of moisture it is conceivable that the oxygen compounds, viz., the hydroxides and water in the compounds, are linked to the metallic atoms in trialkyltin halides by the auxiliary valencies. The linkages are explained by the

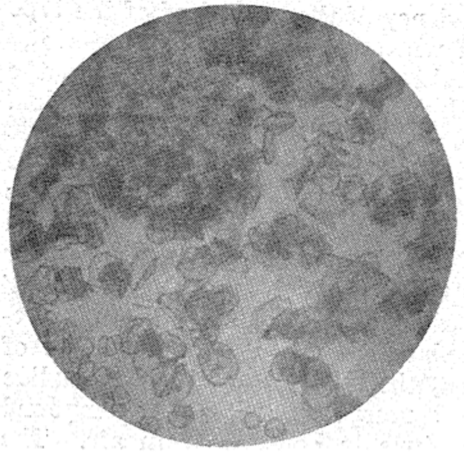


Fig. 1. $[(C_2H_5)_3SnOH]_2Sn(C_2H_5)_3ClH_2O$ Crystals.

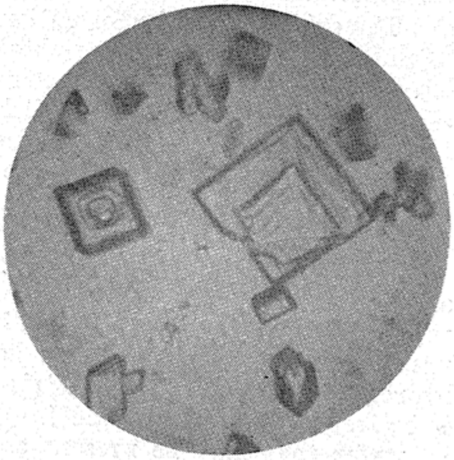


Fig. 2. $H[Sn(C_2H_5)_2O]_3OHSn(C_2H_5)_2I_2$ Crystals.

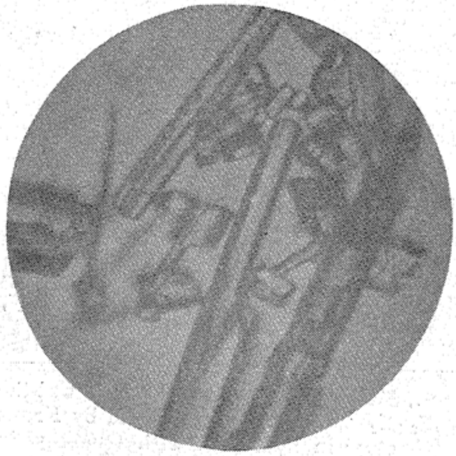


Fig. 3. $C_2H_5[Sn(CH_3)_2O]_3OC_2H_5\cdot Sn(CH_3)_2I_2$ Crystals.

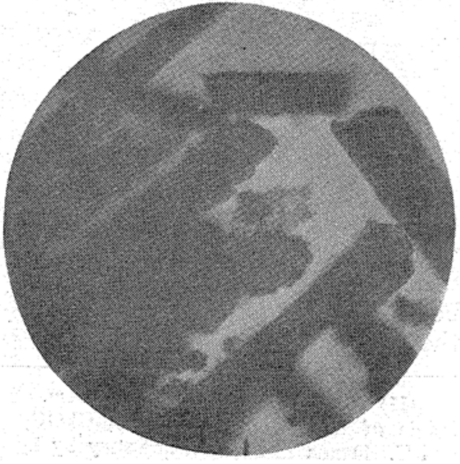


Fig. 4. $H[Sn(CH_3)_2O]_3OHSn(CH_3)_2I_2$ obtained by exposing of $C_2H_5[SnCH_3)_2O]OC_2H_5\cdot Sn(CH_3)_2I_2$ to moisture.

Fig. 5. $Sn(C_2H_5)_2OSn(C_2H_5)_2Br_2$
Crystals.

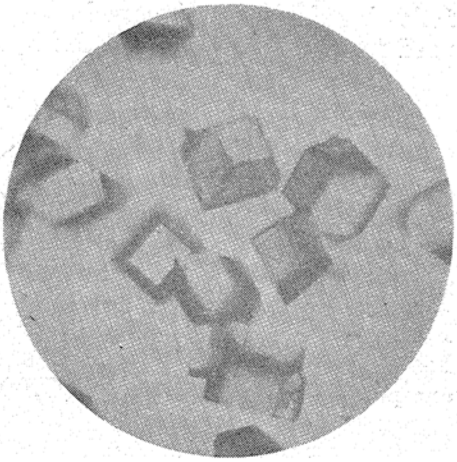


Fig. 6. $[Sn(C_2H_5)_2O]_3Sn(C_2H_5)_2(OAc)_2$
Crystals.

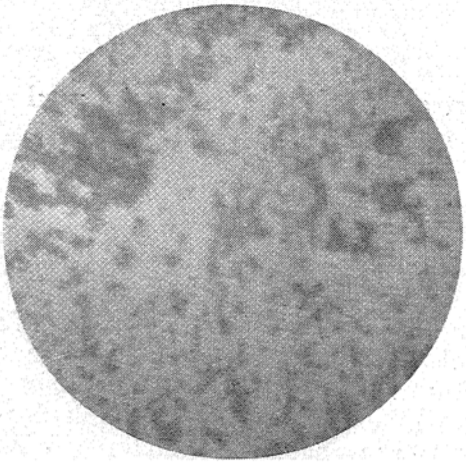


Fig. 7. $[(CH_3)_2SnO]_2Sn(CH_3)_2Cl_2$
precipitate-like crystals.

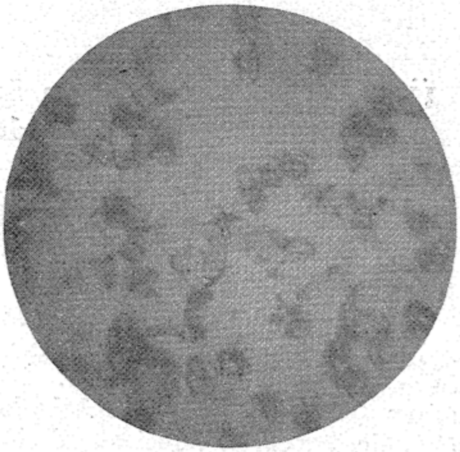


Fig. 8. $(CH_3)_2SnOSn(CH_3)_2(OAc)_2$
Crystals.

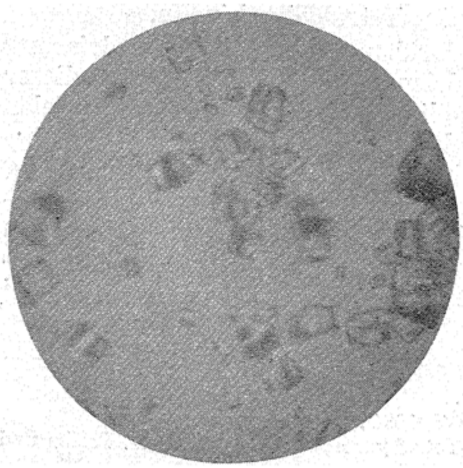


Fig. 9. $(CH_3)_3SnOHSn(CH_3)_3ClH_2O$
Crystals.

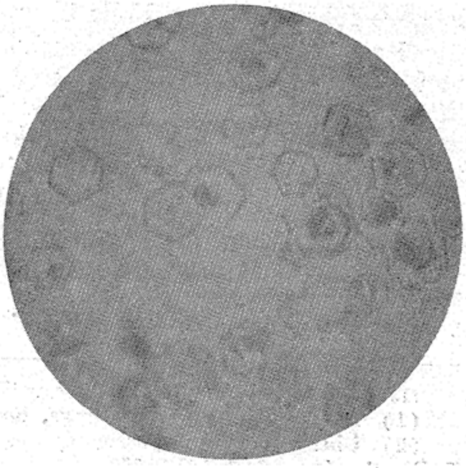
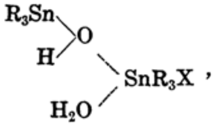
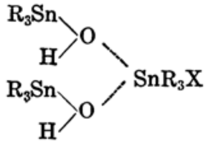


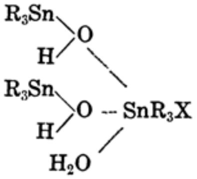
Fig. 10. $[(CH_3)_3SnOH]_2Sn(CH_3)_3Cl$
Crystals.

following formulae (anomalous oxonium salts) in a similar manner as used for the expression of the hydrates of hydrogen chloride:





and



The water in the compounds can be demonstrated without difficulty. For example when $(CH_3)_3SnOHSn(CH_3)_3ClH_2O$ (m.p. 81–95°C) is heated with $HCCl_3$ the water separates floating on the top while the compound $[(CH_3)_3SnOH]Sn(CH_3)_3Cl$ (m.p. 85–91°C)(13) does not.

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(13) T. Harada, unpublished observations.