



Initial organotin chemistry

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ABSTRACT

In 1849, attempts to isolate free alkyl groups led to discovery of an organostannane, $(C_2H_5)_2SnI_2$, which was analyzed in 1852. Coevally, aims at extension of trialkylstibine and trialkyl bismuth chemistry yielded $[(C_2H_5)_2Sn]_n$, finally consisting rather of (cyclic) oligostannanes than polystannanes; the latter might have been degraded to the former though. Further, those reports described conversion of $(C_2H_5)_2SnI_2$ or $[(C_2H_5)_2Sn]_n$ to $(C_2H_5)_2SnO$, in fact a polymer, $[(C_2H_5)_2SnO]_n$. These three substances were employed as starting materials for exploration of new alkylstannanes, and moreover some of the compounds thus obtained were used for synthesis of other organostannanes. Thus, e.g., dialkylstannanes $(C_2H_5)_2SnX_2$ ($X = Br, Cl$, nitrate, formate, acetate) and a number of corresponding methyl derivatives were prepared, as well as $(C_2H_5)_2SnSO_4$, $(CH_3)_2SnSO_4$, $(C_2H_5)_2Sn(C_2O_4)$ and tetraalkylstannanes. Dinuclear tin compounds were also addressed, in particular $(C_2H_5)_3Sn-Sn(C_2H_5)_3$, $(C_2H_5)_2ISn-Sn(C_2H_5)_2I$, and $(C_2H_5)_3SnOSn(C_2H_5)_3$. The latter arose as a reversibly formed dehydration product of $(C_2H_5)_3SnOH$. This hydroxide and $(CH_3)_3SnOH$ served for the synthesis of trialkylstannanes R_3SnX ($R = ethyl$; $X = Br, Cl$; $R = ethyl$ or methyl; $X = formate, acetate, butyrate$), $[(C_2H_5)_3Sn]_2SO_4$, $[(CH_3)_3Sn]_2SO_4$ and $[(C_2H_5)_3Sn]_2(C_2O_4)$. Among the synthesis routes substitution and addition reactions were applied, and even the so-called Kocheshkov redistribution reaction (Kocheshkov comproportionation) was already described, namely by Buckton who thus obtained $(C_2H_5)_3SnCl$. Hence, already by 1860 a diversity of organotin compounds and related reactions was established, and the base for methodical exploration of organotin compounds was laid.

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1. Introduction

This article highlights the historic development of organotin chemistry, based on original publications up to 1860, with emphasis on compounds characterized by elemental analysis. Notably, original formulae derived from those analyses can look mistakenly to present-day readers although the old formulae inherently reflect the correct atomic compositions of the regarded compounds. The reason for such discrepancies originates in the evaluation method of atomic compositions, which requires specification of relative atomic masses. Initially, relative atomic masses were derived by comparison of elements' mass ratios in different compounds [1,2]. However, it was already recognized by contemporary chemists that this method could not provide definite certainty in relative atomic masses [1,2]. Accordingly, it was noted that the evaluated relative atomic masses rather corresponded to mixture-based mass ratios [2] or chemical equivalents [1]. Nonetheless, hydrogen was frequently used as a reference center for relative atomic masses, because hydrogen was found to be the

lightest element, and arbitrarily tagged with the relative atomic mass of 1 [1,2]. Other scales of relative atomic masses referred to oxygen since this element was known as a component in a particularly wide variety of important compounds [1,2], and a relative atomic mass of 1 [1], 10 [1] or 100 [1,2] was conveniently attributed to oxygen atoms.

The chemical analysis of water disclosed an oxygen to hydrogen mass ratio of exactly 8:1 [2], and it was assumed that this mass ratio also reflects the atomic mass ratios of oxygen and hydrogen. Therefore the scale with hydrogen as a reference center entailed a relative atomic mass of oxygen of 8 [1,2]. As a consequence, the chemical formula of water was designated as OH [3], and the relative atomic masses based on 100 for oxygen were then converted to those based on 1 for hydrogen by division of the former by 12.5 [1]. Evaluation of chemical analyses of various compounds led to relative atomic masses (based on 1 for hydrogen) of, e.g., 6 for carbon [1], 14.15 for nitrogen [4] (also called azote [1,5]), 16.09 for sulfur [4], 35.42 for chlorine [4] and 58.82 for tin (calculated from the value of 735.23 on the basis of 100 for oxygen) [6]. Since a number of chemists were of the opinion that all relative atomic masses must be multiples by whole numbers of the atomic mass of hydrogen [4,7], rounded values were also common [4,8] (e.g. 58 [6,8] or 59 [9] for

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tin). It is instantly evident that relative atomic masses of some elements derived as indicated above deviate from the relative masses established nowadays by a factor of 2.

However, a part of the chemists considered the possibility that water comprises an O to H atomic ratio of 1:2 instead of 1:1 [1,2] because the ratio of 1:2 reflected the volume ratio of the respective gases when water was synthesized from oxygen and hydrogen [2], or because the masses of the same volume of oxygen and hydrogen gas amount to 16:1 instead of 8:1 [10]. This had impact on relative atomic masses of a number of elements, leading, for example, to a value of 16.03 for oxygen [11] instead of 8. Thus, different relative atomic masses were applied by different chemists [5,12,13], which eventually led to confusion [12]. For example, the chemical formula of silicon tetrachloride was indicated by SiCl , SiCl_2 , SiCl_3 or SiCl_4 , depending on the atomic masses used by the respective chemists [13]. Although chemical formulae consistent with present-day relative atomic masses were available by 1860 [14], the use of atomic equivalent masses differing by multiples from relative atomic masses used nowadays was then still common [15]. In fact, all chemical formulae in the articles cited in the following still reflect relative atomic mass ratios of C:H, O:H and Sn:H differing by a factor of two compared to those established nowadays, while the N:H, Cl:H, I:H or Na:H mass ratios are not affected. As a consequence, the formula “ C_2H_3 ” for methyl has to be transformed to 2CH_3 , “ C_4H_5 ” for ethyl to $2\text{C}_2\text{H}_5$, “SnI” for stannous iodide to SnI_2 , “ SnI_2 ” for stannic iodide to SnI_4 , “ SnC_4H_5 ” for stanethylum to $[\text{Sn}(\text{C}_2\text{H}_5)_2]_n$, “ $\text{C}_4\text{H}_5\text{SnO}$ ” for oxide of stanethylum to $[(\text{C}_2\text{H}_5)_2\text{SnO}]_n$, “ $\text{C}_4\text{H}_5\text{SnI}$ ” for iodide of stanethylum to $(\text{C}_2\text{H}_5)_2\text{SnI}_2$, “ $\text{Sn}_2(\text{C}_4\text{H}_5)_3\text{Cl}$ ” for chloride of distannic triethyl to $2\text{Sn}(\text{C}_2\text{H}_5)_3\text{Cl}$, “ $\text{Sn}_2(\text{C}_4\text{H}_5)_3\text{O,HO}$ ” for oxide of sesquistannethylum to $2(\text{C}_2\text{H}_5)_3\text{SnOH}$, etc.

As another aspect, attention must be paid to the denomination radical in reports of the 19th century. Nowadays this term is applied for a species with an unpaired electron, however, this concept did not exist yet when the first organotin compounds were synthesized. In that era an organic radical was considered as an immutable assembly of atoms which was preserved upon chemical reactions [16]. Examples were methyl or ethyl radicals, i.e. methyl or ethyl groups in present-day notations. Around 1850, efforts were undertaken to isolate such radicals [16–19], while it was also discussed if radicals indeed consist of unalterable groups of atoms [20]. Frankland reported in 1849 [18] that Löwig had tried to obtain free ethyl radicals by treatment of chloroethane with potassium but did not succeed. Presumably Löwig intended to make use of the high reactivity of potassium and its affinity to chlorine in order to isolate ethyl according to the reaction $\text{Cl-ethyl} + \text{K} \rightarrow \text{KCl} + \text{ethyl}$. However, Frankland believed [18] that pure methyl radical had been isolated previously by the action of potassium upon “cyanide of ethyl” (a compound with the atomic ratio of C:H:N of 3:5:1 [21]) [17], whereat the high reactivity of potassium led to decomposition of “ C_4H_5 ” (ethyl) into “ C_2H_3 ” (methyl) and “ C_2H_2 ” [18]. Accordingly, Frankland attempted to isolate the ethyl radical employing milder agents in order to avoid decomposition of ethyl, and used consequently iodoethane (he was aware that the bond strength between ethyl and iodine was weaker than that with chlorine) and metals with lower oxidation potential (“less electro-positive character”) [18]. In the course of those experiments, it was briefly noted that tin reacted with iodoethane in temperature regions of 150–200 °C to yield a crystalline mass, which was, however, not analyzed [18]. Yet three years later analytical results of such crystals after purification were presented, disclosing $(\text{C}_2\text{H}_5)_2\text{SnI}_2$ [22,23], and in the same period reactions involving iodoethane and tin gave rise to synthesis of other organotin compounds [9,22] (see below). Thus the diversity of tin compounds became significantly extended as previously only a limited number of tin compounds was known, all of inorganic nature, such as tin oxides and oxide hydrates, tin sulfides, SnCl_2 , SnCl_4 and SnI_2 [2].

2. Initial organotin chemistry

2.1. Alkyltin halides

Frankland described the synthesis of $(\text{C}_2\text{H}_5)_2\text{SnI}_2$ (iodide of stanethylum) in detail in 1852 [22]. Tin foil was cut into narrow slips and exposed to iodoethane in sealed tubes. Conducting the reaction at 180 °C evoked danger of explosion. Therefore, synthesis under the action of light for a few days at moderate temperatures was preferred. For this purpose, bright sunlight was concentrated by means of an 18-inch parabolic reflector to the reaction tube which was placed near the focus and immersed in water to keep the reaction temperature near room temperature. Alternately, copper(II) sulfate solution was applied to remove a part of the solar radiation in the visible spectral range. Toward the end of the reaction, temperature was risen by 20–30 °C above ambient temperature. After a purification procedure, $(\text{C}_2\text{H}_5)_2\text{SnI}_2$ was obtained as transparent, slightly straw-colored needles.

At the same time (1852), Cahours and Riche, inspired by experiments of Frankland (see Introduction), exposed tin flakes to iodoethane (éther iodhydrique) at 160–180 °C in a sealed tube for 20–24 h [23]. The formed $(\text{C}_2\text{H}_5)_2\text{SnI}_2$ (iodure de stannéthyle) was separated from the reaction mixture by dissolution in ethanol and was after subsequent steps finally obtained as colorless needles [23]. This reaction was apparently optimized later, when 2.5–3 parts iodoethane per part of tin (probably mass parts) were converted at 150 °C for 20–30 h to yield prismatic crystals of $(\text{C}_2\text{H}_5)_2\text{SnI}_2$ [24]. Furthermore, exposure of $[\text{Sn}(\text{C}_2\text{H}_5)_2]_n$ (see below) to iodine in diethylether also resulted in formation of $(\text{C}_2\text{H}_5)_2\text{SnI}_2$ by Löwig [9].

Ethanol solutions of $(\text{C}_2\text{H}_5)_2\text{SnI}_2$ were found to react with silver sulfate, silver nitrate, silver acetate or silver cyanide, presumed under release of silver iodide [24]. In addition, exposure of ethanolic $(\text{C}_2\text{H}_5)_2\text{SnI}_2$ solutions to oxalic acid or oxalates led to white precipitates [24]. However, analyses of the corresponding reaction products were not reported.

Within the following years, a number of organotin halides of the formula R_2SnX_2 and R_3SnX (with $\text{R} = \text{C}_2\text{H}_5$ or CH_3 and $\text{X} = \text{I}$, Br or Cl) were prepared by a variety of synthetic routes, as indicated in Table 1. These include direct reaction of iodoalkanes with tin, conversion of oligo(dialkylstannane)s or poly(dialkylstannane)s with bromine or iodine, dialkyltin oxides with hydrochloric acid or hydrobromic acid, trialkyltin hydroxides with hydrochloric acid or hydrobromic acid, and tetraalkylstannanes and iodine or tin tet-

Table 1

Dialkyltin dihalides and trialkyltin halides reported between 1852 and 1860.

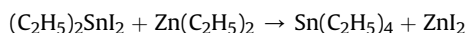
Compound	Method of synthesis	References
$(\text{C}_2\text{H}_5)_2\text{SnI}_2$	Irradiation or heating of $\text{Sn}/\text{C}_2\text{H}_5\text{I}$ mixtures $[\text{Sn}(\text{C}_2\text{H}_5)_2]_n$ and I_2 in diethylether	[22–24] [9]
$(\text{C}_2\text{H}_5)_2\text{SnBr}_2$	$[\text{Sn}(\text{C}_2\text{H}_5)_2]_n$ and Br_2 in ethanol $[(\text{C}_2\text{H}_5)_2\text{SnO}]_n$ and HBr (aq)	[22] [24]
$(\text{C}_2\text{H}_5)_2\text{SnCl}_2$	Probably $[(\text{C}_2\text{H}_5)_2\text{SnO}]_n$ and HCl (aq) (only analysis reported)	[24]
$(\text{CH}_3)_2\text{SnI}_2$	Heating of 2.5–3 parts CH_3I per part Sn in sealed tubes at 150–160 °C, after extended sample workup and fractionation	[24]
$(\text{CH}_3)_2\text{SnBr}_2$	$[(\text{CH}_3)_2\text{SnO}]_n$ and HBr (aq)	[24]
$(\text{CH}_3)_2\text{SnCl}_2$	$[(\text{CH}_3)_2\text{SnO}]_n$ and HCl (aq)	[24]
$(\text{C}_2\text{H}_5)_3\text{SnI}$	$\text{Sn}(\text{C}_2\text{H}_5)_4$ and I_2 Side product from exposure of $\text{C}_2\text{H}_5\text{I}$ to Sn or, more efficiently, to Na/Sn alloys	[25] [24]
$(\text{C}_2\text{H}_5)_3\text{SnBr}$	$(\text{C}_2\text{H}_5)_3\text{SnOH}$ and HBr (aq)	[24]
$(\text{C}_2\text{H}_5)_3\text{SnCl}$	$(\text{C}_2\text{H}_5)_3\text{SnOH}$ and HCl (aq) 3 equiv $\text{Sn}(\text{C}_2\text{H}_5)_4$ per equivalent SnCl_4	[24] [27,28]
$(\text{CH}_3)_3\text{SnI}$	Heating of 2.5–3 parts CH_3I per part Sn in sealed tubes at 150–160 °C, after extended sample workup and fractionation	[24]

rachloride (as referred to below in more detail).

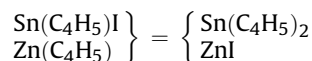
Notably, there was no systematic search for compounds of the formula $R\text{SnX}_3$ at that time. Related compounds would have corresponded to dinuclear compounds in then used formulae, such as “ $\text{Sn}_2(\text{C}_4\text{H}_5)\text{X}_3$ ” for $R = \text{ethyl}$ or “ $\text{Sn}_2(\text{C}_2\text{H}_5)\text{X}_3$ ” for $R = \text{methyl}$, i.e. substances which were in those terms not of straightforward mononuclear nature and therefore probably less obvious to exist potentially.

2.2. Tetraalkylstannanes

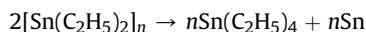
By 1859, Frankland realized that compounds of the composition SnX_2 were known for $X = \text{I}$ and $X = \text{ethyl}$ while SnX_4 had been reported for $X = \text{I}$ but not for $X = \text{ethyl}$ [25]. Hence he concluded that the latter, i.e. $\text{Sn}(\text{C}_2\text{H}_5)_4$ (stannic ethide or binethide of tin), should also exist [25]. Consequently he attempted to prepare this compound, and succeeded in this purpose by means of the reaction



or in the original formulation [25]

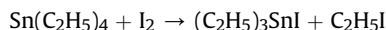


Thus $(\text{C}_2\text{H}_5)_2\text{SnI}_2$ (stannic ethiodide) crystals were added to a concentrated solution of an excess of diethylzinc in diethylether, and after workup of the reaction mixture finally $\text{Sn}(\text{CH}_2\text{CH}_3)_4$ was obtained by distillation as a colorless liquid. Also, Buckton synthesized $\text{Sn}(\text{C}_2\text{H}_5)_4$ (stannic bis-ethyle), by addition of molten $(\text{C}_2\text{H}_5)_2\text{SnI}_2$ to a retort containing $\text{Zn}(\text{C}_2\text{H}_5)_2$, and he finally obtained the product after sample workup by distillation [26]. Moreover, Frankland assumed from preliminary experiments that thermal decomposition of $\text{Sn}(\text{CH}_2\text{CH}_3)_2$ (i.e. $[\text{Sn}(\text{C}_2\text{H}_5)_2]_n$) should also yield $\text{Sn}(\text{CH}_2\text{CH}_3)_4$, according to the reaction



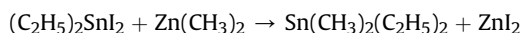
This was confirmed by Cahours, who observed formation of a liquid of the composition $\text{Sn}(\text{C}_2\text{H}_5)_4$ (distannéthyle) in this process [24], as well as by Buckton [27,28].

It was found that $\text{Sn}(\text{C}_2\text{H}_5)_4$ was not susceptible to addition reactions but to substitution reactions [25]. Thus, $(\text{C}_2\text{H}_5)_3\text{SnI}$ (stannic iodotriethide, “ $(\text{Sn}_2(\text{C}_4\text{H}_5)_3)\text{I}$ ”) was isolated by conversion of $\text{Sn}(\text{C}_2\text{H}_5)_4$ with iodine, according to the reaction



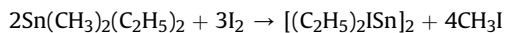
When $\text{Sn}(\text{C}_2\text{H}_5)_4$ was exposed to hydrochloric acid at 80–90 °C for 12–18 h, a gas evolved [25]. This gas was shown to be ethane and designated as hydride of ethyl, “ $\text{C}_4\text{H}_5\text{H}$ ”, i.e. ethane was considered as a combination of an ethyl moiety with a separate hydrogen atom. Besides it was supposed that in this reaction $(\text{C}_2\text{H}_5)_3\text{SnCl}$ formed as the predominant tin species [25].

As $\text{Sn}(\text{C}_2\text{H}_5)_4$ could be prepared by reaction of $(\text{C}_2\text{H}_5)_2\text{SnI}_2$ with $\text{Zn}(\text{C}_2\text{H}_5)_2$, Frankland concluded that an analogous procedure should allow synthesis of tetraalkylstannanes with a variety of alkyl groups by application of $(\text{C}_2\text{H}_5)_2\text{SnI}_2$ and ZnR_2 with $R = \text{methyl}$, pentyl (amyl) or any other homologous group (radical) [25]. He accomplished this route on the example of $R = \text{methyl}$, according to the reaction

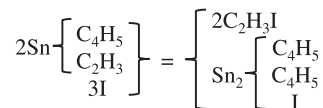


When $\text{Sn}(\text{CH}_3)_2(\text{C}_2\text{H}_5)_2$ (stannic ethylomethide) was exposed to iodine, iodomethane was detected and a product was isolated whose elemental analysis agreed well with the dinuclear

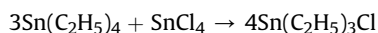
compound $(\text{C}_2\text{H}_5)_2\text{Sn}(\text{CH}_3)_2$. The formation of this product is in line with the reaction



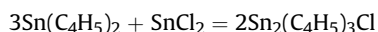
or in the original formulation [25]



Finally, Buckton reported in 1859 that $\text{Sn}(\text{C}_2\text{H}_5)_4$ (stannic diethyl) and SnCl_4 (bichloride of tin) reacted with each other to yield an oily body composed predominantly of $\text{Sn}(\text{C}_2\text{H}_5)_3\text{Cl}$ (chloride of distannic triethyl) [27,28], according to the reaction



or in the original formulation [27,28]



Notably the discovery of this type of reaction is ascribed to Kocheshkov and called Kocheshkov redistribution reaction or Kocheshkov disproportionation reaction, although Buckton referred to this reaction already decades before Kocheshkov (as we have indicated previously [29]). As a side remark, Buckton [27,28] as well as Kocheshkov [30] pointed to the strongly exothermic reaction starting upon mixing $\text{Sn}(\text{C}_2\text{H}_5)_4$ and SnCl_4 .

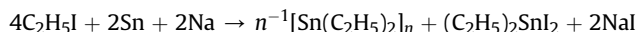
2.3. Oligostannanes and polystannanes

In extension of experiments on the synthesis of trialkylstibines and trialkyl bismuth compounds by conversion of iodoalkanes (RI with $R = \text{methyl}$, ethyl or pentyl) with potassium alloys of antimony or bismuth, Löwig explored related reactions also with tin [9]. Accordingly, he exposed iodoethane to potassium–tin and sodium–tin alloys, at different ratios of the metals in the alloys and at different reaction conditions. Quartz sand was used to control the reaction rate. Sodium–tin alloys were found to be more suited, in particular at a sodium/tin ratio of 1:6. In a complex procedure, partially in sealed reaction vessels, various products were isolated by separation procedures. However, Löwig considered only one compound to be pure, of the composition “ $\text{Sn}(\text{C}_4\text{H}_5)$ ” (Stannäthyl), i.e. $\text{Sn}(\text{C}_2\text{H}_5)_2$. Indeed, a few years later Strecker [31] arrived at the conclusion that some of the various compounds described by Löwig were identical to Stannäthyl while others were of different composition than suggested by Löwig. Remarkably, Strecker attributed the formula “ $n(\text{SnC}_4\text{H}_5)$ ” to Stannäthyl [31] which implies an oligomeric or polymeric nature. In fact, depending on the reaction conditions the procedure of Löwig may produce predominantly cyclic oligomers or considerable quantities of polymers, both of the composition $[\text{Sn}(\text{C}_2\text{H}_5)_2]_n$ [32].

Löwig gained $[\text{Sn}(\text{C}_2\text{H}_5)_2]_n$ as a highly viscous oil [9], indicating (cyclic) oligomers or polymers of low molar mass. Other experiments performed later by Cahours with a sodium/tin ratio of 1:4 also yielded, amongst others, a viscous oil of the composition $\text{Sn}(\text{C}_2\text{H}_5)_2$, and hexaethyldistannane (sesquiéthylure d’étain), $(\text{C}_2\text{H}_5)_3\text{Sn}(\text{C}_2\text{H}_5)_3$ [24]. Note that poly(dialkylstannane)s rapidly degrade in solution if not protected from light, and in this process cyclic oligo(dialkylstannanes)s can be formed, depending on the conditions [33]. Thus, if Löwig or Cahours obtained

poly(diethylstannane) of high molar mass subsequent degradation upon workup of the reaction products was expected because there is no evidence that those authors carried out their operations under exclusion of light.

Löwig considered “Sn(C₄H₅)” as a new radical (in the sense of a firm moiety) and provided two possible explanations for its formation [9]. One explanation based on direct formation of [Sn(C₂H₅)₂]_n by reaction of iodoethane with Na/Sn alloy under release of sodium iodide. The primary formed [Sn(C₂H₅)₂]_n was supposed to react again with iodoethane to yield (C₂H₅)₂SnI₂ while the ethyl groups thus generated by decomposition of iodoethane were assumed to react with tin to form [Sn(C₂H₅)₂]_n. In the second explanation, the reaction was proposed to proceed as follows:

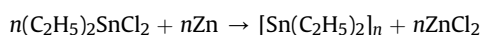


or in the original formulation (Ae = ethyl, i.e. “C₄H₅”, Jd = I, note that the relative atomic masses of Sn and C compared to H differ by a factor of 2 to the presently established values, in contrast to those of Na and I) [9]



The formed (C₂H₅)₂SnI₂ was thought to be subsequently reduced completely or partially by sodium [9]. In fact, a related path was established decades later on the example of poly(dimethylstannane) synthesis by reaction of (C₂H₅)₂SnBr₂ with sodium [34].

Frankland synthesized [Sn(C₂H₅)₂]_n by a different method. Upon treatment of a zinc strip with a compound supposed to be (C₂H₅)₂SnCl₂ at application of a gentle heat a thick, heavy oil assembled at the bottom of the reaction vessel, which could be removed from the supernatant liquid with a pipette [22]. The analysis of this oil, of a yellow color (characteristic for poly-(dialkylstannane)s) disclosed the elemental composition Sn(C₂H₅)₂ (stanethylium) and was assumed to be formed according to the reaction (using actual notation) [22]:

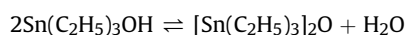


2.4. Alkyltin oxides, hydroxides, nitrates, carboxylates and sulfates

Dialkyltin oxides with linear alkyl groups ranging from methyl to at least butyl are in fact polymers of complicated structure comprising penta-coordinated tin atoms [35]. Such materials of the composition [(C₂H₅)₂SnO]_n (oxide of stanethylium) were synthesized in the middle of the 19th century when (C₂H₅)₂SnI₂ was treated with ammonia solution to yield a precipitate which was heated with ammonia for a few minutes, filtered and washed with water [22]. Similarly, [(C₂H₅)₂SnO]_n (oxyde de stannéthyle) was obtained when a gel resulting by treatment of (C₂H₅)₂SnI₂ with ammonia was washed on a filter with water and then with hot ethanol [24]. In a different route, a solution of [Sn(CH₂CH₃)₂]_n in diethylether was allowed to stand in the air and the solvent was subsequently evaporated, whereupon [(C₂H₅)₂SnO]_n (Stannäthyloxyd) formed [9]. [(C₂H₅)₂SnO]_n was found to be white [9,24] and insoluble in water, ethanol and diethylether but soluble in solutions of various acids [22,24]. Also, the corresponding methyl derivative, [(CH₃)₂SnO]_n, was prepared by one of the above methods, namely by treatment of (CH₃)₂SnI₂ with ammonia [24].

A polymeric structure with penta-coordinated tin atoms has been established in the solid state for (C₂H₅)₃SnOH [36], which may be regarded as a coordination polymer with hydroxide groups acting as bridging units to (C₂H₅)₃Sn⁺ ions. In water, however, the dissolved materials are likely not to persist as polymers, because (C₂H₅)₃SnOH

(and other trialkyl compounds with an anionic forth group) may dissociate in (C₂H₅)₃Sn(H₂O)_n⁺ [37]. A compound of the composition (C₂H₅)₃SnOH (oxyde de sesquistannéthyle) was synthesized by Cahours in 1860 by exposure of (C₂H₅)₃SnI to aqueous potassium hydroxide solution [24]. Upon partial evaporation of water by heating, (C₂H₅)₃SnOH precipitated, and after a purification procedure colorless prisms were obtained. The chemical formula of this compound was indicated as “Sn₂(C₄H₅)₃O,OH” (note that “OH” corresponds to present-day H₂O, see Introduction). Thus, (C₂H₅)₃SnOH was considered to be a hydrate [24]. This view appeared to be confirmed by evolution of water upon heating, yielding an oily substance, which transformed again to the initial material upon addition of water [24]. However, these phenomena reflect instead another process. (C₂H₅)₃SnOH condenses in dry atmosphere to generate the oily dinuclear compound (C₂H₅)₃SnOSn(C₂H₅)₃, which again reacts in ambient humidity to form the hydroxide again, according to the equilibrium reaction [38]



Analogously, (CH₃)₃SnOH was synthesized [24]. The dialkyltin oxides and trialkyltin hydroxides were used as a source for the synthesis of organotin nitrates, sulfates and carboxylates (Table 2). For this purpose [(C₂H₅)₂SnO]_n, [(CH₃)₂SnO]_n, (C₂H₅)₃SnOH and (CH₃)₃SnOH were converted with acids of the type H₂X or HY.

Finally, as an alternative route for the synthesis of organotin sulfates or nitrates, combination of dialkyltin diiodides or trialkyltin iodides with silver salts was employed (Table 2). This method yielded the compounds R₂Sn(NO₃)₂ and (R₃Sn)₂SO₄ with R = methyl and ethyl.

3. Conclusions

Driven by the search for isolation of free alkyl groups (then termed as radicals), tin and iodoethane were combined at high temperatures in 1849. Yet instead of free ethyl, (C₂H₅)₂SnI₂ was obtained, probably the first reported organotin compound, which was, however, characterized by elemental analysis only in 1852. In the same year, trialkylstibine and trialkyl bismuth chemistry was attempted to be transferred to tin on the example of reaction of iodoethane with potassium–tin and sodium–tin alloys. These experiments yielded [(C₂H₅)₂Sn]_n, whereat rather (cyclic) oligostannanes than polystannanes were finally obtained, while polystannanes might have

Table 2

Overview on dialkyltin and trialkyltin compounds with sulfates, oxalates, nitrates and carboxylates [24].

Compound	Method of synthesis
(C ₂ H ₅) ₂ SnSO ₄	Exposure of [(C ₂ H ₅) ₂ SnO] _n to dilute sulfuric acid
(C ₂ H ₅) ₂ Sn(C ₂ O ₄)	[(C ₂ H ₅) ₂ SnO] _n and oxalic acid
(C ₂ H ₅) ₂ Sn(NO ₃) ₂	(C ₂ H ₅) ₂ SnI ₂ and ammonium oxalate
(C ₂ H ₅) ₂ Sn(CHOO) ₂	[(C ₂ H ₅) ₂ SnO] _n and HNO ₃ solution
(C ₂ H ₅) ₂ Sn(CH ₃ COO) ₂	[(C ₂ H ₅) ₂ SnO] _n and dilute formic acid
(C ₂ H ₅) ₃ Sn(CHOO)	[(C ₂ H ₅) ₂ SnO] _n and dilute acetic acid
(C ₂ H ₅) ₃ Sn(CH ₃ COO)	(C ₂ H ₅) ₃ SnOH and formic acid
(C ₂ H ₅) ₃ Sn(C ₃ H ₇ COO)	(C ₂ H ₅) ₃ SnOH and acetic acid
[(C ₂ H ₅) ₃ Sn] ₂ SO ₄	(C ₂ H ₅) ₃ SnOH and butyric acid
[(C ₂ H ₅) ₃ Sn] ₂ (C ₂ O ₄)	(C ₂ H ₅) ₃ SnOH and dilute sulfuric acid
(CH ₃) ₂ SnSO ₄	(C ₂ H ₅) ₃ SnI and Ag ₂ SO ₄ solution
(CH ₃) ₃ Sn(CHOO)	Ethanol solution of (C ₂ H ₅) ₃ SnOH and oxalic acid
(CH ₃) ₃ Sn(CH ₃ COO)	[(CH ₃) ₂ SnO] _n and dilute sulfuric acid
(CH ₃) ₃ Sn(C ₃ H ₇ COO)	Ethanol solution of (CH ₃) ₂ SnI ₂ and Ag ₂ SO ₄
[(CH ₃) ₃ Sn] ₂ SO ₄	(CH ₃) ₃ SnOH and formic acid
	(CH ₃) ₃ SnOH and acetic acid
	(CH ₃) ₃ SnOH and butyric acid
	(C ₂ H ₅) ₃ SnOH and sulfuric acid
	(C ₂ H ₅) ₃ SnI and Ag ₂ SO ₄ solution

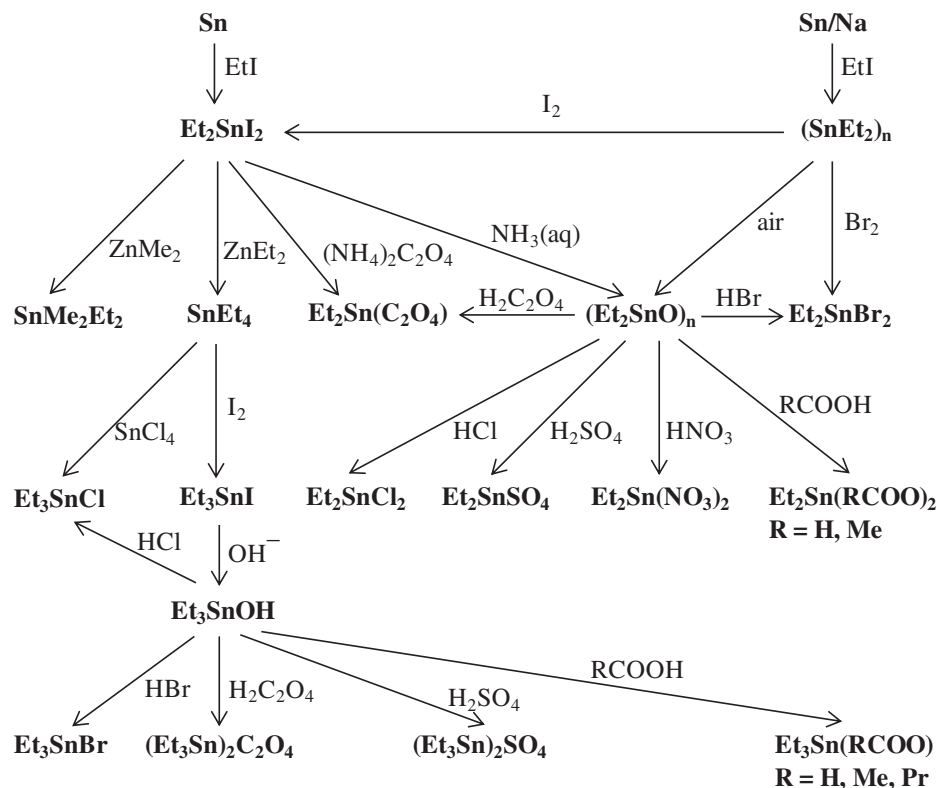


Fig. 1. Overview on reactions for generation of ethyltin derivatives up to the year of 1860. Me = methyl, Et = ethyl, Pr = propyl. Generation of SnEt_4 was also reported to originate upon thermal decomposition of $(\text{SnEt}_2)_n$ (see text). Not included are reactions leading to dinuclear compounds. A number of methyltin derivatives were prepared analogously.

formed initially and subsequently degraded under the action of light. Moreover, $(\text{C}_2\text{H}_5)_2\text{SnO}$, of the polymeric structure $[(\text{C}_2\text{H}_5)_2\text{SnO}]_n$, was prepared from the initially synthesized organostannanes either by exposure of $(\text{C}_2\text{H}_5)_2\text{SnI}_2$ to an alkaline solution or by oxidation of $[(\text{C}_2\text{H}_5)_2\text{Sn}]_n$ in the air.

In the following years, $(\text{C}_2\text{H}_5)_2\text{SnI}_2$, $[(\text{C}_2\text{H}_5)_2\text{Sn}]_n$ and $[(\text{C}_2\text{H}_5)_2\text{SnO}]_n$ as well as the related methyl derivatives $(\text{CH}_3)_2\text{SnI}_2$ and $[(\text{CH}_3)_2\text{SnO}]_n$ were employed as starting materials for the synthesis of other organotin compounds, some of which were converted further (examples in Fig. 1). Thus a variety of dialkyltin and trialkyltin derivatives were obtained. These include compounds of the type R_2SnX_2 ($\text{R} = \text{ethyl or methyl}$, $\text{X} = \text{Cl, Br, nitrate or carboxylates}$), $(\text{C}_2\text{H}_5)_2\text{Sn}(\text{C}_2\text{O}_4)$, R_2SnSO_4 , $\text{Sn}(\text{CH}_3)_2(\text{C}_2\text{H}_5)_2$ and $\text{Sn}(\text{C}_2\text{H}_5)_4$, as well as compounds of the type R_3SnI ($\text{R} = \text{ethyl or methyl}$, $\text{X} = \text{I, Cl, Br, OH, or carboxylates}$), $[(\text{C}_2\text{H}_5)_3\text{Sn}]_2(\text{C}_2\text{O}_4)$ and $[(\text{C}_2\text{H}_5)_3\text{Sn}]_2\text{SO}_4$. Formation of dinuclear tin compounds such as $(\text{C}_2\text{H}_5)_2\text{ISn-Sn}(\text{C}_2\text{H}_5)_2\text{I}$, $(\text{C}_2\text{H}_5)_3\text{Sn-Sn}(\text{C}_2\text{H}_5)_3$ and $(\text{C}_2\text{H}_5)_3\text{SnOSn}(\text{C}_2\text{H}_5)_3$ was also indicated. Besides addition and substitution reactions applied for synthesis of organotin compounds, the so-called Kocheshkov redistribution reaction (Kocheshkov comproportionation) was discovered by Buckton, who therewith generated $(\text{C}_2\text{H}_5)_3\text{SnCl}$.

The above examples illustrate that some organotin basic structures were established within only ten years. Concomitantly various different synthesis routes in organotin chemistry were introduced. These factors constituted a solid fundament for development of organotin chemistry.

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