Journal of Organometallic Chemistry 751 (2014) 20–24

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Initial organotin chemistry

Walter Caseri

Eidgenössische Technische Hochschule Zürich (ETH), Department of Materials, Wolfgang-Pauli-Strasse 10, 8093 Zürich, Switzerland

ARTICLE INFO

Article history:
Received 30 May 2013
Received in revised form
5 August 2013
Accepted 6 August 2013

Keywords:
Historical perspective
Organotin chemistry
Organotin compounds
Organotin halides
Oxides and hydroxides
Organometallic polymers

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.

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

E-mail address: walter.caseri@mat.ethz.ch.

0022-328X/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jorganchem.2013.08.009

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 $2C_2H_5$, "SnI" for stannous iodide to SnI_2, "SnI_2" for stannic iodide to SnI_4, "SnC_4H_5" for stanethylium to $[Sn(C_2H_5)_2]_n$, "C_4H_5SnO" for oxide of stanethylium to $[(C_2H_5)_2SnO]_n$, "C_4H_5SnI" for iodide of stanethylium to $(C_2H_5)_2SnI_2$, "$Sn_2(C_4H_5)_3Cl$" for chloride of distannic triethyl to $2Sn(C_2H_5)_3Cl$, "$Sn_2(C_4H_5)_3$,O,HO" for oxide of sesquistannethylium to $2(C_2H_5)_3SnOH$, 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 Cl–ethyl + K → KCl + 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 $(C_2H_5)_2SnI_2$ [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 $(C_2H_5)_2SnI_2$ (iodide of stanethylium) 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, $(C_2H_5)_2SnI_2$ 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 $(C_2H_5)_2SnI_2$ (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 $(C_2H_5)_2SnI_2$ [24]. Furthermore, exposure of $[Sn(C_2H_5)_2]_n$ (see below) to iodine in diethylether also resulted in formation of $(C_2H_5)_2SnI_2$ by Löwig [9].

Ethanolic solutions of $(C_2H_5)_2SnI_2$ 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 $(C_2H_5)_2SnI_2$ 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 $R = C_2H_5$ or CH_3 and X = 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
Dialkyltindihalides and trialkyltin halides reported between 1852 and 1860.

Compound	Method of synthesis	References
$(C_2H_5)_2SnI_2$	Irradiation or heating of Sn/C_2H_5I mixtures	[22–24]
	$[Sn(C_2H_5)_2]_n$ and I_2 in diethylether	[9]
$(C_2H_5)_2SnBr_2$	$[Sn(C_2H_5)_2]_n$ and Br_2 in ethanol	[22]
	$[(C_2H_5)_2SnO]_n$ and HBr (aq)	[24]
$(C_2H_5)_2SnCl_2$	Probably $[(C_2H_5)_2SnO]_n$ and HCl (aq) (only analysis reported)	[24]
$(CH_3)_2SnI_2$	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]
$(CH_3)_2SnBr_2$	$[(CH_3)_2SnO]_n$ and HBr (aq)	[24]
$(CH_3)_2SnCl_2$	$[(CH_3)_2SnO]_n$ and HCl (aq)	[24]
$(C_2H_5)_3SnI$	$Sn(C_2H_5)_4$ and I_2	[25]
	Side product from exposure of C_2H_5I to Sn or, more efficiently, to Na/Sn alloys	[24]
$(C_2H_5)_3SnBr$	$(C_2H_5)_3SnOH$ and HBr (aq)	[24]
$(C_2H_5)_3SnCl$	$(C_2H_5)_3SnOH$ and HCl (aq)	[24]
	3 equiv $Sn(C_2H_5)_4$ per equivalent $SnCl_4$	[27,28]
$(CH_3)_3SnI$	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]