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# A CONVENIENT SYNTHESIS OF MONOOCTYLTIN(IV) COMPOUNDS FROM 1-, 2-, OR 3-OCTENES

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## Summary

Zirconocene (n-octyl) chloride, $[(\eta^5\text{-}C_5H_5)_2Zr(\text{n-Oct})Cl]$, prepared in situ from 1-, 2-, or 3-octene and zirconocene hydrogen chloride, has been found to react smoothly with 0.5 molar equivalents of stannic chloride to give moderate to high yields of n-octyltin(IV) trichloride at room temperature.

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## Introduction

Monooctyltin(IV) compounds have in recent years been used as additives in dioctyltins used for stabilizing polyvinyl chloride plastics, often being introduced in amounts approaching 30 wt.% [1,2]. The important halide intermediates for these two octyltin compounds are prepared industrially by the Kocheskov redistribution reaction using tetra(n-octyl)tin(IV) and tin tetrahalide in the appropriate stoichiometries [3]. However, it is difficult to obtain the monooctyltin halides in reasonable yields by this method at the reaction temperatures of about 200 °C. An alternative synthesis described in the patent literature involves the oxidative addition of octyl halides to stannous halides in the presence of quaternary ammonium or phosphonium catalysts [4], or trialkylantimony compounds [5]. These reactions, in general, occur more readily with organic bromides and stannous bromide than with the corresponding chlorides, and in the case of n-$OctSnBr_3$ gives over 90% yield with $Et_3Sb$ as catalyst (18 h, 150 °C, $N_2$ atmosphere) [5].

An attempted ambient temperature synthesis of monoorganotin trichlorides involving the addition of trichlorostannane, $[HSnCl_3]$, to olefins was found to afford rather poor yields (< 10%), but high yields were obtained when carbonyl-activated olefins were used [6,7]. The $[HSnCl_3]$ reagent required for this purpose is conveniently generated in situ by passing gaseous anhydrous HCl into an ethereal solution of $SnCl_2$ at 20 °C, and the method is already in use commercially for the production of "estertins" (AKZO process). The apparent failure of the AKZO reaction with non-activated olefins can be readily attributed to the competitive

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addition of HCl to the olefinic double bonds and to self-polymerisation in the case of some olefins. Procedures aimed at external activation of the olefinic bonds have generally not proved fruitful. Thus, we have found that the organometallic moiety, $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]^+$, which is known to form $\pi$-bonded complexes with olefins [8] and consequently deactivate them towards electrophilic attack [9,10], when used with 1-octene under the AKZO conditions leads to formation of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2SnCl_3]$ to the virtual exclusion of any octyltin compound [11]. This led us next to explore the use of zirconocene hydrogen chloride, $[(\eta^5\text{-}C_5H_5)_2Zr(H)Cl]$, {[Zr]*H*}, a reagent known to react under mild conditions with a variety of olefins to form isolable alkylzirconium(IV) complexes, $[(\eta^5\text{-}C_5H_5)_2Zr(R)Cl]$, {[Zr]*R*}, in which the zirconium is attached to the least-hindered primary carbon, irrespective of the original location of the double bond in the olefin chain [12–14]. We report here the results of our investigation on the synthesis of n-octyltin trichloride by this route.

## Experimental

### *Reaction of [Zr]octyl with $SnCl_4$*

In a typical experiment, a mixture of 15 ml benzene, 0.60 g (2.3 mmol) of [Zr]*H* and 0.26 g (2.3 mmol) of 1-octene, was stirred for ca. 2 h at room temperature under nitrogen until a clear yellow solution of [Zr]*octyl* resulted. A solution of 0.27 g (1.1 mmol) anhydrous $SnCl_4$ in 5 ml of n-hexane was then added dropwise, and after stirring for a further 1 h 30 ml of n-hexane were added to precipitate the zirconocene dichloride by-product, which was filtered off (ca. 0.55 g, m.p. 245–247 °C (dec)). The filtrate was concentrated and the residue extracted with 3 × 10 ml n-hexane. The combined extracts were concentrated and made up to 100 ml with methanol to give a solution, subsequently referred to as the stock solution. An aliquot of this solution was used to determine the monooctyltin content by titration with EDTA [15]. Thus, 10 ml of the stock solution was pipetted into a conical flask containing 30 ml each of methanol and chloroform and after thorough mixing. ca. 16 drops of 0.1% methanolic pyrocatechol violet indicator were added, and the resulting blue solution titrated with 0.02 *M* EDTA solution to a reddish-violet end-point. The titration was carried out in triplicate. The presence of dioctyltin(IV) compounds (detected here only in trace amounts by TLC: silica gel, elution with 9/1 chloroform-acetic acid) does not interfere with the titrimetric analysis. That the monooctyltin(IV) compound formed in the reaction was indeed $n\text{-}OctSnCl_3$ was confirmed by isolation of the complex, $n\text{-}OctSnCl_3 \cdot phen$, which was formed immediately when an aliquot of the stock solution (ca. 30 ml) was added to ca. 10 ml of a methanolic solution of 0.13 g of 1,10-phenanthroline · $H_2O$. Anal Found: C, 46.61; H, 4.88; N, 5.30. $C_{20}H_{25}N_2Cl_3Sn$ calcd.: C, 46.32; H, 4.82; N, 5.40%. m.p. 231–233 °C (dec).

### *Attempted reaction of [Zr]octyl with $n\text{-}OctSnCl_3$*

This reaction, performed with 1 or 2 equivalents of $n\text{-}OctSnCl_3$ in the manner described above for $SnCl_4$, yielded no $n\text{-}Oct_2SnCl_2$ even under reflux in the presence of added solvents such as $n\text{-}Bu_2O$ and DMF. An attempt was also made to generate octylcopper(I) from [Zr]*octyl* to facilitate the formation of $n\text{-}Oct_2SnCl_2$ from the monochloride. However, the attempted transmetalation involving reaction of [Zr]*octyl* with a stoichiometric amount of CuI in sulfolane at 0°C was unsuccessful (in contrast to the success reported with alkenylzirconocene chloride [16]).

## Results and discussion

Table 1 summarises the results of the experiments using [Zr]*H*. Although the yields were not optimised, the following observations are noteworthy:

(a) A 2/1 stoichiometry of [Zr]*H* to $SnCl_4$ is required to obtain moderate to high yields of n-$OctSnCl_3$;

(b) The reaction offers a clean route to monooctyltin trichloride, only trace amounts of dioctyltin dichloride being detected by TLC analysis;

(c) The somewhat lower yields with the 2- and 3-octenes are probably explicable in terms of their slower reaction with [Zr]*H* at room temperature; the identity of the n-$OctSnCl_3$ product formed in each case with the octene isomers was established by preparation of the adduct n-$OctSnCl_3$-1,10-phenanthroline;

(d) Whereas increasing the ratio [Zr]*H*/$SnCl_4$ to 4/1 gave approximately equal amounts (35%) of monooctyltin trichloride and dioctyltin dichloride, use of n-$OctSnCl_3$ in place of $SnCl_4$ did not lead to formation of dioctyltin dichloride even under somewhat forcing conditions;

(e) A reasonable yield of the corresponding monoorganotin trichloride was obtained from styrene, but methyl methacrylate yielded no organotin product, presumably because of the preferential attack of [Zr]*H* at the carbonyl rather than the olefinic site [13].

The above results indicate that organozirconium(IV) compounds are weak alkylating agents towards $SnCl_4$ compared with organolithium or Grignard reagents.

TABLE 1

SYNTHESIS OF MONOORGANOTIN(IV) TRICHLORIDES VIA ORGANOZIRCONIUM(IV) DERIVATIVES OF OLEFINS [a]

| Olefin | Mole ratio ([Zr]*H*/$SnCl_4$) [b] | Yield (%) $RSnCl_3$ [c] |
|---|---|---|
| 1-Octene | 1 | 43 |
| (*Z*/*E*)-2-Octene | 1 | 25 |
| (*Z*)-3-Octene | 1 | 21 |
| 1-Octene | 2 | 81 |
| (*Z*/*E*)-2-Octene | 2 | 58 |
| (*Z*)-3-Octene | 2 | 61 |
| 1-Octene | 4 | 35 [d] |
| 1-Octene | 2 | 76 [e] |
| 1-Octene | 2 | 65 [f] |
| 1-Octene | 2 | 62 [g] |
| Styrene | 2 | 59 |
| Methyl methacrylate | 2 | n.d. [h] |

[a] Reaction carried out at room temperature under nitrogen. [b] [Zr]*H* denotes $(\eta^5\text{-}C_5H_5)_2Zr(H)Cl$. [c] Yield determined by EDTA titration using pyrocatechol violet as indicator [15] and based on $SnCl_4$ used; the presence of dioctyltins does not interfere with the determination. [d] Yield of $Oct_2SnCl_2$ estimated by conversion into dioctyltin oxide is 35%. [e] Refluxed for 1 h following addition of $SnCl_4$. [f] In the presence of added DMF (5/1 mole ratio w.r.t. $SnCl_4$). [g] In the presence of added $I_2$ (1/10 mole ratio w.r.t. $SnCl_4$). [h] n.d. denotes not detected.

Although the exact mechanism of the reaction is unknown, it is unlikely that [$HSnCl_3$] is involved as an intermediate, since the addition of $SnCl_4$ to [Zr]*H* followed by the addition of octene did not produce any octyltin compound at ambient or reflux temperatures. An appealing feature of the present investigation is that the zirconocene dichloride, [$(\eta^5\text{-}C_5H_5)_2ZrCl_2$], which is obtained as a by-product, can be reconverted into the reactant [Zr]*H*, for example, by treatment with either $LiAlH(t\text{-}BuO)_3$ or $NaAlH_2[OCH_2CH_2OMe]_2$ [14].

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