

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

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Summary

Zirconocene (n-octyl) chloride, $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Zr}(\text{n-Oct})\text{Cl}]$, 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.

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, $[\text{HSnCl}_3]$, to olefins was found to afford rather poor yields (< 10%), but high yields were obtained when carbonyl-activated olefins were used [6,7]. The $[\text{HSnCl}_3]$ 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

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, $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]^+$, which is known to form π -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 $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{SnCl}_3]$ to the virtual exclusion of any octyltin compound [11]. This led us next to explore the use of zirconocene hydrogen chloride, $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Zr}(\text{H})\text{Cl}]$, $\{[\text{Zr}]\text{H}\}$, a reagent known to react under mild conditions with a variety of olefins to form isolable alkylzirconium(IV) complexes, $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Zr}(\text{R})\text{Cl}]$, $\{[\text{Zr}]\text{R}\}$, 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 $[\text{Zr}]\text{H}$ 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 $[\text{Zr}]\text{octyl}$ 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 mono-octyltin 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 mono-octyltin(IV) compound formed in the reaction was indeed n-Oct SnCl_3 was confirmed by isolation of the complex, n-Oct $\text{SnCl}_3 \cdot \text{phen}$, 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 $\cdot \text{H}_2\text{O}$. Anal Found: C, 46.61; H, 4.88; N, 5.30. $\text{C}_{20}\text{H}_{25}\text{N}_2\text{Cl}_3\text{Sn}$ calcd.: C, 46.32; H, 4.82; N, 5.40%. m.p. 231–233°C (dec).

Attempted reaction of [Zr]octyl with n-Oct SnCl_3

This reaction, performed with 1 or 2 equivalents of n-Oct SnCl_3 in the manner described above for SnCl_4 , yielded no n-Oct $_2\text{SnCl}_2$ even under reflux in the presence of added solvents such as n-Bu $_2\text{O}$ and DMF. An attempt was also made to generate octylcopper(I) from $[\text{Zr}]\text{octyl}$ to facilitate the formation of n-Oct $_2\text{SnCl}_2$ from the monochloride. However, the attempted transmetalation involving reaction

of $[\text{Zr}]_{\text{octyl}}$ 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 $[\text{Zr}]H$. Although the yields were not optimised, the following observations are noteworthy:

- A 2/1 stoichiometry of $[\text{Zr}]H$ to SnCl_4 is required to obtain moderate to high yields of $n\text{-OctSnCl}_3$;
- The reaction offers a clean route to monooctyltin trichloride, only trace amounts of dioctyltin dichloride being detected by TLC analysis;
- The somewhat lower yields with the 2- and 3-octenes are probably explicable in terms of their slower reaction with $[\text{Zr}]H$ at room temperature; the identity of the $n\text{-OctSnCl}_3$ product formed in each case with the octene isomers was established by preparation of the adduct $n\text{-OctSnCl}_3\text{-1,10-phenanthroline}$;
- Whereas increasing the ratio $[\text{Zr}]H/\text{SnCl}_4$ to 4/1 gave approximately equal amounts (35%) of monooctyltin trichloride and dioctyltin dichloride, use of $n\text{-Oct-SnCl}_3$ in place of SnCl_4 did not lead to formation of dioctyltin dichloride even under somewhat forcing conditions;
- 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 $[\text{Zr}]H$ 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 ($[\text{Zr}]H/\text{SnCl}_4$) ^b	Yield (%) RSnCl_3 ^c
1-Octene	1	43
(<i>Z/E</i>)-2-Octene	1	25
(<i>Z</i>)-3-Octene	1	21
1-Octene	2	81
(<i>Z/E</i>)-2-Octene	2	58
(<i>Z</i>)-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 $[\text{Zr}]H$ denotes $(\eta^5\text{-C}_5\text{H}_5)_2\text{Zr(H)Cl}$. ^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 $\text{Oct}_2\text{SnCl}_2$ 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 $[\text{HSnCl}_3]$ is involved as an intermediate, since the addition of SnCl_4 to $[\text{Zr}]H$ 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, $[(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrCl}_2]$, which is obtained as a by-product, can be reconverted into the reactant $[\text{Zr}]H$, for example, by treatment with either $\text{LiAlH}(\text{t-BuO})_3$ or $\text{NaAlH}_2[\text{OCH}_2\text{CH}_2\text{OMe}]_2$ [14].

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