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THE REACTION OF ORGANOTIN HALIDES WITH ZINC. THE OCCURRENCE OF 1,2-INTERMETALLIC SHIFTS

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SUMMARY

The reaction of organotin halides with zinc proceeds via the initial formation of reactive organotin–zinc compounds. The nature of the final reaction products depends on the reaction conditions. In aprotic solvents, in the absence of strongly coordinating ligands, tetraorganotin compounds are formed via alkylation or arylation by intermediate organozinc compounds. The latter are produced by 1,2-intermetallic shifts of organic groups in the initial organotin–zinc reaction product, and from redistribution and transmetallation reactions. In the presence of proton donors, the organozinc intermediates are protolysed to the corresponding hydrocarbons. Strongly coordinating ligands prevent the 1,2-shifts, and hexaalkyl- or hexaarylditin compounds are formed. The unexpected formation of tetramethyltin from the reaction of mixed methylphenyl–tin monochlorides with zinc appears to involve a redistribution reaction between tetraorganotin compounds and zinc chloride. The reactions of diphenyltin dichloride and phenyltin trichloride with zinc give triphenyltin chloride, again via initially-formed organotin–zinc compounds.

INTRODUCTION

The reactions between organotin halides and Group I or Group II metals have been the subject of a large number of investigations[1]. These reactions have generally been assumed to involve the formation of ditin compounds, which are then converted into tin–metal compounds by reaction with an excess of the metal. (Alkyltin)zinc halides have been proposed as intermediates in the reaction of alkyltin chlorides with zinc in triethylamine solution[2]. Closer study of the reaction of organotin chlorides with zinc has shown that different products can be formed, depending on the reaction conditions[3]. In the present paper these investigations are described in detail.

RESULTS AND DISCUSSION

Triphenyltin chloride

In aprotic solvents such as diethyl ether, THF, or toluene, triphenyltin chloride does not react with zinc metal. However, when the highly reactive zinc–copper couple (Zn/Cu) of LeGoff[4] is employed in THF at room temperature, after two to three weeks tetraphenyltin, tin metal, and zinc chloride have been formed quantitatively (1).

$$4\ \mathrm{Ph_3SnCl} + 2\ \mathrm{Zn/Cu} \rightarrow 3\ \mathrm{Ph_4Sn} + \mathrm{Sn} + 2\ \mathrm{ZnCl_2} \qquad (1)$$

Since hexaphenylditin does not react with Zn/Cu under these conditions, it is not an intermediate in this reaction.

In the presence of protic reagents, such as water or methanol, under otherwise similar conditions, the reaction of triphenyltin chloride with Zn/Cu gives nearly quantitative yields of benzene and tin metal:

$$\mathrm{Ph_3SnCl} + 2\ \mathrm{Zn} + 3\ \mathrm{MeOH} \rightarrow 3\ \mathrm{C_6H_6} + \mathrm{Sn} + \mathrm{ClZnOMe} + \mathrm{Zn(OMe)_2} \qquad (2)$$

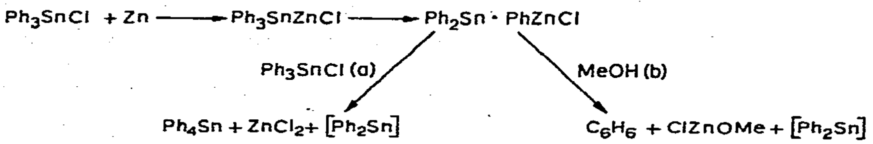
All the phenyl groups of triphenyltin chloride react to yield benzene. Since, in contrast to phenyl–zinc bonds, phenyl–tin bonds are generally only slightly susceptible to protolysis, migration of phenyl groups from tin to zinc is likely to be involved in this reaction.

In the presence of strongly coordinating ligands such as TMED or Bipy*, hexaphenylditin is the major product formed in the reaction of triphenyltin chloride with Zn/Cu:

$$2\ \mathrm{Ph_3SnCl} + \mathrm{Zn/Cu} + \mathrm{TMED} \rightarrow \mathrm{Ph_3Sn{-}SnPh_3} + \mathrm{ZnCl_2 \cdot TMED} \qquad (3)$$

In the presence of TMED the $\mathrm{Ph_6Sn_2/Ph_4Sn}$ ratio is 16, and with Bipy this ratio is 6; the yields are 65–80%.

The chemical behaviour of (triphenyltin)zinc chloride in similar solvent systems[5] readily accounts for the results of the reactions described above. The first reaction steps in THF (a), or in THF in the presence of methanol (b), can be formulated as follows:



As regards the fate of the "diphenyltin" formed in these reactions, the formation of three moles of benzene under protic conditions [eqn. (2)] excludes the possibility of disproportionation into tetraphenyltin and tin metal. In the absence of protic species, disproportionation of "diphenyltin" is not likely to occur either, since elevated temperatures and the presence of strong Lewis acids such as $\mathrm{BF_3}$ are usually required[6]. Redistribution [eqn. (4)] and transmetallation [eqn. (5)] reactions account for the stoichiometry observed in eqn. (1). In ref. 5 the redistribution equilibrium (4)

$$[\mathrm{Ph_2Sn}] + \mathrm{ZnCl_2} \leftrightarrows [\mathrm{PhSnCl}] + \mathrm{PhZnCl} \qquad (4)$$

has been discussed. "Phenyltin chloride", formed in this way, may react with Zn/Cu

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* Tetramethylethylenediamine, 2,2′-bipyridine.

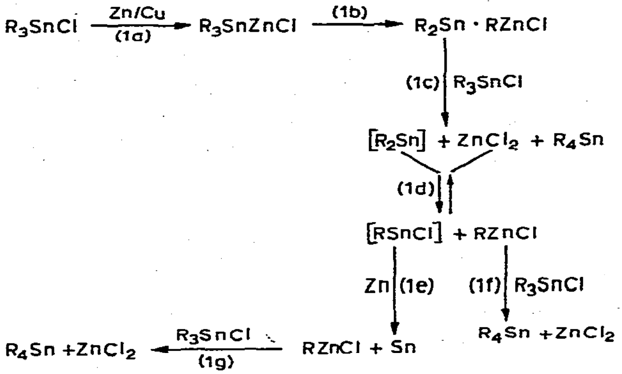
affording phenylzinc chloride and tin metal [eqn. (5), *cf.* the reaction of $SnCl_2$ with zinc], causing equilibrium (4) to shift to the right.

$$[PhSnCl] + Zn \rightarrow PhZnCl + Sn \qquad (5)$$

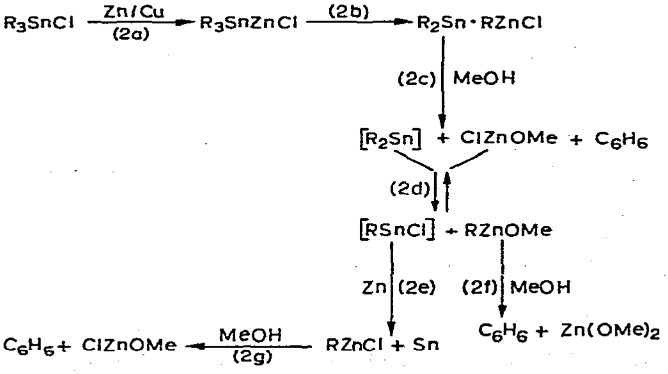
Phenylzinc chloride formed in reactions (4) and (5) reacts with triphenyltin chloride to yield tetraphenyltin.

Similar redistribution and transmetallation reactions take place in the THF/methanol system. Schemes 1 and 2 (R = Ph) account for the products formed in the reactions (1) and (2).

SCHEME 1 (aprotic conditions)



SCHEME 2 (protic conditions)



In the light of the previously reported chemistry of $Ph_3SnZnCl \cdot TMED^5$, the formation of Ph_6Sn_2 in reaction (3) is straightforward:

$$Ph_3SnCl \xrightarrow[TMED]{Zn/Cu} Ph_3SnZnCl \cdot TMED \xrightarrow{Ph_3SnCl} Ph_6Sn_2 + ZnCl_2 \cdot TMED$$

The corresponding reactions of triphenyltin bromide and iodide follow a wholly similar course.

Trimethyltin chloride

The reaction of trimethyltin chloride with Zn/Cu in THF affords tetramethyltin and tin metal in 90% yield:

$$4\ Me_3SnCl + Zn/Cu \rightarrow 3\ Me_4Sn + Sn + 2\ ZnCl_2 \qquad (6)$$

Under protic conditions (THF/methanol) 3 moles of methane and tin metal are formed:

$$Me_3SnCl + 2\ Zn/Cu + 3\ MeOH \rightarrow 3\ CH_4 + Sn + ClZnOMe + Zn(OMe)_2 \qquad (7)$$

Schemes 1 and 2 (R = Me) account for these results.

Strongly coordinating ligands do influence the course of this reaction, although not as markedly as in the corresponding reactions of triphenyltin chloride. In the presence of TMED only a small amount of hexamethylditin is formed in addition to tetramethyltin. The Me_6Sn_2/Me_4Sn ratio varied in a series of experiments from 0.03 to 0.17. The influence of Bipy is more pronounced, the Me_6Sn_2/Me_4Sn ratio varying from 1.19–1.75. Coordination saturation of the zinc atom in organotin–zinc compounds prevents the 1,2-intermetallic shift[5], and thereby also the formation of R_4Sn products. Thus, the R_6Sn_2/R_4Sn ratio increases with increasing stability of the intermediate $R_3SnZnCl \cdot L$ complexes (L = Bipy or TMED). Organozinc–Bipy complexes containing electron-donating groups bound to zinc are less dissociated than the corresponding TMED complexes[7,8]. Since the trimethyltin group is more electron donating than the triphenyltin group[9], the influence of Bipy on reactions of trimethyltin chloride with Zn/Cu in THF should be more pronounced than that of TMED, whereas in the reactions of triphenyltin chloride the influence of TMED should be the greater, as actually observed.

Methylzinc chloride is a key intermediate in Scheme 1, R = Me. The NMR spectrum of the reaction mixture of trimethyltin chloride with Zn/Cu in the presence of TMED shows the CH_3Zn signal for $MeZnCl \cdot TMED$ at δ −0.99 ppm[5]. Addition of methanol results in a fast evolution of methane and simultaneous disappearance of this signal.

The presence of $MeZnCl \cdot TMED$ in the final reaction mixture is connected with an increase in the rate of formation of (trimethyltin)zinc chloride [step (1a)], due to the presence of TMED. The following reaction with trimethyltin chloride, affording tetramethyltin [step (1c)], is very fast. Therefore trimethyltin chloride is consumed very quickly in these reactions, and is not available to react with the $MeZnCl \cdot TMED$ [steps (1f) and (1g)] formed more slowly in steps (1d) and (1e).

Dimethylphenyltin chloride and methyldiphenyltin chloride

The reaction of $Me_2PhSnCl$ with Zn/Cu in THF gives a mixture of products:

$$\begin{aligned} 4\ Me_2PhSnCl + 2\ Zn/Cu \rightarrow\ & 0.42\ Me_4Sn + 0.57\ Me_3PhSn \\ & + 1.35\ Me_2Ph_2Sn + 0.99\ Sn \qquad (8) \end{aligned}$$

A mixture is similarly obtained from the reaction of $MePh_2SnCl$:

$$\begin{aligned} 4\ MePh_2SnCl + 2\ Zn/Cu \rightarrow\ & 0.02\ Me_4Sn + 0.07\ Me_3PhSn \\ & + 0.47\ Me_2Ph_2Sn + 1.81\ MePh_3Sn + 0.78\ Sn \qquad (9) \end{aligned}$$

In the presence of methanol both compounds react with the formation of methane, benzene, and tin metal in the expected amounts:

$$\mathrm{Me_2PhSnCl + 2\ Zn/Cu + 3\ MeOH \rightarrow 2\ CH_4 + C_6H_6 + Sn} \qquad (10)$$

$$\mathrm{MePh_2SnCl + 2\ Zn/Cu + 3\ MeOH \rightarrow CH_4 + 2\ C_6H_6 + Sn} \qquad (11)$$

1,2-Shifts of organic groups (both Me and Ph)[5], redistribution and transmetallation reactions similar to those represented in Scheme 1 are involved in the formation of Me_3PhSn, Me_2Ph_2Sn and $MePh_3Sn$ in reactions (8) and (9). The formation of Me_4Sn, at first sight unexpected, is explained in terms of equilibrium (12):

$$\mathrm{Me_3PhSn + ZnCl_2 \leftrightarrows Me_3SnCl + PhZnCl} \qquad (12)$$

Me_3SnCl either is methylated by intermediate methylzinc species or may react with Zn/Cu according to eqn. (6). The reaction of mixed methyl,phenyl tetraorganotin compounds with zinc chloride has been shown to involve preferential transfer of a phenyl group. Benzene is the only hydrocarbon formed if such reactions are carried out in the presence of methanol:

$$\mathrm{Me_{\mathit{n}}Ph_{4-\mathit{n}}Sn + ZnCl_2 \xrightarrow{THF,MeOH} Me_{\mathit{n}}Ph_{3-\mathit{n}}SnCl + C_6H_6} \qquad (13)$$

Diphenyltin dichloride and phenyltin trichloride

In contrast to triphenyltin chloride, diphenyltin dichloride and phenyltin trichloride react with unactivated zinc metal at room temperature. Diphenyltin dichloride reacts with zinc powder to yield triphenyltin chloride and tin metal, according to eqn. (14).

$$\mathrm{3\ Ph_2SnCl_2 + 2\ Zn \rightarrow 2\ Ph_3SnCl + Sn + 2\ ZnCl_2} \qquad (14)$$

In the presence of methanol this reaction affords benzene and tin metal, indicating that phenyl–zinc bonds are involved:

$$\mathrm{Ph_2SnCl_2 + 2\ Zn + 2\ MeOH \rightarrow 2\ C_6H_6 + Sn + 2\ ClZnOMe} \qquad (15)$$

These results suggest that it should be possible to synthesise triphenyltin chloride from diphenyltin dichloride (or tin tetrachloride) by phenylation with phenylzinc compounds. Attempted phenylation of $SnCl_4$ with phenyllithium or phenylmagnesium bromide in 1/3 ratio leads to the formation of mixtures of phenyltin compounds containing considerable amounts of tetraphenyltin. When phenylzinc chloride was added to tin tetrachloride in a 3/1 ratio, triphenyltin chloride uncontaminated with tetraphenyltin could, in fact, be isolated in 40–50% yield.

Phenyltin trichloride reacts with zinc powder at room temperature affording triphenyltin chloride and tin metal:

$$\mathrm{3\ PhSnCl_3 + 4\ Zn \rightarrow Ph_3SnCl + 2\ Sn + 4\ ZnCl_2} \qquad (16)$$

The reactions of both diphenyltin dichloride and phenyltin trichloride with Zn/Cu yield tetraphenyltin and tin metal. Triphenyltin chloride is an intermediate, as shown by TLC. Apparently, in all these reactions 1,2-intermetallic shifts of phenyl groups from tin to zinc take place in intermediately-formed organotin–zinc compounds.

EXPERIMENTAL

General

All reactions were carried out under dry nitrogen. Elemental analyses were performed at the Microanalytical Department of the Institute for Organic Chemistry TNO, Utrecht. GLC analyses were made using the following column: 6′ Stainless Steel $\frac{1}{4}$″ O.D. filled with 10% Ucon Lubricant water-insoluble +10% Silicone Fett Bayer/H on Diatoport WAW 60–80 mesh. NMR spectra were recorded on a Varian HR 100A spectrometer. For TLC on silica gel the following solvent systems were used: system 1; cyclohexane/dioxane 1/1 (v/v) and system 2; cyclohexane/carbon tetrachloride 1/1 (v/v). The spots were detected with iodine vapour.

Starting materials

THF was distilled from $LiAlH_4$ and stored over molecular sieve 4A under nitrogen. Zinc–copper couple (Zn/Cu) was prepared according to LeGoff[4]. The washings with Et_2O were preceded by two washings with THF (50 ml portions) in order to remove the acetic acid more thoroughly. Dimethylphenyltin chloride and methyldiphenyltin chloride were prepared similarly, as described by Janssen and Luijten[10] for the corresponding ethyl derivatives. Other starting materials were prepared according to well known procedures.

TABLE 1

THE REACTIONS OF ORGANOTIN CHLORIDES WITH EXCESS Zn/Cu UNDER VARIOUS CONDITIONS

Organotin chloride/ Reactant (m/m)	*Time (days)*	*Temp. (°C)*	*Products (mol/mol of organotin chloride)*
Ph_3SnCl	19	20	Ph_4Sn (0.74), Sn (0.34)
$Ph_3SnCl/MeOH^a$	7	20	C_6H_6 (2.65), Sn (0.9)
$Ph_3SnCl/TMED$ (1/1)	2	70	Ph_6Sn_2 (0.41), Ph_4Sn (0.03), C_6H_6 (0.34), Sn (0.09)
$Ph_3SnCl/Bipy$ (1/1)	2	70	Ph_6Sn_2 (0.26), Ph_4Sn (0.06), C_6H_6 (0.62), Sn (0.29)
Me_3SnCl	2	70	Me_4Sn (0.68), Sn (0.29)
$Me_3SnCl/MeOH^a$	3	70	CH_4 (3.0)
$Me_3SnCl/TMED$ (1/1)	$\frac{1}{4}$	70	MeZnCl (0.53), Me_6Sn_2 (0.044), Me_4Sn (0.256), Sn (0.265)
$Me_3SnCl/Bipy$ (1/1)	$\frac{1}{4}$	70	Me_6Sn_2 (0.246), Me_4Sn (0.125), Sn (0.03)
$Me_2PhSnCl/MeOH^a$	1	70	CH_4 (2.05), C_6H_6 (0.89), Sn (0.9)
$MePh_2SnCl/MeOH^a$	1	70	CH_4 (1.02), C_6H_6 (1.54), Sn (0.85)
$Me_2PhSnCl$	25	20	Me_4Sn (0.1), C_6H_6 (0.14), Sn (0.24), Me_3PhSn (0.14), Me_2Ph_2Sn (0.34)
$MePh_2SnCl$	31	20	Me_4Sn (0.006), C_6H_6 (0.08), Sn (0.19), Me_3PhSn (0.16), Me_2Ph_2Sn (0.12), $MePh_3Sn$ (0.45)
$Ph_2SnCl_2{}^b$	3	20	Ph_4Sn (0.017), Ph_3SnCl (0.5)
Ph_2SnCl_2	14	20	Ph_4Sn (0.23)
$Ph_2SnCl_2/MeOH^a$	6	20	C_6H_6 (1.8), Sn (0.91)
$PhSnCl_3{}^b$	11	20	Ph_3SnCl (0.16)
$PhSnCl_3$	5	20	Ph_4Sn (0.11), Ph_3SnCl^c

[a] THF/MeOH 2/1 (v/v) was used as solvent. [b] Zinc powder in stoichiometric amount was used instead of excess Zn/Cu. [c] The exact amount was not determined.

The reactions of organotin chlorides with zinc–copper couple

The tin metal formed in these reactions forms a deposit on the Zn/Cu, effectively deactivating it towards further reaction. Therefore, repeated addition of Zn/Cu is necessary to drive the reaction to completion, and a great excess of Zn/Cu was used in all reactions unless stated otherwise. The reactions were stopped by filtration. In experiments in which tetraphenyltin and/or hexaphenylditin were formed, these products were extracted from the residue with boiling benzene. The filtration of reaction mixtures containing volatile reaction products (benzene, tetramethyltin) was carried out with suction via a cold trap (−78°); subsequently the solvent and volatiles in the filtrate were distilled into this same cold trap. The distillate was examined by GLC.

The various reaction products were identified and their quantities were determined as follows: Tetraphenyltin: m.p., mixed m.p. and TLC (systems 1 and 2). Hexaphenylditin: m.p., mixed m.p. and TLC (system 2). Mixtures of hexaphenylditin and tetraphenyltin were separated by fractional crystallisation from benzene; the residue after evaporation was analysed for tin and the ratio was calculated from the tin content. Triphenyltin chloride: m.p., mixed m.p. and TLC (system 1). Tetramethyltin: GLC and NMR (δ 0.07). Hexamethylditin: GLC and NMR (δ 0.21). Benzene: GLC. Trimethylphenyltin, dimethyldiphenyltin and methyltriphenyltin: NMR (δ 0.27; 0.47 and 0.68 ppm, respectively). Methylzinc chloride·TMED: NMR (δ −0.99 ppm) and hydrolysis (methane formation). Methane: GLC and IR. Tin metal: determined iodometrically after dissolving the metallic residue in 38% HCl.

The reactions were carried out with about 20 mmoles of organotin chloride in about 50 ml of THF. The results and reaction conditions are summarised in Table 1.

Redistribution reactions between mixed tetraorganotin compounds and zinc chloride

Trimethylphenyltin. A solution of 2.35 g (9.7 mmol) of trimethylphenyltin and 2.4 g (17.4 mmol) of anhydrous zinc chloride in 75 ml of THF and 6 ml of methanol was refluxed for 4 days. No gas evolution occurred. The volatiles were distilled into a cold (−78°) trap. The distillate contained 0.88 ml (9.9 mmol) of benzene (GLC). The residue contained trimethyltin chloride (TLC, system 1).

Dimethyldiphenyltin. A similar experiment with 2.86 g (9.45 mmol) of dimethyldiphenyltin and 4.0 g (29.3 mmol) of zinc chloride in 60 ml of THF and 6 ml of methanol yielded 1.68 ml (18.8 mmol) of benzene, and no methane, after 6 days of reaction.

Methyltriphenyltin. In a similar experiment 3.20 g (8.8 mmol) of methyltriphenyltin was reacted with 5.8 g (42.5 mmol) of zinc chloride in 90 ml of THF and 6 ml of methanol to give 1.46 ml (16.4 mmol) of benzene, no methane being evolved. Methyldiphenyltin was formed as was shown by TLC (system 1).

The preparation of triphenyltin chloride from phenylzinc chloride and tin tetrachloride

A solution of 200 mmol of phenylzinc chloride in 350 ml of Et_2O (prepared *in situ* from 0.2 mol of phenyllithium and 0.25 mol of zinc chloride) was added to 17.6 g (67 mmol) of tin tetrachloride in 200 ml of Et_2O cooled in ice. After 1 h of stirring at room temperature the mixture was hydrolysed with 250 ml of 10% HCl. The ether layer was dried on magnesium sulfate and concentrated to a small volume *in vacuo*; 12.5 g (32.5 mmol, 46%) of triphenyltin chloride with m.p. 104–105° was obtained.

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