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A highly selective synthesis of R_2SnX_2 (R = alkyl, X = Br, Cl) species directly from tin and alkyl halides *

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Abstract

The reaction: $Sn + 2RX \rightarrow SnR_2X_2$ (X = Cl, Br) occurs at relatively low temperature (80–120 °C) and with selectivities as high as 95–99% in the presence of a catalytic system formed by a crown ether and potassium iodide. The reaction is favoured by aprotic dipolar solvents such as dimethylformamide; the presence of an alkyl iodide as cocatalyst has a positive effect, the selectivity remaining unchanged.

Introduction

Dialkyltin dihalides are important starting materials for the preparation of specific organotin products used as stabilizers for polymers or as biocides [1]. The industrial preparation of these intermediates usually involves the following steps:

$$4RMgX + SnCl_4 \rightarrow SnR_4 + 4MgXCl \quad (1)$$

$$SnR_4 + SnCl_4 \rightarrow 2SnR_2Cl_2 \quad (2)$$

The direct synthesis

$$Sn + 2RX \rightarrow SnR_2X_2$$

$$(X = Cl, Br, I) \quad (3)$$

should be economically more attractive, but it takes place at relatively low temperatures only when X = I [2]. When X = Br or Cl the reaction occurs at higher temperatures, and often only in the presence of a suitable promotor containing iodine [3,4]; the best catalysts reported in literature are the onium salts and in particular the quaternary ammonium salts [5–7]. However such catalytic systems show relatively low selectivities: the expected dialkyltin dihalides are never obtained with selectivities higher than 90%, the major by-product being the corresponding

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* Dedicated to Prof. L. Sacconi.

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Table 1

Direct synthesis of SnR_2X_2 species ($R = n\text{-}C_4H_9$, $n\text{-}C_8H_{17}$) with a quaternary ammonium salt as catalyst. Reactions conditions are described in the Experimental section. Yields are based on converted tin

R	X	Solvent	Sn conversion (%)	Selectivity (%)	
				SnR_2X_2	SnR_3X
$n\text{-}C_4H_9$	Br	–	3	50	50
$n\text{-}C_4H_9$	Br [a]	–	63	48	52
$n\text{-}C_4H_9$	Br	DMF(HMPA) [b]	36 (59) [b]	86 (85) [b]	11 [c] (15) [b]
$n\text{-}C_4H_9$	Cl	–	1–2	54	46
$n\text{-}C_4H_9$	Cl [d]	DMF	31.5	88	12
$n\text{-}C_4H_9$	Cl [e]	–	100	66	34
$n\text{-}C_8H_{17}$	Cl [f]	–	100	70	30

[a] Amount of $n\text{-}C_4H_9Br$, 1.6×10^{-1} mol; the catalytic system was $[(n\text{-}C_4H_9)_4N]I$ 6.25×10^{-3} mol and $n\text{-}C_4H_9I$ 1.25×10^{-3} mol. [b] HMPA as solvent. [c] Small amounts (3%) of $n\text{-}C_4H_9SnBr_3$ were formed. [d] Amount of $[(n\text{-}C_4H_9)_4N]I$, 1×10^{-3} mol. [e] Amount of $[(n\text{-}C_4H_9)_4N]I$, 1×10^{-3} mol and that of $n\text{-}C_4H_9I$ 5×10^{-3} mol. [f] Amount of $[(n\text{-}C_4H_9)_4N]I$ 1.5×10^{-3} mol, and that of $n\text{-}C_8H_4I$ 5×10^{-3} mol.

R_3SnX species. In addition when $X = Cl$ rather high temperatures are required. These last aspects provide the major obstacle to the industrial development of the direct synthesis (eq. 3). Obviously it is of interest to find and develop a catalytic system characterised by a high selectivity towards the direct formation of SnR_2X_2 species, and we report here the results of research directed towards this goal.

Results

In Table 1 we show, as background material, the best results achievable when a quaternary ammonium iodide salt is used as catalyst ($R =$ butyl and octyl). The reaction occurs with good conversion of tin at temperatures which are dependent upon the nature of the halide. As expected, the alkyl bromides are more reactive than the corresponding chlorides, and the reactions take place at 80–100 °C and 120 °C, respectively. The reaction and selectivity are favoured by dipolar aprotic solvents: the best solvents are dimethylformamide (DMF) and hexamethylphosphoramide (HMPA), with other solvents, such as acetonitrile, the conversion of tin is much lower. The presence of relatively low amounts of an alkyl iodide, which acts as a promotor, greatly increases the reactivity without affecting the selectivity strongly. Under the conditions reported in Table 1 the dialkyltin dihalides are obtained with selectivities between 70–90%.

We have confirmed the good activity and the associated low selectivity of these particular catalytic systems even when working under the best experimental conditions. In addition we have found [8] that other catalytic systems, which play the same role as the quaternary ammonium salts in so-called phase transfer catalysis [9], are not only slightly more active than the quaternary ammonium salts but much more selective for the direct synthesis of SnR_2X_2 ($X = Cl$, Br) compounds. These catalysts are various commercially available, crown ethers, used in the presence of an excess of potassium iodide (Table 2). It is necessary to work in a solvent: again the best solvents are dipolar aprotic solvents and in particular DMF (Table 2). With DMF as solvent the crown ether based catalytic systems are evidently quite active, since some tin conversion can be achieved with alkyl halides of low reactivity, such

Table 2

Direct synthesis of SnR_2X_2 ($R = n\text{-}C_4H_9$, $n\text{-}C_8H_{17}$) with crown ethers as catalyst. Reaction conditions were as described in the Experimental section. Yields are relative to converted tin. The solvent was DMF

R	X	Catalyst	Sn (%) conversion	Selectivity (%)	
				SnR_2X_2	SnR_3X
$n\text{-}C_4H_9$	Br [a]	Dibenzo-18-crown-6 (7×10^{-4} mol)	100	84	16
$n\text{-}C_4H_9$	Cl [b]	Dibenzo-18-crown-6 (7×10^{-4} mol)	100	98	2
$n\text{-}C_4H_9$	Cl	18-Crown-6 (10^{-3} mol)	41	95	6
$n\text{-}C_4H_9$	Cl [c]	18-Crown-6 (5×10^{-4} mol)	95	95	5
$n\text{-}C_4H_9$	Cl	Dicyclohexyl-18-crown-6 (5×10^{-4} mol)	40	99	1
$n\text{-}C_4H_9$	Cl [c]	Dicyclohexyl-18-crown-6 (10^{-3} mol)	100	99	1
$n\text{-}C_8H_{17}$	Cl [d]	Dibenzo-18-crown-6 (7×10^{-4} mol)	100	95	5
$n\text{-}C_4H_9$	Cl [e]	Dibenzo-18-crown-6 (7×10^{-4} mol)	100	98	2

[a] Amount of solvent, 15 ml. [b] Amount of solvent is 15 ml, that of KI 550 mg and that of $n\text{-}C_4H_9I$ as cocatalyst 10^{-2} mol. [c] Amount of $n\text{-}C_4H_9I$ as cocatalyst 5×10^{-3} mol. [d] The amount of solvent 15 ml; temperature 160 °C. [e] Amount of solvent 15 ml and that of $n\text{-}C_8H_{17}I$ as cocatalyst 5×10^{-3} mol.

as alkyl chlorides, even at 100 °C. (The reaction does not occur at 100 °C with an ammonium quaternary salt as catalyst.)

Moreover good conversions of tin can be achieved even in the absence of an alkyl iodide as cocatalyst, although even with our catalytic systems this promoter always has an accelerating action (Table 2). The selectivity of the reaction is excellent (95–99%), even for reactions at temperatures as high as 160 °C (see the reaction with $n\text{-}C_8H_{17}Cl$). We examined the possibility that butyl iodide alone or a mixture of potassium iodide and butyl iodide might have a similar catalytic effect. We found that butyl iodide alone in DMF is an acceptable catalyst even at 100 °C, but its effect is characterised by a low selectivity (the tin conversion is ca. 100% at 120 °C but the selectivity towards SnR_2X_2 is ca. 70%); higher selectivities of ca. 90%, but much lower activities, of ca. 40–50% of tin conversion, are obtained from reactions at ca. 100 °C (Table 2).

It follows that the high activity and selectivity reported in this work can be ascribed completely to the catalytic system formed by a crown ether and an excess of potassium iodide, even when an alkyl iodide is present as promotor. Finally we should point out that in the dipolar aprotic basic solvents used in this work, the final products are the octahedral complexes $Sn(S)_2R_2X_2$ and $Sn(S)_2R_3X$ (where S is the solvent). However the tetrahedral tin organometallic species can be liberated either by treatment with concentrated HCl (followed by extraction with an organic solvent) or by simple thermal decomposition of the octahedral compounds followed by distillation.

Conclusions and discussion

The role of the catalytic system could be to assist the following nucleophilic reactions:

$$RX + I^- \rightarrow RI + X^- \quad (4)$$

(X = Br, Cl)

$$SnR_2I_2 + 2X^- \rightarrow SnR_2X_2 + 2I^- \quad (5)$$

The real direct synthesis must involve the alkyl iodide continuously formed by the nucleophilic exchange (eq. 4), because it is known that the reaction (eq. 6) of addition of an alkyl iodide to metallic tin is a relatively facile reaction [2]:

$$2RI + Sn \rightarrow SnR_2I_2 \qquad (6)$$

It is well-known that reaction 4 is catalysed by phase transfer catalysts even in one single organic phase [10]; in addition we have confirmed by NMR spectroscopy that, for $R = CH_3$, reaction 5 is also catalysed by phase transfer catalysts, even in non polar solvents such as $CHCl_3$. The system formed by reactions 4, 5 and 6 could thus generate a catalytic cycle corresponding to reaction 3, the direct synthesis from metallic tin and RX (X = Cl, Br).

However such an interpretation is too simple because nucleophilic exchange reactions are favoured by the dipolar aprotic solvents used in this work, but in these solvents the presence of the so called phase transfer catalysts usually does much increase the overall reactivity. In agreement with this, we have found that the reaction occurs, although less easily, when RI is used alone as the catalyst and the source of iodine. Furthermore, other solvents, in which transfer catalysis would be expected to facilitate nucleophilic exchange reactions, such as 4 and 5, are either unsuitable ($CHCl_2$–$CHCl_2$) or give rather poor results (CH_3CN). It follows that both the dipolar aprotic solvents and our catalyst must play a role, and probably mainly in the addition reactions 6.

The addition reactions are formally oxidative addition reactions, and by a analogy with what is known of the kinetics and mechanism of oxidative additions to transition metal complexes, a strong positive action of dipolar aprotic solvents would be expected [11]. However a positive role of a phase transfer catalyst such as a crown ether on reaction 6 is difficult to rationalise. The large change in selectivity on going from quaternary ammonium iodides to the crown ether plus potassium iodide system cannot be easily explained.

The formation of SnR_3X as the major by-product has been explained in terms of the interaction of SnR_2X_2 with excess metallic tin in the presence of an excess of RX [12], according to reaction 7. Reaction 7 is favoured by polar solvents, the presence of basic compounds, and low temperatures:

$$SnR_2X_2 + Sn + RX \rightarrow SnR_3X + SnX_2 \qquad (7)$$

Since our reactions are carried out in polar solvents and at relatively low temperatures, the action of crown ethers may be due to a strong negative effect on reaction 7, an effect which cannot be easily rationalised. Such an unexpected property of crown ethers is worthy of detailed investigation from the mechanistic point of view.

Because the species $SnRX_3$ was found in one or two cases as a very minor reaction product we also checked that reaction 8 is not involved by adding preformed SnR_2X_2 (X = Cl, Br) to a DMF solution containing our catalytic systems:

$$2SnR_2X_2 \rightarrow SnR_3X + SnRX_3 \qquad (8)$$

In all cases the original product SnX_2R_2 was recovered unchanged. Finally we should point out that the high selectivity, found even for reactions at temperatures as high as 160 °C, makes our catalytic systems acceptable even with a very volatile alkyl halide such as methyl chloride, which would require use of both high temperatures and high pressures. It is relevant in this connection to note that methyltin derivatives are today important intermediates for the preparation of the most interesting PVC stabilizers.

Experimental

Materials

Tin was of reagent grade, and was used without further purification. Tetraalkylammonium salts, potassium iodide, and the crown ethers were of reagent grade, and were used without purification. The alkyl halides and the solvents were of reagent grade and were distilled before use.

Reactions

The reagents, the catalytic system and the solvent were placed in a glass autoclave (8–10 atm) fitted with a magnetic stirrer. The reaction was carried out at controlled temperature ($\pm 1\,°C$) maintained by a thermostated oil bath. After completion of the reaction, the autoclave was cooled and the product mixture analysed by GLC.

The standard reaction conditions with a quaternary ammonium salt such as $[(n\text{-}C_4H_9)_4N]I$ were: 100 °C, 5 h, 10 ml of solvent ($n\text{-}C_4H_9Br$) and 120 °C, 24 h, 10 ml of solvent ($n\text{-}C_4H_9Cl$) unless otherwise stated (see Table 1). The amounts of alkyl halides $n\text{-}C_4H_9X$ were 1.25×10^{-1} ($X = Br$) and 9.5×10^{-2} ($X = Cl$) mol, respectively, unless otherwise stated (see Table 1). The amounts of quaternary ammonium salt and tin were 1.4×10^{-3} mol and 2.5×10^{-2} g-atoms, respectively.

The standard reaction conditions with a crown ether catalyst were: 100 °C, 6 h, 10 ml of solvent ($n\text{-}C_4H_9Br$) and 120 °C, 24 h, 10 ml of solvent ($n\text{-}C_4H_9Cl$) unless otherwise stated. The solvent was always DMF. The amount of alkyl halides was 1.25×10^{-1} mol of $n\text{-}C_4H_9Br$, 9.5×10^{-2} mol of $n\text{-}C_4H_9Cl$, or 9.5×10^{-2} mol of $n\text{-}C_8H_{17}Cl$. The amount of crown ether was ca. 10^{-3}–10^{-4} mol (see Table 2), that of tin 2.5×10^{-2} g-atoms. The amount of KI was 350 mg unless otherwise stated.

Reactions were carried out in DMF (10 ml) at 120 °C for 24 h with $n\text{-}C_4H_9I$ (5×10^{-3} mol) as catalyst ($n\text{-}C_4H_9Cl$ and tin 9.5×10^{-2} mol and 2.5×10^{-2} g-atoms, respectively), and at 100 °C and 6 h in DMF (25 ml) with $n\text{-}C_4H_9I$ (1.3×10^{-2} mol) as catalyst ($n\text{-}C_4H_9Cl$ and tin 4×10^{-2} mol and 2.5×10^{-2} g-atoms, respectively). Conversions (and selectivity) were 100 (70% SnR_2Cl_2 and 30% SnR_3Cl) and 34% (95% SnR_2Cl_2 and 5% SnR_3Cl), respectively.

Analysis

Two analytical methods were used:

(a) In the case of n-butyl derivatives, direct injection, after addition of the internal standard, of the reaction mixture into the gas chromatograph without any purification; a Carlo Erba Model G with double column, temperature programming, and thermal detection was used. The head of the column was shielded by a 5 cm glass protector between the injector and the column. The analytical conditions were as follows: a steel column of 2 m and 4 mm of diameter (Chromosorb 80–100 mesh, methylsilicone SE 30 6% in weight); injector temperature 300 °C, detector temperature 200 °C, programmed temperature from 180 to 220 °C with increase of

2.5 °C/min; final isotherm of 5 min. The carrier gas was H_2 with a flow rate of 150 ml/min. The internal standard was dibutyldihexyltin.

(b) With both n-butyl and n-octyl derivatives alkylation with CH_3MgBr of the alkyltin halides after purification of the product mixture. The purification was carried out as follows: The reaction mixture was cooled and filtered, and the solvent and the excess of volatile reagents were evaporated off under vacuum (60 °C/0.3 mmHg for 4 h). The residual solid was treated with 100 ml of an anhydrous organic solvent (benzene, toluene or ether) and the solution was filtered and treated slowly with a titrated solution of CH_3MgBr (containing three times the assumed stoichiometric amount). The mixture was refluxed for 2 h and the excess of the Grignard reagent decomposed by addition of a solution of NH_4Cl in dilute HCl. The final mixture was treated with an excess of the organic solvent (100 ml), and the organic layer was separated and dried over $MgSO_4$. After filtration, the solvent was evaporated to about 25% of its original volume and then analysed by GLC.

Analytical conditions were:

(1) For the n-butyl derivatives, a steel column of 2 m and 5 mm of diameter (Chromosorb 80–100 mesh, methylsilicone SE 30 5–6% in weight); injector temperature 280 °C, detector temperature 200 °C, isotherm at 190 °C. The carrier gas was H_2 with flow rate of 30 ml per 17 s. The internal standard is α-methylnaphthalene.

(2) For the n-octyl derivatives, a steel column of 1 m and 5 mm of diameter (Silanised Chromosorb 80–100 mesh, silicon oil 10% in weight); injector temperature 350 °C, detector temperature 300 °C, programmed temperature from 230 to 270 °C with increase of 3 °C/min. The carrier gas was H_2 with a flow rate of 30 ml per 11.5 s. The internal standard was dioctyldihexyltin. The analytical results for the n-butyl tin species obtained by the two procedures were in good agreement; such agreement was also found in tests on standard solutions of SnR_2X_2 and SnR_3X species in DMF in the presence of excess of tin.

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