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Journal of Organometallic Chemistry 655 (2002) 111–114

Journal of Organometallic Chemistry

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Tin–magnesium transmetallation reactions

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Received 24 January 2002

Abstract

Sulfur-functionalized methyltin compounds $n\mathrm{Bu_3SnCH_2S(O)}_i\mathrm{R}$ ($i = 0$, 1, 2; R = Me, Ph) underwent transmetallation with Grignard compounds MgR′X (R′ = Me, *n*Bu, Ph; X = Cl, Br, I) and diorganomagnesium compounds MgR′R″ (R′/R″ = Me/Me, *n*Bu–*s*Bu) to provide $\mathrm{Sn}(n\mathrm{Bu})_3\mathrm{R}$ and $\mathrm{Mg[CH_2S(O)}_i\mathrm{R]X}$ and $\mathrm{Mg[CH_2S(O)}_i\mathrm{R]R''}$, respectively. Analogously, the reaction of $n\mathrm{Bu_3SnCH_2P(O)Ph_2}$ with Mg(*n*Bu)Br afforded quantitatively $\mathrm{Mg[CH_2P(O)Ph_2]Br}$ and $\mathrm{Sn}(n\mathrm{Bu})_4$. Transmetallations between $n\mathrm{Bu_3SnCH_2YMe_2}$ (Y = N, P) and $\mathrm{MgMe_2}$ proceeded only in the presence of catalytic amounts (10–20 mol%) of Li*n*Bu yielding $\mathrm{Mg(CH_2YMe_2)Me}$ and $\mathrm{Sn}(n\mathrm{Bu})_3\mathrm{Me/Sn}(n\mathrm{Bu})_4$. © 2002 Elsevier Science B.V. All rights reserved.

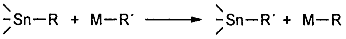
Keywords: Transmetallation reactions; Organotin compounds; Organomagnesium compounds; Functionalized methyl carbanions

1. Introduction

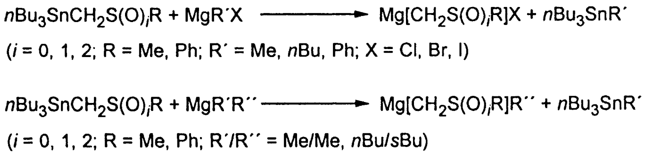
In 1941 Gilman [1] discovered that $\mathrm{SnR_4}$ (R = aryl) reacts with butyllithium yielding LiR and $\mathrm{SnBu_4}$. Since then organotin compounds rank amongst the most potent and versatile reagents for transmetallation reactions according to Scheme 1 both in stoichiometric reactions to prepare other organometallics and in catalytic C–C bond formation reactions using them as starting materials. Since the 1970s, Sn–Li transmetallations have been broadly applied for the preparation of functionalized methyllithium compounds $\mathrm{LiCH_2YR}_n$ ($\mathrm{YR}_n = \mathrm{NR_2}$, OR, SR, ...) [2]. Surprisingly, Sn–Mg transmetallations were described only very recently, namely those of tetraalkynylstannanes with Grignard reagents [3]. Here, we report on a broader scope Sn–Mg transmetallation reactions of functionalized methyltin compounds $n\mathrm{Bu_3SnCH_2Y(O)}_i\mathrm{R}_x$ ($\mathrm{Y(O)}_i\mathrm{R}_x$ = SR, S(O)R, $\mathrm{S(O)_2R}$, $\mathrm{P(O)Ph_2}$) and of $n\mathrm{Bu_3SnCH_2YMe_2}$ (Y = P, N) using Li*n*Bu as precatalyst.

2. Results and discussion

Diorganomagnesium and Grignard reagents were found to react with sulfur-functionalized methyltin compounds $n\mathrm{Bu_3SnCH_2S(O)}_i\mathrm{R}$ ($i = 0$, 1, 2) in 1:1 molar ratio yielding sulfur-functionalized methylmagnesium compounds (Scheme 2). These Sn–Mg transmetallation reactions were performed in THF, THF–$\mathrm{Et_2O}$ or THF–heptane at room temperature. Results are shown in Table 1. The transmetallation reactions of sulfinylmethyl- ($i = 1$) and sulfonylmethyltin compounds ($i = 2$) were complete within 1 h. On the other hand, sulfanylmethyltin compounds $n\mathrm{Bu_3SnCH_2SR}$ reacted within 9–12 days to a small extent only, except for reactions of $n\mathrm{Bu_3SnCH_2SPh}$ with MgMeX and $\mathrm{MgMe_2}$ (entries 2 and 8). In these cases, the degree of conversion amounts to > 85% within 9 days. Interestingly, use of



Scheme 1.



Scheme 2.

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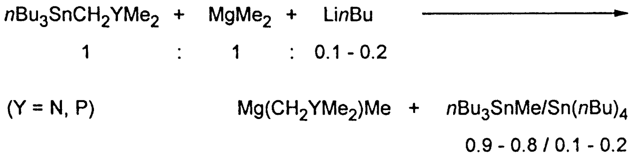
PII: S0022-328X(02)01430-4

Mg(*n*Bu)*s*Bu in 1:1 molar ratio (entries 9 and 10) resulted in the transfer of the *n*-butyl group that was sometimes accompanied by a transfer of the *s*-butyl group to a small extent (< 10%). Using an excess of tin compound (nBu$_3$SnCH$_2$S(O)$_i$R : Mg(*n*Bu)*s*Bu = 2–3 : 1) a further transmetallation yielding Mg[CH$_2$S(O)$_i$R]$_2$ took place—if to any—to a small extent only.

Analogous reactions were carried out with other heteroatom-functionalized methyltin compounds using *n*-butylmagnesium halides as organomagnesium reagents. Aminomethyltin compounds nBu$_3$SnCH$_2$NR$_2$ (NR$_2$ = NMe$_2$, NMePh, NPh$_2$) did not undergo Sn–Mg transmetallation (10 h, r.t.). Phosphinomethyltin compounds nBu$_3$SnCH$_2$PPh$_2$ and nBu$_3$SnCH$_2$PMe$_2$ reacted to an extent of 5–10% and 1–3% (10 h, r.t.), respectively. Under the same reaction conditions, the phosphinoylmethyl compound nBu$_3$SnCH$_2$P(O)Ph$_2$ was found to react quantitatively with Mg(*n*Bu)Br yielding Sn(*n*Bu)$_4$ and Mg[CH$_2$P(O)Ph$_2$]Br.

As shown for dimethylamino- and dimethylphosphinomethyltin compounds nBu$_3$SnCH$_2$YMe$_2$ (Y = N, P), Sn–Mg transmetallation can be enforced by addition of substoichiometric amounts of *n*-butyllithium (Scheme 3, Table 2): At first, to these tin compounds 10–20 mol% of Li*n*Bu (entries 1–4) was added forming the corresponding amounts of Sn(*n*Bu)$_4$ and LiCH$_2$YMe$_2$. The following addition of equimolar amounts of MgMe$_2$ resulted in complete conversion of the remained nBu$_3$SnCH$_2$YMe$_2$ yielding Sn(*n*Bu)$_3$Me and Mg(CH$_2$YMe$_2$)Me within 1 day (Y = N) and 4 days (Y = P).

The mechanism of these Sn–Mg transmetallations catalyzed by organolithium compounds has not been investigated yet. As experimentally proved by ^{119}Sn-NMR spectroscopy and described in lit. [4], the first step is a Sn–Li transmetallation yielding LiCH$_2$YMe$_2$ (Scheme 4, a). Then, the reaction could proceed via Mg–Li (b) and Sn–Li transmetallations (c). On the other hand, LiCH$_2$YMe$_2$ could form with MgMe$_2$ a magnesate complex Li[MgMe$_2$(CH$_2$YMe$_2$)] being capable to undergo Sn–Mg transmetallation due to enhanced carbanionoid character of the methyl groups [5].



Scheme 3.

Dimethylmagnesium, prepared by the 'dioxane method' [6], contained 1–5% residual halide. Therefore, a corresponding amount of the organolithium compound was deactivated in a metathesis reaction (MgRX + LiR′ → MgRR′ + LiX). Thus, the amount of Li*n*Bu to be added has to exceed the halide content. Entry 5 in Table 2 makes clear that a content of about 2 mol% of active organolithium compound is sufficient to catalyze the Sn–Mg transmetallation reaction.

All Sn–Mg transmetallation reactions described here are in accordance with the general trend for transmetallations in Scheme 1, that the more electronegative ligand tends to be bound to the more electropositive metal [2a,7]. Thus, dipole stabilized carbanions [8] $^{-}$CH$_2$Y(O)$_i$R$_x$ (i = 1, 2) are significantly more reactive than those without such dipole stabilization (i = 0). In the latter case the transmetallation may be enforced to proceed by adding catalytic amounts of organolithium compounds. Further investigations are in progress to elaborate the synthetic potential of these new transmetallation reactions.

3. Experimental

3.1. General comments

Functionalized methyltin compounds nBu$_3$SnCH$_2$Y(O)$_i$R$_x$ (Y = S, P, N) were prepared according to published procedures and in analogy to that [4,9].

Table 1
Degree of conversion (in%) [a] and reaction time at room temperature for Sn–Mg transmetallation reactions according to Scheme 2

Entry		R	nBu$_3$SnCH$_2$SR		nBu$_3$SnCH$_2$S(O)R	nBu$_3$SnCH$_2$S(O)$_2$R
	Reaction time		12 days	9 days	1 h	1 h
1	MgMeX (X = Cl, Br, I)	Me	10–30			> 95
2		Ph		85–95	> 95	> 95
3	Mg(*n*Bu)X (X = Cl, Br)	Me	< 5			80–95
4		Ph		< 10	> 95	90–95
5	MgPhX (X = Cl, Br)	Me	< 5			95
6		Ph		< 5	> 95	80–90
7	MgMe$_2$	Me	10			> 95
8		Ph		> 95	> 95	> 95
9	Mg(*n*Bu)*s*Bu	Me	< 5			> 95
10		Ph		< 5	> 95	> 95

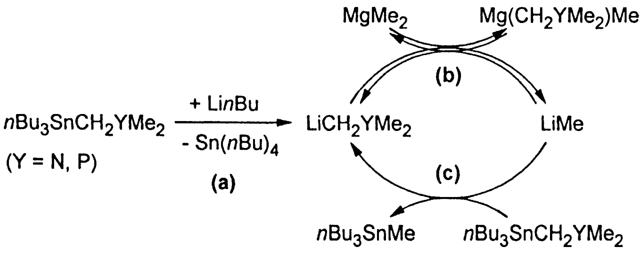
[a] Determined by ^{119}Sn-NMR spectroscopy.

Table 2
Sn–Mg transmetallation reactions in the presence of substoichiometric amounts of Li*n*Bu according to Scheme 3 (degree of conversion > 95%)

Entry	Y in $n\text{Bu}_3\text{SnCH}_2\text{YMe}_2$	[Sn]:[MgMe_2]:[Li*n*Bu]	Solvent	[$n\text{Bu}_3\text{SnMe}$]:[$\text{Sn}(n\text{Bu})_4$]
1	P	1:1:0.2 [a]	Hexane–Et_2O	0.8:0.2
2	P	1:1:0.1 [a]	Hexane–Et_2O	0.9:0.1
3	P	1:1:0.2 [b]	Hexane–THF	0.8:0.2
4	N	1:1:0.1 [b]	Hexane–THF	0.9:0.1
5	N	1:1:0.07 [b]	Hexane–THF	0.93:0.07

[a] MgMe_2 contains ca. 1 mol% Br^-.

[b] MgMe_2 contains ca. 5 mol% Cl^-.



Scheme 4.

Grignard reagents (1–3 M in THF or Et_2O), Mg(*n*Bu)*s*Bu (1 M in *n*-heptane) and Li*n*Bu (1.6 M in *n*-hexane) were commercially (Aldrich, Fluka) available. MgMe_2 in THF with a residual content of about 5 mol% Cl^- and in Et_2O with a residual content of about 1 mol% Br^-, respectively, was prepared from Mg(Me)Cl and Mg(Me)Br according to the 'dioxane method' [6]. NMR spectra were recorded on Varian NMR spectrometers (Gemini 2000, Unity 500) using SnMe_4 (internal reference) and H_3PO_4 (external reference) for ^{119}Sn and ^{31}P measurements, respectively. GC–MS investigations were carried out on an HP 5890 Series II/HP 5972 (Hewlett–Packard).

3.2. Sn–Mg transmetallation reactions (Table 1)

Reactions were performed in NMR tubes strictly under anaerobic conditions. The NMR tubes were filled in a Glove Box (Fa. M. Braun, Garching) with, typically, $n\text{Bu}_3\text{SnCH}_2\text{S(O)}_i\text{R}$ (0.2 mmol), magnesium reagent (0.2 mmol using 1–3 molar solutions), SnMe_4 as internal standard (ca. 0.08 mmol) and THF (0.5 ml). Reactions were monitored by ^{119}Sn-NMR spectroscopy. No other signals were detected than those from the (unreacted) starting compound ($n\text{Bu}_3\text{SnCH}_2\text{S(O)}_i\text{R}$) and the formed tin compound ($n\text{Bu}_3\text{SnR}'$, $\text{R}' = \text{Me}$, *n*Bu, *s*Bu, Ph). Their identities were confirmed by measuring the chemical shifts of authentic substances under the same conditions and in selected cases also by GC–MS after hydrolysis.

*3.3. Sn–Mg transmetallation reactions catalyzed by Li*n*Bu (Table 2)*

At −78 °C, to $n\text{Bu}_3\text{SnCH}_2\text{YMe}_2$ (Y = N, P; 1.0 mmol) in *n*-hexane (5 ml) Li*n*Bu (0.07–0.2 mmol) in *n*-hexane was added. After stirring for 15 min at room temperature (r.t.), MgMe_2 (1.0 mmol) in THF or ether was added at −78 °C. After stirring for 30 min, the reaction mixture was allowed to warm to r.t. Reactions were complete after 1 day (Y = N) and 4 days (Y = P). Products were identified by ^{119}Sn-NMR spectroscopy and after hydrolysis with H_2O–THF (1/4) at −78 °C by means of GC–MS.

3.4. ^{119}Sn chemical shifts

$n\text{Bu}_3\text{SnCH}_2\text{SR}$: δ −17.6 (R = Me), −12.5 (R = Ph) (a). $n\text{Bu}_3\text{SnCH}_2\text{S(O)Ph}$: δ −20.1 (a). $n\text{Bu}_3\text{SnCH}_2\text{S(O)}_2\text{R}$: δ −15.8 (R = Me), −12.7 (R = Ph) (a). $n\text{Bu}_3\text{SnCH}_2\text{NR}_2$: δ −34.1 ($\text{R}_2 = \text{Me}_2$), −20.7 ($\text{R}_2 = \text{MePh}$), −24.7 ($\text{R}_2 = \text{Ph}_2$) (b). $n\text{Bu}_3\text{SnCH}_2\text{PR}_2$: δ −10.6, $^2J_{^{119}\text{Sn},^{31}\text{P}} = 73.3$ Hz ($\text{R}_2 = \text{Me}_2$), δ −10.2, $^2J_{^{119}\text{Sn},^{31}\text{P}} = 81.0$ Hz ($\text{R}_2 = \text{Ph}_2$) (b). $n\text{Bu}_3\text{SnCH}_2\text{P(O)Ph}_2$: δ −6.4, $^2J_{^{119}\text{Sn},^{31}\text{P}} = 55.0$ Hz (b). (a) Relative to SnMe_4 as internal reference; solvent: THF accompanying the organomagnesium starting materials solvent (diethyl ether–heptane). (b) Relative to SnMe_4 as external reference, solvent: CDCl_3.

Acknowledgements

Financial support from the Deutsche Forschungsgemeinschaft and Fonds der Chemischen Industrie as well as gifts of chemicals by Merck (Darmstadt) are gratefully acknowledged.

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