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Journal of Organometallic Chemistry 689 (2004) 3421–3425

Journal of Organo metallic Chemistry

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Preparation of lithium stannide mixtures in organic solvents. A alternate source of lithium in organolithium chemistry

Reuben D. Rieke *, Jun-sik Lee [1], Young-Sik Kye [2], Gerard S. Harbison

Department of Chemistry, University of Nebraska, Lincoln, Nebraska, NE 68588-0304, USA

Received 22 January 2004; accepted 27 April 2004

Abstract

Lithium stannides were prepared from lithium naphthalenide and tin (II) chloride or tin (0) powder in THF solvent at room temperature under dry argon atmosphere. They were characterized with elemental analysis, XRD, and solid ^{6,7}Li NMR. Stabilities and reactivities of lithium stannides prepared from different conditions were tested and showed they were stable for a limited time at low temperatures. Best reactivity was obtained when they were prepared from tin (II) chloride and an excess of lithium naphthalenide. The lithium stannide mixture can reductively cleave carbon–halogen bonds and yield pinacol coupling with aldehydes. Organolithium compounds prepared from lithium stannides and organic halides add to ketones or aldehydes under Barbier conditions.

Keywords: Lithium stannide; Organolithium; ^{6,7}Li NMR; Reductive cleavage of C–X bond

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1. Introduction

The first organolithium compound was prepared by a transmetallation reaction of diethylmercury with lithium metal in 1917 by Schlenk and Holtz [1]. In the 1930s, Gilman et al. [2], Wittig and Leo [3], and Ziegler and Colonius [4] independently prepared organolithium compounds by a metal–halogen exchange reaction of organic halides with lithium metal. Simple organolithium compounds, mainly butyllithium and phenyllithium, which were prepared from above mentioned methods were used to prepare other organolithium compounds by metallation (metal–hydrogen exchange) reaction with acidic organic compounds [5] and halogen–lithium exchange reaction with organic halides [5,6].

Recently Yus and Ramon [7] reported a new approach for the preparation of organolithium compounds using naphthalene or 4,4′-di-*tert*-butylbiphenyl and lithium metal. Reductive cleavage of carbon–oxygen, carbon–nitrogen, and carbon–sulfur bond and reductive opening of saturated heterocycles produced organolithium compounds.

Lithium stannides were electrochemically prepared by Furuya et al. [8], producing several distinct species, identified by deconvolving poorly resolved ^{7}Li solid-state NMR spectra; the ^{7}Li resonances were conjecturally assigned using Knight shifts and T_1 values. We have been able to produce a mixture of lithium stannides as a black slurry by treating preformed lithium naphthalenide with tin (II) chloride or tin powder under stirring for 10 min at 298 K in THF under argon.

2. Results and discussion

Several lithium stannides [9] were prepared by mixing lithium and tin metal or tin alloy at high temperature in the previous reports. But the purpose of the previous

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* Corresponding author.

E-mail address: rrieke@unl.edu (R. D. Rieke).

[1] Present address: Rieke Metals, Inc. 1001 Kingbird Road, Lincoln, NE 68521 USA.

[2] Present address: Department of Chemistry, Korea Military Academy, Seoul, Korea.

0022-328X/$ - see front matter © 2004 Published by Elsevier B.V.
doi:10.1016/j.jorganchem.2004.04.037

reports was analysis of the structure with XRD and no application in organic chemistry was performed with lithium stannides.

At first, active tin was prepared by reacting 2 equivalents of preformed lithium naphthalenide with tin chloride and then reacted with *n*-octyl bromide. But no reaction was detected. Then, excess (3.3 equivalents) amount of preformed lithium naphthalenide was reacted with tin chloride and the resulting black slurry in THF was reacted with *n*-octyl bromide and produced several products including elimination, reduction, and homocoupling product.

Lithium stannide mixtures were characterized by elemental analysis and solid-state ^{6}Li and ^{7}Li magic angle spinning (MAS) NMR. Elemental analysis data showed a Li:Sn ratio for the slurry varying from 0.8 to 1.8, increasing as the initial lithium was increased. The elemental composition of the lithium stannide mixture did not appear to depend on the tin source (tin (II) chloride or commercial tin (0) powder). When lithium was added as single large piece with a catalytic amount of naphthalene, the preparation time took 3 h, but not all of the initial lithium was converted into lithium stannide.

XRD measurement showed only tin (0) and did not detected lithium stannides. The possible explanation might be the decomposition of lithium stannides in the air during the sample preparation.

^{7}Li solid-state NMR of the lithium stannides mixture using static samples at a field of 7 T, showed poorly resolved spectra that qualitatively resembled those obtained by Furuya et al. [8]. However, under MAS, resolution was markedly improved. Fig. 1(a) shows the ^{7}Li MAS NMR spectrum of a sample prepared with 3.3 mol Li per mol $SnCl_2$, over a 24 h reaction time (prep. 8 in Table 1). In this spectrum, several distinct, Knight-shifted ^{7}Li resonances can be observed, flanked by the usual sidebands at integer multiples of the rotation frequency. However, the spectral resolution is still comparatively poor, and the relative contributions of the central 1/2 to $-1/2$ and the satellite transitions to the isotropic peaks cannot accurately be determined. Overlap of sidebands with isotropic peaks also complicates the picture. We therefore turned to ^{6}Li NMR, with remarkable results. With the availability of higher magnetic fields, the less receptive ^{6}Li nucleus has become an attractive alternative to the more abundant ^{7}Li spin, whose spectroscopy is complicated by a larger quadrupole constant. ^{6}Li has been used to study the state of the lithium cation in minerals [10], battery materials [11–13], ceramics [14], and glasses [15]. ^{6}Li, while it is a spin 1 nucleus, has negligible quadrupole couplings; while ^{6}Li NMR is less sensitive than ^{7}Li NMR, the absence of substantial homonuclear dipolar and quadrupolar interactions, makes the resolution considerably better (Fig. 1(b)).

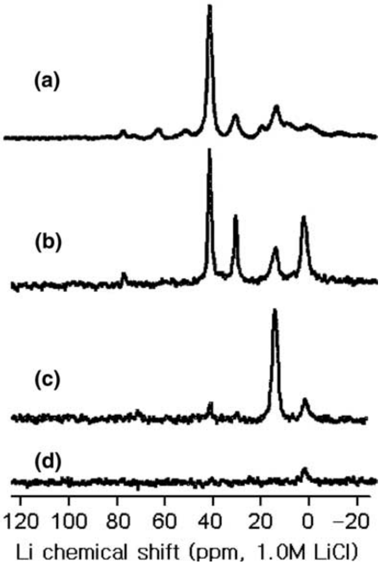


Fig. 1. (a) ^{7}Li MAS NMR spectrum of lithium stannides prepared with 3.3 mol Li per mol $SnCl_2$. (b) ^{6}Li MAS NMR spectrum of lithium stannides prepared with 3.3 mol Li per mol $SnCl_2$. (c) ^{6}Li MAS NMR spectrum of lithium stannides prepared with 4.5 mol Li per mol $SnCl_2$. (d) ^{6}Li MAS NMR spectrum of lithium stannides prepared with 2.5 mol Li per mol Sn.

This enhanced resolution allows us to determine that the resonance reported [8] at ~38 ppm and assigned to LiSn, is in fact two peaks in a 2:1 ratio, at 42 and 31 ppm. Since these peaks seem to vary in synchrony, it is possible they arise from a single lithium stannide; and while the evidence this species is LiSn is by no means conclusive, there certainly exist other compounds of formula AX with two chemically distinct A and two distinct X atoms, each in a 2:1 ratio.

Fig. 1(c) and (d) show the ^{6}Li MAS spectra of the products of prep. 4 and prep. 11, respectively; these spectra allow us to identify the resonances tentatively assigned to $LiSn_2$ at 76 ppm; Li_5Sn_2 at 15 ppm, and Li_7Sn_2 at 3 ppm. Materials with lower Li content could not be spun in the magnetic field due to their conductivity, but static ^{7}Li NMR showed them to contain a high fraction of the putative $LiSn_2$. Irrespective of assignment, the well-resolved lithium NMR signals surely indicate well-defined, crystalline lithium stannides.

To determine the reduction potential of the lithium stannide mixtures, it was reacted with several molecules of varying reduction potential to yield an approximate reduction potential. Benzophenone (−1.72 eV, DMF), anthracene (−1.92 eV, DMF), stilbene (−2.14 eV, DMF), and 2-methylpyrazine (−2.23 eV, DMF) showed the characteristic color change when they were reacted with lithium stannide. The redox potential should be lower than naphthalene (−2.54 eV in DMF) because lithium stannide was prepared from lithium naphthalenide [16]. From the above data, the redox potential of the lithium stannide mixture can be approximated to be in the range from −2.23 to ~−2.54 eV.

Table 1
Reactivity of lithium stannide prepared from different conditions

Entry	Tin source	Method[a]	Li[b]	Np[b]	Time	Yield (%)[c]
1	$SnCl_2$	A	3.49	0.12	8 h	88
2	$SnCl_2$	A	3.40	3.81	1.5 h	99
3	$SnCl_2$	B	3.36	0.12	10 min	99
4	$SnCl_2$	B	4.51	4.97	10 min	57[d]
5	$SnCl_2$	B	4.15	4.51	10 min	81[e]
6	$SnCl_2$	B	2.98	3.30	10 min	75
7	$SnCl_2$	B	3.03	3.29	10 min	99[f]
8	$SnCl_2$	B	3.35	3.82	24 h	35
9	Sn (0)	A	1.07	0.13	12 h	30
10	Sn (0)	B	1.20	1.33	10 min	37
11	Sn (0)	B	2.50	2.77	10 min	55[d]
12	Sn (0)	B	2.15	2.34	10 min	73[e]

[a] Method A: Tin compound, lithium, and naphthalene were reacted at the same time. Method B; Tin compound was reacted with lithium naphthalenide which was prepared right before it was used.

[b] Equivalent amount of lithium and naphthalene compare to 1 equivalent of tin compound.

[c] The yields were obtained by GLC using internal standard (*n*-decane) and anisole.

[d] 1.25 equivalent of 2-bromoanisole was used.

[e] 1 equivalent of 2-bromoanisole was used.

[f] 0.35 equivalent of 2-bromoanisole was used.

The stability of the lithium stannide mixtures was tested by reacting 2-bromoanisole with 2 equivalents of lithium stannide which had been stored under various conditions. Lithium stannide mixtures in THF can be stored 1 week in a freezer (−13 °C) without change of chemical reactivity, but the reactivity is reduced by 18% on 4 weeks storage. Storage for the same duration in ether or hexane resulted in even further reduced reactivity (57% and 38%). When mixtures were stored free of solvent, all reactivity was lost within 2 weeks.

The reactivity of the lithium stannide mixtures was determined using the reductive cleavage of 2-bromoanisole to yield anisole. The results are found in Table 1. The most reactive alloy was obtained from $SnCl_2$ and 3–3.5 equivalents of preformed lithium naphthalenide. In all cases, lithium stannides produced from $SnCl_2$ yielded better results than the lithium stannides generated from tin (0) powders.

The lithium stannide mixture successfully cleaves carbon–halogen bonds at room temperature within 10 min with good to excellent yields (Table 2). Most bromide substrates gave quantitative yields. Lithium stannides prepared from 4.5 or 5.0 equivalents of lithium naphthalenides gave better results for the chloride substrates. For the cyanide-containing aryl bromide, THF/$HNEt_2$ (80/20) solvent mixture was used to prevent the attack of the generated organolithium on the cyanide group. Amino- and hydroxy-containing aryl halides were also successfully reduced. A large excess of lithium stannides (6 equivalents) was required for phenolic halides.

Table 2
Reductive cleavage of aryl halides

Entry	ArX	$SnCl_2$:Li:ArX	Time	Yield (%)[a]
1	2-OMePhBr	1.00:3.44:0.45	10 min	99
2	3-OMePhCl	1.00:3.41:0.46	3 h	55
3	3-OMePhCl	1.00:4.54:0.44	10 min	72
4	2-CNPhBr	1.00:3.39:0.30	10 min	69[b]
5	2-NH_2PhBr	1.00:3.50:0.49	10 min	99
6	2-NH_2PhCl	1.00:5.05:0.46	1 h	88
7	2-OHPhBr	1.00:3.50:0.16	7 h	99

[a] The yields were obtained by GLC using internal standard (*n*-decane or *n*-nonane) and reduced compounds.

[b] THF–$HNEt_2$ (80–20%) mixture solvent was used.

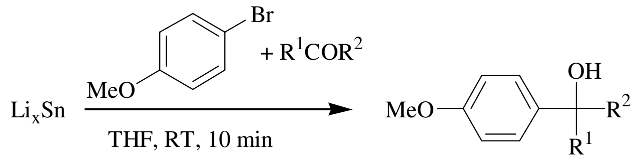
The organolithium compounds prepared from lithium stannides and aryl halides failed to add to ketones or aldehydes in normal conditions, but the addition reactions were successful under Barbier conditions. The preliminary addition reactions of organolithium with aldehydes and ketones are presented in Scheme 1.

In conclusion, this study has yielded a fast and convenient method of preparing lithium stannides of exceptional reactivity. The lithium stannides react with aldehydes to yield pinacols, and can readily reductively cleave carbon–halogen bonds. Preliminary experiments showed organolithium compounds prepared from lithium stannide successfully add to aldehydes and ketones under Barbier conditions.

3. Experimental

3.1. Preparation of lithium stannides

Lithium (10.2 mmol) and naphthalene (11.2 mmol) were weighed into a 50 ml centrifuge tube. Tin (II) chloride (3 mmol) was weighed into a 50 ml two-neck round flask that was equipped with argon gas/vacuum two-way manifold. All the weighing procedures were done inside of the dry box. 20 ml of dry THF was added to the



R^1 = Me $R^2 = PhCH_2CH_2$ **1a** 77%

R^1 = H R^2 = Ph **1b** 57%

Scheme 1.

centrifuge tube and 10 ml of dry THF was added to the two-neck round flask and both tube and flask were stirred for 1 h at room temperature under dry argon gas. Tin (II) chloride solution was cannulated into the centrifuge tube which containing lithium naphthalenide solution. The mixture solution was stirred for 10 min at room temperature and then centrifuged for 10 min at 2000 rpm to separate the lithium stannide from the solvent, naphthalene, and LiCl. The upper solution was removed through the cannula and 10 ml of dry THF was added to the residue. The mixture was stirred for 10 min and then centrifuged again for 10 min at 2000 rpm to wash one more time. The upper solution was removed via cannula and 20 ml of dry THF was added

3.2. XRD analysis

Lithium stannides were prepared as mentioned above and vacuum dried for 24 h at room temperature under dry argon atmosphere. Then they were brought into the dry box and crashed to a fine powder with mortar and pestle. The fine powder sample was transferred into the one-side sealed capillary tube under argon gas and the other side was sealed with para film. The para film treated side was sealed over the flame. But the signal from the sample in a capillary tube was too small. The actual XRD analysis was done after the sample was treated with silicon grease under atmosphere condition.

3.3. Elemental analysis

Lithium stannides were prepared as mentioned above and vacuum dried for 24 h at room temperature under dry argon atmosphere and then sent to analyze with atomic absorption spectroscopy.

3.4. Solid ^{6,7}Li NMR analysis

1.0 M aqueous solution of lithium chloride was used as a reference in ^{6,7}Li NMR experiment and the chemical shift of reference was set to 0 ppm. Lithium stannides were prepared as mentioned above and vacuum dried for 24 h at room temperature under dry argon atmosphere. Then they were brought into the dry box and crashed to a fine powder with mortar and pestle. The fine powder sample was transferred into the 8 mm diameter, 25 mm height dimension of small glass tube. A rubber septum was placed on the glass tube and analyzed with Bruker 600 MHz solid state NMR.

3.5. Stability study

Lithium stannides were prepared as mentioned before and kept in the freezer (−13 °C) for a specific time in different solvent. Then they were warmed to room temperature and reacted with 2-bromoanisole for 10 min 1 equivalent of 2-bromoanisole was used for 2 equivalents of lithium stannide. The reaction yields were obtained by GLC using internal standard (*n*-decane) and anisole.

3.6. Reactivity study

Lithium stannides were prepared from specific conditions of different time, tin source, stoichiometry, etc. The lithium stannides prepared from each condition reacted with 2-bromoanisole with a ratio of 1–2 of 2-bromoanisole and lithium stannide except few experiments specified. The reaction yields were obtained by GLC using internal standard (*n*-decane) and anisole.

3.7. Reductive cleavage of aryl halides

Lithium stannides (3 mmol) were prepared as mentioned before. Neat aryl halides (1.35 mmol) and internal standard (*n*-decane or *n*-nonane) was added to the lithium stannides via syringe and the reaction mixture was stirred for 10 min at room temperature. The hydrolyzed aliquot was extracted with ether and dried over $MgSO_4$ and injected into the GLC. The reduction yield was obtained from the calibration curve.

3.8. Addition of organolithium compounds to the aldehydes and ketones

Lithium stannides (3 mmol) were prepared as mentioned before. A mixture of aryl halide (1.35 mmol) and aldehyde or ketone (1.05 mmol) in THF (5 ml) was added to the lithium stannides via cannula and the reaction mixture was stirred for 10 min at room temperature. The reaction mixture was quenched with saturated aqueous solution of ammonium chloride and organic layer was extracted with ether (2×10 ml) and then dried over $MgSO_4$. The organic solvent was evaporated and the product was separated by the flash column chromatography (ethyl acetate/hexane).

α-(4-Methoxyphenyl)-α-methylbenzenepropanol (**1a**): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.52 (s, 3H), 2.04 (t, $J = 8.58$ Hz, 2H), 2.36–2.62 (m, 3H), 3.68 (s, 3H), 6.83 (app d, $J = 8.59$ Hz, 2H), 7.05–7.11 (m, 3H), 7.16–7.21 (m, 2H), 7.34 (app d, $J = 8.59$ Hz, 2H); ^{13}C NMR

($CDCl_3$, 75 MHz) δ 30.72, 31.03, 46.55, 55.56, 74.70, 113.96, 126.14, 126.54, 128.79, 140.34, 142.87, 158.62.

4-Methoxy-α-phenylbenzenemethanol (**1b**): ^1H NMR ($CDCl_3$, 300 MHz) δ2.74 (s, 1H), 3.70 (s, 3H), 5.66 (s, 1H), 6.77–6.82 (m, 2H), 7.17–7.32 (m, 7H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 55.78, 76.22, 114.39, 127.00, 127.91, 128.49, 128.96, 136.82, 144.66, 159.50.

Acknowledgement

This work was supported by a research grant from the National Science Foundation.

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