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Solvent free hydrostannation and Stille reactions using ionic liquid supported organotin reagents

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ABSTRACT

Hydrostannation reactions were performed cleanly using ionic liquid supported organotin reagents. These green reducing agents were used both under free radical and palladium-catalyzed conditions. One of the new ionic liquid supported organotin reagents so obtained was evaluated successfully in Stille cross-coupling reactions to give aryl-substituted allylic alcohols in solvent free conditions.

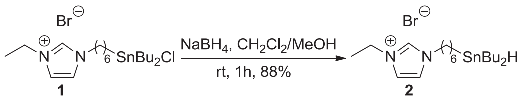
1. Introduction

During the past decades, many versatile and efficient synthetic methods using organotin reagents (Stille coupling, radical reactions, allylation reactions…) have emerged as powerful tools for organic chemists. However, despite such impressive synthetic potential, reactions involving organotin compounds display drawbacks, such as pollution of products by tin salts and difficulties of separation at the end of the synthesis. As a result, ongoing efforts have been devoted to overcome these problems by using solid phase synthetic methods,[1] phosphonium grafted organotins,[2] catalytic Stille couplings,[3] and other modified organotin reagents.[4] As a part of our ongoing research program on the discovery of potentialities of TSILs (task specific ionic liquids),[5] we became interested in investigating the use of organotin reagents supported on ionic liquids for hydrostannation reaction.

Vinylstannanes are useful intermediates for organic synthesis. Among the various methods to obtain vinylstannanes, the most studied and frequently used one is the addition of a tin hydride species to an alkyne.[6] Following this strategy, Cai et al.[7] described palladium-catalyzed hydrostannation reactions of various alkynes in ionic liquids. Recently, we reported the synthesis of organotin reagents supported on ionic liquid bearing a vinyl moiety. These compounds were obtained after reaction of a Grignard reagent with an organotin chloride derivative.[5e] As it is somehow difficult to prepare functionalized vinyl Grignard reagents, we report herein the synthesis of a series of alkenes supported on ionic liquids using hydrostannation reactions. A preliminary study concerning their use in Stille cross-coupling reactions is also described in this work.

2. Results and discussion

As an initial assay, hydrostannation reactions under free radical conditions were investigated using ionic liquid-supported organotin hydride **2**. This compound was obtained by reduction of **1**[5c] in presence of sodium borohydride and methanol (Scheme 1).



Scheme 1. Preparation of organotin hydride supported on ionic liquid.

In a general manner, ionic liquids were isolated with moderate yields (40–55%) as highlighted in Table 1. The hydrostannation of phenyl acetylene (Table 1, entry 1) proceeded with no selectivity. When using propargyl alcohol as substrate (Table 1, entry 2), selectivity was improved in favor of *trans*-isomer. Unfortunately,

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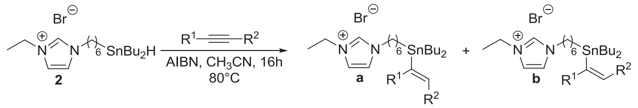
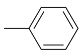
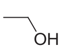
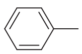
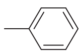
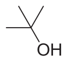
Table 1
Hydrostannation reactions under free radical conditions



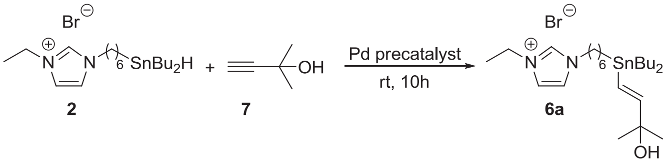
Entry	R^1	R^2	Ratio **a**/**b**[a]	Yield (%)
1	H		**3a**/**3b** 50:50	40
2	H		**4a**/**4b** 82:18	42
3			**5a**/**5b** 2:98	48
4	H		**6a**/**6b** 98:2	55

[a] Determined by ^{1}H NMR.

isomers **3a**/**3b** and **4a**/**4b** could not be separated by silica gel column chromatography. With a symmetrical alkyne (Table 1, entry 3) and a sterically demanding alkyne (Table 1, entry 4), one isomer was mainly obtained, (*Z*)- and (*E*)-isomer, respectively.

The reactivity of tin hydride **2** has been evaluated in palladium-catalyzed hydrostannation reactions with different precatalysts (3 mol %) under solvent free conditions by using 3-methyl-3-hydroxybut-1-yne **7** as a benchmark substrate. Results are summarized in Table 2.

Table 2
Precatalyst effect on palladium-catalyzed hydrostannation reactions



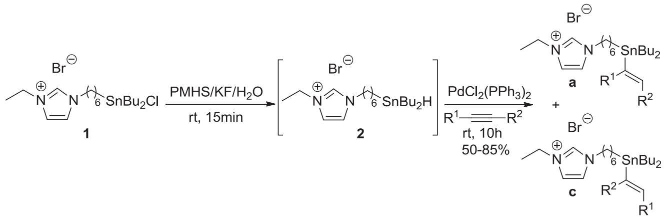
Entry	Precatalyst	Yield (%)
1	[Pd/C]	—
2	[Pd(OAc)$_2$]/2PPh$_3$	18
3	[PdCl$_2$]/2PPh$_3$	21
4	[Pd(PPh$_3$)$_4$]	78
5	[PdCl$_2$(PPh$_3$)$_2$]	85
6	[PdCl$_2$(PPh$_3$)$_2$][a]	80

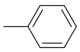
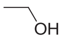
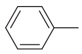
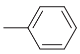
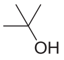
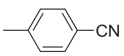
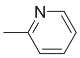
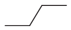
[a] THF was used as co-solvent.

No conversion was observed with Pd/C (Table 2, entry 1). When using [Pd(OAc)$_2$] or [PdCl$_2$] both with 2 equiv of triphenylphosphine (Table 2, entries 2 and 3), the reaction proceeded with only 18–21% conversion. Then, the use of [Pd(PPh$_3$)$_4$] allowed the formation of compound **6a** with 78% yield (Table 2, entry 4). Interestingly, the highest conversion (85%) was observed when using [PdCl$_2$(PPh$_3$)$_2$] as precatalyst (Table 2, entry 5). To further optimize reaction conditions, the influence of a co-solvent was investigated (Table 2, entry 6). Noteworthy, the use of THF as additive did not improve the yield.

With these optimized conditions in hand, we decided to investigate the scope of our catalytic system. Indeed, the hydrostannation of a series of alkynes was studied and the results are depicted in Table 3. We have shown that the palladium-catalyzed hydrostannation reaction could be done with in situ tin hydride generation. This species was generated in situ with hypercoordinate polymethylhydroxysilane[3] (PMHS+fluoride source).

Table 3
Palladium-catalyzed hydrostannation reactions

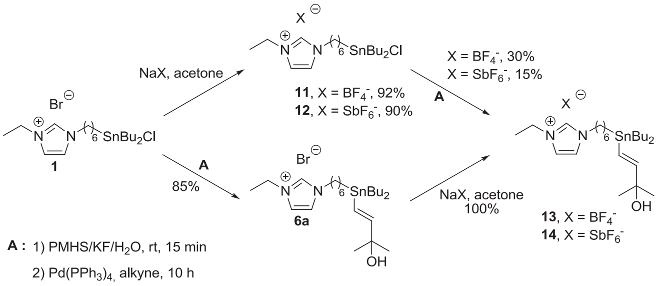


Entry	R^1	R^2	Ratio **a**/**c**[a]	Yield (%)
1	H		**3a**/**3c** 40:60	65
2	H		**4a**/**4c** 12:88	72
3			**5a**	75
4	H		**6a**/**6c** 95:5	85
5	H		**7a**/**7c** 5:95	77
6	H		**8a**/**8c** 62:38	50
7	H		**9a**/**9c** 40:60	52
8	H		**10a**/**10c** 95:5	76

[a] Determined by ^{1}H NMR.

Using our optimized conditions, hydrostannation products were obtained in moderate to good yields following mild reaction conditions. It should be noted that good regioselectivities were observed with sterically demanding alkynes (Table 3, entries 4 and 8) leading mainly to one isomer in case of **6a** and **10a**.

The influence of the ionic liquid's counter anion on the hydrostannation reaction has been investigated (Scheme 2). It has been shown that this parameter strongly influences the yield of the reaction. Indeed, anionic metathesis reactions between bromide and tetrafluoroborate or hexafluoroantimonate anions have to be achieved after hydrostannation reaction, otherwise low yields are obtained (30 and 15%, respectively). This phenomenon is probably connected to the strength of cation–anion interaction[8] $SbF_6^- > BF_4^- > Br^-$, also confirmed by the ^{1}H chemical shifts of the proton at C2 position of imidazolium ring.



Scheme 2. Influence of ionic liquid's counter anion on hydrostannation.