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Hydrostannation of activated alkynes mediated by Stryker's reagent*

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Abstract: The treatment of activated alkynes with catalytic amounts of Stryker's reagent and tributylstannane resulted in hydrostannation. The reaction proceeds with high regioselectivity to produce α-stannated vinylstannanes exclusively.

Keywords: copper; regioselectivity; vinylstannanes; alkynes; hydrostannation.

INTRODUCTION

Stryker's reagent $[(Ph_3P)CuH]_6$ **1** [1], is a well-characterized, relatively nonbasic copper hydride, readily synthesized [2] and available commercially. The most popular application of this reagent is in the conjugate reduction of activated alkenes [3]. This reduction is chemoselective, and isolated olefins remain inert.

More recently, it has been demonstrated that the Stryker reduction of enones and enoates is an avenue for the synthesis of copper enolates, which can further engage in carbon–carbon bond-forming reactions. In this respect, we have demonstrated that various reductive aldol reactions are induced by Stryker's reagent (Scheme 1). We have shown that enediones undergo stoichiometric reductions in tandem with intramolecular aldol reactions to afford good yields of diastereoselective aldol products [4]. The site of enolate formation is at the alkene in conjugation with the electron-withdrawing group. Thus, it is possible to generate ester enolates in the presence of more reactive ketones and direct their intramolecular aldol reaction. Similarly, a reductive intramolecular Henry aldol reaction has been realized by the treatment of nitroalkenes with **1** [5]. Alkynediones such as **2** have been transformed into β-hydroxyenones by **1**, and this reaction also proceeds catalytically using silane as the stoichiometric reductant (Scheme 2) [6].

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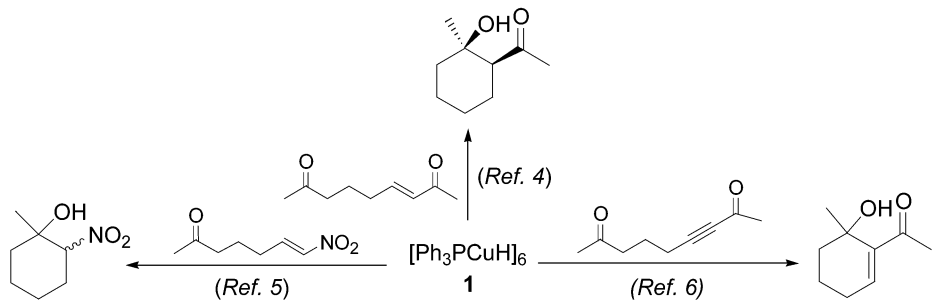
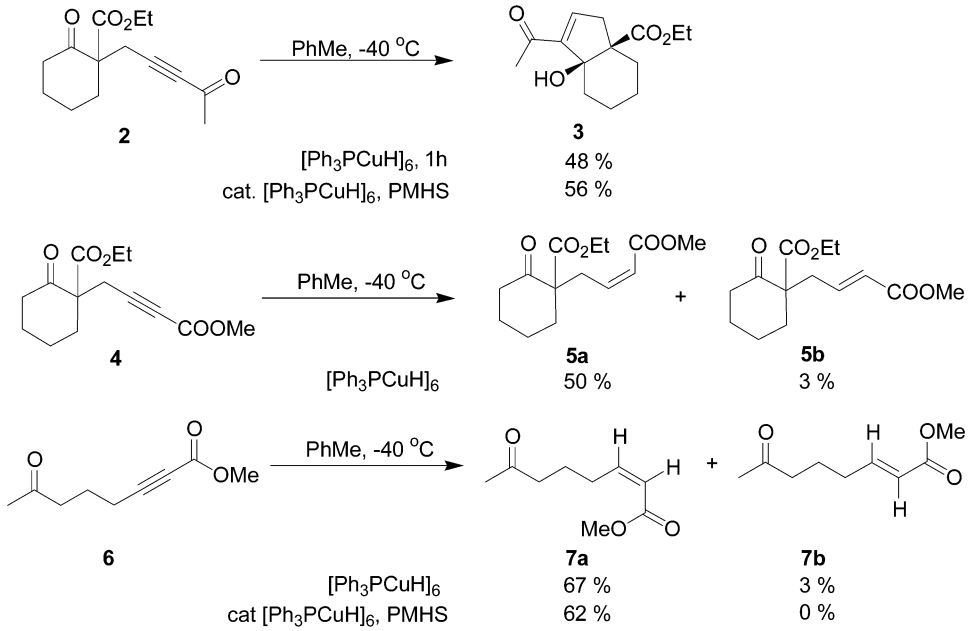


Scheme 1

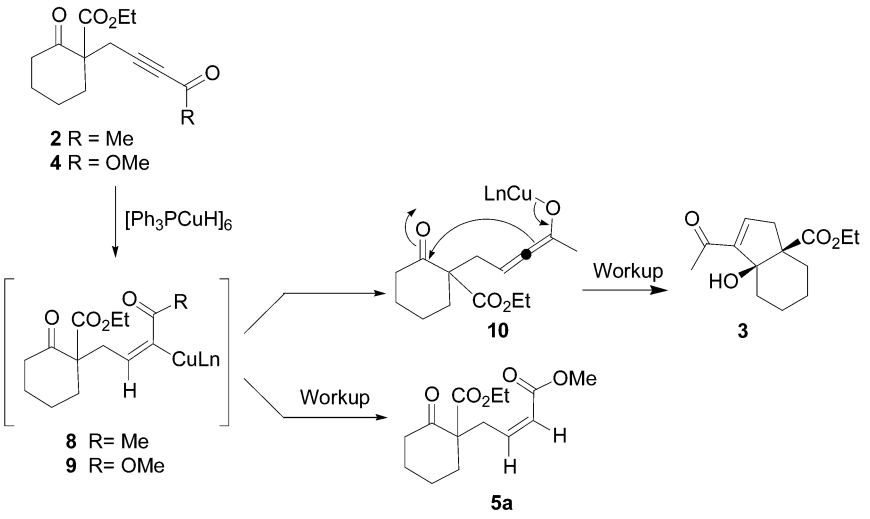
RESULTS AND DISCUSSION

After studying alkynones as substrates, the Stryker reduction was further investigated in the context of alkynoates such as **4** and **6** (Scheme 2). However, under the same reaction conditions, the expected reductive aldol reaction did not proceed. Instead, the major product isolated was the reduction products **5** and **7**. Simple reduction occurred under both the stoichiometric as well as the catalytic reaction conditions. Moreover, it was observed that the *cis*-reduction product **5a** or **7a** was favored or exclusive.



Scheme 2

This suggested that a hydrocupration reaction was responsible for the rise of **5a** and **7a** (Scheme 3). When the electron-withdrawing group in conjugation with the alkyne is an ester, the hydrocuprated intermediate **9** appears to be relatively stable and largely remains until workup to yield the *cis*-reduction product **5a**. If the electron-withdrawing group were a ketone, the vinylcopper intermediate **8** must be able to isomerize to the allenolate **10** in order to undergo the observed intramolecular aldol reaction.



Scheme 3

It was then considered whether the vinylcopper intermediate **9** could be transmetallated via another hydride other than silane, to furnish a new organometallic while perpetuating the catalytic cycle. Stannanes appeared to be a suitable candidate because previous reports by Lipshutz had demonstrated the ability of tin hydride to regenerate Cu hydride [7]. This catalytic reaction would constitute a hydrostannation of an alkyne to produce a vinylstannane, which is an important building block in synthetic organic chemistry granted by its indispensable role in the Stille coupling reaction [8].

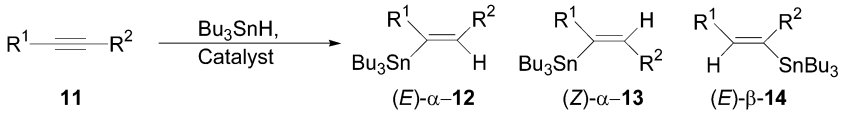
Presently, of the various approaches to the synthesis of vinylstannanes, metal-catalyzed hydrostannation of alkynes is the most common [9]. Due to the difficulty in separating diastereomeric vinylstannanes and their tendency toward decomposition, the hydrostannation reaction should ideally be highly selective. The typical catalysts for the hydrostannation of alkynes are complexes of Pd [10]. Although they mediate the hydrostannation of alkynes efficiently, mixtures of α/β-stannylated regioisomers are frequently obtained. For example, the Pd-catalyzed hydrostannation of **11a** yielded (*E*)-α- and (*E*)-β-stannylated alkenoates **12a** and **14a** as a 4:1 mixture (Table 1, entry 1).

The reaction of **11a** with catalytic amount of **1** and tributylstannane was thus examined (Table 1, entry 1). Gratifyingly, the reaction proceeded smoothly. Moreover, the regioselectivity was exclusive for α-stannation, and the addition of tin hydride was syn, resulting in (*E*)-α-stannylated alkenoate **12a** as the only stannylated product [11]. To the best of our knowledge, this is the first report in the literature of Cu complexes being able to catalyze the hydrostannation reaction. The only side-product obtained, in <10 % yield, is the protodestannylated product**.**

Other alkynes were examined for hydrostannation mediated by **1** (Table 1). In general, polarized alkynes were hydrostannated smoothly. Alkynoates underwent hydrostannation, and compared to the reaction under Pd catalysis, similar yields of vinylstannanes were produced (Table 1, entries 1–3). But in all cases, the selectivity in the reaction mediated by **1** was exclusive for α-stannation. For the isobutyl alkynoate in which the direction provided by steric and electronic factors are antagonistic, hydrostannation catalyzed by Pd proceeded with poor regioselectivity (Table 1, entry 3). However, even in this case, the selectivity for α-stannation is maintained under catalysis by **1**. Alkynones underwent hydrostannation mediated by **1** with expected exclusive α-stannation (Table 1, entries 4–5). But the addition of tin hydride became anti to give **13d** and **13e** as products, whereas both syn and anti additions have been reported under Pd catalysis [10d,e]. Whether catalyzed by **1** or by Pd, the yields of the vinylstannanes were plagued by protodestannylation during isolation and purification. However, the hydrostannation of unpolarized alkynes such as propargyl alcohol derivatives, alkyl and aryl alkynes, were

uniformly unsuccessful under catalysis by **1**, although Stryker had previously shown that **1** induced the reduction of unpolarized alkynes [12] (Table 1, entry 6).

Table 1 Hydrostannation of various alkynes.



11 (*E*)-α–**12** (*Z*)-α–**13** (*E*)-β-**14**

Entry	Substrates	R^1	R^2	Catalyst	Yield of products (%)		
					12	**13**	**14**
1	**11a**	COOMe	*n*-C_6H_{13}	$Pd(PPh_3)_4$	60	–	15
				1	70	–	–
2	**11b**	COOMe	Me	$Pd(PPh_3)_4$	58	–	21
				1	62		–
3	**11c**	COO*i*-Bu	*n*-C_6H_{13}	$Pd(PPh_3)_4$	55	22	–
				1	77	–	–
4	**11d**	COMe	Et	$Pd(PPh_3)_4$ [10c]	–	58	–
				1	–	55	–
5	**11e**	COMe	*n*-C_6H_{13}	$PdCl_2(PPh_3)_2$ [10d]	100 (0)	–	–
				1	–	48	–
6	**11f**	Ph	H	$Pd(PPh_3)_4$ [10b]	48		48
				1	Low yield, nonselective		

The regioselectivity for α-stannation can be correlated to the tendency to deliver hydride to the β-position. Although more studies are required to elucidate the reaction mechanism and the identity of the active species for the Cu-mediated hydrostannation, from the observed exclusive reactivity with polarized alkynes, the hydridic nature of this active species is inferred.

CONCLUSION

Stryker's reagent **1** has been found to mediate the hydrostannation of activated alkynes. The yields of hydrostannation are comparable to that under Pd catalysis, but superior diastereoselectivities are observed. The regioselectivity for α-stannation is exclusive. However, this hydrostannation is limited to polarized alkynes. This reaction represents a useful alternative hydrostannation methodology for the preparation of this family of vinylstannanes.

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