Available online at www.sciencedirect.com
ScienceDirect
Tetrahedron 63 (2007) 6737–6740
Tetrahedron

Regioselective hydrostannation of activated alkynes catalyzed by in situ generated copper hydride

Ru Miao, Shuoliang Li and Pauline Chiu*

Department of Chemistry and Open Laboratory of Chemical Biology of the Institute of Molecular Technology for Drug Discovery and Synthesis, The University of Hong Kong, Pokfulam Road, Hong Kong, PR China

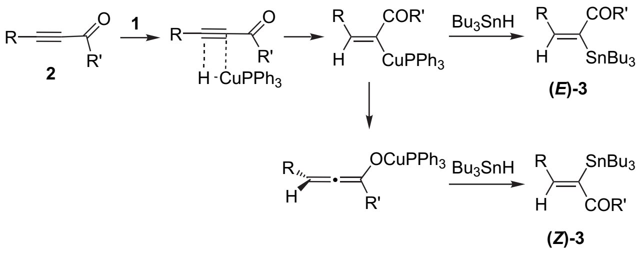
Received 4 January 2007; revised 25 April 2007; accepted 26 April 2007
Available online 3 May 2007

Abstract—The hydrostannation of activated alkynes proceed in good yields and high regioselectivities catalyzed by CuCl, in the presence of potassium *tert*-butoxide, triphenylphosphine, and tributylstannane, by generating copper hydride in situ.
© 2007 Elsevier Ltd. All rights reserved.

1. Introduction

The Stille coupling is one of the most extensively utilized palladium-catalyzed carbon–carbon bond forming reactions, and numerous examples of its application in the syntheses of natural products are found.[1] The application of the Stille vinylation reaction is dependent on the availability of vinylstannanes as precursors. Hydrostannation of alkynes is presently the most common way to gain access to vinylstannanes, with palladium complexes being the dominant catalyst for this reaction.

In this connection, we had previously reported on the use of copper as an alternative transition metal catalyst for hydrostannation in the form of hydrido(triphenylphosphine)copper(I) hydride hexamer, $[(Ph_3P)CuH]_6$ (**1**),[2] known popularly as Stryker's reagent.[3,4] The hydrostannation appears to be initiated by the copper hydride undergoing hydrocupration with an activated alkyne substrate (Scheme 1). Transmetallation of the vinylcopper with tin produces the vinylstannane.



Scheme 1. Hydrostannation catalyzed by **1**.

The overall reduction delivers hydride at the electrophilic β-position, resulting in only α-stannylated vinylstannanes with comparable or superior regioselectivity than that obtained in palladium-catalyzed hydrostannations.[5] This improved selectivity is important and has significant practical advantages, since isomeric vinylstannanes are often hard to separate chromatographically and succumbs to decomposition over time on silica gel.

Although this hydrostannation is more regioselective and economical than palladium for hydrostannation of activated alkynes, it uses discreet copper hydride **1** as catalyst, which needs to be purchased or synthesized in the laboratory.[6] Thus an alternative protocol using a more common and convenient source of copper for hydrostannation, which still achieves high regioselectivity would be practical and desirable.

2. Results and discussion

Recently we found that copper(I) chloride, with potassium *tert*-butoxide and triphenylphosphine, all of which can be weighed in open air without the aid of a dry box,[7] directly promotes hydrostannation in the presence of tributylstannane, thus obviating the need to separately prepare, isolate, and purify **1**.

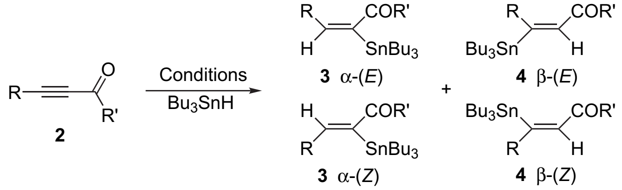
Copper chloride with only KO*t*-Bu or with Ph_3P alone does not promote the hydrostannation. This improved hydrostannation procedure presumably generates the required copper hydride in situ, since CuCl, KO*t*-Bu, and Ph_3P in the presence of hydrogen or hydrosilane are the starting materials for the preparation of **1**. In this improved hydrostannation protocol, the addition of hydrosilane is not required as tin hydride serves both as the reductant as well as the stannylating agent.[8] The reddish brown color of the reaction mixture generated upon mixing of these reagents bears resemblance to the color of **1**.

Keywords: Hydrostannation; Reductions; Stannanes; Catalysis; Regioselectivity.

* Corresponding author. Tel.: +852 2859 8949; fax: +852 2857 1586; e-mail: pchiu@hku.hk

0040–4020/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2007.04.085

Table 1. Hydrostannation of activated alkynes



Entry	Substrate	R	R′	Conditions[a]		
				A: Yield[b] (**3**:**4**)	B: Yield[b] (**3**:**4**)	C: Yield (**3**:**4**)
1	**2a**	Et	OEt	78% (>20:1)[c]; *E*	81% (>20:1)[c]; *E*	92% (15:1)[e]; *E*
2	**2b**	TBSOCH$_2$	OEt	74% (>20:1)[c]; *E*	83%[d] (>20:1)[c]; *E*	84% (91:9)[f]; *E*
3	**2c**	*n*-Bu	OEt	71% (>20:1)[c]; *E*	75%[d] (>20:1)[c]; *E*	83% (3:1)[g]
4	**2d**	*n*-C$_6$H$_{13}$	OMe	71% (>20:1)[c]; *E*	70%[d] (>20:1)[c]; *E*	75% (4:1)[d]
5	**2e**	*n*-C$_6$H$_{13}$	OEt	78% (>20:1)[c]; *E*	71% (>20:1)[c]; *E*	
6	**2f**	*n*-C$_6$H$_{13}$	O*i*-Bu	79% (>20:1)[c]; *E*	77%[d] (>20:1)[c]; *E*	83% (2:1)[d]
7	**2g**	Ph	OEt	74% (>20:1)[c]; *E*/*Z*=3.1:1[i]	65% (>20:1)[c]; *E*/*Z*=2.4: 1[i]	71% (9:1)[f]; *E*
8	**2h**	Ar[h]	OMe	73% (>20:1)[c]; *E*/*Z*=4.7:1[i]	73% (>20:1)[c]; *E*/*Z*=3.8:1[i]	83% (2.8:1)[j]; *E*
9	**2i**	Et	Me	61% (>20:1)[c]; *Z*	55%[d] (>20:1)[c]; *Z*	58%; *Z*[k]
10	**2j**	*n*-C$_6$H$_{13}$	Me	55% (>20:1)[c]; *Z*	48%[d] (>20:1)[c]; *Z*	≥61% (not isolated); *E*[g]
11	**2k**	*n*-Bu	Me	73% (>20:1)[c]; *Z*	77% (>20:1)[c]; *Z*	
12	**2l**	*n*-Bu	Et	68% (>20:1)[c]; *E*/*Z*=1:20[i]	69%[d] (>20:1)[c] *E*/*Z*=1:7.3	
13	**2m**	*n*-Bu	*t*-Bu	64% (>20:1)[c]; *E*/*Z*=1:4[i]	61%[d] (>20:1)[c]; *E*/*Z*=1:4	

[a] Conditions A: 10% CuCl, 10% KO*t*-Bu, 15% Ph$_3$P, 1.5 equiv Bu$_3$SnH, PhMe; conditions B: 10% **1**, 1.5 equiv Bu$_3$SnH, PhMe; conditions C: 10% Pd(PPh$_3$)$_4$, 1.5 equiv Bu$_3$SnH.

[b] Isolated yields after chromatography.

[c] Only regioisomer **3** observed by ^{1}H NMR of the crude product mixture.

[d] Ref. 2a.

[e] Ref. 9a.

[f] Ref. 9b.

[g] Ref. 9c.

[h] Ar=5-benzo[1,3]dioxo-.

[i] Ratio of *E*/*Z* isomers determined from ^{1}H NMR of the crude product mixture.

[j] Ref. 9d.

[k] Ref. 9e.

The reaction conditions for hydrostannation were explored for **2a** using 10% CuCl, 10% KO*t*-Bu while varying the amount of Ph$_3$P (Table 1). At 10, 15, 20, and 30 mol % Ph$_3$P, the yields of **3a** obtained were 65%, 78%, 71%, and 52%, respectively, after about 30 min of reaction. The lower yield at 30 mol % Ph$_3$P is due to a slower rate of reaction, resulting in incomplete reaction of **2a** after 30 min, while conversions were complete at 10, 15, and 20 mol % Ph$_3$P.

Using these optimized conditions, the hydrostannation of various alkynes catalyzed by 10% CuCl/10% KO*t*-Bu/15% Ph$_3$P (conditions A), by 10% **1** (conditions B), and by catalytic palladium (conditions C) were compared (Table 1). Notably, the results of the present hydrostannation catalyzed by the in situ generated copper hydride (conditions A) provide vinylstannanes with similar yields and regioselectivities to hydrostannation catalyzed by **1** (conditions B). Exclusive α-stannation was observed for all acetylenic substrates without exception, showing again similar or superior regioselectivity compared to palladium-catalyzed hydrostannation (conditions C), although the latter reaction system is clearly more reactive and the corresponding reaction time is shorter. Under conditions A, some destannylation was observed as a side reaction.

Entries 1–8 (Table 1) show the results of the hydrostannation of acetylenic esters. α-Stannation in all cases was exclusive in the copper-catalyzed hydrostannation to give vinylstannanes **3a–h**, and this stands in contrast to the palladium-catalyzed reaction, where β-stannylated vinylstannanes **4a–h** in yields varying from 6–33% were produced as mixtures with **3a–h**.

Aryl-substituted alkynes have not been previously examined in the hydrostannation catalyzed by **1** and thus alkynoates **2g** and **2h** are included in the present study. It was found that, while copper-catalyzed hydrostannation of **2g** still generated exclusively α-stannated vinylstannane **3g**, it was obtained as a 3:1 mixture of *syn*- and *anti*-hydrostannated (*E*)-**3g** and (*Z*)-**3g** (entry 7). Similarly, both (*E*)-**3h** and (*Z*)-**3h** were obtained from the reaction of **2h** (entry 8). The two modes of addition presumably resulted from initially a *syn* hydrometallation, followed by an isomerization of the vinyl organometallic via a putative allenoate to the *anti*-hydrometallated product (Scheme 1). Apparently, in both of the copper-catalyzed hydrostannation reactions, this isomerization is facilitated by aryl groups in conjugation (R=Ph, 5-benzo[1,3]dioxo-). In the palladium-catalyzed hydrostannation of acetylenic esters, although mixtures arising from non-regioselective stannylation were obtained, isomerization resulting in *syn*- and *anti*-hydrometallated products was not observed.

Entries 9–13 (Table 1) show the hydrostannation of acetylenic ketones. Acceptable yields of α-stannated vinyl ketones **3** were obtained despite the sensitivity of these compounds to protodestannylation.[10] For methyl acetylenic ketones **2i–k** (R′=Me), both copper and palladium catalyzed-hydrostannation resulted in full isomerization to give exclusively the

Download English Version:

https://daneshyari.com/en/article/5230235

Download Persian Version:

https://daneshyari.com/article/5230235

Daneshyari.com