



Hydrochalcogenation of Terminal Alkynols Mediated by Zinc Organyl Chalcogenolate

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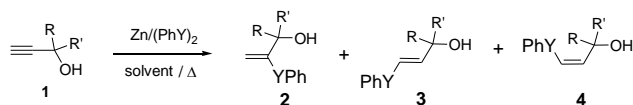
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INTRODUCTION

Preparation of olefins with a rigorous regio- and stereochemical control is of great interest. Many protocols leading to vinyl chalcogenides are described in the literature.¹ The most frequently employed method for preparation of (*Z*)-vinyl chalcogenides (*anti*-Markovnikov isomer) is the hydrochalcogenation of terminal and internal alkynes using nucleophilic organyl chalcogenolate anions, generated *in situ* from diorganyl dichalcogenide in the presence of a reducing agent (as NaBH₄, Li, Sn, Cu, In and Zn) or from elemental chalcogen in the presence of alkyl lithium.¹ On the other hand, Markovnikov regioisomers can be achieved by adding PhSeBr to terminal olefins under rigid kinetic conditions (-78°C) followed by the dehydrohalogenation. Nevertheless, *anti*-Markovnikov *E* and *Z* stereoisomers adduct were obtained at high temperatures.²

In this study, we describe a new chemo- regio and stereoselective hydrochalcogenation of terminal alkynols mediated by zinc organyl chalcogenolate generated *in situ*, affording preferentially Markovnikov adducts in mild reaction conditions (Scheme 1).



Y = S, Se, Te

Scheme 1. Hydrochalcogenation of terminal alkynols.

RESULTS AND DISCUSSION

Several parameters were studied, and the best conditions found for the hydrochalcogenation of terminal alkynes were the addition of zinc dust, diaryl dichalcogenide, NH₄OH and the appropriate alkyne suspended in water under nitrogen atmosphere, at reflux for 1 h (method A) or in 1,4-dioxane under nitrogen atmosphere, at reflux for 24h (Method B). Our results are summarized in Table 1 and Table 2.

Table 1. Hydrochalcogenation of alkynols by method A

Entry	1	Zn(YPh) ₂	(2:3:4)	Yield
1		(SePh) ₂ (SPh) ₂	(20:1:6) (24:3:1)	100% 93%
2		(SePh) ₂ (SPh) ₂	(1.6:1.3:1) (0:3:2)	34% 40%
3		(SePh) ₂	(1:2:2)	64%
4		(SePh) ₂	(10:5:1)	39%
5		(SePh) ₂	(1:0:0)	44%
6		(SePh) ₂	(8:1:19)	82%

Table 2. Hydrochalcogenation of alkynols by method B

Entry	1	Zn(YPh) ₂	(2:3:4)	Yield
1		(SePh) ₂ (SPh) ₂ (TePh) ₂	(39:1:10) (24:3:1) (3: 0:1)	72% 82% 60%
2		(SePh) ₂ (SPh) ₂ (TePh) ₂	(3.2:1:3.8) (1.5:1:0) (1:0:15))	60% 99% 4%
3		(SePh) ₂	(22:1:40)	40%

CONCLUSION

Herein, we present a new protocol for the hydrochalcogenation of alkynols applying green, mild and relatively cheaper system Zn(PhY)₂/NH₄OH with high chemo-, regio- and stereoselectivity.

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