Chinese Chemical Letters Vol. 14, No. 3, pp 255 – 256, 2003
http://www.imm.ac.cn/journal/ccl.html

Stereoselective Synthesis of δ-Selanyl Allylic Alcohols by Hydrozirconation of Propargyl Selenides

Mei Hua XIE[1], Lu Ling WU[1], Xian HUANG[1, 2]*

[1]Department of Chemistry, Zhejiang University, Xi-xi Campus, Hangzhou 310028
[2]State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032

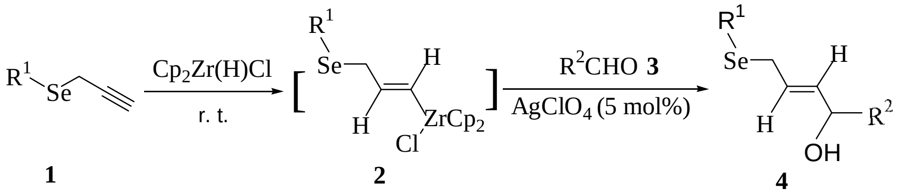
Absrtact: Hydrozirconation of propargyl selenides afford (E)-3-selanyl vinylzirconocenes chlorides **2**. Intermediates **2** reacted with aldehydes to obtain δ-selanyl allylic alcohols.

Keywords: Hydrozirconation, propargyl selenides, aldehydes, allylic alcohols.

Functionality-bearing allylic alcohols are the vital structure units of biologically active compounds[1,2]. Allylic selenides are important intermediates in organic synthesis[3,4]. So regio- and stereoselective synthesis of δ-selanyl allylic alcohol which combine the allylic alcohol and allylic selenide units together is of interest in organic synthesis. Hydrozirconation has emerged as a unique hydrometallation with some attractive features[5,6]. Recently we have reported the stereoselective synthesis of α-heteroatom substituted allylic alcohols by hydrozirconation of heteroatom substituted alkynes[2]. As an extention of our studies, we wish to report herein the hydrozirconation of propargyl selenides and its application in the synthesis of δ-selanyl allylic alcohols.

The (*E*)-3-selanyl vinylzirconocene chlorides **2** can be synthesized regio- and stereoselectivitely by hydrozirconation of propargyl selenides **1**. The intermediates **2** react with aldehydes **3** in CH_2Cl_2 at room temperature in the presence of $AgClO_4$ to afford δ-selanyl allylic alcohols (**Scheme 1**). The results are summarized in **Table 1**.

Scheme 1



---

[*]E-mail: huangx@mail.hz.zj.cn

Table 1 Yields of δ-hydroxy allylic selenides **4a~g**[a]

Entry	R^1	R^2	Product	Yield (%)[b]
1	C_6H_5-	*p*-$CH_3C_6H_4$-	**4a**	55
2	C_6H_5-	C_6H_5-	**4b**	63
3	C_6H_5-	*p*-ClC_6H_4-	**4c**	76
4	C_6H_5-	*p*-$NO_2C_6H_5$-	**4d**	75
5	Et	*p*-$CH_3C_6H_5$-	**4e**	58
6	Et	C_6H_5-	**4f**	61
7	Et	*p*-$NO_2C_6H_5$-	**4g**	73

[a] 1 mmol of propargyl selenides, 1.2 mmol of $Cp_2Zr(H)Cl$, 1.0 mmol of aldehydes were used. [b] Isolated yields based on propargyl selenides. All products were characterized by IR, ^1H NMR, MS spectra and elemental analysis.

The (E)-configuration of all products **4a**~**g** was demonstrated by the coupling constants of the vinylic protons (15.1 – 15.7 Hz).

In conclusion, hydrozirconation of propargyl selenides provide a convenient method for the synthesis of functionalized allylic alcohols. The present procedure has the advantages of readily available starting materials, simple procedures, mild reaction conditions and regio- and stereoselectivity. The application of the allylic alcohols in organic synthesis is in progress in our laboratory.

General procedure: A mixture of hydrozirconocene chloride (1.2 mmol) and propargyl selenide (**1**) (1.0 mmol) in CH_2Cl_2 was stirred at room temperature for 20 min. To the resulting clear solution aldehyde **3** (1.0 mmol) was added followed by $AgClO_4$ (5 mol%). The reaction mixture turned dark brown gradually. After stirring at room temperature for 2-3hr, the reaction mixture was quenched with saturated $NaHCO_3$ aqueous solution. Extractive workup (EtOAc) followed by purification with flash chromatography (silica/hexanes-EtOAc 4:1) gave δ-selanyl allylic alcohols **4a**~**g**.

Acknowledgment

The project was supported by the National Natural Science Foundation of China (No. 29772007).

References

1. J. Shimada, S. L. Schreiber, *Chem. News*, **1995**, *73*, 27.
2. X. Huang, A. M. Sun, *J. Chem. Research (S)*, **1999**, 292 and references therein.
3. a. H. J. Reich, *J. Org. Chem.*, **1975**, *40*, 2570. b. H. J. Reich, M. C. Clark, W. W. Jr. Willis, *J. Org. Chem.*, **1982**, *47*, 1618.
4. H. Takei, M. Miura, K. Kosugi, H. Takei, *Tetra. Lett.* , **1980**, *21*, 87.
5. a. J. Schwartz, *J. Organomet. Chem., Library*, **1976**, *1*, 461. b. D. W. Hart, T. F. Blackburn, J. Schwartz, *J. Am. Chem. Soc.*, **1975**, *97*, 679.
6. a. Review: P. Wipf, H. Jahn, *Tetrahedron*, **1996**, *52*, 12853. b. M. J. Dabdoub, M. L. Begnini, P. G. Jr. Guerrero, *Tetrahedron*, **1998**, *54*, 2371.

Received 29 April, 2002