Chinese Chemical Letters Vol. 16, No. 3, pp 325-326, 2005
http://www.imm.ac.cn/journal/ccl.html

Stereoslective Synthesis of (*Z*)-1, 2-Bis(arylseleno)-1-alkene by Addition of Cesium Arylselenolate to Alkynyl Selenide

Rui Liang LU, Xin Hua XU*, Wen Qi LIU, Qiu Lin ZHANG, Xiong CHEN

State Key Laboratory of Chemo/Biosensing and Chemometrics, College of Chemistry and Chemical Engineering, Hunan University, Changsha 410082

Abstract: Alkynyl selenide reacted with cesium arylselenolate in commercial THF at r.t under N_2 to afford (*Z*)-1, 2-bis(arylseleno)-1-alkene in high yields.

Keyword: (*Z*)-1,2-Bis(arylseleno)-1-alkene, alkynyl selenide, cesium arylselenolate.

Vicinal bisselenides is one of the important bifunctional compounds due to the varied reactivity of their selenium atoms[1-7]. Their synthesis generally is through the additions of diselenides to acetylenes, which include photo or thermal-initiated free-radical addition, palladium- catalyzed addition[8-10] and base-catalyzed addition[11-12]. The radical reactions preferentially provided (*E*)-1, 2-bis(phenylseleno)-1-alkenes, palladium or base-catalyzed addition afforded preferentially (*Z*)-1,2-bis (phenylseleno)-1-alkenes. But among these methods, there were competitive thermal addition. Herein, we wish to report the stereoslective synthesis of (*Z*)-1, 2-bis(arylseleno)-1-alkene by addition of cesium arylselenolate to alkynyl selenide.

We investigated the addition reaction of ArSeCs to alkynyl selenides. The experiment showed that the reaction readily occurred at room temperature and gave the (*Z*)-1,2-bis(arylseleno)-1-alkene in high yield. The experiment results were summarized in **Table 1.**

At room temperature ArSeNa did not react with alkynyl selenides. Only under refluxing ethanol the reaction occured and gave a mixture consisted of *cis*, *trans* and *gem*-bis(phenylseleno) alkenes and alkynyl selenide. This indicated that the $ArSe^-$ in ArSeCs has greater nucleophility than $ArSe^-$ in ArSeNa. It may owe to the less static electricity between $ArSe^-$ and Cs^+.

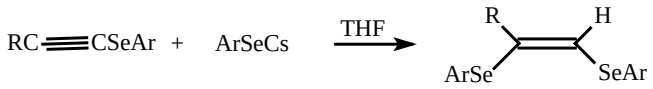
The stereochemistry of the adducts was determined by NOE experiments and the respective ^{77}Se NMR spectra of compound **3a**. Irradioation of the peak of vinylic proton (δ 7.37) responded to the CH_2 (δ 3.96) with 6% enhancement. ^{77}Se NMR are 391.709 and 437.988 ppm. $J_{Se\text{-}Se}$ is 82 ppm. These facts indicated that the reaction provided (*Z*)-1, 2-bis (arylseleno)-1-alkene.

The present method has advantages of mild condition, high stereoselectivity and

* E-mail: xhx1581@21cn.com

yields. It provides an efficient and practical path for the synthesis of (*Z)*-1, 2-bis (arylseleno)-1-alkene.

The typical procedure is as follows: The mixture of alkynyl selenide (1.1 mmol) and ArSeCs (1.0 mmol) in 10 mL THF was stirred under N_2 at room temperature. Then it was diluted with 60 mL of ether, washed with saturated brine and dried over $MgSO_4$. The solvent was evaporated. The crude product was subjected to column chromatography using light petroleum-ether as eluent (30:1).



1 **2** **3**

Table 1 Synthesis of (*Z*)-1, 2-bis (arylseleno) -1- alkene

Entry	R	Ar	Time(h)	Yield (%)
3a	CH_3OCH_2	Ph	3	91
3b	CH_3OCH_2	*p*-$CH_3C_6H_4$	3	93
3c	$HOCH_2$	Ph	2	90
3d	$HOCH_2$	*p*-$CH_3C_6H_4$	2	85
3e	$PhOCH_2$	Ph	3	95
3f	$PhOCH_2$	*p*-$CH_3C_6H_4$	4	89
3g	Ph	Ph	5	88

The structure of **3a-3g** were confirmed by ^{1}H NMR, ^{13}CNMR and MS.

Acknowledgments

We are grateful to the National Natural Sciences Foundation of China (20372020) for financial support.

References and Notes

1. S. M. Ma, X. S. Hao, X. Huang, *Chem. Cumm.*, **2003**, 1082.
2. X. H. Xu, W. Q. Liu, *Chin. Chem. Lett*., **2002**, *13*(4), 283.
3. M. H. Xie, L. L. Wu, X. Huang, *Chin. Chem. Lett*., **2003**, *14*(*3*) 255.
4. X. J. Zhao, H. R. Zhao, X. Huang, *Chin. Chem. Lett*., **2002**, *13*(5) 396.
5. M. Tingoli, M. Tiecco, L. Testaferri, R. Balducci, *Synlett.*, **1993**, (3) 211.
6. D. H. Wadsworth, M. R. Detty, *J. Org. Chem*., **1980**, *45*, 4611.
7. I. Johannaen, L. Henriksen, H. Eggert, *J. Org. Chem*., **1986**, *51*, 1567.
8. A. Ogawa, H. Yokoyama, ,*J. Org. Chem*., **1991**, *56*, 5271.
9. T. G. Back, M. V. Krishna, *J. Org. Chem.*, **1988**, *53*, 2533.
10. A. Ogawa, M. Sekiguchi, H. Shibuya, *Chem. Lett*., **1991**, 1805, 2241.
11. H. Kuniyasu, A. Ogawa, *J. Am. Chem. Soc*., **1991**, *113*, 9796.
12. T. G. Back, R. J. Bethell, M. Parvez, *J. Org. Chem*., **1998**, *63*, 7908.
13. Compound **3a**: ^{1}H NMR, δ ppm: 3.29(s, 3H), 3.98(d, 2H, J=1.2Hz), 7.27-7.35(m, 6H), 7.38(t, 1H, J=1.2Hz), 7.56-7.66(m, 4H). ^{13}C NMR, δ ppm: 133.296, 133.072, 132.635, 130.525, 129.315, 129.138, 129.098, 128.878, 127.689, 127.432, 76.685, 57.917. MS: 45(100), 77(52.6), 91(11.8), 102(11.3), 115(47.3), 131(5.5), 147(31.5), 157(40.2), 195(39.2), 225(6.7), 384(M^+, 31.8).

Received 23 February, 2004