Chinese Chemical Letters Vol. 10, No. 6, pp. 437–440, 1999

A Novel Stereoseletive Approach to (E)-Vinylic Selenides

Jun Hua WANG, Xian HUANG*

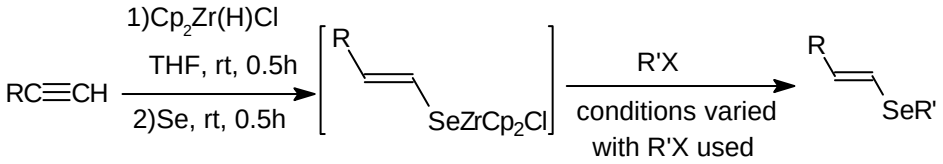
Department of Chemistry, Zhejiang University (Campus Xixi), Hangzhou 310028

Abstract: The insertion of elemental selenium into the Csp^2-Zr bond of alkenylchloro-zirconocenes affords (E)-vinylseleno zirconocenes, which were trapped by alkyl halides giving (E)-vinylic selenides in moderate to good yields.

Keywords: Hydrozirconation reaction, insertion, vinylseleno zirconocenes, vinylic selenides.

Vinylic selenides are important intermediates in organic synthesis, and their promising potential could be anticipated by the combination of the special reactivity of selenium and the reactivity associated with carbon-carbon double bond, particularly they are extremely useful in highly stereoselective C-C bond formation process[1]. Various preparations of these compounds have been reported, but most of these methods involved the disposal of highly toxic selenides, such as RSeX, RSeSeR and RSeH. Futhermore, many of these methods are not stereocontrolled and give mixture of isomers[1]. Recently transition metal selenolates have been widely used in synthesis of selenides[2]. The following intermediates have been reported: $ArSeZnCl$[2], $ArSeCu$[3], $ArSeSmI_2$[4], $Cp_2TiSeAr$[5], $Cp_2Zr(SeMe)_2$[6], $Cp_2Hf(SeMe)_2$[6] and $Cp_2ZrSe_2C_6H_4$-o[7], and they have complemented in reactivity the known main group metal selenolates. According to our knowledge, vinylseleno transition metal complexes have not yet been reported, herein we report the first example of these intermediates, and its application in facile synthesis of (E)-vinylic selenides from alkynes, elemental selenium and alkyl halides.

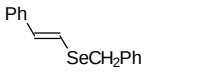
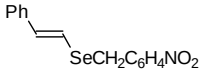
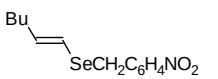
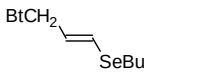
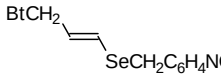
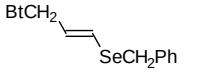
Scheme 1



The insertion of elemental selenium into Csp^2—Zr bond proceeds smoothly in THF at room temperature and usually terminate within 30 minutes, affording a deep red solution. The produced vinylseleno zirconocenes were trapped by alkyl halides under different conditions according to the reactivity of the alkyl halides used. The outcomes were summarized in **Table 1**.

The stereochemistry of these vinylic selenides was easily established, since the ^{1}H-NMR spectra of the products give doublets at δ6-7 with coupling constants 15-16Hz, typical of *trans*- positioned vinylic protons[8]. Besides, it has been well established that syn-addition of $Cp_2Zr(H)Cl$ onto carbon-carbon triple bond of 1-alkynes gives (E)-alkenylchlorozirconocenes[9], and the insertion of several species into the Csp^2-Zr bond proceeds with retention of the stereochemistry of the carbon-carbon double bond[10].

Table 1. Stereoselective synthesis of (E)-vinylic selenides from alkynes, elemental selenium and alkyl halides.

RC≡CH R	R'X	Conditions	Products[a)] (2a-af)	Yields (%)[b)]
Ph	$PhCH_2Br$	50°C , 1h		72
Ph	$p\text{-}O_2NC_6H_4CH_2Br$	40°C , 1h		75
n-Bu	$p\text{-}O_2NC_6H_4CH_2Br$	40°C , 1h		73
$BtCH_2$[c)]	n-BuBr	reflux, 8h		38
$BtCH_2$	$p\text{-}O_2NC_6H_4CH_2Br$	40°C , 1h		66
$BtCH_2$	$PhCH_2Br$	50°C , 1h		71

[a)]All these compounds were characterized by ^{1}H-NMR, IR and MS. [b)]Isolated yields.
[c)]Bt=benzotriazol-1-yl.

It should be pointed out that besides the 1-alkynes employed in **Scheme 1**, various alkynes including functionalized alkynes can undergo hydrozirconation reaction smoothly and stereoselectively[9]. As a result, the present method has provided a stereocontrolled, environmental-friendly route to various vinylic selenides.

Experimental

IR spectra were recorded on a PE-683 spectrometer, and ^{1}H-NMR spectra were recorded on a JEOL-PMX60 spectrometer in CCl_4 solution using hexamethyldisilane as internal standard. MS were obtained on a HP5989B spectrometer. THF was newly distilled from sodium/benzophenone before use. $Cp_2Zr(H)Cl$ was prepared according to the literature procedure[11].

Typical procedure: To a stirred suspension of 1.2 mmol (0.308 g) $Cp_2Zr(H)Cl$ in 8 ml THF under N_2 atmosphere was added 1.0 mmol (0.157 g) 1-propargyl-1H-benzotriazole. When the mixture turned into a clear solution, it was

transferred *via* a syringe into a stirred suspension of 1.0 mmol (0.080 g) selenium powder in 2 ml THF, the color of the mixture turned from a dark yellow-green into a deep red during 0.5h. A solution of 1.0 mmol (0.216 g) 4-nitrobenzyl bromide in 2 ml THF was added and the mixture was stirred for another 1h at 40°C. The solvent was removed in vacuum, and the product was extracted with CH_2Cl_2-diethyl ether (v/v1:1, 4x10 ml). The solvents were removed under reduced pressure and the residue was purified by preparative TLC on silica gel (light petroleum ether -diethyl ether -CH_2Cl_2 (2:1:1) as the eluent). (E)-3-(benzotriazol-1-yl)propenyl 4-nitrobenzyl selenide (**2e**) was obtained as a yellow oil in 66% yield.

Compound 2a: yellow oil. IR (cm^{-1}): 3090, 3060, 1620, 1510, 950, 735, 700. ^{1}H-NMR: δ7.40-6.90 (m, 10H), 6.86 (d, J=15Hz, 1H), 6.56 (d, J=15Hz, 1H), 3.86 (s ,2H). MS (m/z): 274 (m^+, ^{80}Se).

Compound 2b: yellow solid, mp 56-58°C. IR (cm^{-1}): 3100, 3044, 1650, 1622, 1612, 1584, 1530, 1352, 956, 946, 868, 754, 740, 730, 700. ^{1}H-NMR: δ8.20-7.94 (m, 2H), 7.54-7.08 (m, 9H), 6.96 (d, J=15Hz, 1H), 6.70 (d, J=15Hz, 1H), 3.90 (s, 2H). MS (m/z): 319 (m^+, ^{80}Se).

Compound 2c: yellow oil. IR (cm^{-1}): 1610, 1525, 1352, 946, 858, 750, 692. ^{1}H-NMR: δ8.20-8.0 (m, 2H), 7.56-7.20 (m, 2H), 6.22 (d, J=15.4Hz, 1H), 5.92 (dt, J=15.4 and 5.4Hz, 1H), 3.80 (s, 2H), 2.20-1.90 (m, 2H), 1.58-1.10 (m, 6H), 0.90 (t, J=4.4Hz, 3H). MS (m/z): 313 (m^+, ^{80}Se).

Compound 2d: yellow oil. IR (cm^{-1}): 1650, 1630, 1510, 960, 750. ^{1}H-NMR: δ8.24-7.95 (m, 1H), 7.70-7.20 (m, 3H), 6.76 (d, J=15Hz, 1H), 5.90 (dt, J=15 and 5Hz, 1H), 5.30 (d, J=5Hz, 2H), 2.64 (t, J=6.8Hz, 2H), 1.90-1.10 (m, 4H), 0.90 (t, J=4Hz, 3H). MS (m/z): 296 (m^++1, ^{80}Se).

Compound 2e: yellow oil. IR (cm^{-1}): 3140, 3110, 1645, 1628, 1618, 1532, 1514, 1360, 1280, 1246, 1172, 1122, 1110, 960, 870, 808, 788, 778, 755, 706. ^{1}H-NMR ($CDCl_3$, TMS): δ8.30-7.85 (m, 3H), 7.68-7.10 (m, 5H), 6.54 (d, J=15.4Hz, 1H), 6.03 (dt, J=15.4 and 5.2Hz, 1H), 5.28 (d, J=5.2Hz, 2H), 3.90 (s, 2H). MS (m/z): 374 (m^++1, ^{80}Se).

Compound 2f: yellow oil. IR (cm^{-1}): 3100, 1642, 1630, 1610, 1512, 954, 700. ^{1}H-NMR: δ8.26-7.96 (m, 1H), 7.64-7.02 (m, 8H), 6.68 (d, J=15.2Hz, 1H), 5.96 (dt, J=15.2 and 5.8Hz, 1H), 5.24 (d, J=5.8Hz, 1H), 3.86 (s, 2H). MS (m/z): 330 (m^++1, ^{80}Se).

Acknowledgments

Projects 29672008 and 29772007 are supported by the National Natural Science Foundation of China. This work was also supported by the Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Academic Sinica.

References

1. For reviews see:
   (a) J. V. Comasseto, *J. Organomet. Chem*., **1983**, *253*, 131.
   (b) J. V. Comasseto, L. W. Ling, N. Petragnani, H. A. Stefani, *Synthesis*, **1997**, 373.

2. X. Huang, X. Xu, *Synth. Commun*., **1998**, *28*, 807 and references therein.
3. A. Osuka, N. Ohmasa, H. Suzuki, *Synthesis*, **1982**, 857.
4. S. I. Fukuzawa, Y. Nimoto, T. Fujinami, S. Sakai, *Heteroatom. Chem*., **1990**, 49.
5. X. Xu, X. Huang, *Synth. Commun*., **1997**, *27*, 3797.
6. B. Gautheron, G. Tainturier, P. Meunier, *J. Organomet. Chem*., **1981**, *209*, C49.
7. B. Gautheron, G. Tainturier, S. Pouly, F. Theobald, H. Vivier, A. Laarif, *Organo- metallics*, **1984**, *3*, 1495.
8. A. L. Braga, A. Reckziegel, C. C. Silveira, *Synth. Commun*., **1994**, *24*, 1165.
9. Reviews:
   (a) J. Schwartz, J. A. Labinger, *Angew. Chem. Int. Ed. Engl.*, **1976**, *15***,** 333.
   (b) J. A. Labinger, in "*Comprehensive Organic Synthesis*", B. M. Trost and I. Fleming Ed., Pergamon: Oxford, 1991, Vol.8, p667.
   (c)P. Wipf, H. Jahn, *Tetrahedron*, **1996**, *52*, 12853.
   (d) E. Negishi, T. Takahashi, *Synthesis*, **1988**, 1.
10. See 9(c) and references therein.
11. S. L. Buchwald, S. J. LaMaire, R. B. Nielsen, B. T. Watson, S. M. King, *Tetrahedron Lett.*, **1987**, *28*, 3895.

Received 7 January 1999