STEREOSELECTIVE SYNTHESIS OF (Z)-1-ALKYLSELENO-1-ALKENES BY Ni-CATALYZED COUPLING REACTION OF (Z)-DIALKYLSELENOETHENES WITH ORGANOZINC HALIDES

Xian Huang* and Ai Ming Sun

Department of Chemistry, Hangzhou University, Hangzhou 310028, China

Abstract: (Z)-Dialkylselenoethenes 2, prepared conveniently from the hydrozirconation of dialkylselenoacetylenes 1 with $Cp_2Zr(H)Cl$ in THF followed by protonolysis, react readily at $-10^{\circ}C$ in THF with organozinc halides in the presence of a catalytic amount of NiCl₂ (dppe) to give (Z)-1-alkylseleno-1alkenes 3 with retention of the configuration.

Many methods for the synthesis of symmetric and asymmetric substituted ethenes have been reported¹, but the control of stereochemistry can be difficult and procedures of various degrees of complexity and validity have been proposed. Although a number of methods for the synthesis of vinyl selenides have been reported², the stereoselective synthesis of such vinylic selenides has been little explored³, especially for (Z)-alkylselenoalkenes^{3e}. Such vinylic selenides can be stereospecifically converted into the corresponding disubstituted ethenes by Ni-catalyzed coupling reaction with Grignard reagents⁴. Herein we wish to report a new and convenient method for the synthesis of (Z)-vinyl selenides by the coupling of (Z)-dialkylselenoethenes with organozinc halides in the presence of a catalytic amount of NiCl₂(dppe).

^{*} To whom correspondence should be addressed.

The coupling reaction of (Z)-dialkylselenoethenes 2, derived from the hydrozirconation of dialkylselenoacetylenes 1 with Cp₂Zr (H) Cl followed by protonolysis, at room temperature in THF with Grignard reagents in the presence of NiCl₂ (PPh₃)₂ according to the method reported by Hercsi⁴ was carried out, and was expected to afford vinyl selenides 3. The products were obtained in low yields, however and the reaction proceeded with poor stereoselectivity even under low reaction temperature conditions. However, on switching from Grignard reagents to organozinc halides, using a catalytic amount of NiCl₂(dppe) (5% mol) and lowering the reaction temperature, the reaction took readily place and we obtained (Z)-1-alkylseleno-alkenes 3 in good to excellent yields (Scheme 1). An investigation of crude products by GLC showed that the (Z)-isomer formed was more than 95%. The results, listed in Table 1, confirm that the coupling of (Z)-diselenoethene with organozinc halide in the presence of 5% mol of NiCl₂(dppe) takes readily place under mild conditions and with high stereoselectivity.

Scheme 1



The stereochemistry of compounds **3** was established by a characteristic coupling constant (J=8, 7-10 Hz) of (Z)-isomer between two olefinic protons in ¹H NMR spectrum.

Entry	R	R ¹	Х	Yield ^a (%)
a	Me	CH ₂ =CHCH ₂	Br	84
b	Me	n-C₄H ₉ C≡C	Cl	75
с	Et	$CH_2 = CHCH_2$	Br	87
d	Et	PhC=C	Cl	73
e	n-C ₅ H ₁₁	PhCH ₂	Br	80
f	n-C ₅ H ₁₁	HC≡≡C	Cl	81

Table 1 The synthesis of (Z)-1-alkylseleno-alkenes 3

*Isolated yield.

We also carried out the coupling reaction of (Z)-1-methylseleno-1,4-pentadiene³ 3a at room temperature in THF with phenylzinc chloride in the presence of 5% mol of NiCl₂(dppe) to provide (Z)-1-phenyl-1,4-pentadiene 4 in 86% isolated yield with the retention of the configuration (Scheme 2). Although the Ni-catalyzed coupling of carbon-carbon could also be carried out by the methods previously reported⁴, the present method is particulaily attractive because of the mild conditions.

Scheme 2



Experimental

IR spectra were obtained as films on a Shimadzu IR-435 spectrometer. ¹H NMR spectra (chemical shifts in *ppm* from internal TMS) were measured on an AZ-300 MHz (300 MHz) spectrometer with $CDCl_3$ as solvent. Elemental

analyses were conducted using a Yanaco MT-3CHN elemental analyser. All reactions were carried out under a stream of dry nitrogen. All solvents were dried, deoxygenated and redistilled before use. Dialkylselenoacetylenes⁵, Cp_2Zr (H)Cl⁶, organozinc halides⁷, and NiCl₂(dppe)⁸ were prepared according to the literature methods, respectively.

General procedure for the preparation of (Z)-dialkylselenoethenes 2

To a dry 50 ml flask charged with Cp₂Zr(H)Cl (10 mmol) was injected CH₂Cl₂ (15 ml), followed by the addition of 1 (10 mmol) at room temperature. The mixture was stirred under same temperature for 1 h, and then treated with sat. NH₄Cl (8 ml). The product was extracted into light petroleum (bp 30-60 °C). The organic layer was separated, dried over MgSO₄ and filtered. After removal of the solvent *in vacuo* the residue was separated by flash chromatography on a 3 ft×1 in column (100-200 mesh) by elution with petroleum (bp 30-60 °C) to give 2. For example, (Z)-dimethylselenoethene 2a: ¹H NMR, δ 6. 83(s,2 H), 2. 19(s,6 H). MS m/z,214 (M⁺+2,52.52),212(M⁺+,48.23),199(M⁺+2 -Me,27.89),1.97(M⁺-Me,26.70),119(M⁺+1-SeMe,75.36),105(M⁺+1-CH₂,91.19). Anal. Calc. for C₄H₈Se₂:C⁹₀,22.45; H⁹₀, 3.77. Found: C⁹₀,22.03; H⁹₀,3.58.

General procedure for the preparation of (Z)-1-alkylselenoalkenes 3a-f:

To a freshly prepared (Z)-dialkylselenoethenes 2 (2 mmol) and 5 mol% of NiCl₂ (dppe) in THF (10 ml) at -10 °C was added dropply organozinc halides (2 mmol) in THF (10 ml) over a period of 30 min. After further stirring at -10 °C for 4 h the reaction was allowed to warm slowly to room temp. The product was then extracted into petroleum, dried over MgSO₄ and filtered. After removal

of the solvent *in vacuo* the residue was purified by flash chromatography on a 3 ft $\times 1$ in column (100-200 mesh) with light petroleum (bp 30-60 °C) as eluent to give **3**.

- (Z)-1-Methylseleno-1,4-pentadiene (3a)
- ¹H NMR, δ 6. 69(d,1 H,J=9. 7 Hz), 6. 18(dt,1 H,J=9. 7, 7. 1 Hz), 5. 75(m, 1 H), 5. 0(m, 2 H), 3. 05(m, 2 H), 2. 21(s, 3 H). IR (neat) ν (cm⁻¹), 693. Anal. Calc. for C₆H₁₀Se: C%, 44. 73; H%, 6. 26. Found: C%, 45. 11; H%, 6. 59.
- (Z)-1-Methylseleno-1-ene-3-octyne (3b)

¹H NMR, δ 6. 77(d,1 H,J=10 Hz), 6. 21(dt,1 H,J=10 Hz), 2. 23(s,3 H), 2. 37(t,2 H,J=5. 8 Hz), 1. 25-1. 50(m,4 H), 0. 82(t,3 H,J=6.1 Hz). IR (neat) ν (cm⁻¹), 2251, 705. Anal. Calc. for C₉H₁₄Se; C%, 53. 74; H%, 7. 01. Found; C%, 53. 96; H%, 6. 89.

(Z)-1-Ethylseleno-1,4-pentadiene (3c)

¹H NMR, δ 6. 59(d,1 H, J=9 Hz), 6. 15(dt,1 H, J=9 Hz), 5. 71(m,1 H), 5. 03(m,2 H), 3. 09(m,2 H), 2. 95(q,2 H, J=7. 9 Hz), 1. 62(t,3 H, J=7. 9 Hz). IR(neat) ν (cm⁻¹), 1637, 989, 687. Anal. Calc. for C₇H₁₂Se₂C%, 48. 01; H%, 6. 91. Found C%, 47. 79; H%, 7. 13.

(Z)-1-Ethylseleno-4-phenyl-1-ene-3-butyne (3d)

¹H NMR, δ 7. 15–7. 55(m, 5 H), 6. 81(d, 1 H, J=8. 7 Hz), 6. 27(d, 1 H, J= 8. 7 Hz), 2. 93(q, 2 H, J=7. 6 Hz), 1. 71(t, 3 H, J=7. 6 Hz). IR (neat) ν (cm⁻¹), 2217, 1595, 1562, 597. Anal. Calc. for C₁₂H₁₂Se; C%, 61. 28; H%, 5. 14. Found; C%, 61. 54; H%, 4. 93.

(Z)-1-Pentylseleno-3-phenyl-1-propene (3e)

¹H NMR, δ 7.07–7.51(m,5 H), 6.71(d,1 H,J=9.5 Hz), 6.26(dt,1 H,J=

9.5, 6.9 Hz, 4.05(d, 2 H, J=6.9 Hz), 2.89(t, 2 H, J=7.8 Hz), 1.69(m, 2)

H),1.20-1.55(m,6 H),0.95(t,3 H,J=6.1 Hz). IR(neat) ν (cm⁻¹),1591, 1565,1547,713. Anal. Calc. for C₁₄H₂₀Se: C%,62.91; H%,7.54. Found: C%,62.54; H%,7.85.

(Z)-1-Pentylseleno-1-ene-3-butyne (**3f**) ¹H NMR, δ 6. 65(d,1 H,J=8.8 Hz), 6. 16(d,1 H,J=8.8 Hz), 2. 90(t, 2 H, J = 7. 7 Hz), 1. 97(s,1 H), 1. 67(m, 2 H), 1. 14-1. 50(m, 4 H), 0. 93(t, 3 H, J = 6. 3 Hz). IR (neat) ν (cm⁻¹), 2246, 707. Anal. Calc. for C₉H₁₄Se; C%, 53. 74; H%, 7. 01. Found; C%, 53. 31; H%, 7. 37.

Acknowlegement: This work was supported by the National Natural Science Foundation of China and The Laboratory of Organometallic Chemistry, Chinese Academy of Science.

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- (Received in the UK 20 January 1997)