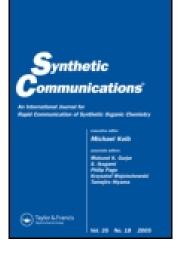
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COUPLING ALKYLATION OF (E)-α-SELANYLVINYLIC ZIRCONIUM COMPOUNDS TO GIVE TRISUBSTITUTED ALKENES

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Abstract: Hydrozirconation of internal acetylenic selenides afforded 1.1bimetalloalkenes. (E)- α -selanylvinylzirconium, which can undergo sequential cross coupling reaction to form two carbon-carbon bonds in the same olefinic carbon leading to trisubstituted alkenes stereoselectively.

Many biologically active compounds occuring in nature possess the structual skeleton of trisubstituted alkenes.¹ Recently, many 1.1-, or 1.2-bimetalloalkenes are used widely in stereoselective synthesis of trisubstituted alkenes. In a previous paper, we have shown the first example of the hydrozirconation of 1-phenylselenoacetylenes to obtain (E)-2-selanylvinylzirconium compounds as a 1.2-bimetalloalkenes of selenium and zirconium, and also have studied their application for synthesis of (E)-disubstituted alkenes. As an extension of our studies, in this paper, we studied the reactivity of hydrozirconation of internal acetylenic selenides, in order to develop a new method for stereoselective synthesis of trisubstituted alkenes.

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The results indicated that internal alkylacetylenic selenides 1 can undergo hydrozirconation easily, the reaction is a *cis* addition, but the regioselectivity is different from the hydrozirconation of 1phenylselenoacetylenes, which obtained (E)-1-selanylvinylic zirconium compounds 2 (R^1 =alkyl). (Scheme 1) Obviously the regiochemistry of this reaction is determined by electrochemical effect. Hydrostannation² and hydroboration³ of internal alkylselenoacetylenes also have the same situations.

$$R^{1} = -SeR^{2} \xrightarrow{Cp_{2}Zr(H)Cl}_{THF,r.t} \left[\begin{array}{c} R^{1} & SeR^{2} \\ H & ZrCp_{2} \\ Cl \end{array} \right]$$

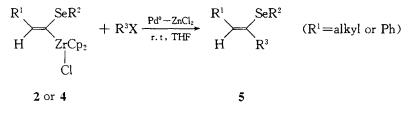
$$1 \qquad 2$$

Scheme 1

The above method can not be suitable to the hydrozirconation of phenylacetylenic selenides even extending the time or raising the temperature. Recently, it was reported that palladium-complexes can catalyze hydrostannation and hydroboration of alkynes.^{4,5} Thus we tried to use the catalytic palladium method on hydrozirconation of phenylacetylenic selenides. The experimental results show that in the presence of 5%mmol Pd (PPh₃)₄, the hydrozirconation of phenylacetylenic selenides can be completed in an hour at room temperature(Scheme 2).

$$Ph = -SeR^{2} \xrightarrow{Cp_{2}Zr(H)Cl}_{Pd^{\circ},r. t. THF} \left(\begin{array}{c} Ph & SeR^{2} \\ H & ZrCp_{2} \\ Cl \\ Cl \end{array} \right)$$

The (E)- α -selanylvinylzirconium compounds 2 and 4 can not need to be isolated and in the presence of Pd (PPh₃)₄ and ZnCl₂ it can take crosscoupling reaction with alkyl halides directly. The experimental results show that intermediates 1,1-bimetalloalkenes cross coupled with alkyl halides to afford a convenient method for the synthesis of disubstituted vinylic selenides 5. (Scheme 3)



Scheme 3

The regio- and stereo- chemistry were established by ¹H NMR measurements. One olefinic proton of (Z)-disubstituted vinylic selenides **5ad** was characteristically split into triplet with coupling contant J about 7. 2 Hz, which indicates that the hydrozirconation of internal alkylselenoacetylenes with $Cp_2Zr(H)Cl$ proceeds with strong preference for the addition of the zirconium atom at carbon adjacent to the alkylseleno group.

(Z)-Disubstituted vinylic selenides are also effective precursors for synthesizing stereodefined trisubstituted alkenes. We carried out the coupling reaction of (Z)-1-ethylseleno-1-phenyl-phenylethene **5f** with Grignard reagent R⁴MgI in the presence of Ni(PPh₃)₂Cl₂ to provide (Z)-1methyl-1-phenyl-phenylethene **6f** (Scheme 4).

As (E)-1-selanylvinylzirconium compounds 2 and 4 undergo a two-step cross-coupling reaction to form two carbon-carbon bonds on the same olefinic carbon and allow the synthesis of trisubstituted alkenes

	(H)Cl followed by cr		
Entry	Internal alkylselenoacetylenes	Disubstituted vinylic selenides	Yield ^a (%)
5a	SeMe	H CH_2Ph	75
5b	∽~-≡- SeEt	H CH2Ph	78
5c	$MeOCH_2 = -SeEt$	$\overset{MeOCH_2}{\underset{H}{\overset{SeEt}{\underset{CH_2Ph}{\overset{SeEt}{}}}}}$	80
5d	$MeOCH_2 - \equiv -SeEt$	MeOCH ₂ SeEt H CH ₃	85
5e	Ph-≡-SeMe ^b	$\overset{Ph}{\underset{H}{\overset{SeCH_{3}}{\longleftarrow}}}$	70
5f	Ph-≡-SeEt ^b	Ph SeEt H Ph	62
a Is R ¹		esence of $Pd(PPh_3)_4$.	$^{1}=Ph,R^{2}=E$
H 5	$= \frac{\operatorname{SeR}^{2}}{\operatorname{R}^{3}} + \operatorname{R}^{4}\operatorname{MgI} \frac{(\operatorname{PPh_{3}})}{\operatorname{THF}},$	r.t. R	³ =Ph,R ⁴ =C ield:63%
	$\left[\begin{array}{c} R^{1} \\ \\ H \end{array}\right]$	$C = C \stackrel{\oplus}{\ominus}$	

Table 1Hydrozirconation of internal acetylenic selenides with Cp2Zr
(H)Cl followed by cross-coupling reaction

stereoselectively, 2 and 4 can be regarded as the equivalent of the cationanion synthon 7. In summary, compared to other methods that have been reported, our method for the synthesis of stereodefined trisubstituted alkenes has the advantages of simple procedure, mild conditions and convenient isolation of products.

Experimental

IR spectra were obtained as films on shimadzu IR-440 spectrometer. ¹H NMR spectra (chemical shifts in ppm from internal TMS) were measured on a Bruker AM-300 spectrometer at 300 MHz with CDCl₃ as solvent. Mass spectra were recorded on Finnigan GC-MS 4021 or MHT8430 mass spectrometers.

A typical procedure for the preparation of 5a-d is as follows

To a solution of Cp₂Zr (H)Cl (4 mmol) in THF (10 ml) was added alkylselenoacetylenes $R^1 - \equiv -SeR^2$ (4 mmol) at room temperature under nitrogen, stirred for about half an hour at r. t, the precipitate dissolved, solution turned from yellow to green. To this mixture was then added ZnCl₂ (4 mmol), Pd (PPh₃)₄ (4×5% mmol), $R^3 \times$ (4 mmol), at r. t stirred for about an hour. The mixture was treated with sat. aq Na₂CO₃ (15ml). The phase was separated, dried (MgSO₄), filtered and concentrated in vacuo. The residue was purifed by flash chromatography on a 3ft × 1 inch column (100-200 mesh) with light petroleum (bp. 30-60°C) as eluent to give **5**.

(Z)-1-methylseleno-1-benzyl-1-hexene (5a)

¹H NMR: $\delta = 7.3 - 7.0(m, 5 H)$, 6. 25(t, 1 H), 4. 31(s, 2 H), 2. 40(s, 3 H), 1.9-2.33(m, 2 H), 0.95-1.58(m, 7 H). IR ν (cm⁻¹): 1630, 807. MS m/z: 268(M-1).

(Z)-1-ethylseleno-1-benzyl-1-hexene (5b)

¹H NMR: $\delta = 7.25 - 7.0(m, 5 H)$, 6. 27(t, 1 H), 4. 33(s, 2 H), 2. 75(q, 2 H), 1. 87 - 2. 25(m, 3 H), 2. 0 - 2. 32(m, 2H), 0. 93 - 1. 84(m, 7 H). IRv (cm⁻¹):1631,808. MS m/z:282(M-1).

(Z)-1-ethylseleno-1-benzyl-3-methoxy-1-propene (5c)

¹H NMR: $\delta = 7.20 - 6.95(m, 5 H)$, 6.29(t,1 H), 4.32(s,2 H), 3.88(d, 2 H), 3.25(s, 3 H), 2.70(q, 2 H), 1.41(t, 3 H). IRv(cm⁻¹):1609,775. MS m/z:269(M-1).

(Z)-1-ethylseleno-1-methyl-3-methoxy-1-propene (5d)

¹H NMR: $\delta = 6.25(t, 1 \text{ H})$, 3.87(d, 2 H), 1.90(s, 3 H), 2.71(q, 2 H), 1.42(t, 3 H). IRv(cm⁻¹):1610,780. MS m/z:193(M-1).

General Procedure for the synthesis of 5e,5f. To a solution of $Cp_2Zr(H)Cl$ (4 mmol) in THF (10 ml) was then added Pd (PPh₃)₄ (4 × 5% mmol), stirred for 30 min to make $Cp_2Zr(H)Cl$ insert to Pd(PPh₃)₄ adequitly. To the solution injected Ph—=-SeR²(4 mmol), stirred at r. t for 1 hr, after the hydrozirconation, the following procedure was the same as the synthesis of 5a-d.

(Z)-1-methylseleno-1-methyl-phenylethene (5e)

¹H NMR: $\delta = 7.50 - 7.0(m, 5 H)$, 6.81(s, 1 H), 1.95(s, 3 H), 2.41(s, 3

H). $IR_{\nu}(cm^{-1})$:1660,1590,1544,805. MS m/z:211(M-1).

(Z)-1-ethylseleno-1-phenyl-phenylethene (5f)

¹H NMR: $\delta = 7.80 - 7.0(m, 10 H)$, 6.78(s, 1 H), 2.74(q, 2 H), 1.48(t, 3 H). IR_v(cm⁻¹):1650,1598,806. MS m/z:288(M-1).

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