Stereoselective Synthesis of 1,1-Bimetalloalkenes of Tin and Selenium, Tin and Tellurium

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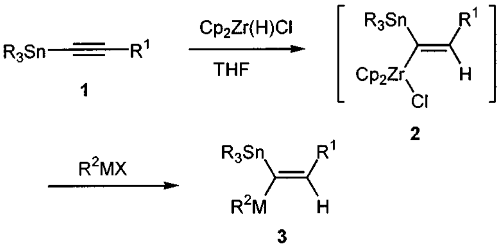
Abstract: 1,1-Bimetalloalkenes(tin and selenium, tin and tellurium) were stereoselectively prepared by a hydrozirconation of acetylenic stannanes followed by transmetallation using tellurenyl iodide and selenenyl bromide. One equivalent of n-BuLi displaced a trialkylstannyl group selectively and lithiated vinyl selenides were reacted with electrophiles to afford *(E)*-internal selenides.

Key words: bimetalloalkene, hydrozirconation, selenide, vinylstannane, tellurium

1,1-Bimetalloalkenes composed of two different carbon-metal bonds play an important role in developing many convenient methods for the synthesis of substituted alkenes. A lot of reports have showed aluminum and titanium,[1(a)] aluminum and zirconium,[1(a)] and zinc and zirconium[1(b)] could behave as alkylidene-transfer reagents. Lipshutz and co-workers have described the 1,1-bimetalloalkenes based on tin and zirconium that underwent selective hydrolysis of the carbon-zirconium bond to provide *(Z)*-vinylstannanes.[1(c)] Other 1,1-bimetalloalkenes containing aluminum and zirconium,[1(d),1(e)] aluminum and hafnium,[1(f)] gallium and zirconium,[1(g)] zinc and boron,[1(h)] copper and boron,[1(h)] tin and boron,[1(i)] and boron and zirconium[1(j)] have also been described. Elaboration of these organometallics involves selective reaction of the more reactive vinyl organometallic center. Although 1,1-bimetalloalkenes of tin and selenium (α-selenenylvinylstannanes) could be very useful specie as a dilithioethene equivalent or cation-anion synthon, there was an only report on the preparation and reactivity, and we could not find a report about synthesis of 1,1-bimetalloalkenes of tin and tellurium. Recently Huang et al. described that hydrostannation of alkynylselenides gave *(E)*-1,1-bimetalloalkenes of tin and selenium under the catalysis of tetrakis(triphenylphospine)palladium and *(E)*-1,1-bimetalloalkenes of tin and selenium afforded trisubstituted alkenes.[2] In a previous papers, we described the stereo- and regio-selective preparation of vinyl tellurides via alkenyl zirconocenes,[3(a)] the hydrozirconation of acetylenic tellurides[3(b)] and the stereoselective preparation of ketene telluroacetalls (1,1-bimetalloalkenes of tellurium and tellurium).[3(c)] We were also interested in concise synthesis of relatively simple natural product that utilized butadienylstannane as a intermediate.[3(d)] As an extension of our studies, we were interested in developing new synthetic routes toward 1,1-bimetalloalkenes of tin and tellurium, tin and selenium. We now describe its simple, stereoselective preparation by the hydrozirconation of acetylenic stannane and then transmetallation using tellurenyl iodide, selenenyl bromide.

Hydrozirconation of acetylenic stannane **1** was found to proceed stereoselectively in *cis* fashion with high regioselectivity affording 1,1-bimetalloalkene of tin and zirconium. From this sampling the most obvious limitation of the method is related to the propensity of this hydride source to reduce aldehyde and ketone competitively with hydrozirconation. Otherwise, the mildness of these conditions tolerates an assortment of desirable functionality.[1(c)]



Scheme 1

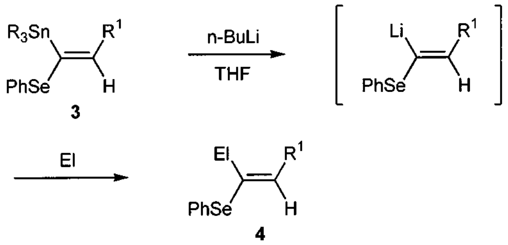
The intermediate **2** was converted to stable 1,1-bimetalloalkenes **3** after treatment with tellurenyl iodide or selenenyl bromide (**Table 1**). The intermediate **2** was cleaved with essentially complete retention of configuration by selenenyl, tellurenyl halide to give stereodefined products. *(Z)*-1,1-Bimetalloalkenes of tin and selenium and *(E)*-1,1-bimetalloalkenes of tin and tellurium are difficult to prepare by other means due to reactivity of functional groups in the same vinyl carbon.[4]

Table 1 Synthesis of 1,1-bimetalloalkenes of Sn-Se, Sn-Te

Entry[a]	R	R^1	R^2M	Yield[b]
a	Me	Bu	SePh	71
b	Me	Bu	TePh	68
c	Bu	CH_2CH_2OTHP	SePh	70
d	Bu	CH_2CH_2OTHP	TePh	67
e	Bu	Bu	SePh	77
f	Bu	Bu	TePh	70
g	Bu	CH_2OCH_2Ph	SePh	69
h	Bu	CH_2OCH_2Ph	TePh	67

[a] All products were characterized using spectroscopic methods
[b] Isolated yields(%) were based on added tellurenyl iodide, selenenyl bromide.

Though selenenyl and trialkylstannyl group both could be used in introduction of a new electrophile to vinyl carbon, one equivalent of n-BuLi displaced a trialkylstannyl group selectively.



Scheme 2

So lithiated vinyl selenide was synthesized and it was reacted with several electrophiles to afford *(E)*-internal selenides[5] which are important intermediates owing to the versatile reactivity of the selenenyl group and the carbon-carbon double bond.[6]

Table 2 Synthesis of internal vinyl selenides from the 1,1-bimetalloalkenes

Entry[a]	R	R^1	El	Yield[b]
a	Bu	Bu	EtI	92
b	Me	Bu	H_2O	90
c	Bu	CH_2OCH_2Ph	EtI	85
d	Bu	CH_2CH_2OTHP	PhCHO	82

[a]All products were characterized using spectroscopic methods
[b]Isolated yields(%) were based on used trialkylstannyl phenylselenenylalkenes.

Although products **3** were isolable by flash column in hexane/ethyl acetate eluent and easily handled in open system, reagents in $CDCl_3$ solution were decomposed in a few days. Synthesis of *(Z)*-1,1-bimetalloalkenes of tellurium and tin will be reported, various manipulations of *(E)*- and *(Z)*-1,1-bimetalloalkenes of tellurium and tin are currently being examined and will be reported in due course.

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(4) **A general procedure for 1,1-bimetalloalkenes(Sn-Se, Sn-Te) preparation is as follows:** $Cp_2Zr(H)Cl$ (1.1mmol) was slurried in 5ml of THF at room temperature under a nitrogen atmosphere, and the acetylenic stannane **1** (1mmol) in 2ml of THF was added via syringe. The mixture was allowed to stir at room temperature for 10-25min., until hydrozirconation was complete, as evidenced by the disappearance of the insoluble hydride and the formation of a clear yellow solution. To a solution of the intermediate **2** was added 1 equivalent of phenylselenenyl bromide, phenyltellurenyl iodide (prepared in situ by the addition of iodine solution to a stirred solution of diphenyl ditelluride).[7] After stirring for 1hr, normal work-up was performed. 1,1-Bimetalloalkene of tellurium and tin, tin and selenium **3** was isolated and purified by column chromatography using hexane/ethyl acetate as eluent. **3e**) ^{1}H NMR (300MHz, $CDCl_3$): δ = 7.40-7.36(2H, m), 7.24-7.10(3H, m), 7.12(1H, t, J = 7.3), 2.15-2.00(2H, m), 1.42-1.34(8H, m), 1.30-1.20(8H, m), 0.92-0.81(18H, m); ^{13}C NMR (75MHz, $CDCl_3$): δ = 152.87, 132.84, 131.68, 130.27, 128.65, 126.33, 36.46, 31.68, 28.96, 27.32, 22.50, 14.01, 13.62, 11.57; exact mass (M^+) calcd for $C_{24}H_{42}SeSn$ 528.1474, found 528.1485. **3f**) ^{1}H NMR (300MHz, $CDCl_3$): δ = 7.62-7.59(2H, m), 7.23-7.16(3H, m), 7.08(1H, t, J = 7.2), 2.15-2.03(2H, m), 1.42-1.32(8H, m), 1.30-1.20(8H, m), 0.91-0.81(18H, m); ^{13}C NMR (75MHz, $CDCl_3$): δ = 159.95, 137.23, 129.01, 127.02, 115.83, 113.79, 39.22, 31.69, 28.95, 27.33, 22.44, 13.96, 13.60, 12.08; exact mass (M^+) calcd for $C_{24}H_{42}SnTe$ 578.1371, found 578.1361.

(5) **A Typical Experimental Procedure for Sn/El transformation is as follows:** Butyllithium (1.6M hexane solution, 1.1mmol) was added to hexane (3.0ml) solution of *(Z)*-1,1-bimetalloalkene of tin and selenium **3** (1.0ml) at -78°C. After stirring for 1hr, the electrophile (1.5mmol) was added at the temperature and the mixture was stirred at r.t. for 3hr and treated with 5% acetic acid solution and the organic layer dried over $MgSO_4$. The solvent was evaporated and the residue was purified by flash silica-gel chromatography eluting with hexane or hexane/ethyl acetate to give the vinyl selenide **4**.

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