



First Example of 1,1-Bimetalloalkenes of Tellurium and Zirconium: Application for Stereoselective Preparation of (Z)- α -Organotelluro- α,β -Unsaturated Carbonyl Compounds

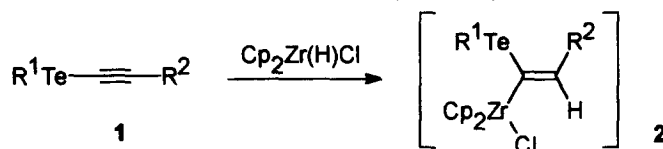
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Abstract : Hydrozirconation of acetylenic tellurides **1** affords the first examples of 1,1-bimetalloalkenes of tellurium and zirconium **2**. Intermediates **2** are reacted with acyl halides to obtain (Z)- α -organotelluro- α,β -unsaturated carbonyl compounds **4** via Zr-Cu transmetalation. Copyright © 1996 Elsevier Science Ltd

1,1-bimetalloalkenes have been prepared in the past, including aluminum and zirconium¹, zinc and zirconium², tin and zirconium³, gallium and zirconium⁴, and boron and zirconium⁵. In this communication we describe the first examples of the preparations and reactions of 1,1-bimetalloalkenes based on tellurium and zirconium.

Hydrozirconation of alkynes offers the simplest and most direct route to alkenylzirconocenes chlorides⁶. So we tried to reduce the acetylenic tellurides **1** using zirconocene hydrochloride to obtain 1,1-bimetalloalkenes of tellurium and zirconium, intermediates **2** (Scheme 1).



Scheme 1

Acetylenic tellurides **1** were synthesized in high yield according to the method of Comasseto⁷. Hydrozirconation of acetylenic tellurides (**1a-1e**) with 1.2 equivalent of zirconocene hydrochloride in THF for 15min at room temperature gave the clear red solutions. Z-vinyl tellurides⁸ **3** were obtained after hydrolysis. But the reaction of **1f** with zirconocene hydrochloride proceeded very slowly. Treatment of **1f** with $\text{Cp}_2\text{Zr(H)Cl}$ for 4hr at room temperature afforded, after hydrolysis, dibutylditelluride (35% isolated yield) and vinyl telluride **3f** (6% isolated yield). A survey of representative examples is given in Table 1. The reaction conditions of our method are milder than those of hydrotelluration of acetylene (reflux, 5hr)^{8b}. There is a regiochemical issue associated with the addition of zirconocene hydrochloride across unsymmetrical acetylenic tellurides. The heteroatoms of α -heteroalkynes determine the regiochemistry of the hydrometallation by polarizing the alkyne bond⁹. The regiochemistry of this reaction was determined

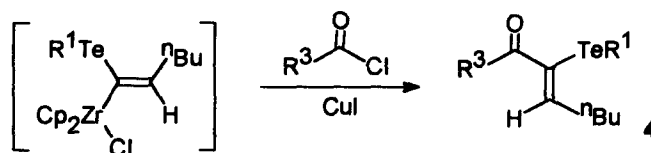
by deuterolysis experiment^{10a} and NMR study^{10b}. There is a strong preference for the attachment of the metal to the α -position. The organotelluro group polarizes the alkyne in a sense opposite to that observed with alkoxyalkynes¹¹. We always observed the corresponding diorganyl ditellurides (3%-8% in entry a-e, 35% in entry f). This is due to the attack of hydride at tellurium atom⁷. The above results indicate that there are two pathways in this reaction, the attack of hydride at the β -position of alkyne bond and at tellurium atom. In the cases of LiAlH_4 and NaBH_4 , the major pathway is the attack of hydride at tellurium atom⁷.

Table 1 : Synthesis of Z-vinyl tellurides via hydrosilylation of acetylenic tellurides.

$\begin{array}{c} \text{R}^1\text{Te} \quad \text{R}^2 \\ \diagdown \quad \diagup \\ \text{H} \quad \text{H} \end{array} \quad \mathbf{3}$				
Entry	R^1	R^2	Product ^a	Yields ^b (%)
a	Et	$n\text{Bu}$	3a	70 (89 ^c)
b	$n\text{Bu}$	$n\text{Bu}$	3b	78 (92 ^c)
c	$\text{CH}_3(\text{CH}_2)_9-$	$n\text{Bu}$	3c	77
d	Ph	$n\text{Bu}$	3d	82 (95 ^c)
e	$n\text{Bu}$	$-(\text{CH}_2)_3\text{OCH}_2\text{Ph}$	3e	72
f	$n\text{Bu}$	Ph	3f	6

^aAll the compounds were characterized. ^bIsolated yields based on acetylenic tellurides after purification by silica gel chromatography using hexane as eluent. ^cNMR yield.

As part of our studies of organotellurium compounds in organic synthesis¹², we are interested in developing new synthetic routes toward highly functionalized organotellurium compounds. Although there are several reports on the synthesis of β -organotelluro- α,β -unsaturated carbonyl compounds¹³, to our knowledge the synthesis of α -organotelluro- α,β -unsaturated carbonyl compounds have not yet been reported. To show the usefulness of intermediates **2** for the synthesis of highly functionalized organotellurium compounds, intermediates **2** were reacted with acyl halides to obtain (Z)- α -organotelluro- α,β -unsaturated carbonyl compounds via Zr-Cu transmetalation¹⁴(Scheme 2, Table 2). Transmetalation from Zr to Cu proceeded predominantly with retention of configuration at carbon¹⁵. Besides CuI, other Cu(I) salts such as CuBr, CuCN and CuBrSMe₂ gave the similar results.



Scheme 2

A typical procedure for the preparation of α -organotelluro- α,β -unsaturated carbonyl compounds is as follows. A suspension of zirconocene hydrochloride (1.2mmol) in THF (2ml) was stirred at room temperature under nitrogen. A solution of acetylenic telluride (1.0mmol) in THF (2ml) was added. After being stirred for 15min, this reaction mixture was transferred to the solution of acyl halide (1.5mmol) and CuI (1.0mmol) in THF (3ml). After being stirred for 8hr at room temperature, the mixture was quenched by pouring it into saturated aqueous NH_4Cl and was extracted with Et_2O . Normal handling and chromatography afforded (Z)- α -organotelluro- α,β -unsaturated carbonyl compound¹⁶.

Table 2 : Synthesis of (Z)- α -organotelluro- α,β -unsaturated carbonyl compounds.

4

Entry	R ¹	R ³	Product ^a	Yields ^b (%)
a	ⁿ Bu	CH ₃ CH ₂ -	4a	60
b	ⁿ Bu	CH ₃ CH ₂ CH ₂ -	4b	71
c	ⁿ Bu	Ph	4c	68
d	Ph	CH ₃ CH ₂ -	4d	57
e	Ph	CH ₃ CH ₂ CH ₂ -	4e	51
f	Ph	Ph	4f	64
g	Ph	PhO	4g	68

^aAll the compounds were characterized. ^bIsolated yields based on acetylenic tellurides.

In summary, hydrozirconation of acetylenic tellurides affords the 1,1-bimetalloalkenes of tellurium and zirconium. For synthetic application of these intermediates **2**, (Z)- α -organotelluro- α,β -unsaturated carbonyl compounds **4** are prepared. Various manipulations of these intermediates **2** are currently being examined and will be reported in due course.

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 10. (a) Deuterolysis ($D_2O/AcOD$) of **2b** and **2d** gave α -deuterized vinylic tellurides (**2b**: 92% D incorporation, **2d**: 94% D incorporation). (b) Zirconium species **2d** was observed by 1H NMR ($CDCl_3$) spectrum of the reaction mixture : 1H NMR (200MHz, $CDCl_3$) δ 7.75-7.65(2H, m), 7.28-7.15(3H, m), 6.25(1H, t, $J=6.9Hz$), 5.80(10H, s), 2.66(2H, q, $J=7.0Hz$), 1.64-1.36(4H, m), 0.96(3H, t, $J=7.0Hz$).
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 16. Spectral data : (**4d**) 1H NMR (200MHz, $CDCl_3$) δ 7.70-7.66(2H, m), 7.28-7.21(3H, m), 6.34(1H, t, $J=7.5Hz$), 2.65(2H, q, $J=7.2Hz$), 2.24(2H, q, $J=7.3Hz$), 1.39-1.28(4H, m), 1.00(3H, t, $J=7.2Hz$), 0.86(3H, t, $J=7.1Hz$). ^{13}C NMR (50MHz, $CDCl_3$) δ 205.43, 149.99, 138.09, 129.55, 128.14, 118.05, 114.15, 35.17, 32.69, 31.33, 22.21, 13.80, 8.16. (**4b**) 1H NMR (200MHz, $CDCl_3$) δ 6.76(1H, t, $J=7.3Hz$), 2.72(4H, t, $J=7.2Hz$), 2.42(2H, q, $J=7.2Hz$), 1.65-1.56(4H, m), 1.45-1.25(6H, m), 0.93-0.81(9H, m). ^{13}C NMR (50MHz, $CDCl_3$) δ 201.15, 152.55, 124.59, 40.54, 37.04, 34.03, 30.70, 24.92, 22.41, 18.44, 13.89, 13.78, 13.33, 7.33.

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