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

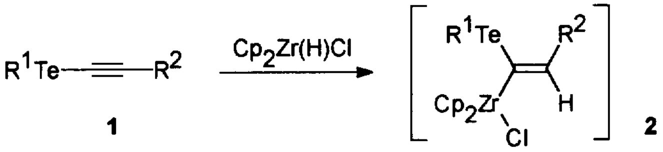
Jin Wuk Sung, Won Bum Jang and Dong Young Oh*

Department of Chemistry, Korea Advanced Institute of Science and Technology,
373-1, Kusung-Dong, Yusung-Gu, Taejon, 305-701, Korea E-mail: dyoh@sorak.kaist.ac.kr

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 transmetallation. Copyright © 1996 Elsevier Science Ltd

1,1-bimetalloalkenes have been prepared in the past, including aluminum and zirconium[1], zinc and zirconium[2], tin and zirconium[3], gallium and zirconium[4], and boron and zirconium[5]. In this communication we describe the first examples of the preparations and reactions of 1,1-bimetalloalkenes based on tellurium and zirconium.

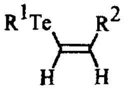
Hydrozirconation of alkynes offers the simplest and most direct route to alkenylzirconocene chlorides[6]. So we tried to reduce the acetylenic tellurides **1** using zirconocene hydrochloride to obtain 1,1-bimetalloalkenes of tellurium and zirconium, intermediates **2** (Scheme 1).



Scheme 1

Acetylenic tellurides **1** were synthesized in high yield according to the method of Comasseto[7]. 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-vinylic tellurides[8] **3** were obtained after hydrolysis. But the reaction of **1f** with zirconocene hydrochloride proceeded very slowly. Treatment of **1f** with $Cp_2Zr(H)Cl$ for 4hr at room temperature afforded, after hydrolysis, dibutylditelluride (35% isolated yield) and vinylic 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 bond [9]. 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 alkoxyalkynes[11]. 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 atom[7]. 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 atom[7].

Table 1 : Synthesis of Z-vinylic tellurides via hydrozirconation of acetylenic tellurides.



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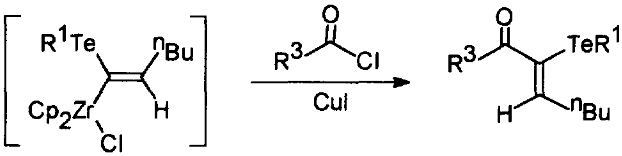
Entry	R^1	R^2	Product[a]	Yields[b](%)
a	Et	^{n}Bu	3a	70 (89^{c})
b	^{n}Bu	^{n}Bu	3b	78 (92^{c})
c	$CH_3(CH_2)_9$-	^{n}Bu	3c	77
d	Ph	^{n}Bu	3d	82 (95^{c})
e	^{n}Bu	-$(CH_2)_3OCH_2Ph$	3e	72
f	^{n}Bu	Ph	3f	6

[a]All the compounds were characterized. [b]Isolated yields based on acetylenic tellurides after purification by silica gel chromatography using hexane as eluent. [c]NMR yield.

As part of our studies of organotellurium compounds in organic synthesis[12], 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 compounds[13], 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 transmetallation[14](Scheme 2, Table 2). Transmetallation from Zr to Cu proceeded predominantly with retention of configuration at carbon[15]. Besides CuI, other Cu(I) salts such as CuBr, CuCN and $CuBr\cdot SMe_2$ gave the similar results.



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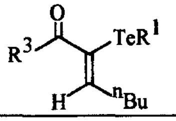
Scheme 2

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 compound[16].

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



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Entry	R^1	R^3	Product[a]	Yields[b](%)
a	^nBu	CH_3CH_2-	4a	60
b	^nBu	$CH_3CH_2CH_2$-	4b	71
c	^nBu	Ph	4c	68
d	Ph	CH_3CH_2-	4d	57
e	Ph	$CH_3CH_2CH_2$-	4e	51
f	Ph	Ph	4f	64
g	Ph	PhO	4g	68

[a]All the compounds were characterized. [b]Isolated yields based on acetylenic tallurides.

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.

References and Notes:

1. (a) Yoshida, T.; Negishi, E. *J. Am. Chem. Soc.*, **1981**, *103*, 1276-1277. (b) Erker, G.; Albrecht, M.; Werner, S.; Nolte, M.; Krüger, C. *Chem. Ber.*, **1992**, *125*, 1953-1956.
2. Tucker, C. E.; Knochel, P. *J. Am. Chem. Soc.*, **1991**, *113*, 9888-9890.
3. Lipshutz, B. H.; Keil, R.; Barton, J. C. *Tetrahedron Lett.*, **1992**, *33*, 5861-5864.
4. Erker, G.; Albrecht, M.; Krüger, C.; Werner, S. *J. Am. Chem. Soc.*, **1992**, *114*, 8531-8536.
5. (a) Deloux, L.; Skrzypczak-Jankun, E.; Cheesman, B. V.; Srebnik, M. *J. Am. Chem. Soc.*, **1994**, *116*,

10302-10303. (b) Deloux, L.; Srebnik, M. *J. Org. Chem.*, **1995**, *60*, 3276-3277. (c) Deloux, L.; Srebnik, M. *J. Org. Chem.*, **1994**, *59*, 6871-6873. (d) Deloux, L.; Srebnik, M. *Tetrahedron Lett.*, **1996**, *37*, 2735-2738.

6. (a) Lipshutz, B. H.; Ellsworth, E. L. *J. Am. Chem. Soc.*, **1990**, *112*, 7440-7441 and references therein. (b) Lipshutz, B. H.; Keil, R. *J. Am. Chem. Soc.*, **1992**, *114*, 7919-7920.
7. Dabdoub, M. J.; Comasseto, J. V. *Organometallics*, **1988**, *7*, 84-87.
8. For the synthesis of vinylic tellurides, see: (a) Dabdoub, M. J.; Dabdoub, V. B.; Comasseto, J. V.; Petragnani, N. J. *J. Organometal. Chem.*, **1986**, *308*, 211-222. (b) Barros, S. M.; Dabdoub, M. J.; Dabdoub, V. M. B.; Comasseto, J. V. *Organometallics*, **1989**, *8*, 1661-1665.
9. Bateson, J. H.; Mitchell, M. B. *Organometallic Reagents in Organic Synthesis*, Academic Press, London, **1994**, pp129-159.
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).
11. For hydrozirconation of 1-alkoxyalkynes, see: (a) Negishi, E.; Takahashi, T.; Baba, S.; Van Horn, D. E.; Okukado, N. *J. Am. Chem. Soc.*, **1987**, *109*, 2393-2401. (b) Hegedus, L. S.; Toro, J. L.; Miles, W. H.; Harrington, P. J. *J. Org. Chem.*, **1987**, *52*, 3319-3322. (c) Negishi, E.; Van Horn, D. E. *J. Am. Chem. Soc.*, **1977**, *99*, 3168-3170.
12. (a) Lee, C. W.; Koh, Y. J.; Oh, D. Y. *J. Chem. Soc., Perkin Trans. 1*, **1994**, 717-719. (b) Sung, J. W.; Lee, C. W.; Oh, D. Y. *Tetrahedron Lett.*, **1995**, *36*, 1503-1504.
13. (a) Detty, M. R.; Murray, B. J.; Smith, D. L.; Zumbulyadis, N. *J. Am. Chem. Soc.*, **1983**, *105*, 875-882. (b) Detty, M. R.; Luss, H. R.; Mckelvey, J. M.; Geer, S. M. *J. Org. Chem.*, **1986**, *51*, 1692-1700. (c) Mo, X. S.; Huang, Y. Z. *Tetrahedron Lett.*, **1995**, *36*, 3539-3542.
14. Wipf, P.; Smitrovich, J. H. *J. Org. Chem.*, **1991**, *56*, 6494-6496.
15. (a) Lipshutz, B. H.; Keil, R. *J. Am. Chem. Soc.*, **1992**, *114*, 7919-7920. (b) Carr, D. B.; Schwartz, J. *J. Am. Chem. Soc.*, **1979**, *101*, 3521-3531.
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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