

Tellurium-Zinc Exchange Between Organotelluronium Salts and Diethylzinc — Reaction of The *In Situ* Generated Mixed Diorganozinc with Carbonyl Compounds

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Received 2 April 1998; accepted 8 June 1998

Abstract

Organotelluronium salts undergo a smooth tellurium-zinc exchange reaction with diethylzinc. The *in situ* generated mixed diorganozinc reagents reacted with carbonyl compounds to give secondary or tertiary alcohols in good to excellent yields. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: organotellurium compounds; diethylzinc; carbonyl addition reaction; tellurium-zinc exchange.

There is a considerable interest in the applications of organotellurium compounds in organic syntheses^[1-5]. Transmetalation of organotellurium compounds gives rise to other organometallic reagents which are often difficult to access by conventional methods^[3]. As compared with tellurium-lithium exchange and tellurium-copper exchange which are well documented^[6-15], little attention has been paid to tellurium-zinc exchange. Recently, Sonoda^[16] has described a method of preparing alkenylzinc reagents from alkenyl tellurides (diorgano-telluride compounds) by tellurium-zinc exchange; and Knochel^[17] has shown that diaryltellurides or diarylditellurides can be successfully employed in a nickel catalyzed tellurium-zinc exchange mediated by diethylzinc. Knochel also showed that there was no reaction between diethylzinc and diaryltelluride in the absence of catalyst. However, no paper has appeared in the literature on tellurium-zinc exchange using organotelluronium salts which are easily prepared and are crystalline solids with excellent shelf-lives as compared with the malodorous and air-sensitive characteristics associated with most of diorgano-tellurides. We have found a quick, direct tellurium-zinc exchange between organotelluronium salts and

diethylzinc without invoking the help of any catalyst. Herein we disclose our preliminary results.

On treatment with Et_2Zn in dichloromethane at room temperature, telluronium salt **1** reacted quickly with carbonyl compounds to give secondary or tertiary alcohols¹, Table 1. When telluronium salt **1a** was used, both aromatic and aliphatic aldehydes were allylated smoothly to give homoallylic alcohols in good to excellent yields. For phenacyl chloride, the corresponding allylated chlorohydrin **2c** was obtained. For α , β -unsaturated ketone or ester, only 1,2-addition products were obtained and no indication of any 1,4-addition product. For the reaction with methyl cinnamate, a bisallylation product was obtained. Entries 5,6,7 and

Table 1
Reaction of organotelluronium salts with carbonyl compounds mediated by Et_2Zn

$ \begin{array}{c} \text{R}_2\text{Te}^+\text{CH}_2\text{E} \\ \text{X}^- \\ \text{1} \end{array} + \begin{array}{c} \text{O} \\ \parallel \\ \text{R}'\text{C}-\text{R}'' \end{array} \xrightarrow[\text{CH}_2\text{Cl}_2, \text{rt}]{\text{Et}_2\text{Zn}} \begin{array}{c} \text{OH} \\ \\ \text{R}'\text{R}''\text{CCH}_2\text{E} \\ \text{2} \end{array} $							
entry	E	R	X	salt	$\text{R}'\text{R}''\text{CO}$	product	yield(%) ^a
1	$\text{CH}=\text{CH}_2$	<i>i</i> -Bu	Br	1a	$\text{C}_6\text{H}_5\text{CHO}$	2a	99
2	$\text{CH}=\text{CH}_2$	<i>i</i> -Bu	Br	1a	Lauraldehyde	2b	84
3	$\text{CH}=\text{CH}_2$	<i>i</i> -Bu	Br	1a	PhCOCH_2Cl	2c	87
4	$\text{CH}=\text{CH}_2$	<i>i</i> -Bu	Br	1a	Methyl cinnamate	2d ^b	64
5	$\text{CH}=\text{CH}_2$	<i>i</i> -Bu	Br	1a	Chalcone	2e	100
6	$\text{CH}=\text{CH}_2$	<i>i</i> -Bu	Cl	1b	Chalcone	2e	96
7	$\text{CH}=\text{CH}_2$	<i>i</i> -Bu	I	1c	Chalcone	2e	95
8	$\text{CH}=\text{CH}_2$	<i>i</i> -Bu	BPh_4	1d	Chalcone	2e	93
9	$\text{C}\equiv\text{CSiMe}_3$	<i>i</i> -Bu	Br	1e	$\text{C}_6\text{H}_5\text{CHO}$	2f	93
10	Ph	ⁿ Bu	Br	1f	<i>p</i> - $\text{ClC}_6\text{H}_4\text{CHO}$	2g	87

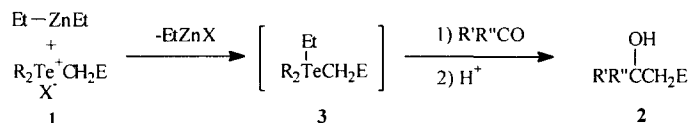
^aIsolated yield based on carbonyl compounds.

^bbisallylation product

8 demonstrate that the effect of the anion on the reaction was not significant. In the case of the telluronium salt **1e** containing the (trimethylsilyl)propargyl group, the propargylation product was obtained in 93% yield while the same product was obtained only in 66% yield^[18] by using (trimethylsilyl)propargylzinc bromide. Benzylolation was also smoothly effected when telluronium salt **1f** was used.

There are two possible mechanisms for this process (Figure 1), i.e., the tetraorganyltellurium mechanism^[19-22] (path A) and the tellurium-zinc exchange mechanism (path B) in which diethylzinc attacks the telluronium salt **1** to generate the mixed diorganozinc salt **5**, probably through a four-membered ring transition state. It has been convincingly documented that tetraorganotellurium species are formed by treating organotelluronium salts or organotellurium halides with alkyllithium or Grignard reagents^[23-26]. However, little is known about the reaction of organotelluronium salts with Et_2Zn , though as early as 1888 Marquardt and Michaelis^[23] made an unsuccessful attempt to prepare tetraethyltellurium by heating triethyltelluronium chloride with Et_2Zn . Considering that telluronium salt **4** is formed in path B, if we could isolate it path B would be a more plausible mechanism. Indeed, we did isolate telluronium salt **4a** in 93% yield² (based on telluronium salt **1**) by filtering the suspension

path A



path B

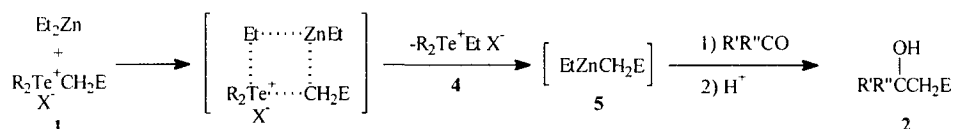


Figure 1 Two possible mechanisms

generated by addition of Et_2Zn to telluronium salt **1e** at room temperature in ether (Figure 2). By further adding benzaldehyde to the filtrate, the propargylation product and the allenylation product **6** were obtained in 51% and 22% yield, respectively. The product **6** resulted from rearrangement of the intermediate **5a** before adding benzaldehyde. The formation of **6** was sharply decreased if benzaldehyde was added before adding diethylzinc to capture the *in situ* generated intermediate **5a** (entry 9 in table 1). A tellurium-zinc exchange mechanism is thus favored based on this experiment, and the key intermediate is the mixed diorganozinc **5**.

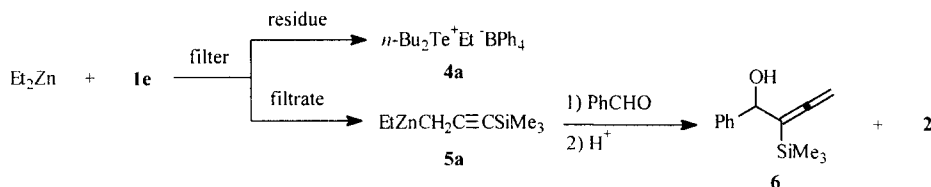


Figure 2 Isolation of telluronium salt **4a**

In summary, we have described a new tellurium-zinc exchange reaction between organotelluronium salts and Et_2Zn . The *in situ* generated mixed diorganozinc reacted smoothly with carbonyl compounds to give alcohols in good to excellent yields. Since diorganozincs have higher enantioselectivity in asymmetric addition to aldehydes than the corresponding organozinc halides^[27], the application of this tellurium-zinc exchange reaction in enantioselective synthesis of a broad range of alcohols can be expected.

Acknowledgment: Financial support from the National Sciences Foundation of China (No.B020205) and Chinese Academy of Sciences is gratefully acknowledged.

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Footnotes

1. **Typical procedure.** Preparation of 1-phenyl-3-buten-1-ol (**2a**). A mixture of allyldiisobutyltelluronium bromide **1a** (435 mg, 1.2 mmol) and benzaldehyde (106 mg, 1.0 mmol) was dissolved in dichloromethane (5 mL) under an Ar atmosphere. A solution of diethylzinc in hexane (1.0M, 1.2 mL, 1.2 mmol) was added dropwise to this mixture at room temperature. The reaction was monitored by TLC. The reaction was quenched by filtering the mixture through a short silica gel column. The filtrate was concentrated and the residue purified by preparative TLC to give homoallylic alcohol **2a** in 99% yield.
2. Analytical data for the dibutylethyltelluronium tetraphenylborate **4a**: ¹H-NMR (300 MHz, CDCl₃) δ 0.92 (t, J = 7.3 Hz, 6 H), 1.36 (m, 7 H), 1.66 (m, 4 H), 2.76 (m, 6 H), 6.80 (t, J = 7.1 Hz, 4 H), 6.94 (t, J = 7.36 Hz, 8H), 7.20 (m, 8 H); IR $\nu_{\text{cm}^{-1}}$ (KBr) 3055, 3000, 1580, 1477, 1458, 1426, 1187, 751, 734, 706, 612; FAB-MS *m/z* (rel. intensity) 273 (¹³⁰Te, 100), 271 (¹²⁸Te, 94), 269 (¹²⁶Te, 66); Anal. Calcd for C₃₄H₄₃BT_e: C, 69.20; H, 7.34; Found: C, 69.29; H, 7.52.