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Tellurium-Zinc Exchange Reaction.
A New Preparative Method of Alkenylzinc Reagents

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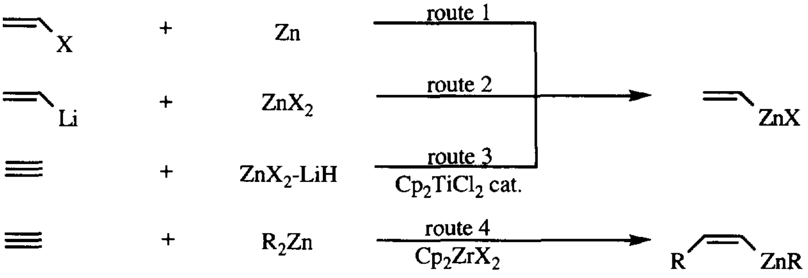
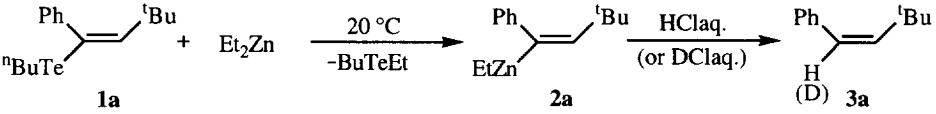
Abstract: Alkenyl tellurides were converted to the corresponding alkenylzinc compounds by the reaction with diethylzinc. The exchange reaction proceeds efficiently in THF at room temperature with retention of the stereochemistry of the starting tellurides. The successive reaction of the formed alkenylzinc with 4-iodotoluene in the presence of $Pd(PPh_3)_4$ afforded a cross-coupling product as a single stereoisomer.

Organozinc compounds are important reagents in organic synthesis[1] especially for asymmetric carbon-carbon bond forming reactions via enantioselective addition to aldehydes catalyzed by chiral ligands.[1d,e,2] Thus, development of useful preparative methods of these compounds is of great significance. Insertion of zinc metal into C-X bonds is a well-known methodology for preparation of organozinc reagents.[1a-c,3] However, the direct reactions of zinc metal with alkenyl halides[4] (route 1 in Scheme 1) do not always afford satisfactory results, since the stereochemistry of the starting halides is not retained completely in the generated alkenylzincs.[4a-c] For this reason, they have usually been prepared by transmetalation of appropriate alkenyllithiums with zinc salts (route 2).[1b,f] For example, alkenylzincs carrying some functionalities, such as cyano or ester groups which are prone to react with organolithiums, have successfully been prepared by generating alkenyllithiums at very low temperatures and subsequent transmetalation with ZnI_2.[5] As an alternative route to alkenylzincs, titanium-catalyzed hydrozincation of internal acetylenes has been reported very recently (route 3).[6] It is also known that Cp_2ZrX_2 promotes carbozincation of terminal alkynes with dialkylzincs which affords the corresponding alkenylalkylzincs with moderate regioselectivities (route 4).[7]



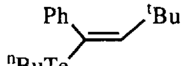
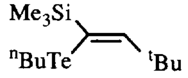
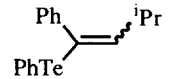
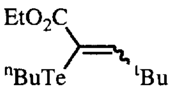
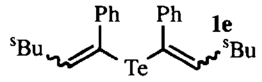
Scheme 1

In this paper, we describe a new preparative method of alkenylzinc compounds by use of a tellurium-zinc exchange reaction under halide-free conditions. A typical procedure is as follows. Into a THF (5 mL) solution of *E*-1-(butyltelluro)-3,3-dimethyl-1-phenyl-1-butene (**1a**) was added diethylzinc (1.0 equiv) at 20 °C. After stirring for 5 h, the reaction mixture was quenched with 1 N HCl at 0 °C. Purification of the resulting mixture by HPLC afforded 3,3-dimethyl-1-phenyl-1-butene (**3a**) in 85% yield with an *E/Z* ratio of 6/94 along with butyl ethyl telluride (BuTeEt) in 89% yield[8] (Scheme 2 and entry 1 in Table 1). This result indicates that **3a** was formed via tellurium-zinc exchange leading to alkenylzinc **2a** followed by protonation. It should be noted that the double bond configuration is fairly well retained during these transformations. Quenching of **2a** prepared under the identical conditions with DCl/D_2O gave deuterated **3a** (*d*-content > 95%, *E/Z* = 5/95, determined by NMR) in 88% yield.



Scheme 2

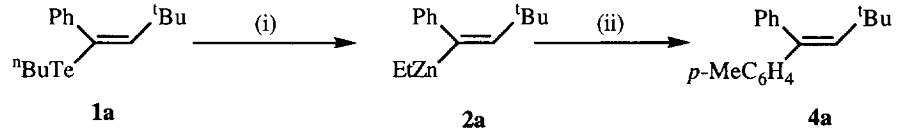
Table 1. Te-Zn Exchange of Alkenyl Tellurides with Diethylzinc

Entry	Telluride	Et_2Zn	Solvent	Time	3	
		(equiv)		(h)	Yield[a] (%)	*E/Z*[b]
1	 **1a** (*E/Z* > 99/1)	1	THF	5	85	6:94
2	**1a**	1.5	THF	5	92	5:95
3	**1a**	3	CH_3CCl_3	5	9	
4	 **1b** (*E/Z* < 1/99)	1.5	THF	24	76	>99:1
5	**1b**	3	THF	5	80	>99:1
6	 **1c** (*E/Z* = 51/49)	3	THF	24	72	32:68
7	 **1d** (*E/Z* = 22/78)	1.5	THF	5	74	82:12
8	 **1e** (*EE/EZ/ZZ* = 12/59/29)	4	THF	36	62[c]	34:66

[a] Isolated yield based on tellurides used. [b] Determined by ^1H NMR and/or GC. [c] Based on the alkenyl groups in **1e**.

The yield increased when 1.5 equiv of diethylzinc was used (entry 2 in table 1), but decreased drastically in a CH_3CCl_3 solvent, suggesting that the exchange reaction is accelerated by the coordinating solvent. Under similar conditions, **3b** was obtained in good yields with complete retention of the stereochemistry. The exchange reaction of **1b** was somewhat slower than in the case of **1a** probably due to the steric bulkiness of the ^{t}Bu group in the *cis* orientation to the ^{n}BuTe group (compare the results in entries 2 and 4). This was supported by the reaction of **1c,** where the Z-isomer of **3c** was formed preferentially from a 1:1 mixture of the stereoisomers (entry 6) and 25% of Z-**1c** was recovered after the reaction. It is interesting that, although **1c** has two similar bonds between tellurium and sp^2-carbons, i.e., Te-vinyl and Te-aryl bonds, the former was cleaved exclusively over the latter resulting in the selective formation of the corresponding alkenylzinc. This was confirmed by the fact that benzene was not detected by the GC analysis of the resulting mixture of entry 6. The tellurium-zinc exchange also proceeded efficiently with **1d** to give an alkenylzinc having an ester group (**2d**). This result demonstrates the synthetic superiority of organozinc compounds over organolithium or -magnesium reagents. When a symmetrical telluride having two alkenyl groups (**1e**) was allowed to react with an excess amount of diethylzinc, both substituents were converted to the corresponding alkenylzinc (entry 8).

Alkenylzinc compounds are known to serve as suitable reagents for cross-coupling reaction with various halides. So, in synthetic application of this tellurium-zinc exchange, we carried out a palladium-catalyzed coupling reaction[1f,9] of 4-iodotoluene with **2a** which was prepared *in situ* by the tellurium-zinc exchange under identical conditions of entry 2 in Table 1 (Scheme 3). Purification of the product by HPLC afforded **4a** as a single stereoisomer in 72% yield. This result indicates that BuTeEt which was produced in the tellurium-zinc exchange process did not affect the palladium-catalyzed coupling reaction.



Reagents and conditions: (i) Et_2Zn (1 equiv), 20 °C, 5 h.
(ii) p-MeC$_6$H$_4$I (1.2 equiv), 5 mol% Pd(PPh$_3$)$_4$, 0~20 °C, 1 h.

Scheme 3

Hitherto known methods (routes 1-4) afford alkenylzincs only in the presence of halide salts as in Scheme 1 and often lack regio-[6] or stereoselectivities.[4a-c] Halide salts sometimes affect stereoselectivities of chelation controlled reactions.[10] The present tellurium-zinc exchange affords halide-free alkenylzinc reagents (RZnEt) from the corresponding alkenyl tellurides with retention of the stereochemistry, which can be prepared easily by regioselective carbotelluration of acetylenes with tellurides.[12] In this respect, the tellurium-zinc exchange provides a useful method for preparation of alkenylzinc reagents. Studies on the scope and limitations of this reaction are currently in progress.

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