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Telluro-Directed Regiospecific and Highly Stereoselective Reaction of Ethyl 5-Telluro-(2*E*,4*Z*)-Pentadienoate with Organocopper Reagents

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Abstract: Ethyl 5-telluro-(2*E*,4*Z*)-pentadienoate **2**, which is prepared by the Wittig olefination of (*Z*)-β-telluroacrolein **1**, reacted very rapidly with organocuprates **3** at -78°C to form exclusively the corresponding 5-substituted products **4** with high stereoselectivity and in excellent yields.

In recent years, vinylic tellurides have surfaced as valuable intermediates in organic synthesis and have been employed in important synthetic transformations.[1] Many methods for preparation of these compounds have hitherto been developed.[2] One of the interests in vinylic tellurides stems from the *Z*-double-bond geometry and the fact that they can function as the precursors of organometallics containing *Z*-vinyl moieties.[3] Vinylic tellurides can be directly metallated with higher-order cyanocuprates to the corresponding *Z*-vinyl cuprates, which can be reacted with enones and epoxides to give the corresponding 4,5-unsaturated compounds or homoallylic alcohols respectively.[3c, 3d] Most recently, however, the cross-coupling reactions (or substitution reactions) of vinylic tellurides with non-higher-order cuprates have been studied,[2,4] and the possible pathway of this substitution reaction described.[4] In the course of searching for synthetically useful functionalized vinyltellurides, we synthesized (*Z*)-β-telluroacroleins **1** (Scheme 1) with high stereoselectivity and in high yield,[5] which on subjection to Wittig olefination would provide conjugated dienyl or trienyl tellurides.[6] We also became aware of an addition-elimination reaction of (*Z*)-β-trifluoroacetylvinyltellurides [7] with organozinc cuprates to (*E*)-α,β-unsaturated trifluoromethyl ketones.[8] As another synthetic application of conjugated dienyl tellurides containing an electron-withdrawing group, here we report the results of the reaction of ethyl 5-telluro-(2*E*, 4*Z*)-pentadienoate **2** with organocuprates.

Ethyl 5-telluro-(2*E*,4*Z*)-pentadienoate **2**,[9] could be obtained as a pure isomer in 94% yield from the olefination of (*Z*)-β-telluroacrolein **1** with (ethoxycarbonylmethenyl)triphenylphosphorane[10] under very mild conditions. Its reaction with a variety of *n*-butylcopper reagents **3** at -78 °C to give the corresponding butylated product **4** was first investigated (Scheme 1). The results are summarized in **Table 1**. The use of 1.2 equiv. of zinc cuprate **3a** didn't cause any reaction even at -78 °C ~ rt for 3h (entry **1**). Obviously, telluride **2** is a less reactive Michael acceptor than (*Z*)-β-trifluoroacetylvinyltellurides.[8] Unexpectedly, however, as soon as 1.2 equiv. of cyanodibutyl lithium cuprate **3b** was added dropwise to the mixture of telluride **2** in THF at -78 °C,

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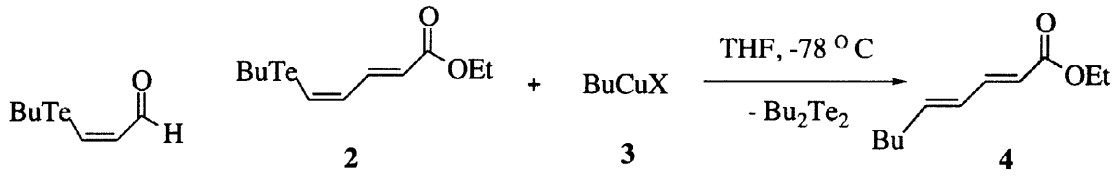
the butylation was complete to give the 5-butylated product **4** in 92% yield (entry **2**). Even at -100 °C, the reaction occurred very rapidly (entry **3**). Similarly, the other butylcopper reagents **3c-e** also reacted very



X =Bu(CN)Li_2, Bu(CN)$(MgBr)_2$, BuLi, BuMgBr, BF_3

Scheme 1

Table 1 The Regiospecific Reaction of Butylcopper Reagents with Telluride 2[a]

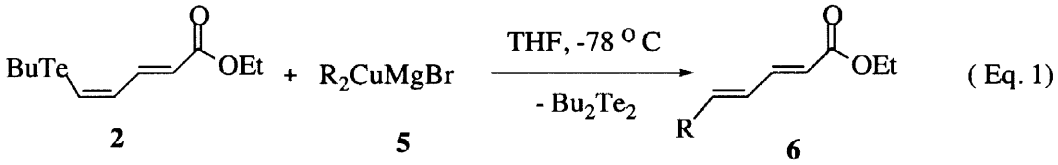
Entry	Butylcopper Reagent (equiv.)	time (min.)	Product 4 (2*E*,4*E*):(2*E*,4*Z*)[b]	Yield (%)[c]
1	$Bu_2Cu(CN)(ZnCl)_2$ **3a** (1.2)	180	---------	0 [d]
2	$Bu_2Cu(CN)Li_2$ **3b** (1.2)	2	81 : 19	92
3	**3b** (1.2)	10 [e]	90 : 10	93
4	**3b** (3.0)	30 [f]	81 : 19	95
5	$Bu_2Cu(CN)(MgBr)_2$ **3c** (1.2)	2	87 : 13	96
6	Bu_2CuLi **3d** (1.2)	2	32 : 68	92
7	$Bu_2CuMgBr$ **3e** (1.2)	2	99 : 1	96
8	**3e** (3.0)	30 [f]	99 : 1	96
9	$BuCu•BF_3$ **3f** (1.2)	2	69 : 31	94

[a] Unless otherwise stated, the reaction was preformed on the 1.0 mmol scale using telluride **2** in THF at -78 °C.[b] Determined by 300 MHz ^1H MNR spectral analysis. [c] Isolated yields on telluride **2**. [d] Telluride **2** was recovered after the reaction mixture was allowed to warm to rt.[e] The reaction proceeded at ca. -100 °C. [f] The reaction finished in 2 min.

quickly with telluride **2** to give exclusively the 5-butylated product **4** in excellent yield. In order to compare the reactivity of telluride **2** with product **4**, three equiv. of cuprate **3b** and **3e** were employed respectively to react with telluride **2** at -78 °C for 30 minutes. In these cases, no dibutylated or other products were detected but only the monobutylated product **4** (entries **4** and **8**). It is noteworthy that in the case of $BuCu•BF_3$ **3f**, the regiochemistry of telluride **2** is in marked contrast to that of the structurally similar methyl sorbate. No 1,4-addition product was detected in the case of telluride **2**, while the 1,4-adduct (93%) along with small amount of 1,6-adduct (7%) was obtained in the case of methyl sorbate.[11] **Table 1** shows that the stereochemistry of product **4** depends strongly on the butylcopper reagent **3** employed. The reaction exhibited high (2*E*,4*E*)-selectivity with cyanocuprates **3b-c**, dibutyl magnesium cuprate **3e**, and $BuCu•BF_3$ **3f**. It is noteworthy that in the case of **3e**, the pure (2*E*,4*E*)-isomer was obtained (>99% selectivity).[12] In contrast, in the case of dibutyllithium cuprate **3d** (entry **6**), the reaction exhibited relatively low (2*E*, 4*Z*)-selectivity. This result appears to be similar to that of the alkylation described by Ogawa et al.[4a]

The scope of this reaction was investigated under the optimum reaction conditions (entries **7** and **8** in **Table 1**)(eq.1). The results are summirazed in **Table 2**. Telluride **2** reacted very rapidly with magnesium

cuprates **5** at -78 °C in THF to give the corresponding detellurolated products **6** with high selectivity and in excellent yield.[13] It is interesting to note that aryl (entries **4-6**) and styryl (entry **7**) copper reagents, which are somewhat unreactive when unsaturated esters are used as Michael acceptors,[14] are so efficient in this reaction that the detellurolated species **6d-g** were obtained as the products in 82-93%.



2 **5** **6** (Eq. 1)

Table 2 The Reaction of Organocuprates 5 with 2

Entry	R in cuprate 5 (equiv.)	Time (min.)	Product 6 (2*E*,4*E*):(2*E*,4*Z*)[a]	Yield (%)[b]
1	n-C_6H_{13} **5a** (1.2)	2	> 98 : 2 **6a**	90
2	n-C_7H_{18} **5b** (1.2)	2	> 98 : 2 **6b**	95
3	n-$C_{10}H_{21}$ **5c** (1.2)	2	> 98 : 2 **6c**	98
4	C_6H_5 **5d** (2.0)	30	> 99 : 1 **6d**	93
5	*p*-$CH_3C_6H_4$ **5e** (2.0)	30	> 99 : 1 **6e**	82
6	*p*-$CH_3OC_6H_4$ **5f** (2.0)	30	> 99 : 1 **6f**	85
7	(*E*)-C_6H_5CH=CH **5g** (2.0)	30	> 99 : 1 **6g**	88

[a] Determined by 300 MHz ^{1}H NMR spectral analysis. [b] Isolated yields based on telluride **2**.

The explanation for the observed results may be related to the telluro group at the terminal position of α,β,γ,δ-unsaturated ester **2**. This can be demonstrated by the following experimental facts: 1) Under the same reaction conditions, product **4** didn't react further with copper reagents **3b** and **3e**. 2) In the case of BuCu•BF_3 **3f**, the butylation of telluride **2** provided only detellurolated product **4** instead of 1,4-adduct. 3) The detellurolation of telluride **2** could proceed very easily even with aryl- and styrylcopper reagents at -78 °C. Probably the telluride **2** was first attacked by the organocopper reagent to form an "ate" complex,[4,15] then a 1,6-addition elimination reaction took place to form the thermodynamically more stable (2*E*, 4*E*)-product along with a substitution reaction to give detallurolated product with retention of olefin geometry.

In conclusion, a regiospecific and highly stereoselective reaction of a vinylic telluride bearing an electron withdrawing group with a wide range of organocopper reagents has been developed. Te reaction is different not only from the transmetallation of vinylic tellurides with higher-order cyanocuprates but also from their cross-coupling with non-higher-order copper reagents.

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13. Typical spectral data for **7g**: ^{1}H NMR (300 MHz, $CDCl_3$/TMS) δ 1.30 (t, J = 7.1Hz, 3H), 4.20 (q, J = 7.1Hz, 2H), 6.0 (m, 2H), 6.24~6.29 (dd, J = 15.5, 10.5Hz, 1H), 6.34~6.37 (d, J = 15.5Hz, 1H), 6.52~6.57 (dd, J = 15.0, 10.2Hz, 1H), 7.0~7.30 (m, 5H), 7.52~7.57 (dd, J = 15.5, 10.8Hz, 1H); IR (neat) *vmax* 1710s, 1630s, 1600s, 1450s, 1250s, 1150s, 1040s, 980s, 730s. Ref. Sossi, R.; Carpita, A.; Lippolis, V. *Syn. commun.* **1991**, 21, 331.
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