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

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Abstract: Ethyl 5-telluro-(2E,4Z)-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. © 1997 Elsevier Science Ltd. All rights reserved.

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-(2E,4Z)-pentadienoate 2,⁹ could be obtained as a pure isomer in 94% yield from the olefination of (Z)- β -telluroacrolein 1 with (ethoxycarbonylmethenyl)triphenylphosphorane¹⁰ 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,

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

$$BuTe H 2 BuCuX - Bu_2Te_2 Bu 4 OEt$$

X =Bu(CN)Li₂, Bu(CN)(MgBr)₂, BuLi, BuMgBr, BF₃

Scheme 1

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Table 1 The Regiospecific Reaction of Butylcopper Reagents with Telluride 2"						
Entry	Butylcopper Reagent (equiv.)	time (min.)	Product 4 $(2E, 4E):(2E, 4Z)^{\circ}$	Yield (%)		
1	$Bu_2Cu(CN)(ZnCl)_2$ 3a (1.2)	180		0 a		
2	$Bu_2Cu(CN)Li_2$ 3b (1.2)	2	81 : 19	92		
3	3b (1.2)	10 °	90:10	93		
4	3b (3.0)	30 ^t	81:19	95		
5	$Bu_2Cu(CN)(MgBr)_2$ 3c (1.2)	2	87:13	96		
6	Bu ₂ CuLi 3d (1.2)	2	32:68	92		
7	Bu ₂ CuMgBr 3e (1.2)	2	99:1	96		
8	3e (3.0)	30 '	99 :1	96		
9	BuCu•BF ₃ 3f (1.2)	2	69 : 31	94		

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* 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.º 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 $BuCu \cdot BF_3$ 3f, the regiochemistry of telluride 2 is in marked contrast to that of the structurally similar methyl sorbate. No 1,4addition 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 (2E,4E)selectivity with cyanocuprates 3b-c, dibutyl magnesium cuprate 3e, and BuCu•BF, 3f. It is noteworthy that in the case of 3e, the pure (2E, 4E)-isomer was obtained (>99% selectivity).¹² In contrast, in the case of dibutyllithium cuprate 3d (entry 6), the reaction exhibited relatively low (2E, 4Z)-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

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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%.

BuTe
$$OEt + R_2CuMgBr = \frac{THF, -78 \circ C}{-Bu_2Te_2} OEt (Eq. 1)$$

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Entry	R in cuprate 5 (equiv.)	Time (min.)	Product 6 (2E,4E):(2E,4Z)*	Yield (%) ⁶
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 ₆ H ₅ 5d (2.0)	30	> 99 : 1 6d	93
5	<i>p</i> -CH ₃ C ₆ H ₄ 5e (2.0)	30	> 99 : 1 6e	82
6	<i>p</i> -CH ₃ OC ₆ H ₄ 5f (2.0)	30	> 99 : 1 6f	85
7	$(E)-C_{6}H_{5}CH=CH 5g (2.0)$	30	> 99 : 1 6g	88

* Determined by 300 MHz¹H 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 $\alpha,\beta,\gamma,\delta$ -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•BF₃ 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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- Typical spectral data for 2: red oil, b. p. 124 °C/3 mmHg; ¹ H NMR (300 MHz, CDCl₃/TMS) δ 0.95 (t, J = 7.30Hz, 3H), 1.30 (t, J = 7.10Hz, 3H), 1.45 (m, 2H), 1.80 (m, 2H), 2.80 (t, J = 7.5Hz, 2H), 4.20 (q, J = 7.10Hz, 2H), 5.95 (d, J = 15.10Hz, 1H), 6.90 (t, J = 10.30Hz, 1H), 7.26 (dd, J = 10.30Hz, J = 15.10Hz, 1H), 7.45 (d, J = 10.30Hz, 1H); IR(neat) *vmax* 1710s, 1620s, 1540w, 1250s, 1150s, 1040m, 980m, 860m, 680m; MS (*m*/z, rel. intensity) 312 (M⁺, ¹³⁰Te, 52), 310 (M⁺, ¹²⁸Te, 50), 308 (M⁺, ¹²⁶Te, 24), 267 (28), 265 (27), 263 (13), 255 (81), 253 (79), 251 (39), 125 (100), 57 (20); HRMS m/z Calcd. for C₁₁H₁₈O₂Te: 312.0369, found: 312.0365.
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- 13. Typical spectral data for 7g: ¹H NMR (300 MHz, CDCl₃/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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