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Highly Stereoselective Preparation of β--(Organotelluro)acroleins and Facile Stereospecific Synthesis of Conjugated Dienols[†]

Xue-Sheng Mo, and Yao-Zeng Huang*

Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Lu, Shanghai 200032, China

Abstract: Diorganoditellurides 1 (1a R = n-Bu; 1b R = Ph), by treated with sodium borohydride, reacted with propargylaldehyde to give corresponding β -(organotelluro)acroleins 2 with high (Z)-stereoselectivity in good yields (2a: Z : E = 89 : 11; 2b: pure Z--isomer); Tellurides 3, on treatment with n-BuLi, reacted with carbonyl compounds to afford conjugated dienols with retention of olefin geometry in high yields.

In recent years, there has been a remarkable interest in preparation of organotellurium compounds and their utilization for organic synthesis.¹ However, limited reports on the synthesis of highly functionalized organotellurium compounds have appeared in the literatures. Uemura et al. reported that ethyl (Z)-- β --(phenyltelluro)acrylate reacted with Grignard reagents catalyzed by the nickel(II)-- or cobalt(II)--phosphine complex to form carbon-carbon bonds.² Detty et al. described the preparation of several β --(aryltelluro)acrylic acid derivatives³ and β --(organotelluro)vinylphenyl ketones.⁴ We now report that n-butyltellurolate(n-BuTeH) and phenyltellurolate(PhTeH) reacted with propargylaldehyde to yield the highly functionalized organotellurium compounds: e.g. β --(n-butyltelluro)acrolein **2a** and β --(phenyltelluro)acrolein **2b** with high Z--stereoselectivity in good yields. We also report that telluride **3**, which were prepared by methylenation of compounds **2**, on treatment with butyllithium, reacted with carbonyl compounds to afford conjugated dienols stereospecifically in good yields.



Thus diorganoditellurides 1 (1a R = n-Bu, 1b R = Ph), after being treated with sodium borohydride, were converted into the corresponding organotellurolates which reacted with propargylaldehyde at $-15 \sim -5^{\circ}$ C in ethanol or methanol to give the corresponding β -(organotelluro)acroleins 2 as shown in equation 1. The reaction

[†]Dedicated to Prof. Shigeru Oae on the occasion of his seventy-fifth birthday.

proceeded in two steps: formation of organotellurolates and their additions to propargylaldedyde. It was necessary that an excess amount of sodium borohydride must be used in order to convert compounds 1 completely into the corresponding organotellurolate in the first step. It seemed to have an effect on the carbonyl groups of propargylaldehyde and β --(organotelluro)acroleins 2 in the second step, in fact, no products of reduction were detected. In the case of Ph₂Te₂ 1b, only β --(phenyltelluro)acrolein 2b with (Z)--configuration was obtained in 80% yield, while in the case of n-Bu₂Te₂ 1a, β -(butyltelluro)acrolein 2a with predominant (Z)-geometry (Z : E = 89 : 11) was obtained in 84% yield, of which E--and Z--isomer could be separated by flash chromatography on silica gel.⁵ The cause which evoked the discrepancy between their stereochemistry was not

Ph₃PCH₃I
$$\xrightarrow{1) t$$
-BuOK/Et₂O, r.t., 30Min.
2) 2, -30~0°C RTe or (eq.2)
(Z) -3 (E) - 3

Compound (Z)--2a, (E)--2a or 2b reacted with triphenylmethylenephosphorane, generated from methyltriphenylphosphonium iodide with potassium tert-butoxide in ether at r.t., to give the corresponding conjugated dienyl telluride (Z)--3a in 92% yield, (E)--3a in 90% yield, and 3b in 89% yield respectively with retention of the olefin geometry (eqn 2).⁶ The conjugated dienyl telluride (Z)--3a, after being treated with butyllithium at -78 °C for 0.5 h in THF, reacted with carbonyl compounds to give Z--conjugated dienols 4 exclusively in good yields via lithium-tellurium exchange reaction (eqn 3). The results are summarized in Table 1. As shown in Table 1, conversion of carbonyl compounds into conjugated dienols usually proceeded completely when the mixture was allowed to warm to room temperature, and the reaction worked well with both aldehydes and ketones, including enolizable aliphatic aldehydes, acetophenone, cyclohexanone and non-enolizable aromatic aldehydes. It is noteworthy that the products obtained were pure Z--isomers. In the case of (E)--3a, only E--product(E--4c) was obtained in 82% yield.⁷

BuTe
$$(Z)-3a$$
 $(Z)-3a$ $(Z)-3a$ (I) n-BuLi/THF, -78°C, 30 Min. R^2 $(eq.3)$
 (I) R^1R^2CO , -78°C~ r.t. R^1 $(eq.3)$

The reaction of conjugated dienyl telluride **3b** mediated by butyllithium with a carbonyl compound was also examined. When n-hexanal was used as a substrate, a mixture of **4e** and 1--phenyhexan--1--ol **5** with the ratio of 10:1 was obtained. Similarly, the reaction of telluride (Z)--**3a** mediated by phenyllithium with n-hexanal led to the same result (eqn. 4). The results showed that 1, 3--conjugated dienyllithium was more stable species than phenyllithium, although phenylcopper is more stable than vinylcopper in the copper-tellurium exchange reaction described by Comasseto.⁸ This BuLi-promoted condensation of telluride (Z)--**3a**, which can be used for direct preparation of terminal (3Z)--1, 3-dienes, with carbonyl compounds giving rise to conjugated dienols stereospecifically is novel, although the lithium-tellurium exchange reaction of organotellurides has been described by the other authors.⁹

$$RTe = \frac{1) R^{1}Li / THF, -78 °C, 30 Min.}{2) n-C_{5}H_{11}CHO} 4e + n-C_{5}H_{11} Ph$$
(eq.4)

$$R=Ph (3b), R^{1}=Bu, 88\% \text{ total yields} 10 : 1$$

$$R=Bu (Z-3a), R^{1}=Ph, 85\% \text{ total yields} 10 : 1$$

011

certain at present.

The β -(organotelluro)acroleins 2, conjugated dienyl tellurides 3, and conjugated dienols 4 reported herein, which are rather readily accessible, are expected to be useful in organic synthesis owing to their novel structures and the presence of several different functional groups. To our knowledge, few methods are available for direct introduction of Z--conjugated dienyl group into organic molecules because the starting materials containing conjugated dienyl moiety are not easily prepared¹⁰. Recently, several reports dealing with the natural products which possess Z--conjugated dienyl groups have been published¹¹. Much attention has been focused on this area.

In summary, a novel method for synthesis of β --(organotelluro)acroleins, conjugated dienyl telluride and conjugated dienols has been established. It is expected that the above described reactions will find considerable application in the synthesis of natural products. Further work in this area is now in progress in our laboratory.

Entry	Carbonyl compound	Product (Z-isomer) ^b	Yield (%) ^c
l	С)-сно		85
2	CH3-CHO		92
3	сі-Д-сно	a-√ 4c	88
4	Br -CHO	Br OH 4d	85
5	n-C ₅ H _{II} CHO	n-C ₅ H ₁₁ - 4e	89
6	n-C ₉ H _p CHO	n-C ₉ H ₁₉ -(4f	92
7		○H 4g	90
8		⟨ → OH → → → → → → → → → → → → → → → → → → →	90

Table 1 The Stereospecific Synthesis of Conjugated Dienols *

^a All the products gave satisfactory elemental analyses and spectral properties (IR, ¹H NMR, and MS).

^b Determined by 300 ¹H NMR spectral analysis. ^c Isolated yields based on carbonyl compounds.

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- 5. (n-Butyltelluro)acrolein Z--2a and E--2a: Z--2a: ¹H NMR (300MHz, CDCl₃) δ 0.85 (t, 7.70Hz, 3H), 1.30-1.45 (m, 2H), 1.72-1.81 (m, 2H), 2.70 (t, 7.40Hz, 2H), 7.40-7.55 (dd, 10.0Hz, 1.50Hz, 1H), 8.73-8.89 (d, 10.0Hz, 1H), 9.90 (d, 1.50Hz, 1H); IR (neat) v_{max} 1640, 1490, 1300, 1180, 970, 820; MS (m/z, rel. intensity) 242 (M⁺, ¹³⁰Te, 40), 240 (M⁺, ¹²⁸Te, 36), 238 (M⁺, ¹²⁶Te, 25), 185 (M⁺-57, ¹³⁰Te, 100), 183 (M⁺-57, ¹²⁸Te, 97), 181 (M⁺-57, ¹²⁶Te, 58); Anal. calc. for C₇H₁₂OTe: C, 35.06; H, 5.05; Found C, 34.79; H, 4.72%. E--2a: ¹H NMR (300MHz, CDCl₃) δ 0.90 (t, 7.70Hz, 3H), 1.30-1.45 (m, 2H), 1.75-1.89 (m, 2H), 2.83 (t, 7.40Hz, 2H), 6.70 (dd, 7.80Hz, 16.0Hz, 1H), 8.60 (d, 16.0Hz, 1H), 9.35 (d, 7.80Hz, 1H); IR (neat) v_{max} 2300, 1670, 1540, 1160, 1080, 950, 700; MS (m/z, rel. intensity) 242 (M⁺, ¹³⁰Te, 61), 240 (M⁺, ¹²⁸Te, 58), 238 (M⁺, ¹²⁶Te, 37), 185 (M⁺-57, ¹³⁰Te, 100), 183 (M⁺-57, ¹²⁸Te, 90), 181 (M⁺-57, ¹²⁶Te, 58); Anal. calc. for C₇H₁₂OTe: C, 35.06; H, 5.05, ¹²⁶Te, 58); Anal. calc. for C₇H₁₂OTe: C, 35.06; H, 5.05, ¹²⁶Te, 58); Anal. calc. for C₇H₁₂OTe: C, 35.06; H, 5.05, ¹²⁶Te, 58); Anal. calc. for C₇H₁₂OTe: C, 37), 185 (M⁺-57, ¹³⁰Te, 100), 183 (M⁺-57, ¹²⁸Te, 90), 181 (M⁺-57, ¹²⁶Te, 58); Anal. calc. for C₇H₁₂OTe: C, 35.06; H, 5.05; Found C, 34.70; H, 4.66%.
- 6. Typical spectral data for Z--3a: ¹H NMR (300MHz, CDCl₃) δ 0.90 (t, 7.30Hz, 3H), 1.35-1.50 (m, 2H), 1.75-1.85 (m, 2H), 2.67-2.73 (t, 7.40Hz, 2H), 5.23-5.26 (d, 9.70Hz, 1H), 5.24-5.32 (dd, 1.20Hz, 16.8Hz, 1H), 6.25-6.40 (td, 9.70Hz, 16.8Hz, 1H), 6.70-6.78 (t, 9.70Hz, 1H), 6.80-6.85 (d, 9.70Hz, 1H); IR (neat) v max 1610, 1540, 1460, 1400, 1300, 1280, 900; MS (m/z, rel. intensity) 240 (M⁺, ¹³⁰Te, 42), 238 (M⁺, ¹²⁸Te, 37), 236 (M⁺, ¹²⁶Te, 25), 183 (M⁺-57, ¹³⁰Te, 100), 181 (M⁺-57, ¹²⁸Te, 92), 179 (M⁺-57, ¹²⁶Te, 54), 57 (C₄H₉⁺, 11), 53 (C₄H₆⁺, 58); Anal. calc. for C₈H₁₄Te: C, 40.41; H, 5.93; Found C, 39.98; H, 5.54%. ¹H NMR spectral data for **E--3a**: (300 MHz, CDCl₃) δ 0.90 (t, 7.40Hz, 3H), 1.40-1.50 (m, 2H), 1.75-1.85 (m, 2H), 2.72-2.79 (t, 7.50Hz, 2H), 4.92-4.98 (d, 10.0Hz, 1H), 5.01-5.09 (dd, 1.10Hz, 16.8Hz, 1H), 6.25-6.38 (td, 10.0Hz, 16.8Hz, 1H), 6.61-6.67 (dd, 10.0Hz, 1H), 6.88-6.92 (d, 16.0Hz, 1H).
- 7. Typical spectral data for Z--4c: ¹H NMR (300 MHz, CDCl₃) δ 1.10 (brs, OH), 5.0-5.04 (d, 10.0Hz, 1H), 5.05-5.12 (dd, 1.75Hz, 16.8Hz, 1H), 5.25 (d, 9.0Hz, 1H), 5.28-5.35 (dd, <u>10.0Hz</u>, 9.0Hz, 1H), 5.82-5.90 (t, <u>10.0Hz</u>, 1H), 6.48-6.60 (td, 10.0Hz, 16.8Hz, 1H), 7.0-7.20 (m, 4H); IR (neat) *v* max 3300, 1600, 1500, 1100, 1020, 920; MS (*m*/z, rel. intensity) 194 (M⁺, ³⁵Cl, 57), 177 (M⁺-OH, ³⁵Cl, 8), 159 (M⁺-³⁵Cl, 12), 141 (³⁷ClC₆H₄CO⁺, 100); Anal. calc. for C₁₁H₁₁ClO: C, 67.86; H, 5.69; Cl, 18.23; Found C, 67.63; H, 5.82; Cl, 17.84%. ¹H NMR spectral data for **E--4c**: (300 MHz, CDCl₃) δ 2.50 (brs, OH), 5.10-5.13 (d, 9.60Hz, 1H), 5.22-5.25 (d, 6.50Hz, 1H), 5.20-5.24 (d, 16.2Hz, 1H), 5.78-5.88 (dd, <u>14.5Hz</u>, 6.50Hz, 1H), 6.23-6.40 (m, 2H), 7.35-7.35 (m, 4H).
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