



0040-4039(95)00580-3

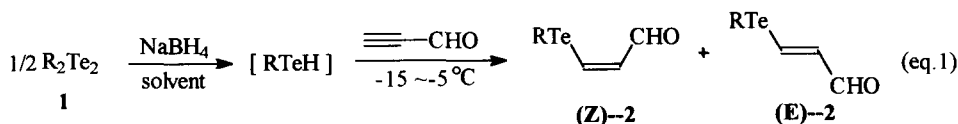
Highly Stereoselective Preparation of β --(Organotelluro)acroleins and Facile Stereospecific Synthesis of Conjugated Dienols[†]

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-butyltelluroate (n-BuTeH) and phenyltelluroate (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.



1a R = n-Bu, (*Z*)--**2a** : (*E*)--**2a** = 89 : 11

1b R = Ph, **2b**: pure *Z*-isomer

Solvent = MeOH or EtOH

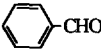
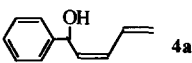

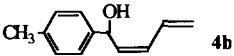
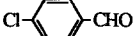
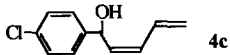
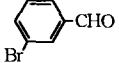
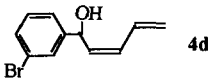
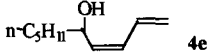
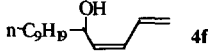

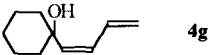
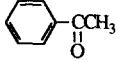
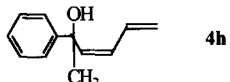
Thus diorganoditellurides **1** (**1a** R = n-Bu; **1b** R = Ph), after being treated with sodium borohydride, were converted into the corresponding organotelluroates which reacted with propargylaldehyde at -15 ~ -5°C in ethanol or methanol to give the corresponding β --(organotelluro)acroleins **2** as shown in equation 1. The reaction

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

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.

Table 1 The Stereospecific Synthesis of Conjugated Dienols ^a

| Entry | Carbonyl compound | Product (<i>Z</i> -isomer) ^b | Yield (%) ^c |
|-------|---|---|------------------------|
| 1 |  |  4a | 85 |
| 2 |  |  4b | 92 |
| 3 |  |  4c | 88 |
| 4 |  |  4d | 85 |
| 5 | $n\text{-C}_7\text{H}_{11}\text{CHO}$ |  4e | 89 |
| 6 | $n\text{-C}_9\text{H}_{19}\text{CHO}$ |  4f | 92 |
| 7 |  |  4g | 90 |
| 8 |  |  4h | 90 |

^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.

Acknowledgement

Thanks are due to the National Natural Science Foundation of China and Chinese Academy of Sciences for their financial support.

References and notes

- (a) Back, T.G. *The Chemistry of Organic Selenium and Tellurium Compounds*, Ed. Patai, S. Wiley, New York, **1987**, Vol. 2, P. 91. (b) Engman, L. *Acc. Chem. Res.* **1985**, *18*, 274. (c) Petragnani, N. and Comasseto, J.V. *Synthesis*, **1986**, 1. (d) Petragnani, N. and Comasseto, J.V. *Synthesis* **1991**, 793 and 898.
- Uemura, S. and Fukuzawa, S. *Tetrahedron Lett.* **1982**, *23*, 1181. (b) Uemura, S.; Fukuzawa, S. and Patil, S.R. *J. Organomet. Chem.* **1983**, *243*, 9.
- Detty, M. R.; Murray, B. J.; Smith, D.L. and Zumbulyadis, N. *J. Am. Chem. Soc.* **1983**, *105*, 875.
- Detty, M. R.; Luss, H. R.; McKelvey, J. M. and Geer, S. M. *J. Org. Chem.* **1986**, *51*, 1692.
- (n-Butyltelluro)acrolein Z--**2a** and E--**2a**: Z--**2a**: ^1H NMR (300MHz, CDCl_3) 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) ν_{max} 1640, 1490, 1300, 1180, 970, 820; MS (m/z , rel. intensity) 242 (M^+ , ^{130}Te , 40), 240 (M^+ , ^{128}Te , 36), 238 (M^+ , ^{126}Te , 25), 185 (M^+ -57, ^{130}Te , 100), 183 (M^+ -57, ^{128}Te , 97), 181 (M^+ -57, ^{126}Te , 58); Anal. calc. for $\text{C}_7\text{H}_{12}\text{OTe}$: C, 35.06; H, 5.05; Found C, 34.79; H, 4.72%. E--**2a**: ^1H NMR (300MHz, CDCl_3) 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) ν_{max} 2300, 1670, 1540, 1160, 1080, 950, 700; MS (m/z , rel. intensity) 242 (M^+ , ^{130}Te , 61), 240 (M^+ , ^{128}Te , 58), 238 (M^+ , ^{126}Te , 37), 185 (M^+ -57, ^{130}Te , 100), 183 (M^+ -57, ^{128}Te , 90), 181 (M^+ -57, ^{126}Te , 58); Anal. calc. for $\text{C}_7\text{H}_{12}\text{OTe}$: C, 35.06; H, 5.05; Found C, 34.70; H, 4.66%.
- Typical spectral data for Z--**3a**: ^1H NMR (300MHz, CDCl_3) 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) ν_{max} 1610, 1540, 1460, 1400, 1300, 1280, 900; MS (m/z , rel. intensity) 240 (M^+ , ^{130}Te , 42), 238 (M^+ , ^{128}Te , 37), 236 (M^+ , ^{126}Te , 25), 183 (M^+ -57, ^{130}Te , 100), 181 (M^+ -57, ^{128}Te , 92), 179 (M^+ -57, ^{126}Te , 54), 57 (C_4H_9^+ , 11), 53 (C_4H_6^+ , 58); Anal. calc. for $\text{C}_8\text{H}_{14}\text{Te}$: C, 40.41; H, 5.93; Found C, 39.98; H, 5.54%. ^1H NMR spectral data for E--**3a**: (300 MHz, CDCl_3) 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, 16.0Hz, 1H), 6.88-6.92 (d, 16.0Hz, 1H).
- Typical spectral data for Z--**4c**: ^1H NMR (300 MHz, CDCl_3) 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, 10.0Hz, 9.0Hz, 1H), 5.82-5.90 (t, 10.0Hz, 1H), 6.48-6.60 (td, 10.0Hz, 16.8Hz, 1H), 7.0-7.20 (m, 4H); IR (neat) ν_{max} 3300, 1600, 1500, 1100, 1020, 920; MS (m/z , rel. intensity) 194 (M^+ , ^{35}Cl , 57), 177 (M^+ -OH, ^{35}Cl , 8), 159 (M^+ - ^{35}Cl , 12), 141 ($^{37}\text{ClC}_6\text{H}_4\text{CO}^+$, 100); Anal. calc. for $\text{C}_{11}\text{H}_{11}\text{ClO}$: 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, CDCl_3) 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, 14.5Hz, 6.50Hz, 1H), 6.23-6.40 (m, 2H), 7.35-7.35 (m, 4H).
- Comasseto, J. V. and Berriel, J. N. *Synth. Commun.* **1990**, *20*, 1681.
- (a) Hiro, T.; Kambe, N.; Ogawa, A.; Miyoshi, N.; Murai, S. and Sonoda, N. *Angew. Chem.* **1987**, *99*, 1221; *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1187. (b) Barros, S. M.; Comasseto, J. V. and Berriel, J. N. *Tetrahedron Lett.* **1989**, *30*, 7353. (c) Hiro, T.; Morita, Y.; Inoue, T.; Kambe, N.; Ogawa, A.; Ryu, I. and Sonoda, N. *J. Am. Chem. Soc.* **1990**, *112*, 455, and references cited therein.
- (a) Block, E. and Aslam, M. *J. Am. Chem. Soc.* **1983**, *105*, 6164. (b) Bloch, R. and Abecassis, J. *Tetrahedron Lett.* **1983**, *24*, 124. (c) Angoh, A. G. and Clive, D. L. J. *J. Chem. Soc., Chem. Commun.* **1984**, 534. (d) Wang, K.K.; Liu, C.; Gu, Y. G. and Burnett, F. N. *J. Org. Chem.* **1991**, *56*, 1914. (e) Gomez, A. M.; Lopez, J. C. and Fraser-Reid, B. *Synthesis* **1993**, *10*, 943, and references cited therein.
- (a) Müller, D. G.; Peters, A.; Gassmann, G.; Boland, W.; Marner, F.-J. and Jaenicke, L. *Naturwissenschaften* **1982**, *69*, 290. (b) Müller, D. G.; Boland, W.; Marner, F.-J. and Gassmann, G. *Naturwissenschaften* **1982**, *69*, 501. (c) Nicolaou, K. C.; Reddy, K. R.; Skokotas, G.; Sato, F. and Xiao, X.-Y. *J. Am. Chem. Soc.* **1992**, *114*, 7935.

(Received in China 11 November 1994; accepted 21 March 1995)