Pergamon

Tetrahedron Letters 39 (1998) 1945–1948

TETRAHEDRON
LETTERS

Conjugated Polyenic Tellurides As Novel Building Blocks: A Facile and Novel Stereoselective Preparation of Conjugated Polyenic Ketones

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Received 9 October 1997; accepted 14 November 1997

Abstract: Upon treatment with butyllithium followed by adding zinc halide, conjugated polyenic tellurides smoothly undergo a Pd(0)-catalyzed cross coupling reaction with acyl chlorides to form the pure thermodynamically more stable conjugated polyenic ketones in good yield, regardless of the configuration of the telluride used. © 1998 Elsevier Science Ltd. All rights reserved.

One of the most important properties of vinylic tellurides is transmetallation. Vinylic tellurides can be metallated with organolithium or higher-order cyanocuprates to give the thermodynamically more stable organometallics.[1] *Z*-Vinylic tellurides are readily accessible by means of the hydrotelluration of acetylenes.[2] This is in contrast to the other hydrometallations of acetylenes which give the *E*-olefins.[3] *Z*-Vinyltellurides obtained in this way can be converted into the corresponding organometallics, and then allowed to react with carbonyl compounds,[4] α,β-unsaturated systems[5] or epoxides[6] to afford the corresponding vinylic alcohols, α,β-unsaturated compounds, or homoallylic alcohols with retention of olefin geometry in good yield. In our previous communication, we described a highly stereoselective preparation of *Z*-telluroacroleins,[7] which were further olefinated to form conjugated vinylic tellurides of *Z*-configuration.[8] One of the olefins, 1-(butyltelluro)-(1*Z*,3)-butadiene **1**, on treatment with butyllithium, reacted with carbonyl compounds to give the conjugated dienols stereospecifically in good yield.[7] In continuation of our studies on the synthetic applications of vinylic tellurides, it was envisioned that by means of tellurium-lithium exchange and transmetallation with zinc chloride, telluride **1** should undergo a Pd(0)-catalyzed cross-coupling reaction with acyl chlorides to form the corresponding terminal dienones with retention of configuration. In the event, only pure *E*-ketones **4** were obtained via this route after the usual workup (Scheme1). In the present communication, we disclose the preparation of conjugated polyenic ketones with high stereoselectivity.

The conversion of 1-(butyltelluro)-(1Z,3)-butadiene **1** into the corresponding dienyllithium reagent was described previously.[7] The corresponding organozinc reagent **2**, which was easily prepared by treating the dienyllithium with zinc chloride, reacted with benzoyl chloride in the presence of a catalytic amount of Pd-catalyst to give dienone **4a** (80% yield) with the pure *E* configuration. This stands in contrast to the parallel chemistry of *Z*-telluride **1** where, owing to the thermodynamical instability of *Z*-**4a** towards isomerization to the

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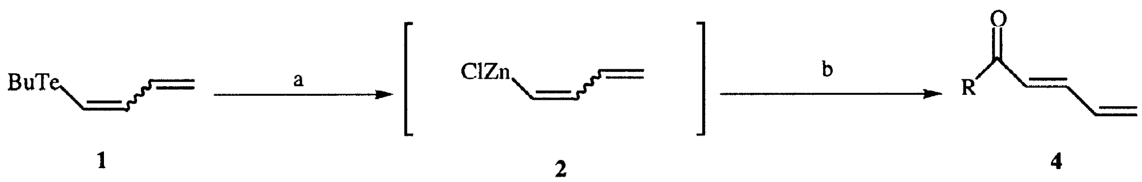
PII: S0040-4039(98)00089-6

more stable *E*-**4a**, *E*-dienes whose configuration could be determined by ^{1}**H NMR** coupling constants, were obtained (Scheme 1, R = Ph). The results for the formation of dienones **4** are summarized in Table 1. In the presence of a catalyst, $Pd(PPh_3)_4$ or $Pd(PPh_3)_2Cl_2$/i-Bu_2AlH (1:2), the cross-coupling reaction of organozinc reagents[9] with acyl chlorides **3** afforded the corresponding pure *E*-dienones **4** in good yield.[10] All the products had satisfactory elemental analyses and spectral properties (**IR, NMR, MS**).[11] For the acylation reactions of alkenylzinc reagents, a Pd-catalyst generated in *situ* from $Pd(PPh_3)_2Cl_2$ and i-Bu_2AlH (1:2) was found to give superior product yields.[12] However, in our reactions (entry 1, 80%; entry 8, 65%), $Pd(PPh_3)_4$ worked as satisfactorily as $Pd(PPh_3)_2Cl_2$/i-Bu_2AlH (1:2) did (entry 2, 82%; entry 9, 66%). Regardless of its stereochemistry, telluride **1** reacted with benzoyl chloride to give the products **4a** with pure *E* olefin geometry. Therefore, it is not necessary to separate the *Z* and *E* mixture (89:11) of β-telluroacrolein, whose Wittig olefination led to **1** as a *Z* and *E* mixture, before application to the precent process. Thus, aromatic (entries 1-6), heteroaromatic (entry 7), and aliphatic (entries 8 and 9) terminal conjugated dienones **4** could be synthesized efficiently with high stereoselectivity via this route.[13]



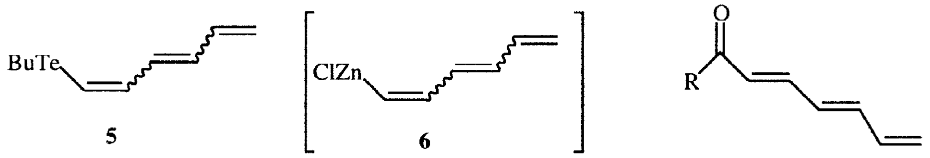
Scheme 1. (a) 1. BuLi, THF, -78 °C, 30 min.; 2. $ZnCl_2$, THF, -78 °C ~ rt;
(b) RC(O)Cl **3**, Pd (5 mole %), -10 ~ 0 °C.

Table 1 Highly Stereoselective Synthesis of (*E*)-Dienones **4** [a]

Entry	Telluride **1**	Catalyst [b]	RC(O)Cl **3**	Product [c]	Yield (%) [d]
1	(*Z*)-	A	Ph	4a	80
2	(*Z*)-	B	Ph	4a	82
3	(*Z*+*E*)-	A	Ph	4a	79
4	(*Z*+*E*)-	A	Ph	4a	76
5	(*Z*+*E*)-	A	*p*-Cl-Ph	4b	78
6	(*Z*+*E*)-	A	*m*-MeO-Ph	4c	73
7	(*Z*+*E*)-	A	2-Furyl	4d	80
8	(*Z*+*E*)-	A	$CH_3(CH_2)_9$	4e	65
9	(*Z*+*E*)-	B	$CH_3(CH_2)_9$	4e	66

[a] The reaction was carried out in 1.0 mmole-scale using telluride **1** in THF. **1**: acyl chloride **3** = 1.0:0.8. All the products were characterized by ^{1}**H NMR, IR, MS** spectra and element analyses. [b] A: $Pd(PPh_3)_4$ (5 mole %); B: $Pd(PPh_3)_2Cl_2$ + i-Bu_2AlH (1:2) (5 mole %). [c] The configurations were determined by ^{1}**H NMR** spectral analysis. [d] Isolated yields based on acyl chlorides **3**.

The acylation reaction of the conjugated trienyl zinc reagent **6** derived from 1-(butyltelluro)-1,3,5-hexatriene **5** was also examined as shown in Scheme 2. Telluride **5**, as an indeterminable mixture, was obtained in 93% yield from the olefination of β-telluroacrolein (*Z*:*E* = 89:11) with allyltriphenylphosphorane, generated from triphenylphosphonium bromide and potassium *tert*-butoxide in ether at room temperature.[7] The procedure for the elaboration of telluride **5** into trienones[8] was the same as described above. The aromatic, heteroaromatic, and aliphatic trienones **5** could be isolated as pure (*E,E*)-isomers in 65~69% yields.[14] Similarly, (1,3-hexadienyl-5-yl-6-trimethylsilyl) butyltelluride **8** (85% yield from Wittig olefination of β-telluroacrolein) can be smoothly converted into the corresponding (2*E*, 4*E*)-dienyl-6-yl ketone **9a** (59% yield) and **9b** (53% yield) with single stereoisomer *via* a coupling reaction of the corresponding zinc reagent with acyl chlorides as shown in Scheme 3. To the best of our knowledge, no report on the preparation of terminal conjugated trienones and conjugated (2,4)-dienyl-6-yl ketone derivatives such as **9a-b** has previously appeared in the literature.



7a, R = Ph, 68 %
7b, R = *p*-Cl-Ph, 65 %
7c, R = *m*-MeO-Ph, 70 %
7e, R = 2-Furyl, 69 %
7f, R = $CH_3(CH_2)_9$-, 66 %

Scheme 2

9a, R = Ph, 59 %
9b, R = *m*-MeO-Ph, 53 %

Scheme 3

In summary, we have established a novel, facile method for efficient synthesis of conjugated dienones and trienones as the pure thermodynamically more stable isomers. This method would be potentially useful for the synthesis of conjugated polyenyl natural products.

Acknowledgments We warmly thank Professors Li-xin Dai, and David Crich (The University of Illinois at Chicago, USA) for their valuable suggestions and correction of the manuscript. Support of this research by the National Natural Science Foundation of China and Chinese Academy of Sciences is gratefully acknowledged.

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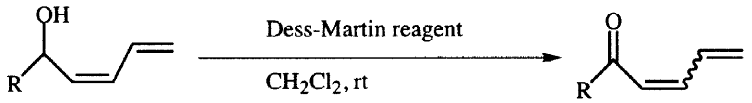
10. *Z*-Dienones **4** could be obtained stereoselectively in good yields by Dess-Martin oxidation of *Z*-conjugated



R = Ph, *Z*:*E* = 7:1, 84 %
R = $CH_3(CH_2)_8$-, *Z*:*E* = 8:1, 88 %

dienols. (For Dess-Martin reagent, see: Dess, D. B.; Martin, J. C. *J. Org. Chem.*, **1983**, 48, 4155.).

11. Typical spectral data for **4a**: ^{1}H NMR (300MHz, $CDCl_3$/TMS) δ 5.10 (d, J = 10.0Hz, 1H), 5.22 (d, J = 16.8Hz, 1H), 6.62 (dt, J = 16.8Hz, J = 10.0Hz, 1H), 7.05 (d, J = 15.2Hz, 1H), 7.35 (dd, J = 15.2Hz, J = 10.0Hz, 1H), 7.50 (m, 3H), 7.95 (m, 2H); IR (neat)ν_{max} 1640s, 1580s, 990s, 910s, 750s, 700s; MS (*m/z*, rel. intensity) 158 (M^+, 83), 131 (15), 105 (62), 77 (100); Anal. calc. for $C_{11}H_{10}O$: C, 83.51; H, 6.37; Found C, 83.26; H, 6.56%.
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14. Typical spectral data for **7a**: ^{1}H NMR (300MHz, $CDCl_3$/TMS) δ 5.35 (d, J = 10.5Hz, 1H), 5.46 (dd, J = 16.7Hz, J = 0.7Hz, 1H), 648 (m, 2H), 6.65 (dd, J = 10.5Hz, J = 15.0Hz, 1H), 7.02 (d, J = 15.0Hz, 1H), 7.50 (m, 4H), 7.90 (m, 2H); IR (neat) ν_{max} 1660s, 1600s, 1600s, 1570m, 1150m, 990s, 750s; MS (*m/z*, rel. intensity) 184 (M^+, 78), 156 (61), 107 (23), 105 (100), 77 (40), 55 (20), 43 (5); Anal. calc. for $C_{13}H_{12}O$: C, 84.75; H, 7.11; Found C, 84.49; H, 7.38%.