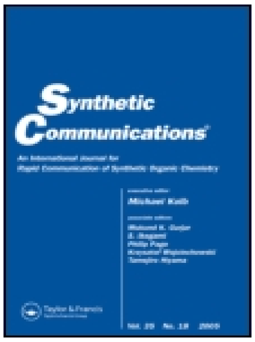

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Synthetic Communications

An International Journal for Rapid Communication of Synthetic Organic Chemistry

ISSN: 0039-7911 (Print) 1532-2432 (Online) Journal homepage: http://www.tandfonline.com/loi/lsyc20

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To cite this article: Xian Huang & Chun-Gen Liang (2000) Stereoselective Synthesis of Z-Vinyltellurides via Hydroboration of Acetylenic Tellurides with DCB and Protonolysis by AcOH, Synthetic Communications, 30:11, 1903-1909, DOI: 10.1080/00397910008087239

To link to this article: http://dx.doi.org/10.1080/00397910008087239

SYNTHETIC COMMUNICATIONS, 30(11), 1903–1909 (2000)

STEREOSELECTIVE SYNTHESIS OF Z-VINYLTELLURIDES VIA HYDROBORATION OF ACETYLENIC TELLURIDES WITH DCB AND PROTONOLYSIS BY AcOH

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Abstract: Hydroboration of acetylenic tellurides with dicyclohexylborane (DCB) gives vinylboranes intermediates **2** and **3**, which react with AcOH to afford Z-vinyltellurides in high yield.

Vinylic tellurium species are of demonstrated utility as synthetic intermediates in a variety of processes[1]. An example is the transmetallation reaction of (Z)-vinylic tellurides leading to (Z)-vinylorganometallic reagents, which are difficult to obtain by other methods presently available.

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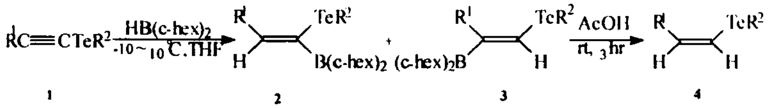
(Z)-Vinylic tellurides have been prepared by several methods: reaction of vinylic Grignard reagents with tellurenylhalides[2], of vinylbromides with tellurolate anions[2], of vinyltellrolate anions with alkylhalides[2], and of tellurols with terminal acetylenes[3]. Alternatively, diorganyltellurides react with acetylene to afford vinylic tellurides in a radical process[4]. Moreover, vinylic tellurides can be prepared by the reduction of acetylenic tellurides with $NaBH_4$/EtOH[5], DIBAL-H[6], or $ZrCp_2Cl(H)$[7]. In the latter two reactions, the C_{sp}-Te bond of was relatively easily broken. We have recently developed a convenient method for preparation of substituted vinylic selenides from reduction of acetylenic selenides with organoboranes [8]. Tellurium is an element homologous with selenium, and this prompted us to apply this procedure to generate vinyltellurides. Here we report hydroboration of acetylenic tellurides with DCB to give vinylboranes which reacted with AcOH to afford Z-vinyltellurides as shown in **scheme 1**. The results are summarized in the **Table**.



R^1=Ph, C_4H_9, CH_3OCH_2; R^2=C_2H_5, C_4H_9.

Scheme 1

One equivalent of acetylenic telluride was treated with DCB in THF for 2h, and then acetic acid was added over 3h at room temperature. Z-vinyltellurides were

Table Compound 4a~f

Product	R^1	R^2	Yield*(%)
4a	C_4H_9	C_4H_9	89
4b	C_4H_9	C_2H_5	85
4c	Ph	C_4H_9	83
4d	Ph	C_2H_5	82
4e	CH_3OCH_2	C_4H_9	85
4f	CH_3OCH_2	C_2H_5	87

*Isolated based on 1-alkyltelluro-1-ynes employed

formed stereoselectively. No diorganoditelluride product of was observed, indicating that dicyclohexylborane did not break the C_{sp}-Te bond in contrast to DIBAL-H[6], ZrCpCl(H)[7].

Hydroboration of acetylenic tellurides with DCB in THF occurs in cis-fashion, forming vinylboranes 2 and 3 **(scheme 1)**, but 2 was the major product, corresponding with that of the hydroboration of 1-alkylthioalk-1-ynes[9] and 1-alkylselenoalk-1-ynes[8]. The proposed regio- and stereochemistry of the intermediates was confirmed by the products of protonolysis and deuterated reactions and by the known retention of configuration in these reactions involving vinylboranes[10]. The stereochemistry of the products obtained was easily determined by the ^{1}HNMR coupling constant data (J=9-11 Hz) to be Z-vinyltellurides. Deuterolysis (AcOD) of 2f and 3f gave α (85%) or β (15%) deuterated vinylic tellurides[11].

Considering the excellent yields, mild reaction conditions, simple procedure and readily available reagents, the transformation described here is a convenient approach to Z-vinyltellurides.

Experimental Section

^1H NMR spectra were recorded on PMX-60 spectrometer, using $CDCl_3$ as the solvent with TMS as an internal standard. IR spectra were determined on a PE-683 spcetrophotometer. MS spectra were obtained on an HP5989A spectrometer, Elemental analyses were conducted using a yanaco MT-3CHN elemental analyser. All reaction were carried out in pre-dried glassware(150℃, 4h) and cooled under a steam of dry nitrogen. Tetrahydrofuran (THF) was distilled over sodium benzophenone immediately before use. Borane[12] was prepared according to literature methods and was standardized by aliquots before use. Acetylenic tellurides[5], AcOD[13] were prepared by methods reported in literature.

A representative procedure for the synthesis of Z-vinyltelluredes4a~f:

To a solution of cyclohexene (5mmol) in THF (5ml) was added a solution of diborane (2.5mmol) in THF at 0℃ with stirring, the precipitate formed (R^2BH) was stirred at 0-5℃ for 1h, and then the reaction mixture was diluted with a solution of internal alkyltelluroacetylene (2.5mmol) in THF (5ml) added at −10°C. The reaction mixture was allowed to warm to 10℃. After the precipitate had dissolved, the resulting solution was stirred for an additional 30 min at this temp, treated with 1ml glacial acetic acid, then stirring of the mixture for 3h at room temp. After reaction, normal work up was performed. All product was isolated and purified by column chromatography eluted with petroleum ether(30~60℃).

4a.oil[7a]. δ_H: 0.87 (t, J=7.0 Hz, 3H), 0.91 (t, J=7.0 Hz, 3H), 1.1-2.2 (m, 10H), 2.65 (t, J=8.0Hz, 2H), 6.11 (m, 1H), 6.55 (d, J=9.5, 1H); IRν (cm^{-1}) 1587.

4b.oil[7b]. δ_H: 0.85 (t, J=7.0 Hz, 3H), 1.0-1.45 (m, 4H), 1.58 (t, J=7.1 Hz, 3H), 1.87 (m, 2H), 2.58 (q, J=7.1 Hz, 2H), 6.04 (m, 1H), 6.58 (d, J=9.2 Hz, 1H); IRν (cm^{-1}) 1585.

4c.oil[5]. δ_H: 0.93 (t, J=7.0 Hz, 3H), 1.1-2.1 (m, 4H), 2.76 (t, J=7.0 Hz, 2H), 7.00 (d, J=11 Hz, 1H), 7.33 (s, 5H), 7.44 (d, J=11 Hz, 1H); IR ν (cm^{-1}) 1590, 755;

4d.oil[5]. δ_H: 1.58 (t, J=7.0Hz, 3H), 2.53 (q, J=7.0Hz, 2H), 6.61 (d, J=11Hz, 1H), 6.95 (s, 5H), 7.05 (d, J=11 Hz, 1H); IR ν (cm^{-1}) 1589.

4e.oil[7a]. δ_H: 0.92 (t, J=7.2 Hz, 3H), 1.39-1.78 (m, 4H), 2.64 (t, J=7.2 Hz, 2H), 3.35 (s, 3H), 3.91 (d, J=5.6Hz, 2H), 6.37 (m, 1H), 6.88 (d, J=10.1 HZ, 1H); IR ν (cm^{-1}) 1589.

4f. Oil. δ_H: 1.58 (t, J=7.1Hz, 3H), 2.53 (q, J=7.1Hz, 2H), 3.20 (s, 3H), 3.80 (d, J=5Hz, 2H), 6.30 (m, 1H), 6.58 (d, J=10.1Hz, 1H); IRν (cm^{-1}) 1585; MS (EI): 230 (19.48, ^{130}Te), 228 (19.38, ^{128}Te), $C_6H_{12}OTe$ Anal. Calcd. for: C% 31.64; H% 5.31, Found C% 31.32; H%5.76.

ACKNOWLEDGMENT: Project 29772007 was supported by the National Nature Science Foundation of China and this work also supported by The Laboratory of Organometallic Chemistry, Chinese Academy of Science.

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11. (a) Deuterolysis (AcOD) of other 2,3 give α-deuterated products in (80%-95%) yield which depended on the size of R^1 and R^2; (b) vinylic proton of boron species (2f, 3f) was observed by ^{1}H NMR spectrum of the reaction mixtures ^{1}H NMR (6.8, s; 5.5, t) .
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Received in the UK 5/17/99