

# Stereoselective synthesis of *E*-vinyltellurides via boron–tellurium exchange

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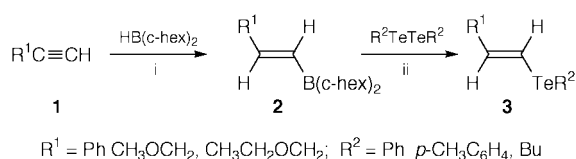
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*E*-Alkenylboranes reacted with diorgano ditellurides in the presence of a palladium complex to afford *E*-vinyltellurides stereoselectively.

Vinyltellurium species are very important intermediates in organic synthesis.<sup>1</sup> *Z*-Isomers have been employed more frequently as intermediates because of the available approaches to these species. Recently, Dabdoub *et al.*<sup>2</sup> reported that *E*-isomers also can be transformed into the  $\alpha,\beta$ -unsaturated esters and carboxylic acids with total retention of both regio- and stereochemistry via vinylolithium intermediates.

*E*-Vinyltellurides have been prepared previously by the reaction of vinylic Grignard reagents with tellurenyl halides,<sup>3</sup> of vinyl bromides with organotelluroate anions,<sup>3</sup> of vinyltelluroate anions with alkyl halides,<sup>3</sup> and of tellurophosphonates with aldehydes.<sup>4</sup> Recently, the transmetalation of *E*-vinylic zirconates<sup>5</sup> and vinylalanes<sup>6</sup> with tellurenyl halides to give the *E*-vinyl tellurides have been reported. In these methods, tellurenyl halides or the organotelluroate must be prepared *in situ*.

Organoboranes offer a wealth of transformations of the C–B bond. In general, the C(sp<sup>2</sup>)–B bond undergoes reactions under milder conditions. This is especially true of transition metal-catalyzed reactions such as the Suzuki–Miyaura cross-coupling reaction of alkenyl/aryl halides with alkenyl/arylboranes<sup>7</sup> or transmetalations of organoboranes to zinc or copper.<sup>8</sup> Diorgano ditellurides can function as either nucleophilic or electrophilic tellurium centers. It could be suggested that vinylboranes would react with diorgano ditellurides in a C-heteroatom coupling reaction in the presence of a palladium complex. Indeed, in this case, *E*-vinyl tellurides **3** were formed stereo- and regioselectively (see Scheme 1).



**Scheme 1** Reagents and conditions: i, THF, –10 ~ 0 °C, 2 h; ii, 3 mol% Pd(PPh<sub>3</sub>)<sub>4</sub>, NaOH, reflux 3 h.

## Results and discussion

The alkenylboranes can be conveniently obtained by hydroboration of a terminal acetylene *e.g.* **1** with dicyclohexylborane.<sup>9</sup> To a solution of the alkenylborane were added sequentially NaOH, a diorgano ditelluride and Pd(PPh<sub>3</sub>)<sub>4</sub>, then the mixture was refluxed for 3 hours under nitrogen. *E*-Vinyltellurides **3** were formed in moderate yields (see Table 1). This reaction did not proceed in the absence of Pd(PPh<sub>3</sub>)<sub>4</sub>. The *E*-geometry of the products was determined by analysis of the coupling-constant data in the <sup>1</sup>H NMR spectra (*J* 16–17 Hz). Only *E*-isomers were observed, indicating that the boron exchanged

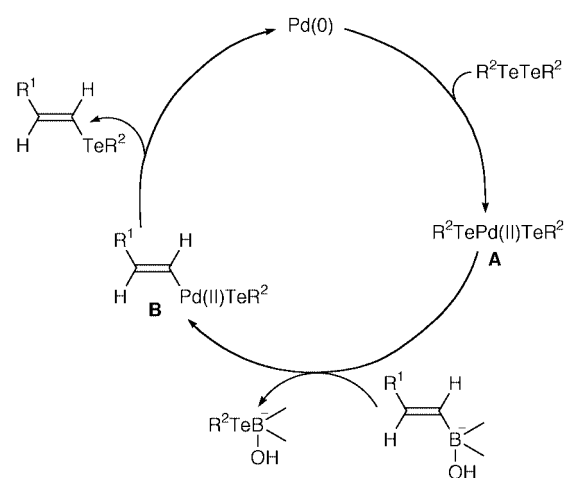
**Table 1** Synthesis of *E*-vinyltellurides **3a–f**

Product	R <sup>1</sup>	R <sup>2</sup>	Yield (%) <sup>a</sup>
<b>3a</b>	Ph	Ph	61
<b>3b</b>	Ph	<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	68
<b>3c</b>	Ph	Bu	63
<b>3d</b>	CH <sub>3</sub> OCH <sub>2</sub>	Ph	65
<b>3e</b>	CH <sub>3</sub> OCH <sub>2</sub>	<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	59
<b>3f</b>	CH <sub>3</sub> CH <sub>2</sub> OCH <sub>2</sub>	Ph	62

<sup>a</sup> Isolated by TLC and based on diorgano ditelluride employed.

with the tellurium stereoselectively with retention of configuration.

Considering the proposed mechanism for the Pd(0) complex-catalyzed cross-coupling reactions of organic halides with vinylboranes<sup>7</sup> and organic tellurides with Grignards,<sup>10</sup> a possible mechanism for the coupling of vinylboranes with diaryl ditellurides shown in Scheme 2 seems to involve the oxidative addition of diorgano ditelluride with a palladium complex to afford intermediate **A**, which is converted by transmetalation with vinylboranes to intermediate **B**, followed by reductive elimination to reproduce the Pd(0) complex and the products.



**Scheme 2**

In conclusion, a new convenient synthetic method for *E*-vinyl tellurides has been developed by the reaction of vinylboranes with diorgano ditellurides in the presence of a Pd(0) complex. Compared with other methods reported, this method has the

advantages of available reagents, excellent regio- and stereo-selectivity, and the simplicity of a 'one pot' procedure which avoids the preparation of intermediate tellurenyl halides.

## Experimental

$^1\text{H}$  NMR spectra were recorded on a PMX-60 and AZ-300 spectrometers, using  $\text{CDCl}_3$  as the solvent with TMS as an internal standard;  $J$ -values are given in Hz. IR spectra were determined on a PE-683 spectrophotometer. Mass spectra were obtained on an HP5989A spectrometer. Mps were measured on a Büchi 535 melting point apparatus and are uncorrected. Elemental analyses were conducted using a Yanaco MT-3CHN elemental analyser. All reactions were carried out in pre-dried glassware ( $150^\circ\text{C}$ ; 4 h) and cooled under dry nitrogen. Tetrahydrofuran (THF) was distilled over sodium benzophenone ketyl immediately before use.

### General procedure for the synthesis of *E*-alkenyltellurides

To a solution of cyclohexene (10 mmol) in THF ( $10\text{ cm}^3$ ) was added a solution of diborane (5 mmol) in THF at  $0^\circ\text{C}$  with stirring; the precipitate thus formed  $[(c\text{-Hex})_2\text{BH}]$  was stirred at  $0^\circ\text{C}$  for 1 h. The reaction mixture was diluted with a solution of a terminal acetylene **1** (5 mmol) added at  $-10^\circ\text{C}$ , and the mixture was kept at  $0^\circ\text{C}$  for 2 h. After the precipitate **2** had dissolved, the resulting solution was treated with 3 M NaOH ( $2\text{ cm}^3$ ), diorgano ditelluride (4 mmol), and 3%  $\text{Pd}(\text{PPh}_3)_4$ , then was refluxed for 3 h under  $\text{N}_2$ . After the reaction was complete, normal work-up was performed. Vinyltellurides **3** were isolated and purified by TLC with petroleum ether (distillation range  $30\text{--}60^\circ\text{C}$ ) as developer.

**3a**.<sup>4</sup> Oil.  $\nu$  (film)/ $\text{cm}^{-1}$  1570, 950;  $\delta_{\text{H}}$  (300 MHz) 7.20 (1H, d,  $J$  16.6), 7.39 (8H, m), 7.64 (1H, d,  $J$  16.6), 7.83 (2H, m).

**3b**. Mp  $51\text{--}52^\circ\text{C}$ ;  $\nu$  (KBr)/ $\text{cm}^{-1}$  1574, 956;  $\delta_{\text{H}}$  (300 MHz) 2.34 (3H, s), 6.8–7.8 (11H, m); MS (EI)  $m/z$  324 (98.7), 322 (100), 195 (62), 179 (82), 91 (39) (Found: C, 55.87; H, 4.43.  $\text{C}_{15}\text{H}_{14}\text{Te}$  requires C, 55.97; H, 4.38%).

**3c**.<sup>3</sup> Oil.  $\nu$  (film)/ $\text{cm}^{-1}$  1570, 930;  $\delta_{\text{H}}$  (60 MHz) 0.91 (3H, m,  $J$  7), 1.1–2.1 (4H, m), 2.80 (2H, t,  $J$  7), 6.98 (1H, d,  $J$  16), 7.30 (5H, m), 7.48 (1H, d,  $J$  16).

**3d**. Oil.  $\nu$  (film)/ $\text{cm}^{-1}$  1580, 950;  $\delta_{\text{H}}$  (60 MHz) 3.29 (3H, s), 3.95 (2H, d,  $J$  5), 6.27 (1H, dt,  $J$  16 and 5), 7.1 (1H, d,  $J$  16), 7.2–7.8 (5H, m); MS (EI)  $m/z$  278 (30.5), 276 (30), 247 (7.5), 245 (6.2), 71 (100) (Found: C, 43.67; H, 4.23.  $\text{C}_{10}\text{H}_{12}\text{OTe}$  requires C, 43.55; H, 4.17%).

**3e**. Oil.  $\nu$  (film)/ $\text{cm}^{-1}$  1580, 947;  $\delta_{\text{H}}$  (60 MHz) 2.31 (3H, s),

3.25 (3H, s), 3.85 (2H, d,  $J$  5), 6.15 (1H, dt,  $J$  17 and 5), 6.95 (1H, d,  $J$  17), 7.02 (2H, d,  $J$  8), 7.60 (2H, d,  $J$  8); MS (EI)  $m/z$  292 (47), 290 (46), 288 (27.8), 261 (13), 259 (12.5), 131 (42.4), 91 (29.2), 71 (100) (Found: C, 45.45; H, 4.91.  $\text{C}_{11}\text{H}_{14}\text{OTe}$  requires C, 45.59; H, 4.87%).

**3f**. Oil.  $\nu$  (film)/ $\text{cm}^{-1}$  1575, 940;  $\delta_{\text{H}}$  (60 MHz) 1.23 (3H, t,  $J$  7), 3.46 (2H, q,  $J$  7), 3.90 (2H, d,  $J$  5), 6.21 (1H, dt,  $J$  16 and 5), 6.9 (1H, d,  $J$  16), 7.0–7.8 (5H, m); MS (EI)  $m/z$  292 (45), 290 (49), 247 (17.7), 245 (17), 117 (42), 85 (100), 57 (63) (Found: C, 45.71; H, 4.93.  $\text{C}_{11}\text{H}_{14}\text{OTe}$  requires C, 45.59; H, 4.87%).

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