

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

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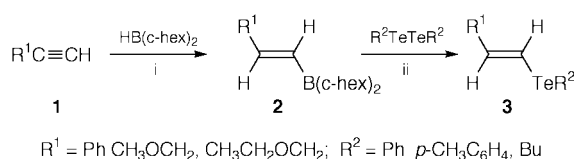
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E-Alkenylboranes reacted with diorgano ditellurides in the presence of a palladium complex to afford *E*-vinyltellurides stereoselectively.

Vinyltellurium species are very important intermediates in organic synthesis.¹ *Z*-Isomers have been employed more frequently as intermediates because of the available approaches to these species. Recently, Dabdoub *et al.*² reported that *E*-isomers also can be transformed into the α,β -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,³ of vinyl bromides with organotelluroate anions,³ of vinyltelluroate anions with alkyl halides,³ and of tellurophosphonates with aldehydes.⁴ Recently, the transmetalation of *E*-vinylic zirconates⁵ and vinylalanes⁶ 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(sp²)–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/arylboranes⁷ or transmetalations of organoboranes to zinc or copper.⁸ 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, $-10 \sim 0^\circ\text{C}$, 2 h; ii, 3 mol% Pd(PPh₃)₄, NaOH, reflux 3 h.

Results and discussion

The alkenylboranes can be conveniently obtained by hydroboration of a terminal acetylene *e.g.* **1** with dicyclohexylborane.⁹ To a solution of the alkenylborane were added sequentially NaOH, a diorgano ditelluride and Pd(PPh₃)₄, 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(PPh₃)₄. The *E*-geometry of the products was determined by analysis of the coupling-constant data in the ¹H NMR spectra (*J* 16–17 Hz). Only *E*-isomers were observed, indicating that the boron exchanged

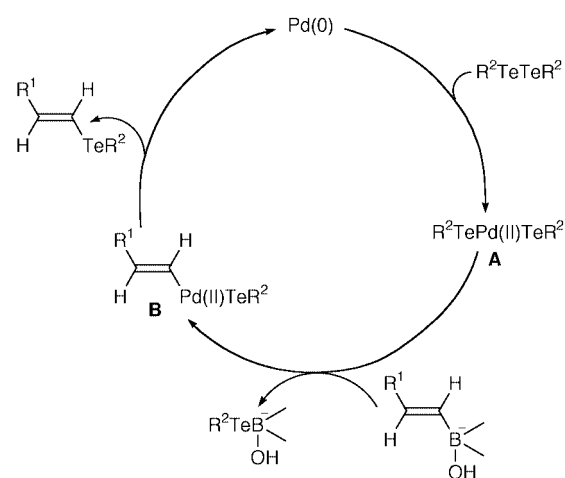
Table 1 Synthesis of *E*-vinyltellurides **3a–f**

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

^a 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 vinylboranes⁷ and organic tellurides with Grignards,¹⁰ 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

^1H NMR spectra were recorded on a PMX-60 and AZ-300 spectrometers, using 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 ($150\text{ }^\circ\text{C}$; 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 cm^3) was added a solution of diborane (5 mmol) in THF at $0\text{ }^\circ\text{C}$ with stirring; the precipitate thus formed $[(c\text{-Hex})_2\text{BH}]$ was stirred at $0\text{ }^\circ\text{C}$ for 1 h. The reaction mixture was diluted with a solution of a terminal acetylene **1** (5 mmol) added at $-10\text{ }^\circ\text{C}$, and the mixture was kept at $0\text{ }^\circ\text{C}$ for 2 h. After the precipitate **2** had dissolved, the resulting solution was treated with 3 M NaOH (2 cm^3), diorgano ditelluride (4 mmol), and 3% $\text{Pd}(\text{PPh}_3)_4$, then was refluxed for 3 h under 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 $30\text{--}60\text{ }^\circ\text{C}$) as developer.

3a.⁴ Oil. ν (film)/ cm^{-1} 1570, 950; δ_{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 $51\text{--}52\text{ }^\circ\text{C}$; ν (KBr)/ cm^{-1} 1574, 956; δ_{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.³ Oil. ν (film)/ cm^{-1} 1570, 930; δ_{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. ν (film)/ cm^{-1} 1580, 950; δ_{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. ν (film)/ cm^{-1} 1580, 947; δ_{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. ν (film)/ cm^{-1} 1575, 940; δ_{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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