A facile stereoselective synthesis of 1,3-dienyltellurides via palladium catalysed cross-coupling reactions

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Hydrozirconation of terminal alkynes **1** gives (*E*)-alkenylzirconium complexes **3**, which cross-couple with (*E*)-α-iodovinyltellurides **4** in the presence of [Pd(PPh$_3$)$_4$] catalyst to afford stereoselectively 1,3-dienyltellurides **5** in good yields.

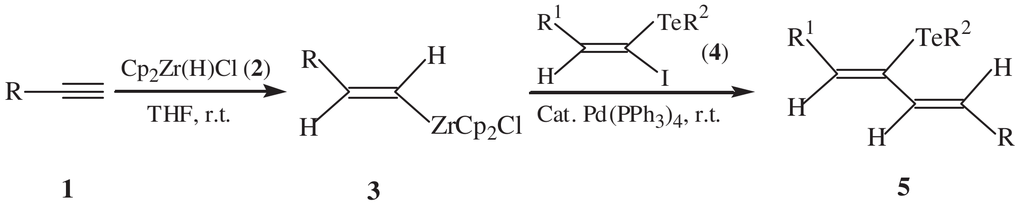
Keywords: palladium; zirconium; tellurium; 1,3-diene; cross-coupling reaction

The stereocontrolled synthesis of 1,3-dienes is of considerable interest in organic synthesis since many natural compounds such as insect sex pheromones and Achilla amide possess the structural skeleton of 1,3-dienes.[1] The synthesis of dienes for use in the preparation of more complex targets *via* the Diels–Alder reaction is still an important challenge in organic synthesis[2] although other elegant uses of these compounds have been developed.[3] Conjugated dienes are usually prepared by utilising either a Wittig type approach[4] or cross-coupling reactions of stereodefined vinyl halides with vinyl organometallic compounds catalysed by transition metals.[5] The metal or heteroatom-containing 1,3-dienes will also be useful as building blocks in organic synthesis because many useful functional group transformations can be achieved by introduction and removal of metal or heteroatom functions. Recently, the stereoselective syntheses of 1,3-dienylsilanes,[6] 1,3-dienyl sulfides,[7] 1,3-dienyl selenides[8] and 1,3-dienylstannanes[9] have been described in the literature. 1,3-Dienyltellurides serve as valuable, versatile intermediates since the tellurium moiety can be replaced by different organic groups always with total retention of the configuration.[10] However, the stereoselective synthesis of 1,3-dienyltellurides has rarely been reported[11] and the stereoselective synthesis of 2-organotelluro-substituted 1,3-dienes has not been reported yet.

The (*E*)-alkenylzirconium complexes, obtained by hydrozirconation of terminal alkynes, can be cross-coupled with alkenyl halides in the presence of a catalytic amount of [Pd(PPh$_3$)$_4$] or [Ni(PPh$_3$)$_4$] to form 1,3-butadienes.[12] We now report that 1,3-dienyltellurides can be synthesised by the cross-coupling reaction of (*E*)-α-iodovinyltellurides with (*E*)-alkenylzirconium complexes in the presence of [Pd(PPh$_3$)$_4$] catalyst.

(*E*)-α-Iodovinyltellurides **4** were prepared according to the literature procedure.[13] Hydrozirconation of terminal alkynes **1** at room temperature in THF for 30 min gave (*E*)-alkenylzirconium complexes **3**, which were cross-coupled with (*E*)-α-iodovinyltellurides **4** in the presence of [Pd(PPh$_3$)$_4$] catalyst at room temperature for 24 h to afford 1,3-dienyltellurides **5** in good yields (Scheme 1). The typical experimental results are summarised in Table 1.

It is well documented that the cross-coupling reaction of alkenylzirconium complexes with alkenyl halides in the presence of a palladium catalyst occurs with retention of configuration.[12] The *E*-configuration of the compounds **5** has been proved by their ^{1}H NMR spectra, which show two doublets for **5a**, **5d**, **5f** and a doublet for **5b**, **5c**, **5e**, **5g**, **5h** at δ = 5.83–7.08 ppm with a coupling constant of 15.2–16.4 Hz. This is also the evidence of the retention of the *E*-configuration of the starting compounds **3**. In addition, the configuration of the 1,3-dienyltelluride **5e** could be confirmed from compound **6**, which was obtained by treatment of **5e** with *n*-butyllithium in THF followed by hydrolysis, a reaction that occurs stereoselectively (Scheme 2). The stereochemistry of compound **6** was easily established, since its^{1}H NMR spectrum (500 MHz) gives rise to a doublet–doublet at δ = 6.97 ppm with coupling constants of 14.7 and 9.1 Hz and a doublet–doublet at δ = 6.68 ppm with coupling constants of 14.6 and 9.0 Hz,



Scheme 1

Table 1 Synthesis of 1,3-dienyltellurides

Entry	R	R^1	R^2	Product^a	Yield^b/%
1	Ph	*n*-C$_4$H$_9$	*n*-C$_4$H$_9$	**5a**	82
2	*n*-C$_6$H$_{13}$	*n*-C$_4$H$_9$	*n*-C$_4$H$_9$	**5b**	80
3	CH$_3$OCH$_2$	*n*-C$_4$H$_9$	*n*-C$_4$H$_9$	**5c**	71
4	Ph	CH$_3$OCH$_2$	Ph	**5d**	75
5	Ph	Ph	*n*-C$_4$H$_9$	**5e**	83
6	Ph	*n*-C$_6$H$_{13}$	*n*-C$_4$H$_9$	**5f**	78
7	CH$_3$OCH$_2$	*n*-C$_6$H$_{13}$	*n*-C$_4$H$_9$	**5g**	69
8	Ph	Ph	Ph	**5h**	85

^{a}All the compounds were characterised using ^{1}H NMR, IR, and MS or elemental analyses.
^{b}Isolated yield based on the compound **4** used.

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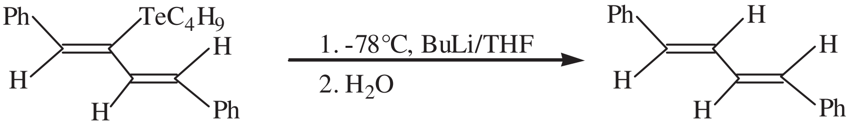

5e **6**

Scheme 2

which is consistent with an (*E,E*)-configuration. The melting point of compound **6** was determined to be 148–149°C which is also consistent with an (*E,E*)-configuration.[14]

In summary, the palladium catalysed cross-coupling reaction of (*E*)-α-iodovinyl tellurides with (*E*)-alkenylzirconium complexes provides a direct route to the stereoselective synthesis of 1,3-dienyltellurides. The method has some attractive advantages such as mild reaction conditions, a simple procedure and good yields. Investigations into the synthetic applications of 1,3-dienyltellurides are currently in progress.

Experimental

^{1}H NMR spectra were recorded on a Bruker AC-P300 (300 MHz) or Bruker AC-P500 (500 MHz) spectrometer with TMS as an internal standard in $CDCl_3$. IR spectra were obtained on a Perkin-Elmer 683 instrument as neat films. Mass spectra were determined on a Finnigan 8230 mass spectrometer. Microanalyses were measured using a Yanaco MT-3 CHN microelemental analyser. All solvent were dried, deoxygenated and freshly distilled before use. $[ZrCp_2(H)Cl]$[15] and $[Pd(PPh_3)_4]$[16] were prepared according to literature methods.

General procedure for the synthesis of 1,3-dienyltellurides **5a–h** A mixture of $[ZrCp_2(H)Cl]$ (1.2 mmol) and alkyne (**1**) (1.2 mmol) in THF (7 ml) was stirred under Ar at r.t. for 30 min to yield a clear solution. Into the resulting solution were added $[Pd(PPh_3)_4]$ (0.05 mmol) and (*E*)-α-iodovinyltelluride (**4**) (1.0 mmol), and the mixture was stirred at r.t. for 24 h. The mixture was diluted with diethyl ether (40 ml), then filtered through a short plug of silica gel and concentrated to give a residue. The residue was purified by flash chromatography on silica gel, eluting with light petroleum (for **5a, 5b, 5e, 5f, 5h**) or light petroleum-diethyl ether (20:1) (for **5c, 5d, 5g**).

(1Z, 3E)-1-Butyl-2-butyltelluro-4-phenyl-1,3-butadiene (**5a**): IR (film): ν (cm^{-1}) 3059, 3023, 2958, 2925, 2857, 1621, 1598, 1492, 1463, 956, 748, 691. ^{1}H NMR ($CDCl_3$): δ 7.45–7.19 (m, 5H), 6.95 (d, *J* = 15.6 Hz, 1H), 6.59 (d, *J* = 15.6 Hz, 1H), 6.02 (t, *J* = 7.2 Hz, 1H), 2.68 (t, *J* = 7.2 Hz, 2H), 2.52–2.46 (m, 2H), 1.73–1.66 (m, 2H), 1.46–1.21 (m, 6H), 0.94–0.86 (m, 6H). MS: *m/z* 370 [M$^+$, 2.9], 185 (6.5), 104 (16.5), 103 (100), 91 (48.9), 77 (29), 57 (13.3). Anal. Found: C, 58.2; H, 6.8. Calc. for $C_{18}H_{26}Te$: C, 58.5; H, 7.0%.

(5Z, 7E)-6-Butyltelluro-5,7-tetradecadiene (**5b**): IR (film): ν (cm^{-1}) 2959, 2928, 2873, 2856, 1638, 1464, 1377, 959, 795. ^{1}H NMR ($CDCl_3$): δ 6.05–5.96 (m, 1H), 5.83 (d, *J* = 15.2 Hz, 1H), 5.76 (t, *J* = 7.2 Hz, 1H), 2.67 (t, *J* = 7.2 Hz, 2H), 2.41–2.34 (m, 2H), 2.08–1.97 (m, 2H), 1.81–1.75 (m, 2H), 1.48–1.20 (m, 14H), 0.96–0.87 (m, 9H). MS: *m/z* 378 [M$^+$, 4.4], 192 (11.4), 185 (8.7), 82 (100), 57 (47.3). Anal. Found: C, 57.4; H, 8.9. Calc. for $C_{18}H_{34}Te$: C, 57.2; H, 9.0%.

(2E, 4Z)-1-Methoxy-4-butyltelluro-2,4-nonadiene (**5c**): IR (film): ν (cm^{-1}) 2958, 2924, 2871, 2856, 1639, 1463, 1377, 1114, 955. ^{1}H NMR ($CDCl_3$): δ 6.88 (d, *J* = 16.0 Hz, 1H), 6.25–6.16 (m, 1H), 5.89 (t, *J* = 7.2 Hz, 1H), 3.95 (d, *J* = 6.8 Hz, 2H), 3.34 (s, 3H), 2.75 (t, *J* = 7.6 Hz, 2H), 2.46–2.36 (m, 2H), 1.81–1.73 (m, 2H), 1.43–1.26 (m, 6H), 0.94–0.86 (m, 6H). MS: *m/z* 338 [M$^+$, 6.2], 153 (8.7), 82 (100), 71 (23.6), 57 (33.4), 45 (25.3). Anal. Found: C, 49.5; H, 7.6. Calc. for $C_{14}H_{26}OTe$: C, 49.8; H, 7.7%.

(1E, 3Z)-1-Phenyl-3-phenyltelluro-5-methoxy-1,3-pentadiene (**5d**): IR (film): ν (cm^{-1}) 3065, 3023, 2923, 2818, 1599, 1574, 1491, 1474, 1434, 1372, 1111, 954, 732, 691. ^{1}H NMR ($CDCl_3$): δ 7.73–7.68 (m, 2H), 7.39–7.16 (m, 8H), 7.02 (d, *J* = 15.6 Hz, 1H), 6.65 (d, *J* = 15.6 Hz, 1H), 6.47 (t, *J* = 7.2 Hz, 1H), 3.97 (d, *J* = 6.4 Hz, 2H), 3.33 (s, 3H). MS: *m/z* 378 [M$^+$, 3.8], 205 (5.9), 173 (7.4), 104 (100), 103 (38.7), 91 (28.6), 77 (37.3), 45 (26.9). Anal. Found: C, 57.0; H, 4.6. Calc. for $C_{18}H_{18}OTe$: C, 57.2; H, 4.8%.

(1Z, 3E)-1,4-Diphenyl-2-butyltelluro-1,3-butadiene (**5e**): IR (film): ν (cm^{-1}) 3065, 3023, 2957, 2854, 1632, 1599, 1576, 1490, 1463, 956, 741, 691. ^{1}H NMR ($CDCl_3$): δ 7.48–7.13 (m, 12H), 7.04 (d, *J* = 16.2 Hz, 1H), 2.74 (t, *J* = 7.6 Hz, 2H), 1.80–1.74 (m, 2H), 1.42–1.31 (m, 2H), 0.90 (t, *J* = 7.2 Hz, 3H). MS: *m/z* 390 [M$^+$, 3.7], 206 (100), 104 (68.9), 103 (31.5), 91 (68.2), 77 (74.5). Anal. Found: C, 61.5; H, 5.5. Calc. for $C_{20}H_{22}Te$: C, 61.6; H, 5.6%.

(1E, 3Z)-1-Phenyl-3-butyltelluro-1,3-decadiene (**5f**): IR (film): ν (cm^{-1}) 3058, 3022, 2957, 2924, 2854, 1619, 1599, 1492, 1463, 956, 748, 691. ^{1}H NMR ($CDCl_3$): δ 7.46–7.19 (m, 5H), 6.94 (d, *J* = 15.2 Hz, 1H), 6.59 (d, *J* = 15.2 Hz, 1H), 6.02 (t, *J* = 7.2 Hz, 1H), 2.68 (t, *J* = 7.6 Hz, 2H), 2.53–2.46 (m, 2H), 1.74–1.66 (m, 2H), 1.47–1.21 (m, 10H), 0.96–0.86 (m, 6H). MS: *m/z* 398 [M$^+$, 3.1], 212 (10.6), 104 (100), 103 (47), 102 (25.5), 91 (20.4), 77 (23.2). Anal. Found: C, 60.1; H, 7.5. Calc. for $C_{20}H_{30}Te$: C, 60.4; H, 7.5%.

(2E, 4Z)-1-Methoxy-4-butyltelluro-2,4-undecadiene (**5g**): IR (film): ν (cm^{-1}) 2958, 2923, 2855, 1640, 1463, 1377, 1112, 959. ^{1}H NMR ($CDCl_3$): δ 6.87 (d, *J* = 16.4 Hz, 1H), 6.26–6.16 (m, 1H), 5.88 (t, *J* = 7.2 Hz, 1H), 3.94 (d, *J* = 6.0 Hz, 2H), 3.33 (s, 3H), 2.74 (t, *J* = 7.6 Hz, 2H), 2.45–2.36 (m, 2H), 1.81–1.72 (m, 2H), 1.42–1.21 (m, 10H), 0.94–0.86 (m, 6H). MS: *m/z* 366 [M$^+$, 9.5], 110 (100), 84 (9.5), 71 (21.8), 45 (22.4). Anal. Found: C, 52.3; H, 8.0 Calc. for $C_{16}H_{30}OTe$: C, 52.5; H, 8.2%.

(1Z, 3E)-1,4-Diphenyl-2-phenyltelluro-1,3-butadiene (**5h**): IR (film): ν (cm^{-1}) 3065, 3024, 1634, 1598, 1575, 1492, 956, 742, 690. ^{1}H NMR ($CDCl_3$): δ 7.72–7.64 (m, 2H), 7.51–7.19 (m, 15H), 7.08 (d, *J* = 16.4 Hz, 1H). MS: *m/z* 410 [M$^+$, 2.3], 206 (78.6), 205 (14.4), 104 (57.5), 91 (64.3), 77 (100). Anal. Found: C, 64.3; H, 4.2 Calc. for $C_{22}H_{18}Te$: C, 64.5; H, 4.4%.

Synthesis of (1E, 3E)-1,4-diphenyl-1,3-butadiene (**6**): *n*-BuLi (1.6 M hexane solution, 1.1 mmol) was added to a THF (5.0 ml) solution of **5e** (1.0 mmol) at –78 °C. After stirring for 10 min, the mixture was hydrolysed with saturated aqueous NH_4Cl and extracted with CH_2Cl_2 (2×10 ml). The organic extract was dried ($MgSO_4$) and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel using light petroleum ether as eluent to give **6** (0.159 g, 77%). M.p. 148–149 °C, lit.[14] m.p. 149–150 °C. IR (KBr): ν (cm^{-1}) 3054, 3015, 1635, 1593, 1490, 992, 739, 690. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.45 (d, *J* = 7.5 Hz, 4H), 7.35–7.22 (m, 6H), 6.97 (dd, *J* = 14.7, 9.1 Hz, 2H), 6.68 (dd, *J* = 14.6, 9.0 Hz, 2H).

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