Stereoselective synthesis of (*Z*)-α-arylsulfenylvinyl tellurides via hydrozirconation of alkynyltellurides

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Hydrozirconation of alkynyltellurides **1** in THF at room temperature gave (*Z*)-α- tellurenylvinylzirconium complexes **2**, which were reacted with arylsulfenyl chlorides **3** to afford stereoselectively (*Z*)-α-arylsulfenylvinyl tellurides **4** in good yields.

Keywords: alkynyltelluride, hydrozirconation, (Z)-α-arylsulfenylvinyl telluride, stereoselective synthesis

Many biologically active compounds occurring in nature possess the structural skeleton of trisubstituted alkenes.[1-3] Difunctional group reagents, which have two different functional groups linked to the olefinic carbon atoms, for example, S–Cu,[4] S–Br,[5] S–B,[6] S–Sn,[7] Te–Zr,[8] Te–Br,[9] and Te–Sn[10] combinations, play an important role in organic synthesis, especially in developing many convenient methods for the stereoselective synthesis of substituted alkenes. Vinylic tellurides are important synthetic intermediates because the tellurium moiety can be replaced by different organic groups always with total retention of the configuration.[11] Vinyl sulfides are also promising synthetic intermediates because they can participate in highly stereoselective carbon–carbon bond formation processes.[12] However, the difunctional group reagents containing sulfur and tellurium have not been reported.

Hydrozirconation has emerged as a unique hydrometallation with some attractive features,[13] such as the high regioselectivity and stereoselectivity observed with alkynes.[14] However, to date, hydrozirconation of alkynyltellurides has received less attention.[15] We now report that (*Z*)-α-arylsulfenylvinyl tellurides could be synthesised by hydrozirconation of alkynyltellurides, followed by treatment with arylsulfenyl chlorides (Scheme 1).

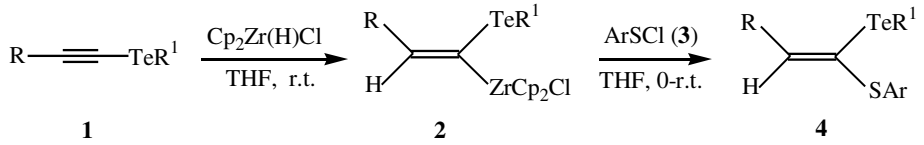
The required starting alkynyltellurides **1** were prepared according to the literature method.[16] Hydrozirconation of alkynyltellurides **1** at room temperature in THF gave (*Z*)-α-tellurovinylzirconium complexes **2**, which were reacted with arylsulfenyl chlorides **3** to afford stereoselectively (*Z*)-α-arylsulfenylvinyl tellurides **4** in good yields. Typical results are summarised in Table 1.

Investigations of the crude products **4** by ^{1}H NMR spectroscopy (300 MHz) showed isomeric purities of more than 96%. One olefinic proton signal of **4** was characteristically split into one triplet with coupling constant J = 7.2 Hz, which indicated that the hydrozirconation of alkynyltellurides had taken place with strong preference for the addition of the zirconium atom at the carbon adjacent to the telluro group. We observed that the Zr/S exchange reaction on intermediates **2** occurs with total retention of the configuration. The configuration of compound **4a** could be confirmed from compound **5** which was obtained by treatment of **4a** with *n*-butyllithium in THF followed by hydrolysis, a reaction which occurs stereoselectively (Scheme 2). The stereochemistry of compound **5** was easily established, since ^{1}H NMR spectrum (300 MHz) of **5** gives rise to a doublet at δ = 6.05 with a coupling constant of 15.2 Hz, which is consistent with a *E*-configuration.

In conclusion, we have developed a direct route to the stereoselective synthesis of (*Z*)-α-arylsulfenylvinyl tellurides via hydrozirconation of alkynyltellurides, followed by treatment with arylsulfenyl chlorides. The present method has the advantages of mild reaction conditions, straightforward and simple procedures and good yields. Investigations on the synthetic applications of (*Z*)-α-arylsulfenylvinyl tellurides are in progress.

Experimental

THF was distilled from sodium-benzophenone immediately prior to use. IR spectra were obtained on a Perkin-Elmer 683 instrument as neat films. ^{1}H NMR spectra were recorded on a Bruker AC-300 (300 MHz) spectrometer using $CDCl_3$ as solvent. Microanalyses were measured using a Yanaco MT-3 CHN microelemental analyser.



Scheme 1

Table 1 Synthesis of (*Z*)-α-arylsulfenylvinyl tellurides **4a–4j**

Entry	R	R^1	Ar	Product[a]	Yield (%)[b]
1	*n*-C_4H_9	Ph	Ph	**4a**	70
2	*n*-C_4H_9	4-$CH_3C_6H_4$	4-$CH_3C_6H_4$	**4b**	65
3	*n*-C_4H_9	4-$CH_3C_6H_4$	4-ClC_6H_4	**4c**	63
4	*n*-C_4H_9	Ph	4-$CH_3C_6H_4$	**4d**	69
5	*n*-C_4H_9	*n*-C_4H_9	Ph	**4e**	61
6	*n*-C_6H_{13}	4-$CH_3C_6H_4$	4-$CH_3C_6H_4$	**4f**	67
7	*n*-C_6H_{13}	4-$CH_3C_6H_4$	Ph	**4g**	64
8	*n*-C_6H_{13}	4-ClC_6H_4	Ph	**4h**	66
9	*n*-C_6H_{13}	4-ClC_6H_4	4-$CH_3C_6H_4$	**4i**	62
10	$PhCH_2O(CH_2)_3$	*n*-C_4H_9	Ph	**4j**	59

[a]All the compounds were characterised by IR, ^{1}H NMR spectra and elemental analyses.[b]Isolated yield based on the **3** used.

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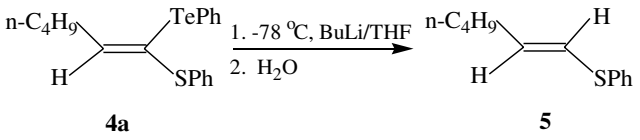

4a **5**

Scheme 2

Arylsulfenyl chlorides **3** were prepared according to literature method.[17] $Cp_2Zr(H)Cl$ was prepared according to the literature procedure.[18]

General procedure for the synthesis of (Z)-α-arylsulfenylvinyl tellurides **4a–j**

A slurry was prepared from $Cp_2Zr(H)Cl$ (1.1 mmol) and 5 ml of THF at room temperature under a nitrogen atmosphere, and the alkynyltelluride **1** (1 mmol) in 2 ml of THF was added via a syringe. The mixture was stirred at room temperature for 20–40 min, until hydrozirconation was complete, as evidenced by the disappearance of the insoluble hydride and the formation of a clear solution. To this solution, which contained the intermediate **2**, was added arylsulfenyl chloride **3** (0.9 mmol) at 0 °C. After stirring for 30 min, the mixture was stirred at room temperature for 2 h and normal work-up was performed. (Z)-α-Arylsulfenylvinyl telluride **4** was isolated and purified by column chromatography using light petroleum as eluent.

Compound **4a:** IR(film): ν(cm^{-1}) 3057, 3026, 2967, 2879, 1657, 1586, 1497, 1473, 1278, 769, 695; ^{1}H NMR: δ_H 7.61–7.04 (m, 10H), 6.31 (t, *J* = 7.2 Hz, 1H), 2.23 (m, 2H), 1.37–1.20 (m, 4H), 0.89 (t, *J* = 7.2 Hz, 3H); Anal. Calcd. for $C_{18}H_{20}STe$: C, 54.60; H, 5.06. Found: C, 54.32; H, 4.87.

Compound **4b:** IR(film): ν(cm^{-1}) 3056, 3017, 2963, 2872, 1647, 1579, 1487, 1463, 1269, 859, 693; ^{1}H NMR: δ_H 7.52–6.97 (m, 8H), 6.18 (t, *J* = 7.2 Hz, 1H), 2.33 (s, 3H), 2.32 (s, 3H), 2.25 (m, 2H), 1.36–1.22 (m, 4H), 0.88 (t, *J* = 7.2 Hz, 3H); Anal. Calcd. for $C_{20}H_{24}STe$: C, 56.66; H, 5.67. Found: C, 56.45; H, 5.73.

Compound **4c:** IR(film): ν(cm^{-1}) 3057, 3024, 2967, 2878, 1650, 1582, 1489, 1464, 1261, 860, 696; ^{1}H NMR: δ_H 7.54–6.94 (m, 8H), 6.38 (t, *J* = 7.2 Hz, 1H), 2.32 (s, 3H), 2.26 (m, 2H), 1.44–1.25 (m, 4H), 0.91 (t, *J* = 7.2 Hz, 3H); Anal. Calcd. for $C_{19}H_{21}SClTe$: C, 51.34; H, 4.73. Found: C, 51.12; H, 4.53.

Compound **4d:** IR(film): ν(cm^{-1}) 3054, 3024, 2956, 2875, 1653, 1582, 1491, 1463, 1268, 857, 760, 691; ^{1}H NMR: δ_H 7.61–7.05 (m, 9H), 6.19 (t, *J* = 7.2 Hz, 1H), 2.31 (s, 3H), 2.25 (m, 2H), 1.43–1.20 (m, 4H), 0.89 (t, *J* = 7.2 Hz, 3H); Anal. Calcd. for $C_{19}H_{22}STe$: C, 55.67; H, 5.38. Found: C, 55.41; H, 5.23.

Compound **4e:** IR(film): ν(cm^{-1}) 3057, 3019, 2958, 2870, 1647, 1598, 1489, 1463, 758, 695; ^{1}H NMR: δ_H 7.42–7.11 (m, 5H), 6.11 (t, *J* = 7.2 Hz, 1H), 3.07 (t, *J* = 7.6 Hz, 2H), 2.19–2.12 (m, 2H), 1.89–1.83 (m, 2H), 1.49–1.18 (m, 6H), 0.94–0.85 (m, 6H); Anal. Calcd. for $C_{16}H_{24}STe$: C, 51.12; H, 6.39. Found: C, 50.89; H, 6.26.

Compound **4f:** IR(film): ν(cm^{-1}) 3053, 3015, 2961, 2871, 1644, 1577, 1484, 1461, 1265, 843; ^{1}H NMR: δ_H 7.62–7.05 (m, 8H), 6.17 (t, *J* = 7.2 Hz, 1H), 2.34 (s, 3H), 2.28 (s, 3H), 2.23 (m, 2H), 1.41–1.20 (m, 8H), 0.88 (t, *J* = 7.2 Hz, 3H); Anal. Calcd. for $C_{22}H_{28}STe$: C, 58.46; H, 6.21. Found: C, 58.23; H, 6.08.

Compound **4g:** IR(film): ν(cm^{-1}) 3057, 3012, 2965, 2877, 1649, 1578, 1483, 1474, 1269, 857, 756, 696; ^{1}H NMR: δ_H 7.59–6.95 (m, 9H), 6.30 (t, *J* = 7.2 Hz, 1H), 2.32 (s, 3H), 2.25 (m, 2H), 1.48–1.25 (m, 8H), 0.89 (t, *J* = 7.2 Hz, 3H); Anal. Calcd. for $C_{21}H_{26}STe$: C, 57.59; H, 5.94. Found: C, 57.43; H, 6.03.

Compound **4h:** IR(film): ν(cm^{-1}) 3059, 3023, 2968, 2879, 1654, 1580, 1486, 1477, 845, 760, 697; ^{1}H NMR: δ_H 7.64–7.21 (m, 9H), 6.23 (t, *J* = 7.2 Hz, 1H), 2.25 (m, 2H), 1.52–1.26 (m, 8H), 0.87 (t, *J* = 7.2 Hz, 3H); Anal. Calcd. for $C_{20}H_{23}SClTe$: C, 52.39; H, 5.03. Found: C, 52.13; H, 5.18.

Compound **4i:** IR(film): ν(cm^{-1}) 3056, 3021, 2963, 2875, 1644, 1575, 1476, 1467, 857; ^{1}H NMR: δ_H 7.65–6.97 (m, 8H), 6.17 (t, *J* = 7.2 Hz, 1H), 2.34 (s, 3H), 2.21 (m, 2H), 1.56–1.22 (m, 8H), 0.84 (t, *J* = 7.2 Hz, 3H); Anal. Calcd. for $C_{21}H_{25}SClTe$: C, 53.38; H, 5.30. Found: C, 53.11; H, 5.23.

Compound **4j:** IR(film): ν(cm^{-1}) 3059, 3020, 2956, 2874, 1627, 1595, 1487, 1464, 756, 697; ^{1}H NMR: δ_H 7.78–7.72 (m, 2H), 7.41–7.22 (m, 8H), 6.70 (t, *J* = 7.2 Hz, 1H), 4.51 (s, 2H), 3.48 (t, *J* = 6.4 Hz, 2H), 3.01 (t, *J* = 7.6 Hz, 2H), 2.34 (m, 2H), 1.81–1.67 (m, 4H), 1.43–1.28 (m, 2H), 0.91 (t, *J* = 7.2 Hz, 3H); Anal. Calcd. for $C_{22}H_{28}OSTe$: C, 56.46; H, 6.01. Found: C, 56.25; H, 5.83.

The synthesis of (E)-1-phenylthio-1-hexene **5**

BuLi (1 ml, 1.1 M hexane solution) was added to a THF (5 ml) solution of **4a** (1.0 mmol) at –78 °C. After stirring for 1 h, the mixture was hydrolysed with saturated aq. NH_4Cl and extracted with Et_2O (2 × 30 ml). The organic extract was washed with water (2 × 10 ml), dried with $MgSO_4$, filtered and concentrated under vacuum. The residue was purified by column chromatography on silica gel, eluting with light petroleum to give (*E*)-1-phenylthio-1-hexene **5** (yield: 78%) as a colourless oil. IR (film): ν (cm^{-1}) 3021, 2927, 2857, 1595, 1450, 956, 786. ^{1}H NMR ($CDCl_3$): δ 7.45–7.08 (m, 5H), 6.05 (d, *J* = 15.2 Hz, 1H), 5.70 (dt, *J* = 15.2, 7.2 Hz, 1H), 2.16–2.09 (m, 2H), 1.42–1.23 (m, 4H), 0.91 (t, *J* = 7.2 Hz, 3H). Anal. Calcd for $C_{12}H_{16}S$: C, 74.94; H, 8.39. Found: C, 74.78; H, 8.44.

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