Stereoselective synthesis of (*E*)-α-silylvinyl tellurides via the hydrozirconation reaction of alkynylsilanes

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(*E*)-α-silylvinyl tellurides have been synthesised stereoselectively via the hydrozirconation of alkynylsilanes, followed by reaction with aryltellurenyl iodides. (*E*)-α-Silylvinyl tellurides can undergo cross coupling reaction with Grignard reagents in the presence of $[NiCl_2(PPh_3)_2]$ catalyst to give (*Z*)-1,2-disubstituted vinylsilanes in good yields.

Keywords: hydrozirconation, (*E*)-α-silylvinyl telluride, alkynylsilane, stereoselective synthesis

Many biologically active compounds occurring in nature possess the structural skeleton of trisubstituted alkenes.[1-3] Bifunctional-group reagents, which have two different functional groups linked to the olefinic carbon atoms, for example, Sn–Si,[4] Se–Si,[5] Zr–Si,[6] Te–Zr,[7]and Te–Br[8] combinations, play an important role in organic synthesis, especially in developing many convenient methods for stereoselective preparation of trisubstituted alkenes. Both vinylsilanes and vinyl tellurides are important intermediates, but the bifunctional-group reagent containing tellurium and silicon has rarely aroused attention. Hydrozirconation is one of the most promising organometallic techniques used in organic synthesis and has emerged as a unique hydrometallation with some attractive features,[9] such as the high regioselectivity and stereoselectivity observed with alkynes[10] and alkynylsilanes.[6] We now report that (*E*)-α-silylvinyl tellurides could be synthesised by hydrozirconation of alkynylsilanes, followed by treatment with aryltellurenyl iodides.

Alkynylsilanes **1** were prepared according to the literature procedure.[11] Hydrozirconation of alkynylsilanes **1** at room temperature in THF for 40 min gave (*E*)-α-silylvinylzirconiums **2**, which reacted with aryltellurenyl iodides **3** to afford (*E*)-α-silylvinyl tellurides **4**. The yields were 64–84% (Scheme 1).

Investigations of the crude products **4** by ^{1}H NMR spectroscopy (300 MHz) showed their isomeric purities to be more than 97%. One olefinic proton signal of **4a–f** splits characteristically into one triplet with a coupling constant J = 7.0 Hz, which indicated that the hydrozirconation of the alkynylsilanes had taken place with strong preference for the addition of the zirconium atom at the carbon adjacent to the silyl group. The results of the reaction are summarised in Table 1.

We have also carried out the cross coupling reaction of compounds **4** with Grignard reagents in the presence of $[NiCl_2(PPh_3)_2]$ catalyst at room temperature in THF for 48 h to give the (*Z*)-1,2-disubstituted vinylsilanes **5** with high stereoselectivity (Scheme 2).

In conclusion, we have developed a direct route to the synthesis of (*E*)-α-silylvinyl tellurides from alkynylsilanes. The method has some attractive advantages such as mild reaction conditions, a simple procedure, shorter reaction times, good yields and high regio- and stereoselectivity. Investigation into the synthetic applications of (*E*)-α-silylvinyl tellurides is in progress.

Experimental

^{1}H NMR spectra were recorded on an AZ-300 MHz spectrometer with TMS as an internal standard in $CDCl_3$ as solvent. IR spectra were obtained by use of neat capillary cells on a Perkin-Elmer 683 instrument. Mass spectra were determined on a Finnigan 8230 mass spectrometer. Microanalyses were measured using a Yanaco MT-3 CHN microelemental analyzer. All solvents were dried, deoxygenated and freshly distilled before use. $[ZrCp_2(H)Cl]$ was prepared according to a literature procedure.[12]

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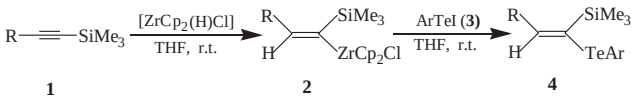
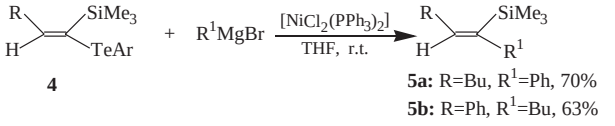


Scheme 1

Table 1 Synthesis of (*E*)-α-silylvinyl tellurides **4**

Entry	R	Ar	Product[a]	Yield[b]/%
1	n-C_4H_9	Ph	**4a**	75
2	n-C_4H_9	4-ClC_6H_4	**4b**	82
3	n-C_4H_9	4-$CH_3C_6H_4$	**4c**	68
4	CH_3OCH_2	Ph	**4d**	74
5	CH_3OCH_2	4-ClC_6H_4	**4e**	78
6	CH_3OCH_2	4-$CH_3C_6H_4$	**4f**	64
7	Ph	Ph	**4g**	80
8	Ph	4-ClC_6H_4	**4h**	84
9	Ph	4-$CH_3C_6H_4$	**4i**	79

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



Scheme 2

General procedure for the synthesis of (E)-α-silylvinyl tellurides **4a-i:** A mixture of $[ZrCp_2(H)Cl]$ (1 mmol) and alkynylsilane **1** (1 mmol) in THF (5 ml) was stirred under N_2 at room temperature for 40 min to yield a clear solution. Into the resulting solution was added a solution of ArTeI **3** (1 mmol) in THF (3 ml) and the mixture was stirred at room temperature for 1 h. The solvent was removed by rotary evaporator under reduced pressure. The residue was extracted with light petroleum (3×10 ml) and filtered through a short plug of silica gel. After evaporation of the filtrate, the residue was purified by column chromatography on silica gel, eluting with light petroleum to give **4a–i** as oils.

Compound **4a:** IR(film): ν(cm^{-1}) 3065, 2955, 1574, 1473, 1433, 1248, 838, 730, 691; ^{1}H NMR: δ_H 7.48–7.04 (m, 5H), 6.88 (t, J = 7.0 Hz, 1H), 2.33 (m, 2H), 1.38–1.19 (m, 4H), 0.85 (t, J = 6.4 Hz, 3H), 0.11 (s, 9H); MS: *m/z* 360 (M^+, 6.4), 73 (100); Anal. calcd. for $C_{15}H_{24}SiTe$: C, 50.06; H, 6.67. Found: C, 49.85; H, 6.43.

Compound **4b:** IR(film): ν(cm^{-1}) 3068, 2955, 1569, 1470, 1248, 1089, 841, 809; ^{1}H NMR: δ_H 7.55 (d, J = 7.8 Hz, 2H), 7.17 (d, J = 7.8 Hz, 2H), 6.98 (t, J = 7.0 Hz, 1H), 2.25 (m, 2H), 1.39–1.20 (m, 4H), 0.91 (t, J = 6.8 Hz, 3H), 0.18 (s, 9H); MS: *m/z* 394 (M^+, 3.4), 73 (100); Anal. calcd. for $C_{15}H_{23}SiClTe$: C, 45.69; H, 5.84. Found: C, 45.44; H, 5.68.

Compound **4c:** IR(film): ν(cm^{-1}) 3064, 2955, 1631, 1574, 1486, 1247, 1013, 838, 797, 755; ^{1}H NMR: δ_H 7.39 (d, J = 7.9 Hz, 2H), 6.91 (d, J = 7.9 Hz, 2H), 6.33 (t, J = 7.0 Hz, 1H), 2.34 (m, 2H), 2.25 (s, 3H), 1.39–1.18 (m, 4H), 0.84 (t, J = 6.5 Hz, 3H), 0.09 (s, 9H); MS: *m/z* 374 (M^+, 3.7), 73 (100); Anal. calcd. for $C_{16}H_{26}SiTe$: C, 51.39; H, 6.96. Found: C, 51.17; H, 6.84.

Compound **4d:** IR(film): ν(cm^{-1}) 3066, 2952, 1574, 1473, 1434, 1249, 1112, 842, 731, 691; ^{1}H NMR: δ_H 7.74–7.20 (m, 5H), 6.70 (t, J = 7.0 Hz, 1H), 3.97 (d, J = 6.4 Hz, 2H), 3.28 (s, 3H), 0.22 (s, 9H); MS: *m/z* 348

(M^+, 11), 73 (100); Anal. calcd. for $C_{13}H_{20}OSiTe$: C, 44.88; H, 5.75. Found: C, 44.63; H, 5.58.

Compound **4e:** IR(film): ν(cm^{-1}) 3069, 2952, 1634, 1568, 1471, 1249, 1089, 1009, 841, 810, 756; ^1H NMR: δ_H 7.63 (d, *J* = 8.1 Hz, 2H), 7.20 (d, *J* = 8.1 Hz, 2H), 6.70 (t, *J* = 7.0 Hz, 1H), 3.97 (d, *J* = 6.4 Hz, 2H), 3.29 (s, 3H), 0.21 (s, 9H); MS: *m/z* 382 (M^+, 14.6), 73 (100); Anal. calcd. for $C_{13}H_{19}OClSiTe$: C, 40.84; H, 4.97. Found: C, 40.71; H, 4.69.

Compound **4f:** IR(film): ν(cm^{-1}) 3064, 2952, 1632, 1579, 1486, 1449, 1249, 1112, 855, 798, 756; ^1H NMR: δ_H 7.62 (d, *J* = 7.9 Hz, 2H), 7.06 (d, *J* = 7.9 Hz, 2H), 6.58 (t, *J* = 7.0 Hz, 1H), 3.95 (d, *J* = 6.4 Hz, 2H), 3.27 (s, 3H), 2.35 (s, 3H), 0.22 (s, 9H); MS: *m/z* 362 (M^+, 7.8), 73 (100); Anal. calcd. for $C_{14}H_{22}OSiTe$: C, 46.46; H, 6.08. Found: C, 46.58; H, 6.14.

Compound **4g:** IR(film): ν(cm^{-1}) 3064, 2952, 1597, 1573, 1473, 1247, 837, 728, 691; ^1H NMR: δ_H 7.81–7.68 (m, 4H), 7.31–7.11 (m, 7H), 0.03 (s, 9H); MS: *m/z* 380 (M^+, 7), 73 (100); Anal. calcd. for $C_{17}H_{20}SiTe$: C, 53.74; H, 5.27. Found: C, 53.52; H, 5.08.

Compound **4h:** IR(film): ν(cm^{-1}) 3055, 2953, 1597, 1567, 1488, 1248, 838, 697; ^1H NMR: δ_H 7.70 (d, *J* = 8.4 Hz, 2H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.30–7.11 (m, 6H), 0.03 (s, 9H); MS: *m/z* 414 (M^+, 2.4), 73 (100); Anal. calcd. for $C_{17}H_{19}ClSiTe$: C, 49.28; H, 4.59. Found: C, 49.07; H, 4.37.

Compound **4i:** IR(film): ν(cm^{-1}) 3062, 3018, 2952, 1631, 1597, 1486, 1248, 839, 797, 749; ^1H NMR: δ_H 7.71–7.56 (m, 4H), 7.29–7.01 (m, 6H), 2.33 (s, 3H), 0.04 (s, 9H); MS: *m/z* 394 (M^+, 28), 73 (100); Anal. calcd. for $C_{18}H_{22}SiTe$: C, 54.88; H, 5.59. Found: C, 54.65; H, 5.43.

General procedure for the synthesis of (Z)-1,2-disubstituted vinylsilanes **5a–b:** To a stirred suspension of $[NiCl_2(PPh_3)_2]$ (0.05 mmol) and (*E*)-α-silylvinyl telluride **4** (1 mmol) in THF (5 ml) was added a solution of R^1MgBr (4 mmol) in THF (6 ml) at room temperature and the mixture was stirred for 48 h. The mixture was treated with sat. aq NH_4Cl (10 ml) and extracted with ether (2×30 ml). The ethereal solution was washed with water (3×20 ml) and dried ($MgSO_4$). Removal of the solvent under reduced pressure gave an oil which was purified by column chromatography on silica gel using light petroleum as eluent.

Compound **5a:** IR(film): ν(cm^{-1}) 3075, 3023, 2957, 1598, 1488, 1249, 837, 765, 700; ^1H NMR: δ_H 7.40–7.03 (m, 5H), 6.08 (t, *J* = 7.5 Hz, 1H), 2.27 (m, 2H), 1.50–1.26 (m, 4H), 0.93 (t, *J* = 6.8 Hz, 3H), 0.13 (s, 9H); Anal. calcd. for $C_{15}H_{24}Si$: C, 77.59; H, 10.34. Found: C, 77.40; H, 10.23.

Compound **5b:** IR(film): ν(cm^{-1}) 3057, 3023, 2956, 2928, 1592, 1491, 1248, 836, 749, 700; ^1H NMR: δ_H 7.41–7.15 (m, 6H), 2.27 (t, *J* = 6.8 Hz, 2H), 1.51–1.25 (m, 4H), 0.94 (t, *J* = 7.0 Hz, 3H), 0.15 (s, 9H); Anal. calcd. for $C_{15}H_{24}Si$: C, 77.59; H, 10.34. Found: C, 77.32; H, 10.19.

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