A facile stereoselective synthesis of (E)-1,2-disubstituted vinylic tellurides via hydromagnesiation of alkylarylacetylenes

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Hydromagnesiation of alkylarylacetylenes **1** in diethyl ether gave (*E*)-α-arylvinyl Grignard reagents **2**, which reacted with aryltellurenyl iodides **3** in THF to afford stereoselectively (*E*)-1,2-disubstituted vinylic tellurides **4** in good yields.

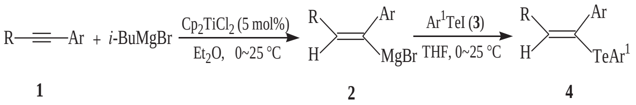
Keywords: hydromagnesiation, alkylarylacetylene, vinyl Grignard reagent, vinylic telluride, stereoselective synthesis

Vinylic tellurides are important synthetic intermediates because the tellurium moiety can be replaced by different organic groups always with total retention of the configuration.[1,2] Due to their synthetic utility, a variety of methods has been developed for their stereoselective preparation including those involving the addition of tellurols (or tellurolate anions) to acetylenes;[3] the reduction of acetylenic tellurides with $NaBH_4$;[4] the hydrozirconation of acetylenic tellurides;[5] zirconium-tellurium transmetalation.[6] Recently, Huang *et al*. have reported the stereoselective synthesis of (E)-vinylic tellurides via boron-tellurium transmetalation of (E)-alkenylboranes with diorgano ditellurides.[7]

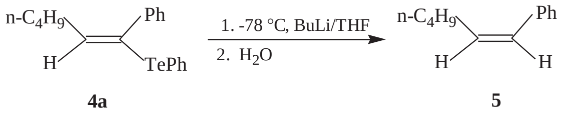
Hydromagnesiation has emerged as a unique hydrometallation with some attractive features such as the high regioselectivity and stereoselectivity observed with alkylarylacetylenes[8] and alkynylsilanes.[9] Very recently, we have reported the stereoselective syntheses of (*E*)-allylic alcohols,[10] (*E*)-α-selenenylvinylsilanes,[11] 1,3- dienylsilanes[12] and (*E*)-α-aryltellurenylvinylsilanes.[13] Herein we wish to report that (E)-1,2-disubstituted vinylic tellurides could be conveniently synthesised via the hydromagnesiation of alkylarylacetylenes, followed by the reaction with aryltellurenyl iodides.

Alkylarylacetylenes **1** were prepared according to the literature procedure.[14] Hydromagnesiation of alkylarylacetylenes **1** at 25°C in diethyl ether for 1 h gave (*E*)-α-arylvinyl Grignard reagents **2**, which reacted with aryltellurenyl iodides **3** in THF to afford stereoselectively (*E*)-1,2-disubstituted vinylic tellurides **4** in good yields (Scheme 1). Typical results are summarised in Table 1.

Investigations of the crude products **4** by ^1H NMR spectroscopy (400 MHz) showed their isomeric purities to be more than 97%. One olefinic proton signal of compounds **4a–l** splits characteristically into one triplet at $\delta = 6.17–6.35$ with coupling constant $J = 7.2$ or 7.6 Hz, which indicated that hydromagnesiation to the alkylarylacetylenes had taken place with strong preference for the addition of the magnesium atom at the carbon adjacent to the aryl group. We observed that the Mg/Te 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 the ^1H NMR spectrum (400 MHz) of **5** gives rise to a doublet at $\delta = 6.45$ with a coupling constant of 11.6 Hz, which is consistent with a Z-configuration.



Scheme 1



Scheme 2

In conclusion, a new convenient synthetic method for (*E*)-1,2-disubstituted vinylic tellurides has been developed by the hydromagnesiation of alkylarylacetylenes, followed by reaction with aryltellurenyl iodides. Compared with other methods reported, this method has the advantages of readily available starting materials, straightforward and simple procedures, mild reaction conditions and good yields.

Experimental

Diethyl ether was distilled from sodium immediately prior to use. IR spectra were obtained on a Perkin-Elmer 683 instrument as neat films. ^1H NMR spectra were recorded on a Bruker AC-400 (400 MHz) spectrometer using $CDCl_3$ as solvent. Microanalyses were measured using a Yanaco MT-3 CHN microelemental analyzer.

General procedure for the synthesis of (E)-1,2-disubstituted vinylic tellurides **4a-l**: To a solution of isobutylmagnesium bromide (2.5 mmol)

Table 1 Synthesis of (E)-1,2-disubstituted vinylic tellurides **4a–l**

Entry	R	Ar	Ar^1	Product	Yield/%[a]
1	n-C_4H_9	Ph	Ph	**4a**	59
2	n-C_4H_9	Ph	4-ClC_6H_4	**4b**	66
3	n-C_4H_9	Ph	4-$CH_3C_6H_4$	**4c**	63
4	n-C_6H_{13}	Ph	Ph	**4d**	62
5	n-C_6H_{13}	Ph	4-ClC_6H_4	**4e**	67
6	n-C_6H_{13}	Ph	4-$CH_3C_6H_4$	**4f**	60
7	n-C_4H_9	4-ClC_6H_4	Ph	**4g**	61
8	n-C_4H_9	4-ClC_6H_4	4-ClC_6H_4	**4h**	65
9	n-C_4H_9	4-ClC_6H_4	4-$CH_3C_6H_4$	**4i**	62
10	n-C_4H_9	4-$CH_3C_6H_4$	Ph	**4j**	60
11	n-C_4H_9	4-$CH_3C_6H_4$	4-ClC_6H_4	**4k**	68
12	n-C_4H_9	4-$CH_3C_6H_4$	4-$CH_3C_6H_4$	**4l**	58

[a]Isolated yield based on the alkylarylacetylene **1** used.

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in diethyl ether (4 ml) was added Cp_2TiCl_2 (25 mg, 0.1 mmol) at 0°C under Ar, and the mixture was stirred for 30 min at that temperature. To this solution was added alkylarylacetylene **1** (2.0 mmol), and the mixture was stirred for 1 h at 25°C. After removal of the Et_2O under reduced pressure (2h, r.t./2 torr), the residue was dissolved in THF (3 ml), cooled to 0°C. Then a solution of aryltellurenyl iodide **3** (2.5 mmol) in THF (3 ml) was added dropwise over 30 min with stirring at 0°C and the mixture was stirred for 6 h at 25°C, quenched with sat. aq. NH_4Cl (15 ml) and extracted with Et_2O (2×30 ml). The organic layer was washed with sat. aq. $Na_2S_2O_3$ (20 ml) and 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.

(E)-1-Phenyl-1-phenyltelluro-1-hexene (**4a**): ν_{max} (film)/cm^{-1} 3053, 2955, 2924, 1597, 1573, 1487, 1473, 758, 731, 698; δ_H ($CDCl_3$) 7.71–7.64 (m, 2H), 7.35–7.14 (m, 8H), 6.29 (t, *J* = 7.6 Hz, 1H), 2.09–2.03 (m, 2H), 1.34–1.19 (m, 4H), 0.84 (t, *J* = 6.8 Hz, 3H); Anal. Calcd for $C_{18}H_{20}Te$: C, 59.34; H, 5.49. Found: C, 59.11; H, 5.25.

(E)-1-Phenyl-1-(4-chlorophenyltelluro)-1-hexene (**4b**): ν_{max} (film)/cm^{-1} 3058, 2957, 2925, 1598, 1568, 1487, 1470, 1089, 1008, 809, 698; δ_H ($CDCl_3$) 7.54 (d, *J* = 8.8 Hz, 2H), 7.26–7.10 (m, 7H), 6.32 (t, *J* = 7.6 Hz, 1H), 2.09–2.03 (m, 2H), 1.34–1.20 (m, 4H), 0.85 (t, *J* = 6.8 Hz, 3H); Anal. Calcd for $C_{18}H_{19}ClTe$: C, 54.27; H, 4.77. Found: C, 54.02; H, 4.56.

(E)-1-Phenyl-1-(4-methylphenyltelluro)-1-hexene (**4c**): ν_{max} (film)/cm^{-1} 3015, 2957, 2924, 1674, 1595, 1486, 1441, 1013, 798, 758, 699; δ_H ($CDCl_3$) 7.59–7.48 (m, 2H), 7.25–6.97 (m, 7H), 6.21 (t, *J* = 7.2 Hz, 1H), 2.32 (s, 3H), 2.07–1.96 (m, 2H), 1.36–1.19 (m, 4H), 0.84 (t, *J* = 6.8 Hz, 3H); Anal. Calcd for $C_{19}H_{22}Te$: C, 60.32; H, 5.82. Found: C, 60.09; H, 5.65.

(E)-1-Phenyl-1-phenyltelluro-1-octene (**4d**): ν_{max} (film)/cm^{-1} 3054, 2954, 2925, 2854, 1598, 1574, 1487, 1473, 1434, 731, 698; δ_H ($CDCl_3$) 7.71–7.64 (m, 2H), 7.34–7.13 (m, 8H), 6.29 (t, *J* = 7.6 Hz, 1H), 2.08–2.02 (m, 2H), 1.34–1.15 (m, 8H), 0.84 (t, *J* = 6.8 Hz, 3H); Anal. Calcd for $C_{20}H_{24}Te$: C, 61.22; H, 6.12. Found: C, 60.94; H, 6.03.

(E)-1-Phenyl-1-(4-chlorophenyltelluro)-1-octene (**4e**): ν_{max} (film)/cm^{-1} 3056, 3018, 2957, 2925, 1597, 1568, 1488, 1471, 1441, 809, 699; δ_H ($CDCl_3$) 7.53 (d, *J* = 8.8 Hz, 2H), 7.26–7.10 (m, 7H), 6.32 (t, *J* = 7.6 Hz, 1H), 2.08–2.02 (m, 2H), 1.35–1.12 (m, 8H), 0.85 (t, *J* = 6.8 Hz, 3H); Anal. Calcd for $C_{20}H_{23}ClTe$: C, 56.34; H, 5.40. Found: C, 56.10; H, 5.42.

(E)-1-Phenyl-1-(4-methylphenyltelluro)-1-octene (**4f**): ν_{max} (film)/cm^{-1} 3014, 2954, 2922, 2854, 1592, 1486, 1441, 1012, 797, 758, 699; δ_H ($CDCl_3$) 7.59–7.49 (m, 2H), 7.25–6.98 (m, 7H), 6.20 (t, *J* = 7.6 Hz, 1H), 2.32 (s, 3H), 2.07–2.00 (m, 2H), 1.33–1.14 (m, 8H), 0.84 (t, *J* = 6.8 Hz, 3H); Anal. Calcd for $C_{21}H_{26}Te$: C, 62.07; H, 6.40. Found: C, 61.90; H, 6.15.

(E)-1-Phenyltelluro-1-(4-chlorophenyl)-1-hexene (**4g**): ν_{max} (film)/cm^{-1} 3054, 2956, 2927, 2870, 1677, 1588, 1573, 1485, 1434, 818, 732, 690; δ_H ($CDCl_3$) 7.71–7.62 (m, 2H), 7.29–7.06 (m, 7H), 6.33 (t, *J* = 7.6 Hz, 1H), 2.08–2.00 (m, 2H), 1.33–1.21 (m, 4H), 0.83 (t, *J* = 6.8 Hz, 3H); Anal. Calcd for $C_{18}H_{19}ClTe$: C, 54.27; H, 4.77. Found: C, 54.12; H, 4.53.

(E)-1-(4-Chlorophenyl)-1-(4-chlorophenyltelluro)-1-hexene (**4h**): ν_{max} (film)/cm^{-1} 3056, 2956, 2927, 1587, 1567, 1485, 1471, 1381, 1089, 1009, 809, 722; δ_H ($CDCl_3$) 7.52 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 7.05 (d, *J* = 8.0 Hz, 2H), 6.35 (t, *J* = 7.2 Hz, 1H), 2.06–1.99 (m, 2H), 1.34–1.19 (m, 4H), 0.84 (t, *J* = 6.8 Hz, 3H); Anal. Calcd for $C_{18}H_{18}Cl_2Te$: C, 49.89; H, 4.16. Found: C, 49.62; H, 3.97.

(E)-1-(4-Chlorophenyl)-1-(4-methylphenyltelluro)-1-hexene (**4i**): ν_{max} (film)/cm^{-1} 3014, 2956, 2923, 1594, 1574, 1486, 1440, 797, 759, 699; δ_H ($CDCl_3$) 7.59–7.49 (m, 2H), 7.26–6.97 (m, 6H), 6.21 (t, *J* = 7.6 Hz, 1H), 2.33 (s, 3H), 2.09–1.98 (m, 2H), 1.33–1.19 (m, 4H), 0.83 (t, *J* = 6.8 Hz, 3H); Anal. Calcd for $C_{19}H_{21}ClTe$: C, 55.34; H, 5.10. Found: C, 55.09; H, 5.02.

(E)-1-Phenyltelluro-1-(4-methylphenyl)-1-hexene (**4j**): ν_{max} (film)/cm^{-1} 3050, 3020, 2957, 2924, 1603, 1574, 1505, 1473, 1434, 815, 731, 691; δ_H ($CDCl_3$) 7.71–7.65 (m, 2H), 7.28–7.02 (m, 7H), 6.26 (t, *J* = 7.6 Hz, 1H), 2.29 (s, 3H), 2.09–2.03 (m, 2H), 1.33–1.19 (m, 4H), 0.81 (t, *J* = 7.2 Hz, 3H); Anal. Calcd for $C_{19}H_{22}Te$: C, 60.32; H, 5.82. Found: C, 60.15; H, 5.59.

(E)-1-(4-Methylphenyl)-1-(4-chlorophenyltelluro)-1-hexene (**4k**): ν_{max} (film)/cm^{-1} 3021, 2959, 2927, 1605, 1567, 1508, 1471, 1381, 808, 721; δ_H ($CDCl_3$) 7.59–7.50 (m, 2H), 7.29–7.02 (m, 6H), 6.29 (t, *J* = 7.2 Hz, 1H), 2.29 (s, 3H), 2.10–2.04 (m, 2H), 1.34–1.20 (m, 4H), 0.82 (t, *J* = 7.2 Hz, 3H); Anal. Calcd for $C_{19}H_{21}ClTe$: C, 55.34; H, 5.10. Found: C, 55.23; H, 5.14.

(E)-1-(4-Methylphenyl)-1-(4-methylphenyltelluro)-1-hexene (**4l**): ν_{max} (film)/cm^{-1} 3018, 2956, 2922, 1603, 1565, 1505, 1485, 1441, 798, 768; δ_H ($CDCl_3$) 7.59–7.54 (m, 2H), 7.11–6.98 (m, 6H), 6.17 (t, *J* = 7.2 Hz, 1H), 2.32 (s, 3H), 2.29 (s, 3H), 2.06–2.01 (m, 2H), 1.33–1.18 (m, 4H), 0.81 (t, *J* = 6.8 Hz, 3H); Anal. Calcd for $C_{20}H_{24}Te$: C, 61.22; H, 6.12. Found: C, 61.05; H, 5.95.

The synthesis of (Z)-1-phenyl-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 hydrolyzed 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 (*Z*)-1-phenyl-1-hexene **5** (yield: 73%) as a colourless oil. IR (film): ν (cm^{-1}) 2926, 2855, 1647, 1595, 1498, 1378. ^{1}H NMR ($CDCl_3$): δ 7.34–7.20 (m, 5H), 6.45 (d, *J* = 11.6 Hz, 1H), 5.70 (dt, *J* = 11.6, 7.2 Hz, 1H), 2.36–2.29 (m, 2H), 1.46–1.32 (m, 4H), 0.93 (t, *J* = 7.2 Hz, 3H). Anal. Calcd for $C_{12}H_{16}$: C, 90.00; H, 10.00. Found: C, 89.73; H, 9.84.

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