SHORT PAPER

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Alkynylsilanes as convenient precursors for the stereoselective synthesis of (*E*)-disubstituted alkenes[†]

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Hydromagnesiation of alkynylsilanes **1** gives (*Z*)-α-silylvinyl Grignard reagents **2**, which are reacted with alkyl iodides or aryl iodides in the presence of CuI or $Pd(PPh_3)_4$ catalysts to afford (*Z*)-1,2-disubstituted vinylsilanes **3** in good yields. Intermediates **3** can undergo a desilylation reaction to give (*E*)-disubstituted alkenes **4** in high yields.

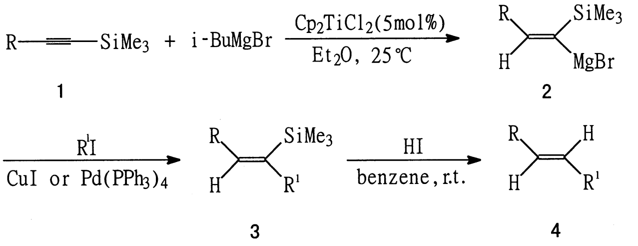
Keywords: hydromagnesiation, (*E*)-disubstituted alkene, stereoselective synthesis

The stereoselective synthesis of (*Z*) and (*E*)-alkenes is of considerable interest since such alkenes are often encountered in natural compounds, such as insect sex pheromones,[1] and are also valuable monomers for polyolefins used in nonenzymic biogenetic-like cyclisations to form polycyclic compounds.[2] Many methods can be used for the synthesis of (*E*)-disubstituted alkenes, such as the base-promoted elimination reactions of β-hydroxyalkylsilanes,[3] the hydroboration of 1-bromo-1-alkynes followed by treatment with sodium methoxide and then protonolysis,[4] the coupling reactions of (*E*)-alkenylzirconium and (*E*)-alkenylaluminum compounds with aryl halides catalysed by Ni or Pd catalysts,[5] by the cross-coupling reactions of (*E*)-alkenyl halides with Grignard reagents catalysed by $Pd(PPh_3)_4$[6] and the palladium-catalysed coupling of (*E*)-alkenylsilacyclobutanes and aryl iodides.[7]

Hydromagnesiation has emerged as a unique hydrometallation reaction with some attractive features, such as the high regioselectivity and stereoselectivity observed with alkynylsilanes.[8,9] However, there are few reports on the application of the reaction in stereoselective synthesis of (*E*)-alkenes. In this paper we will report a facile route for stereoselective synthesis of (*E*)-disubstituted alkenes via the hydromagnesiation of alkynylsilanes (Scheme 1).

Alkynylsilanes **1** were easily prepared according by literature procedures.[10] Hydromagnesiation of alkynylsilanes **1** at 25°C in ether for 6h gave (*Z*)-α-silylvinyl Grignard reagents **2**, which were reacted with methyl iodide at room temperature to give (*Z*)-1,2-disubstituted vinylsilanes **3** in high yields. The intermediates **2** were found to possess low reactivity with alkyl halides other than methyl iodide. However, they were readily alkylated by butyl iodide in the presence of 10mol% CuI. In the presence of 5mol% $Pd(PPh_3)_4$ intermediates **2** could also undergo cross-coupling reactions with aryl iodides at room temperature to give (*Z*)-1,2-disubstituted vinylsilanes **3** in good yields. The experimental results are summarised in Table 1. Investigation of the crude products **3** by ^1H NMR spectroscopy(300MHz) showed isomeric purities of more than 96%. One olefinic proton signal of **3** was characteristically split into a triplet with coupling constant J=7.0Hz, which indicated that the hydromagnesiation of the alkynylsilanes had taken place with strong preference for the addition of the magnesium atom at the carbon adjacent to the alkylsilyl group.

Vinylsilanes are important synthetic intermediates owing to the versatile reactivity of the silyl group and the carbon-carbon double bond.[11] (*Z*)-1,2-disubstituted vinylsilanes **3** are also effective precursors for synthesising (*E*)-disubstituted alkenes. In the presence of a catalytic amount of hydriodic acid they easily undergo desilylation reactions with retention of configuration providing a convenient method to synthesise (*E*)-disubstituted alkenes.[11] Thus, the desilylation reactions of compounds **3** at room temperature in benzene for 2h in the presence of hydriodic acid afforded (*E*)-disubstituted alkenes **4** in high yields. The typical results are summarised in Table 2. The stereochemistry of products **4** was easily established, since ^1H NMR spectra of **4b**, **4d** and **4f** give rise to a doublet at δ6.3-6.4 with a coupling constant of 16Hz, typical of *trans* protons. The products **4a–g** all show strong IR bands at about $965cm^{-1}$, which also indicate the existence of *trans* hydrogen atoms.



Scheme 1

Table 1 Synthesis of (Z)-1,2-disubstituted vinylsilanes **3**

Entry	R	R^1	Catalyst	Product[a]	Yield[b]/%
1	n-C_4H_9	CH_3		**3a**	91
2	n-C_4H_9	n-C_4H_9	CuI	**3b**	86
3	n-C_4H_9	Ph	$Pd(PPh_3)_4$	**3c**	71
4	n-C_4H_9	4-ClC_6H_4	$Pd(PPh_3)_4$	**3d**	74
5	i-C_5H_{11}	n-C_4H_9	CuI	**3e**	87
6	i-C_5H_{11}	4-ClC_6H_4	$Pd(PPh_3)_4$	**3f**	75
7	n-C_6H_{13}	CH_3		**3g**	89
8	n-C_6H_{13}	n-C_4H_9	CuI	**3h**	85
9	n-C_6H_{13}	Ph	$Pd(PPh_3)_4$	**3i**	70
10	n-C_6H_{13}	4-ClC_6H_4	$Pd(PPh_3)_4$	**3j**	72
11	$PhCH_2$	n-C_4H_9	CuI	**3k**	80
12	$PhCH_2$	Ph	$Pd(PPh_3)_4$	**3l**	67

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

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[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

Table 2 Synthesis of (*E*)-disubstituted alkenes 4

Entry	R	R^1	Product^a	Yield^b/%
1	*n*-C_4H_9	*n*-C_4H_9	**4a**	91
2	*n*-C_4H_9	Ph	**4b**	88
3	*i*-C_5H_{11}	*n*-C_4H_9	**4c**	90
4	*i*-C_5H_{11}	4-ClC_6H_4	**4d**	85
5	*n*-C_6H_{13}	*n*-C_4H_9	**4e**	92
6	*n*-C_6H_{13}	Ph	**4f**	87
7	$PhCH_2$	*n*-C_4H_9	**4g**	84

^{a}All compounds were characterised by ^{1}H NMR, IR and elemental analyses.
^{b}Isolated yield based on the (*Z*)-1,2-disubstituted vinylsilane used.

In conclusion, the methodology discussed in this paper provides a convenient and practical route to (*E*)-disubstituted alkenes, which has advantages of readily available starting materials, straightforward and simple procedures, mild reaction conditions and high yields.

Experimental

Tetrahydrofuran (THF) was freshly distilled from sodium-benzophenone prior to its use. IR spectra were obtained on Shimadzu IR-435 instrument, ^{1}H NMR spectra were recorded on an AZ-300MHz spectrometer with TMS as an internal standard in $CDCl_3$ as solvent. Microanalyses were performed on Vario EL and Perkin-Elmer CHN2400.

General procedure for the synthesis of (Z)-1,2-disubstituted vinylsilanes **3a,3g**: To a solution of isobutylmagnesium bromide (4.5mmol) in diethyl ether (7ml) was added Cp_2TiCl_2 (50mg, 0.2mmol) at 0°C under Ar, and the mixture was stirred for 30min at that temperature. To this solution was added alkynylsilane **1** (4.0mmol), and the mixture was stirred for 6h at 25°C. After removal of the ether under reduced pressure (2h, r.t./2torr), the residue was dissolved in THF (6ml) and treated with methyl iodide (0.71g, 5mmol) at 0°C for 10min and then at room temperature for 2h. The resulting mixture was treated with sat.aq NH_4Cl (25ml) and extracted with Et_2O (2×30ml). The ethereal solution was washed with water (3×30ml) and dried ($MgSO_4$). Removal of solvent under reduced pressure gave an oil which was purified by column chromatography on silica gel using light petroleum as eluent.

(Z)-2-Trimethylsilyl-2-heptene(**3a**): υ_{max}(film)/cm^{-1} 2958, 2860, 1620, 1466, 1249, 838; δ_H($CDCl_3$) 0.11(s, 9H), 0.90(t, 3H, *J*=5.4Hz), 1.08–1.60(m, 4H), 1.74(s, 3H), 1.85–2.40(m, 2H), 5.84(t, 1H, *J*=7.0Hz); Anal. calcd for $C_{10}H_{22}Si$: C, 70.59; H, 12.94. Found: C, 70.36; H, 12.79.

(Z)-2-Trimethylsilyl-2-nonene(**3g**): υ_{max}(film)/cm^{-1} 2926, 2856, 1607, 1458, 1248, 837; δ_H($CDCl_3$) 0.11(s, 9H), 0.88(t, 3H, *J*=5.4Hz), 1.10–1.65(m, 8H), 1.73(s, 3H), 1.84–2.41(m, 2H), 5.81(t, 1H, *J*=7.0Hz); Anal. calcd for $C_{12}H_{26}Si$: C, 72.73; H, 13.13. Found: C, 72.51; H, 13.02.

General procedure for the synthesis of (Z)-1,2-disubstituted vinylsilanes **3b, 3e, 3h, 3k**: To a solution of isobutylmagnesium bromide (4.5mmol) in diethyl ether (7ml) was added Cp_2TiCl_2 (50mg, 0.2mmol) at 0°C under Ar, and the mixture was stirred for 30min at that temperature. To this solution was added alkynylsilane 1 (4.0mmol), and the mixture was stirred for 6h at 25°C. After removal of the ether under reduced pressure, the residue was dissolved in THF (7ml), cooled to –10°C, and treated with butyl iodide (0.828g, 4.5mmol) and CuI (76mg, 0.4mmol). The reaction mixture was brought to room temperature gradually and stirred for 2h. After the usual workup (see above) the residue was chromatographed through a silica gel column using light petroleum as eluent.

(Z)-5-Trimethylsilyl-5-decene(**3b**): υ_{max}(film)/cm^{-1} 2954, 2860, 1612, 1466, 1249, 848; δ_H($CDCl_3$) 0.11(s, 9H), 0.66–1.08(m, 6H), 1.10–1.62(m, 8H), 1.78–2.40(m, 4H), 5.83(t, 1H, *J*=7.0Hz); Anal. calcd for $C_{13}H_{28}Si$: C, 73.58; H, 13.21. Found: C, 73.40; H, 13.13.

(Z)-2-Methyl-6-trimethylsilyl-5-decene(**3e**): υ_{max}(film)/cm^{-1} 2955, 2871, 1612, 1466, 1384, 1366, 1248, 835; δ_H($CDCl_3$) 0.12(s, 9H), 0.78–1.05(m, 9H), 1.08–1.64(m, 7H), 1.74–2.38(m, 4H), 5.83(t, 1H, *J*=7.0Hz); Anal. calcd for $C_{14}H_{30}Si$: C, 74.34; H, 13.27. Found: C, 74.19; H, 13.06.

(Z)-5-Trimethylsilyl-5-dodecene(**3h**): υ_{max}(film)/cm^{-1} 2958, 2857, 1612, 1466, 1249, 838; δ_H($CDCl_3$) 0.11(s, 9H), 0.68–1.03(m, 6H), 1.04–1.72(m, 12H), 1.74–2.40(m, 4H), 5.82(t, 1H, *J*=7.0Hz); Anal. calcd for $C_{15}H_{32}Si$: C, 75.00; H, 13.33. Found: C, 75.11; H, 13.24.

(Z)-1-Phenyl-3-trimethylsilyl-2-heptene(**3k**): υ_{max}(film)/cm^{-1} 2956, 2859, 1601, 1494, 1453, 1248, 837; δ_H($CDCl_3$) 0.12(s, 9H), 0.89(t, 3H, *J*=5.4Hz), 1.15–1.74(m, 4H), 2.05–2.41(m, 2H), 3.50(d, 2H, *J*=7.2Hz), 5.90(t, 1H, *J*=7.0Hz), 6.89–7.42(m, 5H); Anal. calcd for $C_{16}H_{26}Si$: C, 78.05; H, 10.57. Found: C, 78.23; H, 10.46.

General procedure for the synthesis of (Z)-1,2-disubstituted vinylsilanes **3c, 3d, 3f, 3i, 3j, 3l**: To a solution of isobutylmagnesium bromide (4.5mmol) in diethyl ether (7ml) was added Cp_2TiCl_2 (50mg, 0.2mmol) at 0°C under Ar, and the mixture was stirred for 30min at that temperature. To this solution was added alkynylsilane **1** (4.0mmol), and the mixture was stirred for 6h at 25°C. After removal of the ether under reduced pressure, the residue was dissolved in THF (7ml), cooled to –10°C, and treated with aryl iodide (4.0mmol) and $Pd(PPh_3)_4$ (0.231g, 0.2mmol). The reaction mixture was brought to room temperature gradually and stirred for 6h. After the usual workup (see above) the residue was chromatographed through a silica gel column using light petroleum as eluent.

(Z)-1-Trimethylsilyl-1-phenyl-1-hexene(**3c**): υ_{max}(film)/cm^{-1} 2956, 2858, 1602, 1249, 839; δ_H($CDCl_3$) 0.12(s, 9H), 0.91(t, 3H, *J*=5.4Hz), 1.20–1.71(m, 4H), 2.01–2.50(m, 2H), 6.01(t, 1H, *J*=7.0Hz), 6.71–7.40(m, 5H); Anal. calcd for $C_{15}H_{24}Si$: C, 77.59; H, 10.34. Found: C, 77.31; H, 10.25.

(Z)-1-Trimethylsilyl-1-(4-chlorophenyl)-1-hexene(**3d**): υ_{max}(film)/cm^{-1} 2957, 2858, 1605, 1485, 1249, 839; δ_H($CDCl_3$) 0.15(s, 9H), 0.90(t, 3H, *J*=5.4Hz),1.21–1.68(m, 4H), 2.06–2.51(m,2H), 5.94(t, 1H, *J*=7.0Hz), 6.78(d, 2H, *J*=9.0Hz), 7.08(d, 2H, *J*=9.0Hz); Anal. calcd for $C_{15}H_{23}SiCl$: C, 67.54; H, 8.63. Found: C, 67.66; H, 8.56.

(Z)-1-Trimethylsilyl-1-(4-chlorophenyl)-5-methyl-1-hexene(**3f**): υ_{max}(film)/cm^{-1} 2955, 2870, 1606, 1486, 1384, 1366, 1249, 838; δ_H($CDCl_3$) 0.12(s, 9H), 0.92(d, 6H, *J*=6.4Hz), 1.15–1.78(m, 3H), 2.00–2.46(m,2H), 5.90(t, 1H, *J*=7.0Hz), 6.74(d, 2H, *J*=9.0Hz), 7.06(d, 2H, *J*=9.0Hz); Anal. calcd for $C_{16}H_{25}SiCl$: C, 68.45; H, 8.91. Found: C, 68.61; H, 8.99.

(Z)-1-Trimethylsilyl-1-phenyl-1-octene(**3i**): υ_{max}(film)/cm^{-1} 2955, 2855, 1602, 1573, 1488, 1249, 837; δ_H($CDCl_3$) 0.11(s, 9H), 0.90(t, 3H, *J*=5.4Hz),1.10–1.78(m, 8H), 2.00–2.50(m,2H), 5.98(t, 1H, *J*=7.0Hz), 6.70–7.32(m, 5H,); Anal. calcd for $C_{17}H_{28}Si$: C, 78.46; H, 10.77. Found: C, 78.22; H, 10.53.

(Z)-1-Trimethylsilyl-1-(4-chlorophenyl)-1-octene(**3j**): υ_{max}(film)/cm^{-1} 2957, 2856, 1605, 1486, 1249, 839; δ_H($CDCl_3$) 0.11(s, 9H), 0.90(t, 3H, *J*=5.4Hz),1.10–1.70(m, 8H), 2.06–2.50(m,2H), 5.93(t, 1H, *J*=7.0Hz), 6.76(d, 2H, *J*=9.0Hz), 7.08(d, 2H, *J*=9.0Hz); Anal. calcd for $C_{17}H_{27}SiCl$: C, 69.27; H, 9.17. Found: C, 69.35; H, 9.30.

(Z)-1-Trimethylsilyl-1,3-diphenyl-1-propene(**3l**): υ_{max}(film)/cm^{-1} 2958, 2860, 1605, 1490, 1249, 839; δ_H($CDCl_3$) 0.12(s, 9H), 3.51(d, 2H, *J*=7.2Hz), 5.96(t, 1H, *J*=7.0Hz), 6.85–7.50(m, 10H,); Anal. calcd for $C_{18}H_{22}Si$: C, 81.20; H, 8.27. Found: C, 81.37; H, 8.41.

General procedure for the synthesis of (E)-disubstituted alkenes **4a–g**: To a solution of (*Z*)-1,2-disubstituted vinylsilane **3** (0.5mmol) in benzene (1ml) was added 0.04ml of hydriodic acid. The mixture was stirred at room temperature for 2h, quenched with sat.aq $NaHCO_3$ (10 ml) and extracted with Et_2O (2×15 ml). The ethereal solution was washed with water (3×10 ml), dried ($MgSO_4$) and concentrated under reduced pressure. The oily residue was purified by flash column chromatography on silica gel using light petroleum as eluent to give **4a–g** as oils.

(E)-5-Decene(**4a**): υ_{max}(film)/cm^{-1} 2955, 2853, 1463, 1377, 967; δ_H($CDCl_3$) 0.66–1.60(m, 14H), 1.95–2.21(m, 4H), 5.42(m, 2H); Anal. calcd for $C_{10}H_{20}$: C, 85.71; H, 14.29. Found: C, 85.53; H, 14.12.

(E)-1-Phenyl-1-hexene(**4b**): υ_{max}(film)/cm^{-1} 2925, 2857, 1651, 1598, 1493, 1378, 963; δ_H($CDCl_3$) 0.91(t, 3H, *J*=6.8Hz), 1.10–1.68(m, 4H), 2.05–2.42(m, 2H), 6.22(m, 1H), 6.38(d, 1H, *J*=16Hz), 6.89–7.42(m, 5H); Anal. calcd for $C_{12}H_{16}$: C, 90.00; H, 10.00. Found: C, 89.79; H, 9.93.

(E)-2-Methyl-5-decene(**4c**): υ_{max}(film)/cm^{-1} 2956, 1613, 1466, 1383, 1366, 968; δ_H($CDCl_3$) 0.68–1.62(m, 16H), 1.98–2.33(m, 4H), 5.40(m, 2H); Anal. calcd for $C_{11}H_{22}$: C, 85.71; H, 14.29. Found: C, 85.50; H, 14.32.

(E)-1-(4-Chorophenyl)-5-methyl-1-hexene(**4d**): υ_{max}(film)/cm^{-1} 2956, 2869, 1651, 1490, 1467, 1384, 1366, 966; δ_H($CDCl_3$) 0.90(d, 6H, *J*=6.4Hz), 1.08–1.70(m, 3H), 2.02–2.40(m, 2H), 6.24(m, 1H), 6.39(d, 1H, *J*=16Hz), 6.81(d, 2H, *J*=9.0Hz), 7.12(d, 2H, *J*=9.0Hz); Anal. calcd for $C_{13}H_{17}Cl$: C, 74.82; H, 8.15. Found: C, 74.51; H, 8.03.

(E)-5-Dodecene(**4e**): υ_{max}(film)/cm^{-1} 2958, 2856, 1656, 1466, 1379, 967; δ_H(CDCl$_3$) 0.68–1.70(m, 18H), 1.85–2.25(m, 4H), 5.33(m, 2H); Anal. calcd for $C_{12}H_{24}$: C, 85.71; H, 14.29. Found: C, 85.50; H, 14.11.

(E)-1-Phenyl-1-octene(**4f**): υ_{max}(film)/cm^{-1} 2928, 2856, 1651, 1600, 1495, 1457, 963; δ_H(CDCl$_3$) 0.90(t, 3H, *J*=6.8Hz), 1.10–1.75(m, 8H), 2.05–2.50(m, 2H), 6.23(m, 1H), 6.38(d, 1H, *J*=16Hz), 6.87–7.41(m, 5H); Anal. calcd for $C_{14}H_{20}$: C, 89.36; H, 10.64. Found: C, 89.50; H, 10.52.

(E)-1-Phenyl-2-heptene(**4g**): υ_{max}(film)/cm^{-1} 2959, 2856, 1651, 1595, 1498, 967; δ_H(CDCl$_3$) 0.90(t, 3H, *J*=6.8Hz), 1.10–1.73(m, 4H), 1.98–2.25(m, 2H), 3.50(d, 2H, *J*=7.2Hz), 5.41(m, 2H), 6.75–7.36(m, 5H); Anal. calcd for $C_{13}H_{18}$: C, 89.66; H, 10.34. Found: C, 89.41; H, 10.17.

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References

1 K. Mori, *The Total Synthesis of Natural Products*, J. ApSimon, Ed., John Wiley and Sons, Inc., New York, 1981, Vol. 4, PP1-183.
2 P.A. Bartlett and W.S. Johnson, *J. Am. Chem. Soc.*, 1973, **95**, 7501; E. E. Van Tamelen, R. G. Lees and A. Grieder, *J. Am. Chem. Soc.*, 1974, **96**, 2255; K. A. Parker and W. S. Johnson, *J. Am. Chem. Soc.*, 1974, **96**, 2556.
3 P.F. Hudrlik and D. Peterson, *J. Am. Chem. Soc.*, 1975, **97**, 1464.
4 G. Zweifel, R.P. Fisher, J.T. Snow and C.C. Whitney, *J. Am. Chem. Soc.*, 1971, **93**, 6309; H.C. Brown and D. Basavaiah, *J. Org. Chem.*, 1982, **47**, 754; H.C. Brown, H.D. Lee and S.U. Kulkarni, *Synthesis*, 1982, 195; H.C. Brown, D. Basavaiah and S.U. Kulkarni, *J. Org. Chem.*, 1982, **47**, 3808.
5 E. Negishi and D.E. Van Horn, *J. Am. Chem. Soc.*, 1977, **99**, 3168; E. Negishi, N. Okukado, A.O. King and B.I. Spiegel, *J. Am. Chem. Soc.*, 1978, **100**, 2254.
6 H. Janowicz and R.G. Bergman, *J. Am. Chem. Soc.*, 1983, **105**, 3929.
7 S.E. Denmark and J.Y. Choi, *J. Am. Chem. Soc.*, 1999, **121**, 5821.
8 F. Sato, H. Watanabe, Y. Tanaka, T. Yamaji and M. Sato, *Tetrahedron Lett.*, 1983, **24**, 1041.
9 F. Sato, *J. Organomet. Chem.*, 1985, **285**, 53.
10 C. Eaborn and D.R.M. Walton, *J. Organomet. Chem.*, 1964, **2**, 95.
11 T.H. Chan and I. Fleming, *Synthesis*, 1979, 761.