***SHORT PAPER***

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# Stereoselective synthesis of (*E*)-α-halovinylsilanes via hydrozirconation of alkynylsilanes†

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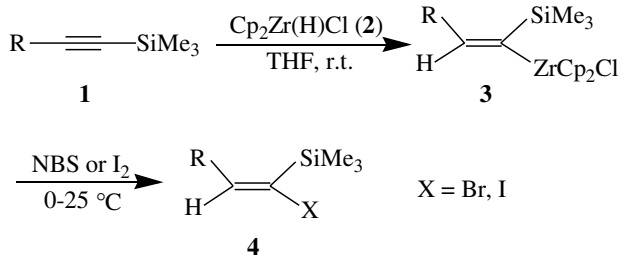
Hydrozirconation of alkynylsilanes **1** at room temperature in THF gave the (*E*)-α- silylvinylzirconium complexes **3**, which were reacted with NBS or iodine to afford stereoselectively (*E*)-α-halovinylsilanes **4** in good yields.

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

Vinylsilanes are useful synthetic intermediates because of the versatile reactivity of the silyl group and the carbon–carbon double bond.[1] Bifunctional group reagents, which have two different functional groups linked to the olefinic carbon atoms, for example, Si–Al,[2] Si–B,[3] Si–Cu,[4] Si–Sn[5] and Si–Se[6] combinations, play an important role in organic synthesis, especially in developing many convenient methods for the stereoselective preparation of substituted alkenes. Both vinylsilanes and vinyl halides are important intermediates, but the bifunctional group reagent containing silicon and halogen has received less attention.[7] Hydrozirconation has emerged as a unique hydrometallation with some attractive features, such as the high regioselectivity and stereoselectivity observed with alkynylsilanes.[8] We now wish to report that (*E*)-α-halovinylsilanes can be synthesised by hydrozirconation of alkynylsilanes, followed by reaction with NBS or iodine.

Alkynylsilanes **1** were prepared according to the literature procedure.[9] Hydrozirconation of alkynylsilanes **1** with $[ZrCp_2(H)Cl]$ **2** at room temperature in THF gave (*E*)-α-silylvinylzirconium complexes **3**, which reacted with NBS or iodine to afford (*E*)-α-halovinylsilanes **4**. The yields were 65–78% (Scheme 1).

Investigations of the crude products **4** by $^1$H NMR spectroscopy (300 MHz) showed their isomeric purities of more than 97%. One olefinic proton signal of **4** splits characteristically into one triplet at δ = 6.7–7.3 with coupling constant *J* = 6.8-8.1Hz, which indicated that the hydrozirconation to the alkynylsilanes had taken place with




**Scheme 1**

**Table 1** Synthesis of (*E*)-α-halovinylsilanes **4**

| Entry | R | X | Product[a] | Yield[b]/% |
|---|---|---|---|---|
| 1 | Ph | Br | **4a** | 73 |
| 2 | Ph | I | **4b** | 68 |
| 3 | n-$C_4H_9$ | Br | **4c** | 72 |
| 4 | n-$C_4H_9$ | I | **4d** | 76 |
| 5 | $CH_3OCH_2$ | Br | **4e** | 70 |
| 6 | $CH_3OCH_2$ | I | **4f** | 65 |
| 7 | n-$C_6H_{13}$ | Br | **4g** | 67 |
| 8 | n-$C_6H_{13}$ | I | **4h** | 78 |

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

strong preference for the addition of the zirconium atom at the carbon adjacent to the silyl group. The other results of the reaction are summarised in the Table 1.

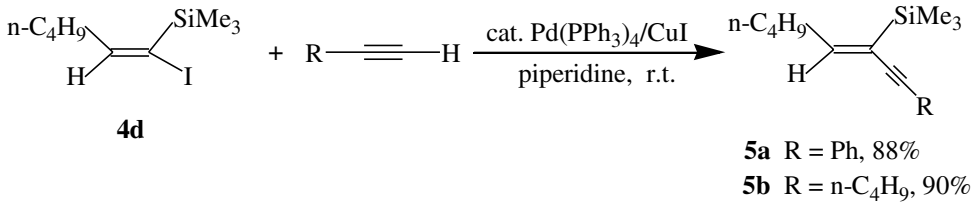
We have also carried out the Sonogashira reaction[10] of the compound **4d** with terminal acetylenes in the presence of 0.05 equiv of $[Pd(PPh_3)_4]$ and 0.1 equiv of CuI in piperidine to give 1,3-enynylsilanes **5** in high yields with high stereoselectivity (Scheme 2).

In summary, our results showed that the hydrozirconation–halogenation sequence of the alkynylsilanes has the advantages of readily available starting materials, straightforward and simple procedures, mild reaction conditions and good yields. Investigation of the synthetic application of (*E*)-α-halovinylsilanes 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. Microanalyses were performed on Vario EL and Perkin Elmer CHN 2400 instruments. The reactions were carried out in pre-dried (150°C, 4 h) glassware and cooled under a stream of dry $N_2$. All solvents were dried, deoxygenated and freshly distilled before use.

*General procedure for the synthesis of (E)-α-halovinylsilanes* **4a–h**: A mixture of $[ZrCp_2(H)Cl]$ (1 mmol) and alkynylsilane **1** (1 mmol) in THF (6 ml) was stirred under $N_2$ at room temperature for 40 min to yield a clear solution. After being cooled to 0 °C, into the




**Scheme 2**

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

resulting solution was added NBS or iodine (1 mmol) and the mixture was stirred at room temperature for 10 min. The solvent was removed by a 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–h** as oils.

*Compound* **4a**: $\nu_{max}$(film)/cm$^{-1}$ 3059, 3026, 2925, 2854, 1601, 1586, 1571, 1490, 1443, 1250, 840, 751, 697; $\delta_H$ 7.95 (s, 1H), 7.36–7.12 (m, 5H), 0.06 (s, 9H); Anal. Calcd for $C_{11}H_{15}SiBr$: C, 51.76; H, 5.88. Found: C, 51.49; H, 5.67.

*Compound* **4b**: $\nu_{max}$(film)/cm$^{-1}$ 3057, 3023, 2954, 2897, 1599, 1578, 1489, 1249, 837, 749, 696; $\delta_H$ 8.34 (s, 1H), 7.39–7.12 (m, 5H), 0.05 (s, 9H); Anal. Calcd for $C_{11}H_{15}SiI$: C, 43.71; H, 4.97. Found: C, 43.50; H, 4.78.

*Compound* **4c**: $\nu_{max}$(film)/cm$^{-1}$ 2958, 2873, 1569, 1466, 1250, 842, 759; $\delta_H$ 6.76 (t, $J$ = 8.1Hz, 1H), 2.07 (m, 2H), 1.45–1.25 (m, 4H), 0.90 (t, $J$ = 6.9Hz, 3H), 0.27 (s, 9H); Anal. Calcd for $C_9H_{19}SiBr$: C, 45.96; H, 8.09. Found: C, 45.68; H, 7.83.

*Compound* **4d**: $\nu_{max}$(film)/cm$^{-1}$ 2956, 2859, 1587, 1465, 1249, 841; $\delta_H$ 7.16 (t, $J$ = 7.9Hz, 1H), 2.08 (m, 2H), 1.39–1.21 (m, 4H), 0.90 (t, $J$ = 6.8Hz, 3H), 0.25 (s, 9H); Anal. Calcd for $C_9H_{19}SiI$: C, 38.30; H, 6.74. Found: C, 38.05; H, 6.49.

*Compound* **4e**: $\nu_{max}$(film)/cm$^{-1}$ 2925, 2855, 1606, 1454, 1251, 1114, 845, 759; $\delta_H$ 6.89 (t, $J$ = 7.2Hz, 1H), 3.93 (d, $J$ = 6.8Hz, 2H), 3.30 (s, 3H), 0.28 (s, 9H); Anal. Calcd for $C_7H_{15}OSiBr$: C, 37.67; H, 6.73. Found: C, 37.42; H, 6.54.

*Compound* **4f**: $\nu_{max}$(film)/cm$^{-1}$ 2924, 2854, 1595, 1459, 1377, 1250, 1109, 846; $\delta_H$ 7.29 (t, $J$ = 6.8Hz, 1H), 3.85 (d, $J$ = 6.8Hz, 2H), 3.33 (s, 3H), 0.28 (s, 9H); Anal. Calcd for $C_7H_{15}OSiI$: C, 31.11; H, 5.56. Found: C, 31.24; H, 5.49.

*Compound* **4g**: $\nu_{max}$(film)/cm$^{-1}$ 2927, 2857, 1600, 1459, 1250, 843, 759; $\delta_H$ 6.76 (t, $J$ = 7.9Hz, 1H), 2.07 (m, 2H), 1.47–1.21 (m, 8H), 0.89 (t, $J$ = 7.0Hz, 3H), 0.26 (s, 9H); Anal. Calcd for $C_{11}H_{23}SiBr$: C, 50.19; H, 8.75. Found: C, 49.89; H, 8.61.

*Compound* **4h**: $\nu_{max}$(film)/cm$^{-1}$ 2926, 2856, 1586, 1465, 1249, 842, 758; $\delta_H$ 7.17 (t, $J$ = 7.9Hz, 1H), 2.06 (m, 2H), 1.45–1.24 (m, 8H), 0.89 (t, $J$ = 6.8Hz, 3H), 0.27 (s, 9H); Anal. Calcd for $C_{11}H_{23}SiI$: C, 42.58; H, 7.42. Found: C, 42.31; H, 7.23.

*General procedure for the synthesis of 1,3-enynylsilanes* **5**: To a stirred solution of the compound **4d** (1 mmol), CuI (0.1 mmol) and [Pd(PPh$_3$)$_4$] (0.05 mmol) in piperidine (1.5 ml) was added a solution of terminal acetylene (2 mmol) in piperidine (1.5 ml) under $N_2$. After stirring at room temperature for 2 h, the mixture was hydrolysed with a saturated aqueous solution of ammonium chloride and extracted with diethyl ether (3×10 ml). The organic extract was washed with water (2×10 ml), dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel, eluting with light petroleum to afford **5a–b** as oils.

*Compound* **5a**: $\nu_{max}$(film)/cm$^{-1}$ 3056, 3031, 2957, 2872, 2188, 1598, 1489, 1465, 1249, 842, 755, 690; $\delta_H$ 0.16 (s, 9H), 0.89 (t, $J$ = 5.4 Hz, 3H), 1.20–1.58 (m, 4H), 2.25 (m, 2H), 6.25 (t, $J$ = 7.0 Hz, 1H), 7.27–7.53 (m, 5H); Anal. Calcd for $C_{17}H_{24}Si$: C, 79.69; H, 9.38. Found: C, 79.47; H, 9.28.

*Compound* **5b**: $\nu_{max}$(film)/cm$^{-1}$ 2958, 2874, 2176, 1583, 1466, 1379, 1249, 841; $\delta_H$ 0.11 (s, 9H), 0.66–1.05 (m, 6H), 1.07–1.68 (m, 8H), 2.08–2.40 (m, 4H), 6.21 (t, $J$ = 7.0 Hz, 1H); Anal. Calcd for $C_{15}H_{28}Si$: C, 76.27; H, 11.86. Found: C, 76.05; H, 11.69.

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