SHORT PAPER

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Stereoselective synthesis of (*E*)-2-alkyl and 2-phenyl-1-silylvinyl sulfides *via* hydrozirconation of alkyl silyl acetylenes[†]

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Hydrozirconation of alkyl silyl acetylenes gave organozirconium complexes, which reacted with aryl or alkyl sulfonyl chlorides to afford (*E*)-1-silylvinyl sulfides in high yields.

Vicinal difunctional compounds containing sulfur and a metal have attracted special attention as important intermediates in various synthetic transformations.[1,2] For example (1-metallovinyl)sulfides can be synthesised stereoselectively by hydroboration[3] and hydrostannylation[4] of alkynyl sulfides. The preparation and application in synthesis of α-silyl substituted vinyl sulfides have been reported.[5–8] However, few convenient routes to (*E*)-2-alkyl-1-silylvinyl sulfides are known. For example, 1-trimethylsilyl vinyl sulfide has been prepared by the addition of phenylsulfenyl chloride to vinyltrimethylsilane followed by dehydrohalogenation with DBU[5], or by the treatment of vinyl sulfides with LDA, followed by chlorotrimethylsilane.[6] However, these methods are not applicable for the more highly substituted derivatives. The chlorination of 1-phenylthio-1-silylalkanes followed by dehydrochlorination afforded a mixture of (*E*) and (*Z*)- 2-alkyl-1-silylvinyl silfides.[7] Some other methods give (*Z*)- 2-alkyl-1-silylvinyl sulfides.[1,8] We have studied the synthesis of (*E*)-2-alkyl-1-silylvinyl selenides[9] and now describe the preparation of (*E*)-2-alkyl and 2-phenyl-1-silylvinyl sulfides *via* the hydrozirconation of alkyl silyl acetylenes and an application of this in the synthesis of a (*Z*)-1-alkyl-2-phenyl vinyl silane.

Hydrozirconation of alkyl and phenyl silyl acetylenes **1** yielded the silyl-substituted alkenyl and aralkenyl zirconium complexes **2**,[10] which reacted with aryl or alkyl sulfenyl chloride at room temperature to afford the corresponding (*E*)-2-alkyl and 2-phenyl-1-silylvinyl sulfides **3** in high yields. The results are summarized in Table 1.

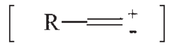
Table 1 Synthesis of compounds **3a–f**

Product	R	R′	Yield (%)[a]
3a	Ph	Ph	81
3b	Ph	$CH_2C_6H_5$	74
3c	n-C_5H_{11}	Ph	84
3d	n-C_4H_9	Ph	80
3e	n-C_4H_9	4-ClC_6H_4	81
3f	Ph	CH_3	70

[a]Isolated yield.

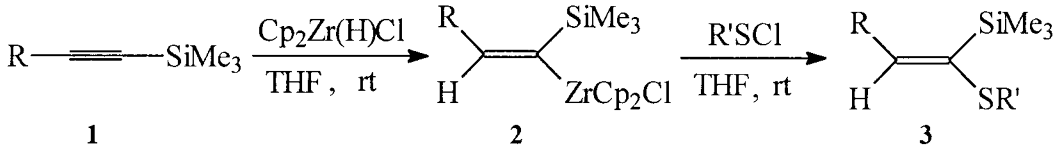
Because the sulfur group is easily substituted by various reagents,[1] the (*E*)-2-alkyl- and 2-phenyl-1-silylvinyl sulfides thus obtained act as vinyl cation equivalent species. Experiment showed that **3a** can couple stereoselectively with Grignard reagents in the presence of $Ni(PPh_3)_2Cl_2$ to give the (*Z*)-1-alkyl-2-phenyl vinyl silane **4** in 78 % yield.

Vinylsilanes have been widely utilized in synthesis of natural products[11] by coupling with electrophiles such as acyl halides,[12] alkenyl or aryl halides[13] as well as arenediazonium ion.[14] Therefore, 1-silylvinyl sulfides **3** can be regarded as the equivalent of the cation–anion synthon **5**.

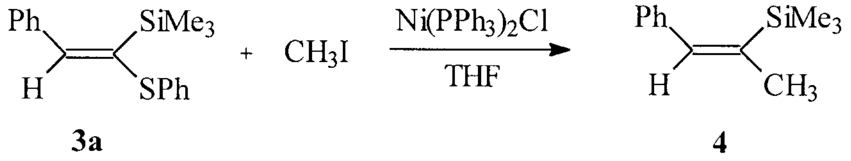


5

The present method has advantages of readily available starting materials, simple procedures and high yields. It provides an efficient and practical path for the synthesis of (*E*)-1-silylvinyl sulfides.



Scheme 1



Scheme 2

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

Experimental

^{1}H NMR spectra were recorded on an AZ-300MHz with TMS as internal standard. Mass spectra were determined using a Finigan 8230 mass spectrometer. IR spectra were obtained neat in a capillary cell on a Shimadzu IR-408 instrument. Microanalyses were performed using a Yamaco MT-3 CHN micro-elemental analyser. The reaction were carried out in pre-dried glassware (150 °C, 4 h) and cooled under a stream of dry nitrogen. All solvents were dried, deoxygenated and redistilled before use.

General procedure for the synthesis of **3a-f**: A mixture of Cp$_2$Zr(H)Cl (1.0 mmol) and silylacetylene **1** (1.0 mmol) in THF (5 ml) was stirred at room temperature for 30 min, during which time the mixture became a clear solution. Into the resulting solution were injected aryl or alkyl sulfinyl chlorides (1.0 mmol) in THF (1 ml). The mixture was stirred at room temperature for 2h. It was then diluted with light petroleum and stirred for a further 10 min. The solvent was removed by rotary evaporation under reduced pressure to give a crude oil, which was purified by preparative TLC (silica gel, hexane: AcOEt = 10 : 1) to give **3a–f.**

3a: oil (81 % yield), δ_H (CDCl$_3$), 7.08–7.42 (m, 11H), 0.03 (s, 9H); IR (film): 3075, 3050, 3020, 2950, 2890, 1600, 1580, 1560, 1490, 1475, 1400, 1250, 1070, 840, 740 cm^{-1}. MS: m/s 284 (M$^+$). Calc for C$_{17}$H$_{20}$SSi: C, 71.77, H, 7.09. Found: C, 71.64, H 7.05 %.

3b: oil (74 % yield), δ_H (CDCl$_3$), 7.12–7.65 (m, 10H, Ph), 7.05 (s, 1H, vinylic H), 3.70 (s, 2H, SCH$_2$), 0.12 (s, 9H, SiMe$_3$); IR (film): 1492, 1450, 1440, 1240, 1060, 840, 750 cm^{-1}. MS: m/s 298 (M$^+$). Calc for C$_{18}$H$_{22}$SSi: C, 72.42, H, 7.43. Found: C, 72.65, H, 7.47 %.

3c: Oil (84 % yield), δ_H (CDCl$_3$), 7.10–7.40 (m, 5H, Ph), 6.35 (t, *J* = 7 Hz, 1H, vinylic H), 2.25 (m, 2H), 1.05–1.60 (m, 6H), 0.90, (t, *J* = 7 Hz, 3H), 0.03 (s, 9H); IR (film): 3070, 3050, 2960, 2920, 2860, 1580, 1480, 1450, 1245, 1020, 840, 740 cm^{-1}. MS: m/s 278 (M$^+$). Calc for C$_{16}$H$_{26}$SSi: C, 69.00, H, 9.41. Found: C, 69.29, H. 9.45 %.

3d: oil (80 % yield), δ_H (CDCl$_3$), 7.10–7.40 (m, 5H, Ph), 6.33 (t, *J* = 7 Hz, 1H, vinylic H), 2.25 (m, 2H), 1.00–1.60 (m, 4H), 0.92 (t, *J* = 7 Hz, 3H), 0.03 (s, 9H): IR (film): 3070, 3050, 2960, 2925, 2865, 1585, 1480, 1455, 1250, 1020, 840, 740 cm^{-1}. MS: m/s 264 (M$^+$). Calc for C$_{15}$H$_{24}$SSi: C, 68.11, H, 9.15. Found: C, 68.47, H, 9.11 %.

3e: Oil (81% yield), δ_H (CDCl$_3$), 7.20–7.50 (AB q, *J* = 8 Hz, 4H), 6.35 (t, *J* = 7Hz, 1H, vinylic H), 2.25 (m, 2H), 1.05–1.60 (m, 4H), 0.90 (t, *J* = 7 Hz, 3H), 0.03 (s, 9H); Ir (film): 3070, 3050, 2960, 2925, 2860, 1585, 1475, 1445, 1250, 1020, 840, 735 cm^{-1}. MS: m/s 298 (M$^+$). Calc for C$_{15}$H$_{23}$ClSSi: C, 60.27, H, 7.75. Found: C, 60.41, H, 7.68 %.

3f: oil (70 % yield), δ_H (CDCl$_3$), 7.20–7.55 (m, 5H), 6.97 (s, 1H, vinylic H), 2.23 (s, 3H), 0.21 (s, 9H); IR (film): 3075, 3015, 1595, 1245, 865 cm^{-1}. MS: m/s 222 (M$^+$). Calc for C$_{12}$H$_{18}$SSi: C, 64.80, H, 8.16, Found: C, 64.49, H, 8.20 %.

General procedure for the synthesis of **4**: Under nitrogen, a 2.0 M THF solution of the CH$_3$MgI (10 mmol) was slowly added to a stirred suspension of NiCl$_2$(PPh$_3$)$_2$ (0.05 mmol) and the (*E*)-α-silyl vinyl sulfide **3a** (1 mmol) in THF (5 ml) at room temperature. The mixture was stirred at reflux temperature until the starting product had disappeared [TLC EtOAc-hexane (1 : 10) as eluent], after which it was quenched with saturated aqueous ammonium chloride and extracted with diethyl ether. The solvent was removed by rotary evaporator under reduced pressure to give a crude oil, which was purified by preparative TLC (silica gel, hexane: AcOEt = 10 : 1) to give **4** in 78 % yield.

4: Oil. δ_H (CDCl$_3$) 7.15–7.35 (m, 6H), 1.97 (d, *J* = 1.5 Hz, 3H), 0.12 (s, 9H); IR (film): 3030, 3010, 2960, 2900, 2850, 1590, 1500, 1260, 840, 745 cm^{-1}. MS: m/s 190 (M$^+$). Calc for C$_{12}$H$_{18}$Si: C, 75.72, H, 9.53, Found, C, 75.43, H, 9.61 %.

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