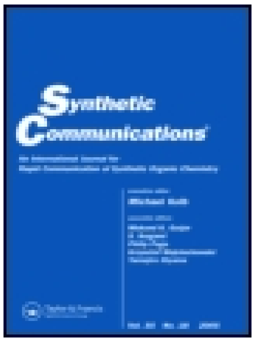

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STEREOSELECTIVE SYNTHESIS OF (E)-(2-ALKYL)- (1-SILYLVINYL) SELENIDES VIA HYDROZIRCONATION OF ALKYL SILYL ACETYLENES

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Abstract: Hydrozirconation of alkyl silyl acetylenes gives organozirconium complexes which reacted with arylselenenyl bromides to afford (E)-(1-silylvinyl)selenides in high yields.

Vicinal difunctional compounds containing selenium and metal have attracted special attention as important intermediates in various synthetic transformation [1-3]. Some methods have been developed to prepare these compounds by our and other laboratories. For example (2-metallovinyl) selenides can been synthesized stereoselectively by hydrozirconation[4], hydrostannation[5] or hydroboration[6] of acetyl selenides. (1-silylvinyl) selenides also are an important (1-metallovinyl) selenides. The preparation and application in synthesis of 1-arylseleno-1-silylethene has been reported[7-8]. But the preparation and application of the E-(2-alkyl)-(1-silylvinyl)selenides has not been reported by literature. We now describe

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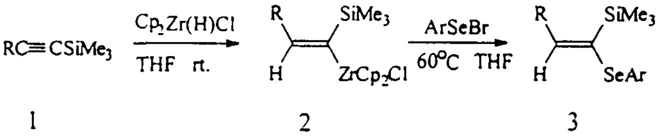
the preparation of E-(2-alkyl)-(1-silylvinyl) selenides via the hydrozirconation of alkyl silyl acetylenes and its application in synthesis of (Z)-(1,2-dialkylvinyl)silanes.

Hydrozirconation of alkyl silyl acetylenes 1 yield the silyl-substituted alkenyl zirconium complexes 2 [9] . We found that at room temperature the 2 do not react with aryl selenenyl bromides. At 60 ℃ the reaction can occur and give the corresponding E-(2-alkyl)-(1-silylvinyl) arylselenieds 3 in high yields. The results are summarized in the table.



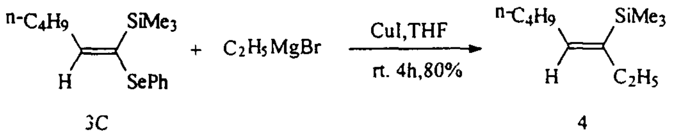
From the above fact, it indicated that 2 have higher stability than the 2-alkyl vinyl zirconium complexes[10]. This is due to the silyl having the ability of stabilizing the carbanions.

Because seleno group is easily substituted by various reagents[11], 3 acts as vinyl cation equivalent species. The experiment showed that 3 can stereoselectively coupled with Grignard reagents in the presence of CuI to give the (Z)-1,2-dialkyl vinyl silane.

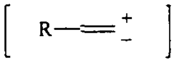
TABLE Compounds 3a-f:

Product	R	Ar	Yield(%)(a)
3a	n-C_6H_{13}	Ph	85
3b	n-C_6H_{13}	p-$CH_3C_6H_4$	87
3c	n-C_4H_9	Ph	80
3d(b)	CH_3OCH_2	Ph	80
3e(b)	CH_3OCH_2	m-$CH_3C_6H_4$	86
3f	Ph	Ph	81

(a) Isolated yield. (b) There is 35% regioisomers



Vinylsilane have been widely utilized in synthesis of natural products[12] by coupling with electrophiles such as acyl halides[13], alkenyl or aryl halides[14] as well as arenediazonium [15] et al. Therefore (1-silyl vinyl) selenides 3 can be regarded as the equivalent of the cation-anion synthon 5.



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The present method has advantages of readily available starting materials simple procectures and high yields. It provides a efficient and practical path for the synthesis of E-(1-silylvinyl) selenides.

Experiment Section

1H NMR Spectra were recorded on PMX-60 spectrometer, using $CDCl_3$ as the solvent with TMS as an internal standard. IR spectra were determined on PE-683 spectrophotometer.MS spectra were determined on HP5989A Spectrometer. Microanalyses were measured using a Yamaco MT-3 CHN micro-elemental analyser. THF was distilled from sodium benzophenone. All reactions were carried out under pure nitrogen.

A representative procedure for the synthesis of E-(1-silyl vinyl) arylselenides 3a-f: A mixture of Cp_2ZrCl_2 (1.0 mmol) and siylacetylenes (1.0 mmol) in THF (5.0 ml) was stirred at room temperature for 20 min. during which the mixture became a clear solution. Into the resulting solution was injected ArSeBr (1.0 mmol) in THF (4 ml) and the mixture was stirred at 60 ℃ for 5h. It was then diluted with light petroleum and stirred for a further 10 min. .The mixture was filtered through a short plug of silica gel. After evaporation of the filtrate the residue was purifed by preparative TLC on silica gel using light petroleum as eluent.

Synthesis of 4 : To the mixture of 3c (1.0 mmol) with CuI (1.0 mmol) in THF (10 ml) was added EtMgBr (1.2 mmol) .The mixture was stirred at 10 ℃ for 2h, then treated as above procedure.

Compound 3a IR (film)/cm^{-1}: 3080, 2990, 1590, 1480, 1250, 840. δ_H 6.95-7.60(m, 5H), 6.55 (t, 1H, J=7Hz),1.9-2.3 (m, 2H), 0.8-1.6 (m, 11H), 0.10 (s, 9H). MS. m/z 339 (5.6), 73 (100), 215 (20), 135 (8.6), 91 (4.0), 43 (7.1), 45 (6.9), 157 (3.2). Calc. for $C_{17}H_{28}SeSi$: C, 60.18, H, 8.26.Found: C, 60.20, H, 8.32%.

Compound 3b IR (film)/cm^{-1}: 3080, 2990, 1590, 1480, 1250, 840. δ_H: 7.33 (d, 2H, J=8Hz), 7.00 (d,2H,J=8Hz), 6.50 (t, 1H, J=7Hz),2.30 (s, 3H),1.9-2.30 (m,2H), 0.8-1.6 (m, 11H), 0.10 (s, 9H). Calc. for $C_{18}H_{30}SeSi$: C, 61.19, H, 8.50. Found: C, 61.10, H,8.32 %.

Compound 3c IR (film)/cm^{-1}: 3080, 2990, 1590, 1480, 1250, 840. δ_H 6.9-7.6 (m,5H), 6.50 (t,1H,J=7Hz),1.9-2.3 (m,2H),0.8-1.6 (m,7H),0.10 (s,9H). Calc. for $C_{15}H_{24}SeSi$: C, 57.88, H, 7.72.Found: C, 57.40, H, 7.65%.

Compound 3d IR (film)/cm^{-1}: 3080, 2930, 1580, 1480, 1250, 1120, 850.δ_H 6.9-7.4 (m,5H), 6.48 (t,1H,J=7Hz), 3.70 (d, 2H, J=7Hz),3.10 (s,3H),0.10 (s,9H). Calc. for $C_{13}H_{20}OSeSi$: C, 52.17, H, 6.69.Found: C, 51.98, H, 6.56%.

Compound 3e IR (film)/cm^{-1}: 2990, 2960, 1600, 1450, 1250, 1100 850.δ_H 6.9-7.6 (m,4H), 6.50 (t,1H,J=7Hz), 3.70 (d, 2H,J=7Hz),3.66 (s, 3h), 2.24 (s, 3H), 0.10 (s,9H). Calc. for $C_{14}H_{22}OSeSi$: C, 53.67, H, 7.03.Found: C, 53.89, H, 7.03%

Compound 3f IR (film)/cm^{-1} 3080, 2940, 1590, 1480, 1445, 1250, 1040, 840 .δ_H 6.8-7.6 (m,11H), 0.10 (s, 9H). Calc. for $C_{17}H_{20}SeSi$: C, 62.13, H, 6.04.Found: C, 62.03, H, 6.09%

Compound 4 b.p.89-91 °C/20mmHg, [59-63 °C]/3mmHg[16] IR: (film)/cm^{-1} 2975, 1611, 1450, 1250, 840, 747, 688. δ_H , 0.10 (s, 9H), 0.9-2.1 (m, 13 H),5.85 (t, 1H, J=7 Hz)

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