Heteroatom Chemistry
Volume 16, Number 7, 2005

A Facile Stereoselective Synthesis of (*E*)-α-Silylvinyl Sulfides via Hydromagnesiation of Alkynylsilanes

Mingzhong Cai,[1] Jun Xia,[1] and Pingping Wang[2]

[1]*Department of Chemistry, Jiangxi Normal University, Nanchang 330027, People's Republic of China*

[2]*Department of Chemistry, Jiujiang College, Jiujiang 332000, People's Republic of China*

Received 2 August 2005; revised 1 September 2005

ABSTRACT: *Hydromagnesiation of alkynylsilanes* **1** *in diethyl ether gave (Z)-α-silylvinyl Grignard reagents* **2**, *which reacted with arylsulfenyl chlorides* **3** *to afford stereoselectively (E)-α-silylvinyl sulfides* **4** *in good yields. (E)-α-Silylvinyl sulfides* **4** *could undergo the cross-coupling reactions with Grignard reagents in the presence of* $NiCl_2(PPh_3)_2$ *to give stereoselectively (Z)-1,2-disubstituted vinylsilanes* **5**. © 2005 Wiley Periodicals, Inc. Heteroatom Chem 16:644–647, 2005; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20165

INTRODUCTION

Difunctional group reagents, which have two different functional groups linked to the olefinic carbon atoms, for example, S-Cu [1], S-B [2], S-Sn [3], Si-Sn [4], and Si-Zr [5] 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 sulfides are important synthetic intermediates; the difunctional group reagents containing sulfur and silicon have attracted special attention as important intermediates in various synthetic transformations since the silyl and thioether functions exert an opposing polarization on the olefinic bond [6–12]. However, few convenient routes to (*E*)-2-alkyl-1-silylvinyl sulfides are known. For example, 1-trimethylsilyl vinyl sulfide has been synthesized by the addition of phenylsulfenyl chloride to vinyltrimethylsilane followed by dehydrohalogenation with DBU [6] or by the treatment of vinyl sulfides with LDA, followed by the reaction with chlorotrimethylsilane [7]. But these methods are not applicable to 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 sulfides [8]. Some other methods give (*Z*)-2-alkyl-1-silylvinyl sulfides [9,10]. Recently, Zhong et al. [13] reported the stereoselective synthesis of (*E*)-2-alkyl-1-silylvinyl sulfides via hydrozirconation of alkynylsilanes.

Hydromagnesiation has emerged as a unique hydrometallation with some attractive features such as the regioselectivity and stereoselectivity observed with alkynylsilanes [14]. Very recently, we have reported the stereoselective syntheses of (*E*)-α-selenenylvinylsilanes [15] and (*E*)-α-aryltellurenylvinylsilanes [16] via hydromagnesiation of alkynylsilanes. Herein, we wish to report that (*E*)-α-silylvinyl sulfides could be conveniently synthesized via the hydromagnesiation of alkynylsilanes, followed by the reaction with arylsulfenyl chlorides.

Correspondence to: Mingzhong Cai; e-mail: caimzhong@163.com.

Contract grant sponsor: National Natural Science Foundation of China.
Contract grant number: 20462002.
Contract grant sponsor: Natural Science Foundation of Jiangxi Province of China.
Contract grant number: 0420015.

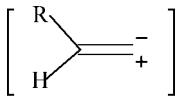
RESULTS AND DISCUSSION

Alkynylsilanes **1** were prepared according to the literature procedure [17]. Hydromagnesiation of alkynylsilanes **1** at 25°C in diethyl ether for 6 h gave (*Z*)-α-silylvinyl Grignard reagents **2**, which reacted with arylsulfenyl chlorides **3** to afford stereoselectively (*E*)-α-silylvinyl sulfides **4** in good yields (Scheme 1). The typical results are summarized in Table 1.

Investigations of the crude products **4** by ^{1}H-NMR spectroscopy (400 MHz) showed their isomeric purities by more than 97%. One olefinic proton signal of compounds **4a–i** splits characteristically into one triplet at $\delta = 6.23$–6.58 with coupling constant $J = 7.6$ Hz, which indicated that the hydromagnesiation to the alkynylsilanes had taken place with strong preference for the addition of the magnesium atom at the carbon adjacent to the silyl group.

(*E*)-α-Silylvinyl sulfides **4** are difunctional group reagents in which two synthetically versatile groups are linked to the same olefinic carbon atom and can be considered both as vinyl sulfides and vinylsilanes. It is known that vinyl sulfides couple with Grignard reagents in the presence of nickel(II)-phosphine complexes to give olefins, with predominant retention of configuration [18]. Phenyl vinyl sulfides containing a trimethylsilyl group in the β-position were coupled with Grignard reagents to synthesize stereospecifically monosubstituted *E*-vinylsilanes [19]. (*Z*)-α- Silylvinyl sulfides were coupled with Grignard reagents in the presence of $NiCl_2(PPh_3)_2$ to give stereoselectively (*E*)-1,2-disubstituted vinylsilanes [10]. (*E*)-α- Silylvinyl sulfides **4** could, in principle, afford (*Z*)-1,2-disubstituted vinylsilanes **5** (Scheme 2). With this aim, a study of $NiCl_2(PPh_3)_2$-catalyzed cross-coupling of **4a** and **4g** with methylmagnesium bromide was carried out; the corresponding (*Z*)-1,2-disubstituted vinylsilanes **5** were obtained in good yields according to Scheme 2.

Vinylsilanes have been widely utilized in the synthesis of natural products [20], by coupling with electrophiles such as acyl halides [21], alkenyl or aryl halides [22] as well as arenediazonium ion [23]. Therefore, (*E*)-α-silylvinyl sulfides **4** can be regarded as the equivalent of the cation–anion synthon **6**.



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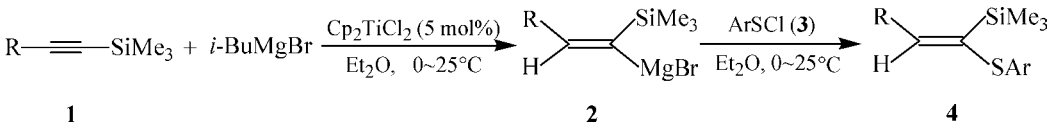
In summary, we have developed a new route to stereoselective synthesis of (*E*)-α-silylvinyl sulfides. Compared to the reported method [13], the present method has advantages of readily available and cheap starting materials instead of the expensive $Cp_2Zr(H)Cl$, straightforward and simple procedures, mild reaction conditions, and good yields.

EXPERIMENTAL

Diethyl ether was distilled from sodium immediately prior to use. THF was freshly distilled from sodium-benzophenone prior to its use. IR spectra were obtained on a Perkin-Elmer 683 instrument as neat films. ^{1}H-NMR spectra were recorded on a Bruker AC-400 (400 MHz) spectrometer using $CDCl_3$



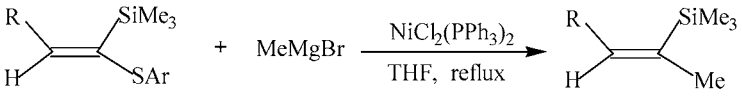
1 **2** **4**

SCHEME 1

TABLE 1 Synthesis of (*E*)-α-Silylvinyl Sulfides **4a–i**

Entry	*R*	*Ar*	*Product*	*Yield(%)*[a]
1	*n*-C_4H_9	Ph	**4a**	76
2	*n*-C_4H_9	4-$CH_3C_6H_4$	**4b**	70
3	*n*-C_4H_9	4-ClC_6H_4	**4c**	73
4	*i*-C_5H_{11}	4-$CH_3C_6H_4$	**4d**	67
5	*i*-C_5H_{11}	4-ClC_6H_4	**4e**	71
6	*n*-C_6H_{13}	Ph	**4f**	66
7	*n*-C_6H_{13}	4-$CH_3C_6H_4$	**4g**	62
8	*n*-C_6H_{13}	4-ClC_6H_4	**4h**	69
9	$PhCH_2$	Ph	**4i**	65

[a]Isolated yield based on the arylsulfenyl chloride **3** used.



4a: R = *n*-C_4H_9, Ar = Ph
4g: R = *n*-C_6H_{13}, Ar = 4-$CH_3C_6H_4$

5a: R = *n*-C_4H_9, Yield: 83%
5b: R = *n*-C_6H_{13}, Yield: 74%

SCHEME 2

as solvent. Mass spectra were determined on a Finnigan 8230 mass spectrometer. Microanalyses were measured using a Yanaco MT-3 CHN microelemental analyzer. Arylsulfenyl chlorides **3** were prepared according to the literature method [24]. Methylmagnesium bromide was purchased from Aldrich, and $NiCl_2(PPh_3)_2$ was prepared according to the procedure described by Venanzi [25].

General Procedure for the Synthesis of (E)-α-Silylvinyl Sulfides **4a–i**

To a solution of isobutylmagnesium bromide (2.5 mmol) 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 alkynylsilane **1** (2.0 mmol), and the mixture was stirred for 6 h at 25°C. After being cooled to 0°C a solution of arylsulfenyl chloride **3** (1.5 mmol) in Et_2O (2 mL) was added dropwise over 30 min with stirring, and the mixture was stirred for 2 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. NH_4Cl (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-Phenylsulfanyl-1-trimethylsilyl-1-hexene **4a**. IR (film): ν (cm^{-1}) 3070, 3051, 2960, 2865, 1585, 1481, 1456, 1250, 1020, 840, 742; ^1H NMR ($CDCl_3$): δ 7.28–7.14 (m, 5H), 6.52 (t, J = 7.6 Hz, 1H), 2.28–2.20 (m, 2H), 1.41–1.28 (m, 4H), 0.92 (t, J = 7.2 Hz, 3H), 0.14 (s, 9H); MS: *m/z* 264 (M^+, 17.2), 249 (33), 207 (26), 187 (27), 77 (19), 73 (100); Anal. found: C, 67.89; H, 8.85. $C_{15}H_{24}SiS$ calcd: C, 68.18; H, 9.09.

(E)-1-(4-Methylphenyl)sulfanyl-1-trimethylsilyl-1-hexene **4b**. IR (film): ν (cm^{-1}) 3071, 3019, 2958, 2925, 1580, 1491, 1464, 1382, 1248, 839, 805, 756; ^1H NMR ($CDCl_3$): δ 7.16 (d, J = 8.0 Hz, 2H), 7.07 (d, J = 8.0 Hz, 2H), 6.36 (t, J = 7.6 Hz, 1H), 2.30 (s, 3H), 2.25–2.17 (m, 2H), 1.38–1.20 (m, 4H), 0.89 (t, J= 7.2 Hz, 3H), 0.15 (s, 9H); MS: *m/z* 278 (M^+, 13), 263 (29), 187 (22), 91 (31), 73 (100); Anal. found: C, 68.78; H, 9.19. $C_{16}H_{26}SiS$ calcd: C, 69.06; H, 9.35.

(E)-1-(4-Chlorophenyl)sulfanyl-1-trimethylsilyl-1-hexene **4c**. IR (film): ν (cm^{-1}) 3076, 2956, 2928, 2873, 1576, 1474, 1389, 1249, 1093, 1012, 839, 735; ^1H NMR ($CDCl_3$): δ 7.07 (d, J = 8.0 Hz, 2H), 7.02 (d, J = 8.0 Hz, 2H), 6.39 (t, J = 7.6 Hz, 1H), 2.15–2.07 (m, 2H), 1.28–1.18 (m, 4H), 0.78 (t, J = 7.2 Hz, 3H), −0.01 (s, 9H); MS: *m/z* 299 (M^+, 10.5), 284 (47), 187 (29), 73 (100); Anal. found: C, 60.25; H, 7.53. $C_{15}H_{23}ClSiS$ calcd: C, 60.20; H, 7.69.

(E)-1-(4-Methylphenyl)sulfanyl-1-trimethylsilyl-5-methyl-1-thexene **4d**. IR (film): ν (cm^{-1}) 3071, 3019, 2956, 2869, 1578, 1490, 1467, 1384, 1249, 839, 806, 757; ^1H NMR ($CDCl_3$): δ 7.04 (d, J = 8.0 Hz, 2H), 6.95 (d, J = 8.0 Hz, 2H), 6.23 (t, J = 7.6 Hz, 1H), 2.18 (s, 3H), 2.14–2.07 (m, 2H), 1.46–1.41 (m, 1H), 1.18–1.10 (m, 2H), 0.78 (d, J = 6.8 Hz, 6H), 0.03 (s, 9H); MS: *m/z* 292 (M^+, 8.3), 277 (47), 201 (35), 91 (25), 73 (100); Anal. found: C, 69.59; H, 9.42. $C_{17}H_{28}SiS$ calcd: C, 69.86; H, 9.59.

(E)-1-(4-Chlorophenyl)sulfanyl-1-trimethylsilyl-5-methyl-1-hexene **4e**. IR (film): ν (cm^{-1}) 3076, 2958, 2870, 1630, 1577, 1474, 1385, 1249, 1092, 1012, 870, 840, 816, 756; ^1H NMR ($CDCl_3$): δ 7.09 (d, J = 8.0 Hz, 2H), 7.02 (d, J = 8.0 Hz, 2H), 6.38 (t, J = 7.6 Hz, 1H), 2.15–2.08 (m, 2H), 1.46–1.39 (m, 1H), 1.18-1.11 (m, 2H), 0.76 (d, J = 6.8 Hz, 6H), 0.01 (s, 9H); MS: *m/z* 313 (M^+, 14), 298 (40), 201 (26), 73 (100); Anal. found: C, 61.07; H, 7.80. $C_{16}H_{25}ClSiS$ calcd: C, 61.34; H, 7.99.

(E)-1-Phenylsulfanyl-1-trimethylsilyl-1-octene **4f**. IR (film): ν (cm^{-1}) 3070, 3022, 2959, 2920, 2865, 1579, 1490, 1468, 1249, 1020, 839, 740; ^1H NMR ($CDCl_3$): δ 7.26–7.14 (m, 5H), 6.51 (t, J = 7.6 Hz, 1H), 2.26–2.19 (m, 2H), 1.46–1.25 (m, 8H), 0.89 (t, J = 7.2 Hz, 3H), 0.14 (s, 9H); MS: *m/z* 292 (M^+, 6.7), 277 (39), 215 (23), 77 (34), 73 (100); Anal. found: C, 69.57; H, 9.62. $C_{17}H_{28}SiS$ calcd: C, 69.86; H, 9.59.

(E)-1-(4-Methylphenyl)sulfanyl-1-trimethylsilyl-1-octene **4g**. IR (film): ν (cm^{-1}) 3072, 3019, 2956, 2923, 1579, 1491, 1456, 1249, 840, 806, 758; ^1H NMR ($CDCl_3$): δ 7.17 (d, J = 8.0 Hz, 2H), 7.08 (d, J= 8.0 Hz, 2H), 6.37 (t, J = 7.6 Hz, 1H), 2.31 (s, 3H), 2.25–2.18 (m, 2H), 1.43–1.22 (m, 8H), 0.91 (t, J = 7.2 Hz, 3H), 0.16 (s, 9H); MS: m/z 306 (M^+, 16), 291 (43), 215 (30), 91 (27), 73 (100); Anal. found: C, 70.33; H, 9.74. $C_{18}H_{30}SiS$ calcd: C, 70.59; H, 9.81.

(E)-1-(4-Chlorophenyl)sulfanyl-1-trimethylsilyl-1-octene **4h**. IR (film): ν (cm^{-1}) 3067, 3022, 2957, 2928, 2857, 1577, 1474, 1388, 1249, 1093, 839, 759, 696; ^1H NMR ($CDCl_3$): δ 7.22 (d, J = 8.0 Hz, 2H), 7.17 (d, J = 8.0 Hz, 2H), 6.54 (t, J = 7.6 Hz, 1H), 2.29–2.20 (m, 2H), 1.44–1.23 (m, 8H), 0.90 (t, J = 7.2 Hz, 3H), 0.14 (s, 9H); MS: m/z 327 (M^+, 5.8), 312 (38), 215 (19), 73 (100); Anal. found: C, 62.11; H, 8.04. $C_{17}H_{27}ClSiS$ calcd: C, 62.39; H, 8.26.

(E)-1-Phenylsulfanyl-1-trimethylsilyl-3-phenyl-1-propene **4i**. IR (film): ν (cm^{-1}) 3070, 3023, 2956, 2859, 1615, 1578, 1496, 1249, 839, 735, 690; ^1H NMR ($CDCl_3$): δ 7.51–7.08 (m, 10H), 6.58 (t, J = 7.6 Hz, 1H), 3.56 (d, J = 7.6 Hz, 2H), 0.11 (s, 9H); MS: m/z 298 (M^+, 9.4), 283 (41), 221 (32), 207 (29), 91 (25), 77 (36), 73 (100); Anal. found: C, 72.21; H, 7.25. $C_{18}H_{22}SiS$ calcd: C, 72.48; H, 7.38.

General Procedure for the Synthesis of (Z)-1,2-Disubstituted Vinylsilanes **5a–b**

A 3.0 M THF solution of MeMgBr (15 mmol) was slowly added, under Ar, to a stirred suspension of $NiCl_2(PPh_3)_2$ (0.03 mmol) and the (*E*)-α-silylvinyl sulfide **4** (1 mmol) in THF (6 mL) at room temperature. The mixture was stirred at reflux temperature for 48 h. After being cooled to room temperature, the mixture was quenched with sat. aq. NH_4Cl (15 mL) and extracted with Et_2O (2 × 30 mL). The organic layer was washed with water (3 × 10 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.

(Z)-2-Trimethylsilyl-2-heptene. IR (film): ν (cm^{-1}) 2958, 2860, 1620, 1466, 1249, 838; ^1H NMR ($CDCl_3$): δ 5.84 (t, J = 7.2 Hz, 1H), 2.16–2.05 (m, 2H), 1.74 (s, 3H), 1.37–1.21 (m, 4H), 0.89 (t, J = 7.2 Hz, 3H), 0.11 (s, 9H); Anal. found: C, 70.36; H, 12.79. $C_{10}H_{22}Si$ calcd: C, 70.59; H, 12.94.

(Z)-2-Trimethylsilyl-2-nonene. IR (film): ν (cm^{-1}) 2926, 2856, 1607, 1458, 1248, 837; ^1H NMR ($CDCl_3$): δ 5.81 (t, J = 7.2 Hz, 1H), 2.17–2.03 (m, 2H), 1.73 (s, 3H), 1.47–1.22 (m, 8H), 0.88 (t, J = 7.2 Hz, 3H), 0.11 (s, 9H); Anal. found: C, 72.51; H, 13.02. $C_{12}H_{26}Si$ calcd: C, 72.73; H, 13.13.

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