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Novel stereoselective synthesis of 1,3-dienylsilanes via hydromagnesiation reaction of alkynylsilanes

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Abstract

Hydromagnesiation of alkynylsilanes gives (*Z*)-α-silylvinyl Grignard reagents, which undergo palladium-catalyzed cross-coupling reactions with alkenyl halides to afford stereoselectively 1,3-dienylsilanes in good yields.

Keywords: Alkynylsilane; Hydromagnesiation; 1,3-Dienylsilane; Cross-coupling reaction; Stereoselective synthesis

1. Introduction

The stereocontrolled synthesis of conjugated dienes is of great interest in organic chemistry since such dienes are often encountered in natural compounds, such as insect sex pheromones [1], and are also valuable intermediates. The synthesis of dienes for use in the Diels–Alder reaction is still an important challenge in organic synthesis [2] although other elegant uses of these compounds have been developed [3].

The synthesis of 1,3-dienes containing functional groups is of considerable interest in recent years. The stereoselective synthesis of 1,3-dienyl sulfides [4], 1,3-dienyl selenides [5] has already been described in the literature. Silyl-substituted 1,3-dienes are versatile building blocks in organic synthesis and many methods can be used for the stereoselective synthesis of 1,3-dienes having a silyl group at the terminal carbon atom [6]. However, to date, the stereoselective synthesis of 1,3-dienes having a silyl group at the internal carbon atom has received less attention [7].

The transition metal-catalyzed cross-coupling reaction is a highly versatile method for carbon–carbon bond formation and has been widely used as synthetic tool [8]. Hydromagnesiation has emerged as a unique hydrometallation with some attractive features, such as the high regioselectivity and stereoselectivity observed with alkynylsilanes [9]. We now wish to report that 1,3-dienylsilanes could be synthesized by hydromagnesiation of the alkynylsilanes, followed by treatment with alkenyl halides in the presence of $Pd(PPh_3)_4$ catalyst.

2. Results and discussion

Alkynylsilanes **1** were prepared according to the literature [10]. Hydromagnesiation of alkynylsilanes **1** at 25 °C in ether for 6 h gave (*Z*)-α-silylvinyl Grignard reagents **2**, which reacted with alkenyl halides **3** in THF in the presence of $Pd(PPh_3)_4$ catalyst to afford stereoselectively 1,3-dienylsilanes **4**. The yields were 76–89% (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 compounds **4a**–**j** but **4c** splits characteristically into one triplet at δ 5.89–6.40 with coupling constant $J = 7.0$ 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. It is well documented that the cross-coupling reaction of vinyl Grignard reagents with alkenyl halides occurs with the configuration

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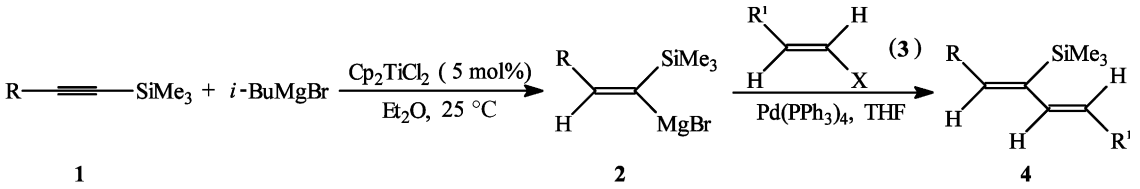

1 2 4

Scheme 1.

retention of both the starting vinyl Grignard reagents and the alkenyl halides [11]. In addition, ^{1}H-NMR spectra of **4a**–**j** but **4c** give rise to a doublet at δ 5.97–6.55 with a coupling constant of 15.0–16.4 Hz, which showed that the cross-coupling reaction had proceeded with the configuration retention of the alkenyl halides. The results of the reaction are summarized in Table 1.

In conclusion, we have developed a novel route to the stereoselective synthesis of 1,3-dienylsilanes **4**. Compared to the reported methods [7], the present method has the advantages of readily available starting materials, simple procedures, mild reaction conditions and good yields. Investigations into the synthetic applications of 1,3-dienylsilanes **4** are currently in progress.

3. Experimental details

^{1}H-NMR spectra were recorded on an AZ-300 MHz spectrometer with TMS as an internal standard. IR spectra were determined on an FTS-185 instrument as neat films. Mass spectra were obtained on a Finigan 8239 mass spectrometer. Microanalyses were measured using a Yanaco MT-3 CHN microelemental analyser. Alkenyl halides were prepared according to the literature [12]. THF was freshly distilled from sodium-benzophenone prior to its use. Diethyl ether was treated with lithium aluminum hydride and distilled before use.

Table 1
Synthesis of 1,3-dienylsilanes **4a**–**j**

Entry	R	R^1	X	Product [a]	Yield [b] (%)
1	n-C_4H_9	n-C_4H_9	I	**4a**	80
2	n-C_4H_9	Ph	I	**4b**	84
3	n-C_4H_9	Ph	Br	**4b**	77
4	n-C_4H_9	CH_3OCH_2	I	**4c**	76
5	n-C_4H_9	n-C_6H_{13}	Br	**4d**	79
6	i-C_5H_{11}	n-C_4H_9	I	**4e**	89
7	i-C_5H_{11}	Ph	I	**4f**	81
8	n-C_6H_{13}	n-C_4H_9	I	**4g**	85
9	n-C_6H_{13}	Ph	I	**4h**	78
10	n-C_6H_{13}	n-C_6H_{13}	Br	**4i**	87
11	$PhCH_2$	n-C_4H_9	I	**4j**	76

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

3.1. General procedure for the synthesis of 1,3-dienylsilanes *4a–j*

To a solution of isobutylmagnesium bromide (4.5 mmol) in diethyl ether (7 ml) was added Cp_2TiCl_2 (50 mg, 0.2 mmol) at 0 °C under Ar, and the mixture was stirred for 30 min at that temperature. To this solution was added alkynylsilane **1** (4.0 mmol), and the mixture was stirred for 6 h at 25 °C. After removal of the ether under reduced pressure (2 h, r.t. (2 Torr)$^{-1}$), the residue was dissolved in THF (6 ml), cooled to 0 °C, and $Pd(PPh_3)_4$ (0.232 g, 0.2 mmol) and alkenyl halide (4.4 mmol) were added with stirring. The reaction mixture was brought to 30 °C gradually and stirred for 5 h, quenched with sat. aq. NH_4Cl (25 ml) and extracted with Et_2O (2 × 30 ml). The organic layer was washed with sat. aq. NH_4Cl (20 ml) and water (3 × 30 ml) 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.

3.1.1. (5Z,7E)-6-Trimethylsilyl-5,7-dodecadiene (*4a*)

IR (film): ν (cm^{-1}) 2957, 2859, 1595, 1466, 1378, 1249, 962, 837. ^{1}H-NMR ($CDCl_3$): δ 6.10 (t, J = 7.0 Hz, 1H), 5.97 (d, J = 15.4 Hz, 1H), 5.48 (m, 1H), 2.18–1.95 (m, 4H), 1.56–1.19 (m, 8H), 0.98–0.78 (m, 6H), 0.15 (s, 9H). MS: m/z 238 [M$^+$, 4.6], 73 (100). Anal. Found: C, 75.44; H, 12.49. $C_{15}H_{30}Si$ Calc.: C, 75.63; H, 12.61%.

3.1.2. (1E,3Z)-1-Phenyl-3-trimethylsilyl-1,3-octadiene (*4b*)

IR (film): ν (cm^{-1}) 3059, 3024, 2957, 2859, 1619, 1587, 1491, 1447, 1249, 960, 840, 746. ^{1}H-NMR ($CDCl_3$): δ 7.46–7.18 (m, 5H), 6.84 (d, J = 16.2 Hz, 1H), 6.51 (d, J = 16.4 Hz, 1H), 6.40 (t, J = 7.0 Hz, 1H), 2.26 (m, 2H), 1.64–1.17 (m, 4H), 0.88 (t, J = 5.4 Hz, 3H), 0.16 (s, 9H). MS: m/z 258 [M$^+$, 1.5], 73 (100). Anal. Found: C, 79.23; H, 10.16. $C_{17}H_{26}Si$ Calc.: C, 79.07; H, 10.08%.

3.1.3. (2E,4Z)-1-Methoxy-4-trimethylsilyl-2,4-nonadiene (*4c*)

IR (film): ν (cm^{-1}) 2956, 2858, 1639, 1606, 1455, 1377, 1249, 1118, 967, 838. ^{1}H-NMR ($CDCl_3$): δ 6.29–6.17 (m, 2H), 5.60 (m, 1H), 3.92 (d, J = 6.3 Hz, 2H), 3.33 (s, 3H), 2.17 (m, 2H), 1.47–1.24 (m, 4H), 0.89 (t,

$J = 5.4$ Hz, 3H), 0.18 (s, 9H). MS: *m/z* 226 [M^+, 4.5], 73 (100). Anal. Found: C, 68.89; H, 11.41. $C_{13}H_{26}OSi$ Calc.: C, 69.03; H, 11.50%.

*3.1.4. (5Z,7E)-6-Trimethylsilyl-5,7-tetradecadiene (**4d**)*

IR (film): ν (cm^{-1}) 2926, 2857, 1621, 1596, 1465, 1378, 1248, 963, 838. ^{1}H-NMR ($CDCl_3$): δ 6.16 (t, $J =$ 7.0 Hz, 1H), 6.01 (d, $J = 15.0$ Hz, 1H), 5.53 (m, 1H), 2.39–2.01 (m, 4H), 1.67–1.18 (m, 12H), 1.01–0.79 (m, 6H), 0.17 (s, 9H). MS: *m/z* 266 [M^+, 2.7], 73 (100). Anal. Found: C, 76.44; H, 12.57. $C_{17}H_{34}Si$ Calc.: C, 76.69; H, 12.78%.

*3.1.5. (5Z,7E)-2-Methyl-6-trimethylsilyl-5,7-dodecadiene (**4e**)*

IR (film): ν (cm^{-1}) 2956, 2872, 1595, 1467, 1384, 1366, 1249, 963, 837. ^{1}H-NMR ($CDCl_3$): δ 6.09 (t, $J =$ 7.0 Hz, 1H), 5.97 (d, $J = 15.3$ Hz, 1H), 5.48 (m, 1H), 2.19–1.94 (m, 4H), 1.60–1.21 (m, 7H), 0.95–0.77 (m, 9H), 0.15 (s, 9H). MS: *m/z* 252 [M^+, 3.7], 73 (100). Anal. Found: C, 76.31; H, 12.65. $C_{16}H_{32}Si$ Calc.: C, 76.19; H, 12.70%.

*3.1.6. (1E,3Z)-1-Phenyl-3-trimethylsilyl-7-methyl-1,3-octadiene (**4f**)*

IR (film): ν (cm^{-1}) 3060, 3024, 2955, 2869, 1596, 1570, 1494, 1466, 1384, 1366, 1248, 960, 840. ^{1}H-NMR ($CDCl_3$): δ 7.48–7.19 (m, 5H), 6.82 (d, $J = 16.0$ Hz, 1H), 6.55 (d, $J = 15.4$ Hz, 1H), 5.89 (t, $J = 7.0$ Hz, 1H), 2.37–2.18 (m, 2H), 1.70–1.24 (m, 3H), 0.89 (d, $J = 6.7$ Hz, 6H), 0.16 (s, 9H). MS: *m/z* 272 [M^+, 14.8], 73 (100). Anal. Found: C, 79.22; H, 10.13. $C_{18}H_{28}Si$ Calc.: C, 79.41; H, 10.29%.

*3.1.7. (5E,7Z)-7-Trimethylsilyl-5,7-tetradecadiene(**4g**)*

IR (film): ν (cm^{-1}) 2957, 2856, 1606, 1465, 1378, 1248, 963, 837. ^{1}H-NMR ($CDCl_3$): δ 6.12 (t, $J = 7.0$ Hz, 1H), 6.01 (d, $J = 15.0$ Hz, 1H), 5.49 (m, 1H), 2.23–1.97 (m, 4H), 1.59–1.18 (m, 12H), 0.98–0.78 (m, 6H), 0.17 (s, 9H). MS: *m/z* 266 [M^+, 5.2], 73 (100). Anal. Found: C, 76.45; H, 12.57. $C_{17}H_{34}Si$ Calc.: C, 76.69; H, 12.78%.

*3.1.8. (1E,3Z)-1-Phenyl-3-trimethylsilyl-1,3-decadiene (**4h**)*

IR (film): ν (cm^{-1}) 3059, 3024, 2956, 2856, 1619, 1587, 1492, 1447, 1248, 960, 839. ^{1}H-NMR ($CDCl_3$): δ 7.49–7.18 (m, 5H), 6.79 (d, $J = 16.2$ Hz, 1H), 6.54 (d, $J = 15.5$ Hz, 1H), 6.38 (t, $J = 7.0$ Hz, 1H), 2.40–2.20 (m, 2H), 1.69–1.20 (m, 8H), 0.88 (t, $J = 5.7$ Hz, 3H), 0.19 (s, 9H). MS: *m/z* 286 [M^+, 1.6], 73 (100). Anal. Found: C, 79.54; H, 10.37. $C_{19}H_{30}Si$ Calc.: C, 79.72; H, 10.49%.

*3.1.9. (7Z,9E)-8-Trimethylsilyl-7,9-hexadecadiene (**4i**)*

IR (film): ν (cm^{-1}) 2957, 2856, 1606, 1466, 1248, 962, 837. ^{1}H-NMR ($CDCl_3$): δ 6.14 (t, $J = 7.0$ Hz, 1H), 6.02 (d, $J = 15.0$ Hz, 1H), 5.49 (m, 1H), 2.26–1.98 (m, 4H), 1.51–1.24 (m, 16H), 0.98–0.79 (m, 6H), 0.18 (s, 9H). MS: *m/z* 294 [M^+, 3.8], 73 (100). Anal. Found: C, 77.32; H, 12.76. $C_{19}H_{38}Si$ Calc.: C, 77.55; H, 12.93%.

*3.1.10. (2Z,4E)-1-Phenyl-3-trimethylsilyl-2,4-nonadiene (**4j**)*

IR (film): ν (cm^{-1}) 3058, 3023, 2859, 1596, 1493, 1446, 1249, 963, 838. ^{1}H-NMR ($CDCl_3$): δ 7.48–7.17 (m, 5H), 6.21 (t, $J = 7.0$ Hz, 1H), 5.99 (d, $J = 15.6$ Hz, 1H), 5.51 (m, 1H), 3.56 (d, $J = 7.2$ Hz, 2H), 2.21–1.98 (m, 2H), 1.55–1.19 (m, 4H), 0.89 (t, $J = 5.4$ Hz, 3H), 0.15 (s, 9H). MS: *m/z* 272 [M^+, 1.8], 73 (100). Anal. Found: C, 79.23; H, 10.14. $C_{18}H_{28}Si$ Calc.: C, 79.41; H, 10.29%.

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