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A facile stereoselective synthesis of (*E*)-1,2-disubstituted vinylstannanes via hydromagnesiation of alkylarylacetylenes

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Abstract

Hydromagnesiation of alkylarylacetylenes **1** in diethyl ether gave (*E*)-α-arylvinyl Grignard reagents **2**, which reacted with trialkylstannyl chlorides **3** in diethyl ether to afford stereoselectively (*E*)-1,2-disubstituted vinylstannanes **4** in high yields.

Keywords: Hydromagnesiation; Alkylarylacetylene; Vinyl Grignard reagent; Tin; Vinylstannane; Stereoselective synthesis

1. Introduction

Vinylstannanes are pivotal intermediates in a wide range of carbon–carbon bond forming reactions [1]. Due to their synthetic utility, a variety of methods have been developed for their preparation including those involving carbonyl addition chemistry [2]; transmetallation of vinylmetallic species [3]; metallometallation of alkynes [4]; and the hydrostannylation of alkynes induced by either radical initiators [5] or Lewis acid [6] or transition metal catalysts [7]. The radical-induced procedure often gives a mixture of the *trans*- and *cis*-hydrostannylation products, since the isomerization of the alkenyltin products occurs in the presence of tin radicals [8]. The transition metal catalyzed hydrostannylation reaction of alkynes proceeds via the *cis*-hydrostannylation pathway [7]. Hydromagnesiation has emerged as a unique hydrometallation with some attractive features such as the high regioselectivity and stereoselectivity observed with alkylarylacetylenes [9]. Recently, we have reported the stereoselective syntheses of (*E*)-disubstituted alkenes, (*E*)-α-selenenylvinylsilanes and (*E*)-allylic alcohols via the hydromagnesiation of alkynylsilanes [10]. Herein, we wish to report that (*E*)-1,2-disubstituted vinylstannanes could be conveniently synthesized via the hydromagnesiation of alkylarylacetylenes, followed by the reaction with trialkylstannyl chlorides.

2. Results and discussion

Alkylarylacetylenes **1** were prepared according to the literature procedure [11]. Hydromagnesiation of alkylarylacetylenes **1** at 25 °C in diethyl ether for 1 h gave (*E*)-α-arylvinyl Grignard reagents **2**, which reacted with trialkylstannyl chlorides **3** in ether to afford stereoselectively (*E*)-1,2-disubstituted vinylstannanes **4** in high yields (Scheme 1). Interestingly, the intermediates **2** in THF were found to possess very low reactivity with trialkylstannyl chlorides and only trace of products **4** were obtained at 60 °C after 8 h. Even in the presence of CuI, the Mg/Sn exchange reaction in THF proceeded slowly at room temperature and the yields were less than 15% after 24 h. However, when diethyl ether was used as the solvent, the Mg/Sn exchange reaction proceeded smoothly at room temperature and the corresponding (*E*)-1,2-disubstituted vinylstannanes were

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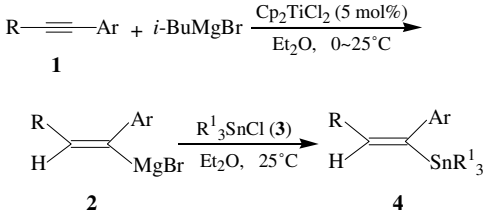


Scheme 1.

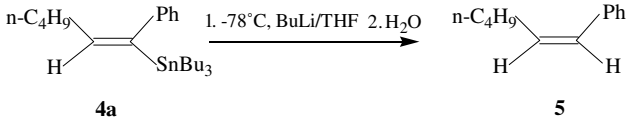
obtained in high yields. The typical results are summarized in Table 1.

Investigations of the crude products **4** by ^{1}H NMR spectroscopy (400 MHz) showed their isomeric purities of more than 97%. One olefinic proton signal of compounds **4a**–**h** splits characteristically into one triplet at $\delta = 5.73$–5.84 with coupling constant $J = 7.0$ Hz, which indicated that the hydromagnesiation to the alkylarylacetylenes had taken place with strong preference for the addition of the magnesium atom at the carbon adjacent to the aryl group. We observed that the Mg/Sn exchange reaction on intermediates **2** occurs with total retention of the configuration. The configuration of compound **4a** could be confirmed from compound **5** which was obtained by treatment of **4a** with *n*-butyllithium in THF followed by hydrolysis, a reaction which occurs stereoselectively (Scheme 2) [12]. The stereochemistry of compound **5** was easily established, since ^{1}H NMR spectrum (400 MHz) of **5** gives rise to a doublet at $\delta = 6.45$ with a coupling constant of 11.6 Hz, which is consistent with a *Z*-configuration.

In summary, our results showed that the hydromagnesiation–stannylation sequence of the alkylarylacetylenes has the advantages of readily available starting materials, straightforward and simple procedures, mild reaction conditions, and high yields.

3. Experimental

Diethyl ether was distilled from sodium immediately prior to 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 $CDCl_3$ as solvent. Mass spectra were determined on a Finnigan 8230 mass spectrometer. Microanalyses were measured using a Yanaco MT-3 CHN microelemental analyzer.



Scheme 2.

3.1. General procedure for the synthesis of (*E*)-1,2-disubstituted vinylstannanes *4a–h*

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 alkylarylacetylene **1** (4.0 mmol) and the mixture was stirred for 1 h at 25 °C. Then, a solution of trialkylstannyl chloride **3** (5.0 mmol) in diethyl ether (2 ml) was added dropwise over 20 min at 0 °C and the mixture was stirred for 2 h at 25 °C, quenched with sat. aq NH_4Cl (25 ml) and extracted with Et_2O (2×40 ml). The organic layer was washed with sat. aq NH_4Cl (25 ml) and water (3×30 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 (for **4a**–**f**) or light petroleum–diethyl ether (20:1) (for **4g**–**h**) as eluent.

3.1.1. (*E*)-1-Phenyl-1-tributylstannyl-1-hexene (*4a*)

IR(film): ν (cm^{-1}) 3073, 2957, 2926, 2854, 1593, 1571, 1486, 1464, 1376, 1071, 700. ^{1}H NMR: δ 7.30–6.94 (m, 5H), 5.76 (t, $J = 7.0$ Hz, 1H), 2.15–2.02 (m, 2H), 1.56–1.24 (m, 16H), 0.97–0.83 (m, 18H). MS: *m/z* 449 (M^+, 2.4), 393 (100), 392 (51), 391 (82), 389 (49), 337(43), 279 (44), 117 (64), 91 (44). Anal. Calc. for $C_{24}H_{42}Sn$: C, 64.14; H, 9.35. Found: C, 63.87; H, 9.18%.

3.1.2. (*E*)-1-Phenyl-1-trimethylstannyl-1-hexene (*4b*)

IR(film): ν (cm^{-1}) 3073, 2957, 2924, 2872, 1593, 1572, 1487, 1466, 1187, 856, 764, 700. ^{1}H NMR: δ 7.32–6.96

Table 1
Synthesis of (*E*)-1,2-disubstituted vinylstannanes **4a**–**h**

Entry	R	Ar	R^1	Product	Yield (%)[a]
1	*n*-C_4H_9	Ph	*n*-C_4H_9	**4a**	87
2	*n*-C_4H_9	Ph	CH_3	**4b**	90
3	*n*-C_4H_9	4-ClC_6H_4	*n*-C_4H_9	**4c**	82
4	*n*-C_4H_9	4-ClC_6H_4	CH_3	**4d**	85
5	*n*-C_6H_{13}	Ph	*n*-C_4H_9	**4e**	88
6	*n*-C_6H_{13}	Ph	CH_3	**4f**	91
7	*n*-C_6H_{13}	4-$CH_3OC_6H_4$	*n*-C_4H_9	**4g**	84
8	*n*-C_6H_{13}	4-$CH_3OC_6H_4$	CH_3	**4h**	86

[a]Isolated yield based on the alkylarylacetylene **1** used.

(m, 5H), 5.81 (t, J=7.0 Hz, 1H), 2.09–2.03 (m, 2H), 1.39–1.24 (m, 4H), 0.86 (t, J=6.8 Hz, 3H), 0.13 (s, 9H). MS: *m/z* 323 (M^+, 4.3), 309 (81), 307 (75), 117 (100), 115 (62), 91(67), 41 (37). Anal. Calc. for $C_{15}H_{24}Sn$: C, 55.73; H, 7.43. Found: C, 55.52; H, 7.26%.

*3.1.3. (E)-1-(4-Chlorophenyl)-1-tributylstannyl-1-hexene (**4c**)*

IR(film): ν (cm^{-1}) 3076, 2925, 2871, 1607, 1587, 1485, 1464, 1377, 1091, 1014, 869, 844, 690. ^1H NMR: δ 7.24 (d, J=8.4 Hz, 2H), 6.86 (d, J=8.4 Hz, 2H), 5.77 (t, J=7.0 Hz, 1H), 2.05–1.99 (m, 2H), 1.49–1.24 (m, 16H), 0.95–0.83 (m, 18H). MS: *m/z* 483 (M^+, 1.2), 427 (87), 425 (63), 179 (84), 177 (100), 175 (67), 151 (79), 125 (71), 115 (74). Anal. Calc. for $C_{24}H_{41}ClSn$: C, 59.63; H, 8.49. Found: C, 59.47; H, 8.32%.

*3.1.4. (E)-1-(4-Chlorophenyl)-1-trimethylstannyl-1-hexene (**4d**)*

IR(film): ν (cm^{-1}) 3075, 2957, 2858, 1609, 1588, 1485, 1466, 1187, 1091, 1014, 871, 844, 816, 768. ^1H NMR: δ 7.29 (d, J=8.4 Hz, 2H), 6.90 (d, J=8.4 Hz, 2H), 5.84 (t, J=7.0 Hz, 1H), 2.08–2.01 (m, 2H), 1.40–1.25 (m, 4H), 0.89 (t, J=6.8 Hz, 3H), 0.15 (s, 9H). MS: *m/z* 358 (M^+, 7.8), 343 (100), 341 (77), 339 (41), 165 (45), 151 (78), 115 (52). Anal. Calc. for $C_{15}H_{23}ClSn$: C, 50.42; H, 6.44. Found: C, 50.20; H, 6.23%.

*3.1.5. (E)-1-Phenyl-1-tributylstannyl-1-octene (**4e**)*

IR(film): ν (cm^{-1}) 3073, 3012, 2924, 2857, 1604, 1593, 1572, 1487, 1464, 1377, 1071, 873, 757, 700. ^1H NMR: δ 7.30–6.94 (m, 5H), 5.78 (t, J=7.0 Hz, 1H), 2.09–2.03 (m, 2H), 1.51–1.22 (m, 20H), 0.93–0.86 (m, 18H). MS: *m/z* 477 (M^+, 1.3), 421 (94), 419 (73), 307 (46), 179 (56), 177(61), 117 (100), 91 (79). Anal. Calc. for $C_{26}H_{46}Sn$: C, 65.41; H, 9.64. Found: C, 65.22; H, 9.47%.

*3.1.6. (E)-1-Phenyl-1-trimethylstannyl-1-octene (**4f**)*

IR(film): ν (cm^{-1}) 3073, 2924, 2855, 1607, 1594, 1572, 1486, 1466, 1378, 1188, 852, 765, 700. ^1H NMR: δ 7.32–6.95 (m, 5H), 5.81 (t, J=7.0 Hz, 1H), 2.08–2.02 (m, 2H), 1.39–1.21 (m, 8H), 0.88 (t, J=6.8 Hz, 3H), 0.13 (s, 9H). MS: *m/z* 351 (M^+, 2.8), 337 (57), 335 (54), 117 (100), 115 (59), 104 (47), 91(67). Anal. Calc. for $C_{17}H_{28}Sn$: C, 58.12; H, 7.98. Found: C, 57.87; H, 7.82%.

*3.1.7. (E)-1-(4-Methoxyphenyl)-1-tributylstannyl-1-octene (**4g**)*

IR(film): ν (cm^{-1}) 3072, 2925, 2875, 1600, 1505, 1464, 1376, 1243, 1041, 863, 824, 723. ^1H NMR: δ 6.87–6.81 (m, 4H), 5.73 (t, J=7.0 Hz, 1H), 3.81 (s, 3H), 2.09–2.02 (m, 2H), 1.49–1.20 (m, 20H), 0.94–0.84 (m, 18H). MS: *m/z* 508 (M^+, 1.2), 451 (19), 179 (19), 177 (24), 175 (18), 147(55), 121 (100), 41 (36). Anal. Calc. for $C_{27}H_{48}OSn$: C, 63.91; H, 9.47. Found: C, 63.69; H, 9.22%.

*3.1.8. (E)-1-(4-Methoxyphenyl)-1-trimethylstannyl-1-octene (**4h**)*

IR(film): ν (cm^{-1}) 3074, 2924, 2855, 1602, 1571, 1505, 1466, 1378, 1243, 1172, 1039, 865, 824, 766. ^1H NMR: δ 6.89–6.82 (m, 4H), 5.76 (t, J=7.0 Hz, 1H), 3.81 (s, 3H), 2.08–2.01 (m, 2H), 1.35–1.15 (m, 8H), 0.86 (t, J=7.2 Hz, 3H), 0.10 (s, 9H). MS: *m/z* 381 (M^+, 4.0), 367 (20), 217 (18), 161 (12), 147 (100), 121(93), 115 (21), 91 (29). Anal. Calc. for $C_{18}H_{30}OSn$: C, 56.69; H, 7.87. Found: C, 56.44; H, 7.61%.

*3.2. The synthesis of (Z)-1-phenyl-1-hexene **(5)***

BuLi (1 ml, 1.1 M hexane solution) was added to a THF (5 ml) solution of **4a** (1.0 mmol) at −78 °C. After stirring for 30 min, the mixture was hydrolyzed with saturated aq. NH_4Cl and extracted with CH_2Cl_2 (2×15 ml). The organic extract was washed with water (2×10 ml), dried with $MgSO_4$, filtered, and concentrated under vacuum. The residue was purified by column chromatography on silica gel, eluting with light petroleum to give (*Z*)-1-phenyl-1-hexene **5** (yield: 79%) as a colorless oil. IR(film): ν (cm^{-1}) 2926, 2855, 1647, 1595, 1498, 1378. ^1H NMR: δ 7.34–7.20 (m, 5H), 6.45 (d, J=11.6 Hz, 1H), 5.70 (dt, J=11.6, 7.2 Hz, 1H), 2.36–2.29 (m, 2H), 1.46–1.32 (m, 4H), 0.93 (t, J=7.2 Hz, 3H). Anal. Calc. for $C_{12}H_{16}$: C, 90.00; H, 10.00. Found: C, 89.73; H, 9.84%.

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