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Stereoselective Synthesis of 1,4-Dienes through Sequential Cross Coupling of (*E*)-α-Selanylvinylstannanes†

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(*E*)-α-Selanylvinylstannanes underwent palladium-catalysed coupling reaction with allyl bromides to give 1,4-dienyl selenides; the products can react with Grignard reagent to afford 1,4-dienes in the presence of Ni(dppp)$_2$Cl$_2$.

The 1,1-dimetallo reagents, such as Sn-Zr, B-Zr, Zr-Zn, Sn-B, Sn-S, offer unique opportunities to effect sequential multiple carbon–carbon bonds and provide access to polysubstituted alkenes of defined stereochemistry.[1–6] However, difunctionalized reagents containing both tributyltin and selanyl groups have aroused little attention. Previously, we have described the synthesis of (*E*)-α-selanylvinylstannanes[7] in which two synthetically versatile groups are linked to the same olefinic carbon atom and can be viewed as either vinylstannanes[8] or vinyl selenides.[9] They can undergo sequential transition metal-catalysed cross-coupling reaction with aryl halides and Grignard reagents, respectively and provide a convenient method for the stereospecific synthesis of trisubstituted alkenes.[7] As an extension of this methodology, we now describe an efficient synthesis of 1,4-dienes.

Table 1 Synthesis of 1,4-dienyl selenides

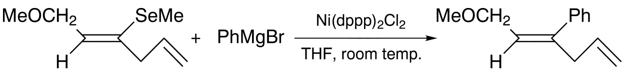
R	R^1	R^2	Product	Yield (%)
MeOCH$_2$	Me	H	**3a**	82
MeOCH$_2$	Ph	H	**3b**	76
Me(CH$_2$)$_4$	Ph	H	**3c**	68
MeOCH$_2$	Me	Ph	**3d**	65
MeOCH$_2$	Me	SiMe$_3$	**3e**	72
MeOCH$_2$	C$_6$H$_4$Cl-*p*	H	**3f**	58

(*E*)-α-Selanylvinylstannanes **1** were prepared conveniently by the hydrostannation of 1-selanylalkynes. Their palladium-catalysed cross-coupling reaction with allyl bromides **2** in DMF at ambient temperature using Ph(PPh$_3$)$_4$ and CuI as cocatalyst (Scheme 1) smoothly afforded the desired 1,4-dienyl selenides **3** (see Table 1) in which the tributylstannanes were selectively replaced by a new carbon–carbon bond with conservation of the configuration of the starting alkenes.

1 **2** **3**

Scheme 1

The stereochemistry of the reaction product was assigned on the basis of the results of the results of differential NOE experiments. Thus irradiation of the ethylenic proton resulted in a positive NOE on the hydrogen atoms of the alkyl groups linked to the other ethylenic carbon atom. The selenium moiety was retained in this first palladium-catalysed cross-coupling. Vinyl selenides are synthetic intermediates owing to the versatile reactivities of the selanyl group and the carbon–carbon double bond.[9] 1,4-Dienyl selenides can undergo cross-coupling reactions with Grignard reagents easily to provide an effective method of stereoselective synthesis of 1,4-dienes (Scheme 2).



3a **4**

Scheme 2

The present method has the advantage of simple starting materials, mild reaction conditions, conditions, convenient manipulation and stereoselectivities.

Experimental

The ^{1}H NMR spectra were recorded in CDCl$_3$ on a AZ-300 instrument, IR spectra on a FTS-185 spectrometer as neat films and mass spectra on a Finnigan 8230 mass spectrometer. Solvents were dried, deoxygenated and distilled before use. All reactions were carried out under nitrogen.

General Procedure for Synthesis of 1,4-*Dienyl Selenides*.—(*E*)-α-Selanylvinylstannanes **1** (1.0 mmol) and allyl bromides **2** (1.0 mmol) were dissolved in DMF (10 ml) under nitrogen at room temperature. The compounds Pd(PPh$_3$)$_4$ (0.05 mmol) and CuI (0.75 mmol) were then added. The mixture was stirred at room temperature and monitored by TLC for the disappearance of the starting organostannanes. Then it was diluted with diethyl ether (20 ml) and the organic layer washed with aqueous NH$_4$Cl (20 ml) and water (30 ml) and dried with MgSO$_4$. The solvent was removed under reduced pressure and the residue purified by column chromatography on silica gel eluting with a mixture of ether and light petroleum.

Compound **3a**. $\tilde{\nu}_{max}$/cm^{-1} 3080, 1625, 1450, 1117; δ_H 5.98 (m, 1 H), 5.85 (t, *J* 6.90, 1 H), 5.15 (m, 2 H), 4.18 (d, *J* 6.90, 2 H), 3.38 (s, 3 H), 3.15 (d, *J* 5.4 Hz, 2 H), 2.12 (s, 3 H); *m*/*z* 206 (7.79), 191 (11.44), 117 (29.17), 45 (100.00%).

Compound **3b**. $\tilde{\nu}_{max}$/cm^{-1} 3082, 3026, 1639, 1579, 1477, 1118; δ_H 7.38–7.08 (m, 5 H), 5.90–5.62 (m, 2 H), 5.10–4.90 (m, 2 H), 3.90 (d, *J* 7.8, 2 H), 3.23 (s, 3 H), 3.01 (d, *J* 7.2 Hz, 2 H); *m*/*z* 268 (68.66), 155 (100.00), 111 (98.85), 77 (80.70), 45 (82.37%).

Compound **3c**. $\tilde{\nu}_{max}$/cm^{-1} 3092, 3038, 1638, 1562, 1458; δ_H 7.38–7.15 (m, 5 H), 6.01–5.62 (m, 2 H), 5.15–4.82 (m, 2 H), 3.12 (d, *J* 7.0 Hz, 2 H), 2.15–1.68 (m, 4 H), 0.89–1.03 (m, 7 H); *m*/*z* 294 (12.62), 137 (68.05), 77 (100.00), 71 (15.00).

Compound **3d**. $\tilde{\nu}_{max}$/cm^{-1} 3089, 3026, 1625, 1599, 1495, 1120; δ_H 7.35–7.10 (m, 6 H), 6.13 (m, 1 H), 5.85 (m, 1 H), 4.02 (d, *J* 6.2 Hz, 2 H), 3.35 (s, 3 H), 3.28 (d, *J* 4.9 Hz, 2 H), 2.06 (s, 3 H); *m*/*z* 282 (5.55), 267 (19.99), 250 (52.77), 155 (100.00), 117 (34.42), 77 (17.79), 45 (42.33%).

Compound **3f**. $\tilde{\nu}_{max}$/cm^{-1} 3089, 3025, 1630, 1545, 1119; δ_H 7.40–7.12 (m, 5 H), 5.80 (m, 1 H), 4.75 (m, 2 H), 3.98 (d, *J* 6.4 Hz, 2 H), 3.35 (s, 3 H), 3.10 (d, *J* 5.0 Hz, 2 H); *m*/*z* 291 (4.30), 237 (100.00), 111 (95.44), 77 (37.11), 45 (50.29).

Compound **3e**. $\tilde{\nu}_{max}$/cm^{-1} 2957, 1612, 1464, 1120; δ_H 5.85 (m, 1 H), 5.67 (m, 1 H), 5.02 (m, 1 H), 3.90 (d, *J* 6.5 Hz, 2 H), 3.25 (s, 3 H), 3.13 (d, *J* 5.2 Hz, 2 H), 2.08 (s, 3 H), 0.05 (s, 9 H); *m*/*z* 278 (9.24), 247 (19.22), 183 (12.49), 83 (27.68), 73 (100.00), 45 (21.43%).

Reaction of the 1,4-*Dienyl selenide* **3a** *with* PhMgBr.—To a stirred suspension of Ni(dppp)$_2$Cl$_2$ [dppp = Ph$_2$P(CH$_2$)$_3$PPh$_2$] (0.05 mmol) and 1,4-dienyl selenide **3a** (1.0 mmol) in THF (5 ml) was added a solution of PhMgBr (2.5 mmol) in THF (5 ml) at room temperature; the mixture was stirred for 48 h. After the usual work-up,

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the residue was chromatographed through a silica gel column using light petroleum as eluent. Yield 65%.

Compound **4**. $\tilde{\nu}_{max}/cm^{-1}$ 3092, 3025, 1610, 1547, 1452, 1119; δ_H 7.35–7.10 (m, 5 H), 6.03 (m, 1 H), 5.86 (t, *J* 7.0, 1 H), 4.13 (d, *J* 7.2, 2 H), 3.38 (s, 3 H), 3.15 (d, *J* 5.6 Hz, 2 H) Found: C, 91.15; H, 8.85. Calc. for $C_{13}H_{15}O$: C, 91.01; H, 8.78%.

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