

Novel stereoselective synthesis of 1,3-dienyl selenides by palladium-copper cocatalyzed cross coupling reactions of (*E*)- α -selanylvinylstannanes

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(*E*)- α -Selanylvinylstannanes are new difunctional reagents which undergo palladium-catalyzed coupling reactions with unsaturated organic halides to give dienyl selenides stereoselectively.

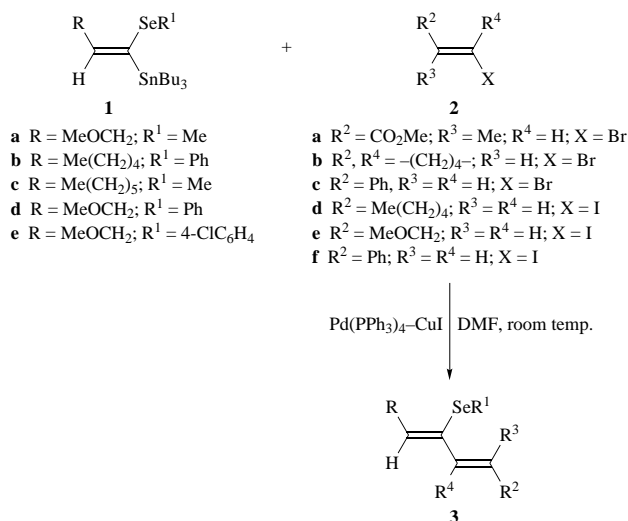
Conjugated dienes are valuable intermediates in organic chemistry. The synthesis of dienes for use in the Diels–Alder reaction is still an important challenge in organic synthesis¹ although recently other elegant uses of these compounds have been developed.^{2,3} Besides, most natural products contain one or more di- or tri-substituted double bonds⁴ often present as a 1,3-diene, with a specific double bond geometry being a requirement for biological activity.

The synthesis of 1,3-dienes containing functional groups is of considerable interest in recent years. The stereoselective synthesis of (*E,E*)-1-trimethylsilylbutadienes,^{5,6} (*E,E*)-1-phenylsulfanylbutadienes⁷ has already been described in the literature. Dienyl selenides serve as valuable versatile intermediates since vinyl selenides are synthetically equivalent to carbonyls and can be stereospecifically converted to alkenes by nickel-catalyzed coupling reactions with Grignard reagents.⁸ However, synthesis of polysubstituted dienyl selenides has rarely been reported.^{8,9} Our research group has reported that arylselanyl ethynes react with $Cp_2Zr(H)Cl$ to form 1,2-difunctional reagents *i.e.* (*E*)- β -arylselanylalkenylzirconium complexes. The cross-coupling reaction of the complexes with alkenyl halides in the presence of $Pd(PPh_3)_4$ provides a method for the synthesis of α -selanyl substituted 1,3-dienes.⁸

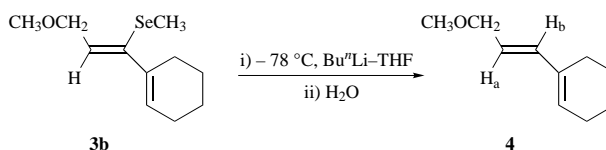
Vinylstannanes are pivotal intermediates in a wide range of carbon–carbon bond forming reactions.¹⁰ Palladium catalyzed hydrostannylation of alkynes provides a simple general route for the synthesis of vinylstannanes.¹¹ We have recently described how 1-selanylalkynes undergo hydrostannylation to afford 1,1-difunctional reagents *i.e.* (*E*)- α -selanylvinylstannanes¹² in which two synthetically versatile groups are linked to the same olefinic carbon atom and can be considered both as vinylstannanes and as vinyl selenides. Here, we have explored the application of (*E*)- α -selanylvinylstannanes in organic synthesis. This is different from the (*E*)- β -arylselanylalkenylzirconium complexes since here we have utilized the cross-coupling reaction of (*E*)- α -selanylvinylstannanes in order to synthesize β -selanyl substituted 1,3-dienes 3.

With a convenient route to the (*E*)- α -selanylvinylstannanes 1 we decided to establish the feasibility of using 1 in cross-coupling reactions. Gratifyingly, when the coupling reaction of 1 with a variety of vinylic halides 2 was conducted in DMF at ambient temperature using $Pd(PPh_3)_4$ and CuI as co-catalyst (Scheme 1) fairly rapid reaction occurred affording the desired coupling products 3 in good yield (Table 1).

It is well documented that the cross-coupling reaction of vinylstannanes with organic halides in the presence of a palladium catalyst occurs with retention of configuration.¹³ In addition, the configuration of the dienyl selenide 3b could be confirmed from compound 4 which was obtained by treatment of 3b with *n*-butyllithium in THF followed by hydrolysis, a



Scheme 1



Scheme 2

reaction which occurs stereoselectively (Scheme 2).¹⁴ Particularly diagnostic for the stereochemistry of 4 was the coupling constant between the vicinal protons H_a and H_b which show a typical value of J_{H-H} of 15.6 Hz which is consistent with an *E* configuration.

In conclusion, we have developed a novel route to the synthesis of 1,3-dienyl selenides 3. The method has the advantages of readily available starting materials, simple procedures, mild conditions and good yields. Investigations into the synthetic applications of 1,3-dienyl selenides 3 are currently in progress.

Experimental

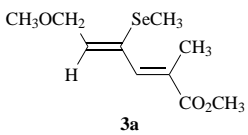
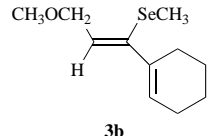
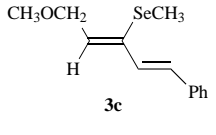
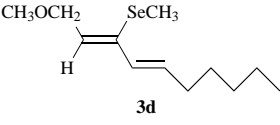
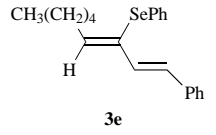
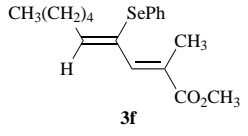
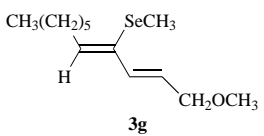
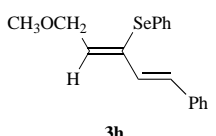
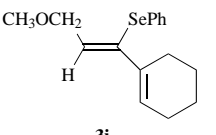
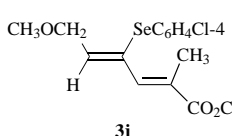
General details

¹H NMR spectra were recorded in $CDCl_3$ on an AZ-300 spectrometer with TMS as internal standard. *J* values are given in Hz. Mass spectra were obtained on a Finigan 8239 mass spectrometer. IR spectra were determined on an FTS-185 instrument as neat films. All reactions were carried out under an inert atmosphere (Ar or N_2). DMF was dried by distillation over calcium hydride. CuI was purified by a literature procedure.¹⁵ Petrol refers to light petroleum with bp 60–90 °C.

General procedure for the cross-coupling reactions

Organostannane 1 (1.0 mmol) and vinyl halide 2 (1.0 mmol) were dissolved in DMF (10 ml) under nitrogen at room tem-

Table 1 Synthesis of 1,3-dienylselenide **3**

Selenylvinyltin	Vinyl halide 2	Product 3	Yield (%)
1a	2a		90
1a	2b		68
1a	2c		82
1a	2d		62
1b	2c		65
1b	2a		78
1c	2e		80
1d	2f		76
1d	2b		63
1f	2a		75

perature. Pd(PPh₃)₄ (0.10 mmol) and purified CuI (0.75 mmol) were then added. The mixture was stirred at room temperature and monitored by TLC (SiO₂) for the disappearance of the starting organostannane. The reaction mixture was diluted with diethyl ether (20 ml) filtered and then treated with 20% aqueous KF (10 ml) for 30 min before being dried and concentrated. The residue was purified by column chromatography on silica gel, eluting either with a mixture of diethyl ether and petrol or just petrol.

Compound 3a. ν_{\max} (film)/cm⁻¹ 2957, 1720, 1610, 1466 and 1116; δ_{H} 7.16 (s, 1H), 5.92 (t, *J* 5.80, 1H), 4.15 (d, *J* 5.80, 2H), 3.78 (s, 3H), 3.38 (s, 3H), 2.09 (s, 3H), 1.97 (s, 3H); *m/z* 264

(16.35), 169 (100.00), 45 (32.29) (Found: C, 45.90; H, 5.68. C₁₀H₁₆O₃Se requires C, 45.63; H, 6.13%).

Compound 3b. ν_{\max} (film)/cm⁻¹ 2980, 1582, 1456 and 1114; δ_{H} 6.35 (t, 1H), 5.65 (t, *J* 5.91, 1H), 3.58 (d, *J* 5.91, 2H), 3.38 (s, 3H), 2.08 (s, 3H), 2.03 (m, 4H), 1.55 (m, 4H); *m/z* 246 (17.26), 151 (43.12), 106 (4.81), 45 (100.00) (Found: C, 53.70; H, 7.20. C₁₁H₁₈OSe requires C, 53.88; H, 7.04%).

Compound 3c. ν_{\max} (film)/cm⁻¹ 3051, 3024, 2995, 1578, 1477 and 1117; δ_{H} 7.46–7.02 (m, 6H), 6.76 (d, *J* 18, 1H), 6.21 (t, *J* 6.02, 1H), 4.36 (d, *J* 6.02, 2H), 3.48 (s, 3H), 2.10 (s, 3H); *m/z* 268 (10.63), 173 (51.99), 141 (100.00), 45 (25.12) (Found: C, 58.94; H, 6.30. C₁₃H₁₆OSe requires C, 58.43, H, 6.04%).

Compound 3d. ν_{\max} (film)/cm⁻¹ 2980, 1580, 1493 and 1114; δ_{H} 6.56–6.28 (dd, 2H), 5.90 (t, *J* 6.10, 1H), 3.78 (d, *J* 6.10, 2H), 3.25 (s, 3H), 2.08 (s, 3H), 1.82–0.90 (m, 11H); *m/z* 261 (26.11), 167 (33.75), 57 (100.00) (Found: C, 55.39; H, 8.90. C₁₂H₂₂OSe requires C, 55.17; H, 8.49%).

Compound 3e. ν_{\max} (film)/cm⁻¹ 3059, 3025, 1578, 1477 and 999; δ_{H} 7.60–7.15 (m, 11H), 6.83 (d, *J* 16.01, 1H), 6.21 (t, *J* 5.91, 1H), 2.25–2.35 (m, 4H), 1.65–0.85 (m, 7H); *m/z* 356 (16.82), 199 (51.48), 103 (38.19), 95 (21.05), 91 (100.00), 77 (79.38) (Found: C, 70.65; H, 6.68. C₂₁H₂₄Se requires C, 70.97; H, 6.80%).

Compound 3f. ν_{\max} (film)/cm⁻¹ 3044, 3015, 2957, 1718, 1586, 1438 and 1118; δ_{H} 7.42–7.15 (m, 5H), 6.91 (s, 1H), 5.98 (t, *J* 5.82, 1H), 3.60 (s, 3H), 1.89 (s, 3H), 1.75 (m, 2H), 1.47–0.92 (m, 9H); *m/z* 352 (5.50), 254 (100.00), 195 (38.35), 77 (17.53) (Found: C, 61.20; H, 6.92. C₁₈H₂₄O₂Se requires C, 61.53; H, 6.89%).

Compound 3g. ν_{\max} (film)/cm⁻¹ 2928, 1601, 1466 and 1120; δ_{H} 6.04 (m, 2H), 5.91 (t, *J* 5.81, 1H), 3.98 (s, 2H), 3.32 (s, 3H), 2.02 (s, 3H), 1.47–1.35 (m, 8H), 1.25–0.97 (m, 5H); *m/z* 276 (37.63), 245 (11.34), 149 (34.50), 110 (100.00), 45 (38.66) (Found: C, 56.21; H, 8.70. C₁₃H₂₄OSe requires C, 56.72; H, 8.78%).

Compound 3h. ν_{\max} (film)/cm⁻¹ 3081, 3059, 1600, 1577, 1494 and 1118; δ_{H} 7.38–7.15 (m, 10H), 6.95–6.78 (dd, *J* 16.04, 2H), 6.18 (t, *J* 5.90, 1H), 4.23 (d, *J* 5.90, 2H), 3.28 (s, 3H); *m/z* 330 (12.15), 173 (50.20), 77 (100.00), 45 (70.35) (Found: C, 65.02; H, 5.30. C₁₈H₁₈OSe requires C, 65.65; H, 5.51%).

Compound 3i. ν_{\max} (film)/cm⁻¹ 3092, 3045, 1580, 1477 and 1116; δ_{H} 7.68–7.15 (m, 5H), 6.34 (m, 1H), 5.91 (t, *J* 5.80, 1H), 4.15 (d, *J* 5.80, 2H), 3.32 (s, 3H), 2.60–2.41 (m, 4H), 1.68–1.13 (m, 4H); *m/z* 308 (72.21), 151 (84.64), 121 (100.00), 77 (26.99), 45 (58.86) (Found: C, 62.20; H, 6.60. C₁₆H₂₀OSe requires C, 62.53; H, 6.56%).

Compound 3j. ν_{\max} (film)/cm⁻¹ 3089, 3043, 1717, 1579, 1438 and 1120; δ_{H} 7.60–7.15 (m, 4H), 6.91 (s, 1H), 6.02 (t, *J* 6.00, 1H), 4.15 (d, *J* 6.00, 2H), 3.68 (s, 3H), 3.32 (s, 3H), 1.89 (s, 3H); *m/z* 360 (15.32), 339 (30.38), 191 (63.10), 169 (58.03), 45 (100.00) (Found: C, 50.60; H, 4.92. C₁₅H₁₇O₃SeCl requires C, 50.09; H, 4.76%).

Compound 4. δ_{H} 1.44–1.63 (m, 4H), 1.97–2.06 (m, 4H), 3.35 (s, 3H), 3.82 (d, *J* 6.02, 2H), 5.85 (dt, *J* 6.02, 15.60, 1H), 6.00–6.10 (m, 1H), 6.45 (d, *J* 15.60, 1H).

Acknowledgements

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References

- H. Wolliveber, *Diels–Alder Reaction*, Georg Thieme Verlag, Stuttgart, 1972; W. Oppolzer, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 876.
- S. Ghosal, S. P. Luke and K. S. Tyler, *J. Org. Chem.*, 1987, **52**, 4296.
- E. Arce, M. C. Carreno, M. B. Cid and J. L. G. Ruano, *J. Org. Chem.*, 1994, **59**, 3421.
- J. F. Normant and A. Alexakis, *Synthesis*, 1981, 841; K. Mori, in *The Total Synthesis of Natural Products*, ed. J. Apsimon, Wiley,

- New York, 1981; M. Abarbri, J. L. Parrann, J. C. Cintrat and A. Duchene, *Synthesis*, 1996, 82.
- 5 V. Fiandanese, G. Marchese, G. Mascolo, F. Naso and L. Ronzini, *Tetrahedron Lett.*, 1988, **29**, 3705.
- 6 T. H. Chan and J. S. Li, *J. Chem. Soc., Chem. Commun.*, 1982, 696.
- 7 F. Naso, *Pure Appl. Chem.*, 1988, **60**, 79.
- 8 J. V. Comasseto, *J. Organomet. Chem.*, 1983, **253**, 131; L. Hevesi, B. Hermans and C. Allard, *Tetrahedron Lett.*, 1994, **35**, 6729; L. S. Zhu, Z. Z. Huang and X. Huang, *Tetrahedron*, 1996, **52**, 9819.
- 9 J. V. Comasseto and C. A. Brandt, *Synthesis*, 1987, 146.
- 10 D. Gschneidner, *J. Am. Chem. Soc.*, 1993, **115**, 6625.
- 11 B. M. Trost and C. J. Li, *Synthesis*, 1994, 1267.
- 12 Y. Ma and X. Huang, *Synth. Commun.*, 1997, **27**, 225.
- 13 J. K. Stille, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 508; T. N. Mitchell, *Synthesis*, 1992, 803.
- 14 B. T. Grobel and D. Seebach, *Chem. Ber.*, 1977, **110**, 867.
- 15 G. B. Kauffman and L. Y. Fang, *Inorg. Synth.*, 1983, **22**, 101.

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