SHORT PAPER

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Stereoselective conversion of dialkylselenaethenylboranes into dialkylselenaalkenes by cross-coupling of carbon–carbon systems†

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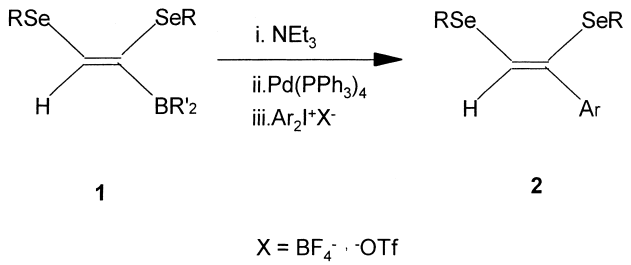
Dialkylselenaethenylboranes reacted with iodonium salts in the presence of a catalytic amount of $Pd(PPh_3)_4$ and NEt_3 at room temperature to provide dialkylselenaalkenes with retention of configuration.

Keywords: dialkylselenaethenylboranes, dialkylselenaalkenes

Few syntheses of diselenaalkenes have been reported to date.[1] However, there are still many classes of diselenaalkenes that can not be sythesised generally, especially dialkylselenaalkenes. We recently reported that the dialkylselenaethenylboranes, in the presence of NaOMe and $[CuBr(SMe_2)]$ at –15°C, reacted with allylic bromide to give a mixture of 1,1-dialkylselenapenta-1,4-dienes and the corresponding (*Z*)-1,2-dialkylselenapenta-1,4-dienes. The major method lead to a mixture of stereoisomers because of the reaction proceeding via the migration of an alkylselenyl group from one olefinic carbon to another.[2] Thus, herein we wish to report a new method for sytheses of (*Z*)-1,2-dialkylselenaalkenes.

Dialkylselenaethenylboranes **1,** readily prepared *in situ* by the hydroboration of dialkylselenaacetylenes in THF with 9-borabicyclo[3,3,1]nonane (9-BBN), were treated with $[Ar_2I]X$ in the presence of 0.4 mol % $[Pd(PPh_3)_4]$ and NEt_3 at room temperature to afford (*Z*)-1,2-dialkylselenaalkenes **2** with retention of configuration (Scheme 1**).** Representative results of the reaction are summarised in Table 1. The coupling reaction



Scheme 1

Table 1 Cross-coupling of dialkylselenaethenylboranes with iodonium salts catalysed by Pd (0) in the presence of organic base

Compounds **2**	R	Ar	Yield/% [a]
a	Me	*p*-$CH_3OC_6H_4$	81
b	Me	Ph	85
c	Et	*p*-$CH_3OC_6H_4$	80
d	Et	Ph	80
e	Bu	Ph	78
f	Pentyl	Ph	74
g	Hexyl	Ph	71
h	Cyclohexyl	Ph	70
i	Ph	Ph	77

[a]Isolated yields based on dialkylselenaacetylenes employed.

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† This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

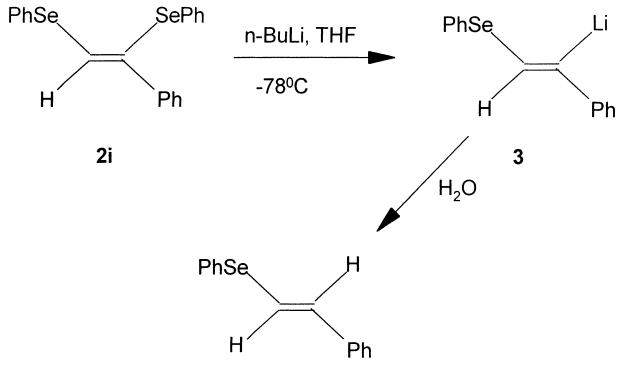
proceeded smoothly under mild conditions. It was found that no alkylselenyl group migrated from one olefinic carbon to another.[3] On the other hand, it (Table 1) shows that the compounds **1** reacted with $[Ar_2I]X$ to give the corresponding (*Z*)-1,2-dialkylselenaalkenes **2** in good yield. The results also indicated that the cross-coupling in each case occurred stereoselectively at the boryl position, and no coupling products at the selenyl position were obtained even under conditions using an excess of iodonium salts or a prolonged time.

The configurations in the structures of the compounds **2** were established by known methods.[4] For example, compound **2i** was lithiated by reaction with one equivalent of n-butyllithium in THF at –78°C. The lithiated species **3**, when trapped with water, lead to (*E*)-phenylselenastyrene (known compound, see ref. 4), showing that the Se–Li exchange reaction occurred stereoselectively because the PhSe group sterically hinders approach to Ph (Scheme 2).

The present reactions not only offer a new synthetic method for (*Z*)-1,2-dialkyselenaalkenes but also inicate that a high stereoselective cross-coupling was accomplished. These dialkylselenaalkenes are expected to be versatile intermediates for the synthesis of trisubstituted alkenes.

Experimental

The ^1H NMR spectra (chemical shifts in ppm) were recorded on an AZ-300 MHz with TMS as internal standard. Mass spectra were determined using a Finigan 8230 mass spectrometer. IR spectra were obtained in neat capillary cells on a Shimadzu IR-408 instrument. Elemental analyses were conducted using a Perkin-Elmer 240B elemental analyser. Silica gel 60 FG_{254} was used for analytical and preparative TLC. Silica gel columns were prepared using silica gel Q/BKUS 3-91(100–200 mesh). The reactions were carried out in pre-dried glassware (150°C, 4h) and cooled under a stream of dry



Scheme 2

dinitrogen. All solvents were dried, deoxygenated and redistilled before use. The dialkylselenaacetylenes,[5] $[Pd(PPh_3)_4]$,[6] 9-BBN,[7] $Ph_2I^+BF_4^-$ [8] and $[4\text{-}CH_3OC_6H_4I]PhOTf$ [9] were prepared according to literature methods.

General procedure for the synthesis of (Z)-1,2-dialkylselenaalkenes 2: To a freshly prepared suspension of 9-borabicyclo[3.3.1]nonane (5 mmol) in THF (10 ml) at 0°C was added dialkylselenaacetylene (5.1 mmol) in THF (2 ml) over 5 min. The reaction mixture was stirred until the precipitate completely disappeared (*ca* 5 h).To the solution was then added NEt_3 (5 mmol) in THF (3 ml) at the same temperature. After being stirred for 30 min, to the solution was added iodonium salts (5.5 mmol) and $[Pd(PPh_3)_4]$ (0.4 mol %,11.40 mg). The reaction temperature was warmed to room temperature and then stirred for a further 1 h. The reaction mixture was quenched with saturated aqueous NH_4Cl then extracted with pentane (15 ml × 13), and the organic layer was dried over anhydrous $MgSO_4$, filtered and evaporated *in vacuo*. The residue was purified by flash chromatography on a 3 ft × 1 inch column with light petroleum (b.p. 30–60°C) as eluent to give **2**.

(Z)-1,2-Dimethylselena-(p-methoxyl)styrene **2a**: *Oil:* R_f 0.61 (pentane). ν_{max}/cm^{-1} 3045 1645, 1579, 805. δ_H ($CDCl_3$) 7.60 (2 H, d, *J* 8 Hz), 6.95 (2 H, d, *J* 8 Hz), 6.45 (1 H, s), 3.9 (3 H, s), 2.25 (3 H, s), 2.11 (3 H, s). *m/z* 322 (M^++2, 16 %) (Found: C, 41.87; H, 3.98. $C_{11}H_{14}OSe_2$ requires C, 41.27; H, 4.41 %).

(Z)-1,2-Dimethylselenastyrene **2b**: *Oil:* R_f 0.63 (pentane). ν_{max}/cm^{-1} 3050, 1651, 1581, 1519, 804. δ_H ($CDCl_3$) 7.05–7.60 (5 H, m), 6.49 (1 H, s), 2.30 (3 H, s), 2.15 (3 H, s). *m/z* 292 (M^+ +2, 15 %) (Found: C, 41.10; H, 3.69. $C_{10}H_{12}Se_2$ requires C, 41.40; H, 3.69 %).

(Z)-1,2-Diethylselena-(p-methoxyl) styrene **2c**: *Oil:* R_f 0.62 (pentane). ν_{max}/cm^{-1} 3045, 1653, 1587, 1521, 810. δH ($CDCl_3$) 7.60 (2 H, d, *J* 8 Hz), 6.95 (2 H, d, *J* 8 Hz), 6.47 (1 H, s), 3.9 (3 H, s), 2.87 (2 H, q, *J* 7.5 Hz), 2.81 (2 H, q, *J* 7.5 Hz), 1.75(3H, t , *J* 7.5 Hz), 1.71(3H, t , *J* 7.5 Hz) (Found: C, 44.40; H, 4.83. $C_{13}H_{18}OSe_2$ requires C, 44.84; H, 5.21 %).

(Z)-1,2-Diethylselenastyrene **2d**: *Oil:* R_f 0.63 (pentane). ν_{max}/cm^{-1} 3050, 1643, 1590, 1555, 1517, 805. δ_H ($CDCl_3$) 7.0–7.60 (5 H, m), 6.45 (1 H, s), 2.90 (2 H, q, *J* 7.5 Hz), 2.85 (2 H, q, *J* 7.5 Hz), 1.75 (3 H, t, *J* 7.5 Hz), 1.71 (3 H, t, *J* 7.5 Hz) (Found: C, 45.11; H, 4.79. $C_{12}H_{16}Se_2$ requires C, 45.30; H, 5.07 %).

(Z)-1,2-Dibutylselenastyrene **2e**: *Oil:* R_f 0.62 (pentane). ν_{max}/cm^{-1} 3050, 1647, 1590, 1560, 1520, 810. δ_H ($CDCl_3$) 7.0–7.60 (5 H, m), 6.47 (1 H, s), 2.75–2.95 (4 H, m), 1.58–1.80 (4 H, m), 1.25–1.55 (4 H, m), 0.98 (3 H, t, *J* 7.0 Hz), 0.91(3 H, t, *J* 6.9 Hz) (Found: C, 51.59; H, 5.99. $C_{16}H_{24}Se_2$ requires C, 51.34; H, 6.46 %).

(Z)-1,2-Dipentylselenastyrene **2f**: *Oil:* R_f 0.62 (pentane). ν_{max}/cm^{-1} 3050, 1651, 1591, 1560, 1519, 811. δ_H ($CDCl_3$) 7.0–7.60 (5 H, m), 6.40 (1 H, s), 2.75–2.90 (4 H, m), 1.55–1.78 (4 H, m), 1.15–1.50 (8 H, m), 0.92 (3 H, t, *J* 7.0 Hz), 0.89 (3 H, t, *J* 6.8 Hz) (Found: C, 54.14; H, 7.43. $C_{18}H_{28}Se_2$ requires C, 53.73; H, 7.02 %).

(Z)-1,2-Dihexylselenastyrene **2g**: *Oil*: R_f 0.62 (pentane). ν_{max}/cm^{-1} 3050, 1649, 1560, 1518, 813. δ_H ($CDCl_3$) 7.0–7.60 (5 H, m), 6.49 (1 H, s), 2.85 (2 H, t, *J* 7.8 Hz), 2.78 (2 H, t, *J* 7.7 Hz), 1.52–1.78 (4 H, m), 1.15–1.48 (12 H, m), 0.93 (3 H, t, *J* 6.8 Hz), 0.88 (3 H, t, *J* 6.8 Hz) (Found: C, 56.27; H, 7.91. $C_{20}H_{32}Se_2$ requires C, 55.81; H, 7.49 %).

(Z)-1,2-Dicyclohexylselenastyrene **2h**: *Oil:* R_f 0.61 (pentane).ν_{max}/cm^{-1} 3050, 1651, 1592,1565, 1518, 814. δ_H ($CDCl_3$) 7.0–7.60 (5 H, m), 6.41 (1 H, s), 2.85–3.05 (2 H, br), 1.15–1.80 (20 H, m), *m/z* 430 (M^++2, 12 %) (Found: C, 55.67; H, 6.83. $C_{20}H_{30}Se_2$ requires C, 56.08; H, 7.06 %).

(Z)-1,2-Diphenylselenastyrene **2i**. *Oil*: R_f 0.59 (pentane). ν_{max}/cm^{-1} 1654, 1595, 1560, 1513, 817. δ_H ($CDCl_3$) 7.0–7.65 (15 H, m), 6.53 (1 H, s). *m/z* 416 (M^++2, 10 %) (Found: C, 57.58; H, 4.27. $C_{20}H_{16}Se_2$ requires C, 57.99; H, 3.89 %).

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