A Regio- and Stereo-selective Synthesis of (*Z*)-Alkylselanylalkenyl Bromides *via* Palladium(0)-catalysed Hydroboration–Bromination from Alkylselanylacetylenes†

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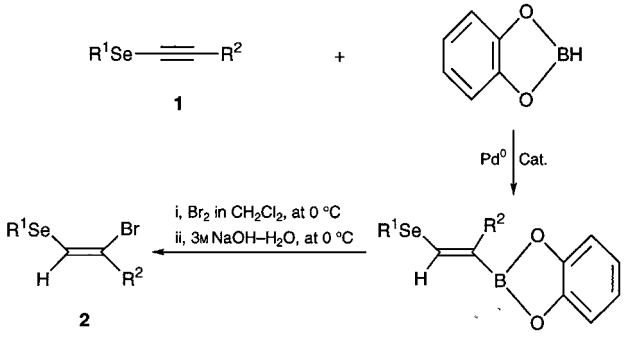
(*Z*)-Alkylselanylalkenyl bromides have been prepared in two steps from alkylselanylacetylenes using palladium(0)-catalytic hydroboration–bromination.

The traditional synthesis of (*E*)-arylselanylvinyl bromides involving the addition of arylselanyl bromide to monosubstituted alkynes has been reported.[1] However, to date no report has been published on the preparation of (*Z*)-alkylselanylalkenyl bromides. We have recently showed that the hydroboration of alkylselanylacetylenes followed by its cross-coupling with alkyl halides gives (*Z*)-1-alkylselanyl-1-alkyl- or -arylalk-1-enes.[2] This uncatalysed hydroboration of alkylselanylacetylenes proceeds with a strong preference for the addition of the boron atom at the carbon adjacent to the alkylselanyl group. We now report a palladium(0)-catalysed hydroboration of alkylselanylacetylenes with 1,3,2-benzodioxaborole and its application to the synthesis of (*Z*)-alkylselanylalkenyl bromides.

The palladium(0)-catalysed hydroboration of terminal alkylselanylacetylenes **1a–c** at room temperature with 1,3,2-benzodioxaborole in benzene, followed by treatment with sodium hydroxide and bromine, resulted in 74–77% yields of (*Z*)-alkylselanylalkenyl bromides **2a–c** (Scheme 1). Investigations of the crude products by ^{1}H NMR spectroscopy (300 MHz) showed isomeric purities of more than 97%. The stereochemistry of **2a–c** was confirmed by an absorption band at 690–699 cm^{-1} in the IR spectrum of each product and a coupling constant of 6.8–6.9 Hz between the vinylic protons in the ^{1}H NMR spectrum. In a similar manner, (*Z*)-alkylselanylalkenyl bromides **2d–g** were better obtained using internal alkylselanylacetylenes **1d–g** in 63–68% yields (Scheme 1). The stereochemistry of **2d–g** was established by metallation of **2e** at −78 °C with *n*-butyllithium in tetrahydrofuran (THF) followed by protonolysis with retention of configuration into the known isomer of (*E*)-1-phenyl-2-phenylselanylethene[3] with a characteristic coupling constant (*J* 16 Hz) of an (*E*)-isomer for its two olefinic proton signals.



Scheme 1

Table 1 Formation of (*Z*)-alkylselanylalkenyl bromides **2** by palladium(0)-catalysed hydroboration–bromination of alkylselanylacetylenes **1**

Product					
No.	R^1	R^2	Yield[a] (%)	ν_{max}/cm^{-1}	*m/z* (FAB, M$^+$)
2a	Me	H	74	690	200
2b	Et	H	77	699	214
2c	*n*-C_6H_{13}	H	75	692	270
2d	Et	Bu^n	68	814	270
2e	Ph	Ph	63	803	338
2f	Bu^n	Bu^n	65	808	298
2g	Et	*n*-C_6H_{13}	67	810	298

[a]Isolated yields.

The results thus indicate that palladium(0)-catalysed hydroboration of all the alkylselanylacetylenes studied (**1a–g**) provides regioselectively the selanylalkenylboronates with the boryl group in the β-position relative to the selenium atom. Even bulky substituents such as phenyl or hexyl (as in **1e** or **g**) do not change the regioselectivity which is likely to be controlled by electronic effects and which is higher than that for the hydroboration of internal alkynes when performed under reflux.[4] In addition, the *in situ* preparation of selanylalkenylboronates by bromination establishes an approach to the synthesis of (*Z*)-alkylselanylalkenyl bromides, compounds which are difficult to obtain by other traditional methods, as these afford the (*E*)-isomers.[1]

Experimental

IR spectra were obtained as films on a Shimadzu IR-408 spectrometer. ^{1}H NMR spectra (chemical shifts in ppm from internal Me_4Si) were measured on a Bruker AM-300 spectrometer at 300 MHz with $CDCl_3$ as solvent; *J* values are given in Hz. Elemental analyses were conducted using a Perkin-Elmer 240B elemental analyser. Mass spectra were determined on a Finigan 8230 spectrometer. All reactions were carried out in pre-dried glassware (150 °C; 4 h) and cooled under a stream of dry nitrogen. All solvents were dried, deoxygenated and redistilled before use. Borane,[5] 1,3,2-benzodioxaborole[6] and the alkylselanylacetylenes[7] were prepared according to literature methods. Similarly, $Pd(PPh_3)_4$ was obtained according to known procedures.[8]

General Procedure for the Synthesis of (Z)-*Alkylselanylalkenyl Bromides* **2a–g**.—A 50 ml dry flask equipped with a septum inlet, magnetic stirring bar and reflux condenser was flushed with nitrogen and charged with $Pd(PPh_3)_4$ (0.15 mmol), dry benzene‡ (20 ml), the terminal methylselanylacetylene **1a** (5 mmol) and freshly distilled 1,3,2-benzodioxaborole (5.5 mmol). The reaction mixture was stirred at room temperature overnight. The mixture was cooled to 0 °C and 3 M sodium hydroxide (10 mmol) was added, followed by addition of bromine[9] (10 mmol) in CH_2Cl_2 (2 ml). The mixture was stirred at 0 °C for 30 min and then allowed to warm to room temperature. The mixture was treated with saturated aqueous NH_4Cl (10 ml). The organic phase was separated, dried ($MgSO_4$) and concentrated *in vacuo*. The residue wsa purified by flash chromatography [3 ft × 1 in column; (100–200 mesh, light petroleum as eluent] to give (Z)-1-*bromo*-2-(*methylselanyl*)*ethene* **2a** as an oil, δ_H 2.21 (3 H, s, $SeCH_3$), 6.67 (1 H, d, *J* 6.8, CH), 7.17 (1 H, d, *J* 6.8, CH) (Found: C, 18.31; H, 2.30. C_3H_5BrSe requires C, 18.02; H, 2.52%). Similarly prepared were the following, all of

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‡**CAUTION:** Because of the hazardous nature of benzene, it is recommended that toluene be used as solvent for these reactions.

which were obtained as oils: (Z)-1-*bromo*-2-(*ethylselanyl*)*ethene* **2b**, δ_H 1.72 (3 H, t, *J* 8.1, CH), 2.80 (2 H, q, *J* 8.1, $SeCH_2$), 6.68 (1 H, d, *J* 6.8, CH), 7.15 (1 H, d, *J* 6.8, CH) (Found: C, 22.17; H, 3.11. C_4H_7BrSe requires C, 22.45; H, 3.30%); (Z)-1-*bromo*-2-(*hexylselanyl*)*ethene* **2c**, δ_H 0.75–1.48 (9 H, m, CH_3, $3 \times CH_2$), 1.68 (2 H, m, CH_2), 2.77 (2 H, t, *J* 8.0, $SeCH_2$), 6.64 (1 H, d, *J* 6.9, CH), 7.09 (1 H, d, *J* 6.9, CH) (Found: C, 35.82; H, 5.87. $C_8H_{15}BrSe$ requires C, 35.58; H, 5.60%); (Z)-2-*bromo*-1-(*ethylselanyl*)*hex*-1-*ene* **2d**, δ_H 0.67–1.51 (7 H, m, CH_3, $2 \times CH_2$), 1.73 (3 H, t, *J* 8.1, CH_3), 2.31 (2 H, t, *J* 6.6, CH_2), 2.79 (2 H, q, *J* 8.1, $SeCH_2$), 6.82 (1 H, s, CH) (Found: C, 35.21; H, 5.97. $C_8H_{15}BrSe$ requires C, 35.58; H, 5.60%); (Z)-1-*bromo*-1-*phenyl*-2-(*phenylselanyl*)*ethene* **2e**, δ_H 6.93 (1 H, s, CH), 7.00–7.75 (10 H, m, $2 \times C_6H_5$) (Found: C, 49.48; H, 3.63. $C_{14}H_{11}BrSe$ requires C, 49.73; H, 3.28%); (Z)-2-*bromo*-1-(*butylselanyl*)*hex*-1-*ene* **2f**, δ_H 0.67–1.52 (12 H, m, $2 \times CH_3$, $3 \times CH_2$), 1.70 (2 H, m, CH_2), 2.30 (2 H, t, *J* 6.5, CH_2), 2.85 (2 H, t, *J* 7.9, $SeCH_2$), 6.80 (1 H, s, CH) (Found: C, 40.05; H, 6.19. $C_{10}H_{19}BrSe$ requires C, 40.29; H, 6.42%); (Z)-2-*bromo*-1-(*ethylselanyl*)*oct*-1-*ene* **2g**, δ_H 0.65–1.53 (11 H, m, CH_3, $4 \times CH_2$), 1.72 (3 H, t, *J* 8.2, CH_3), 2.34 (2 H, t, *J* 6.6, CH_2), 2.82 (2 H, q, *J* 8.2, SeCH), 6.77 (1 H, s, CH) (Found: C, 40.64; H, 6.77. $C_{10}H_{19}BrSe$ requires C, 40.29; H, 6.42%).

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