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Palladium(0)-catalysed Coupling of Organozinc Reagents with (*E*)- or (*Z*)-2-Halo-1-alkylselanylethenes†

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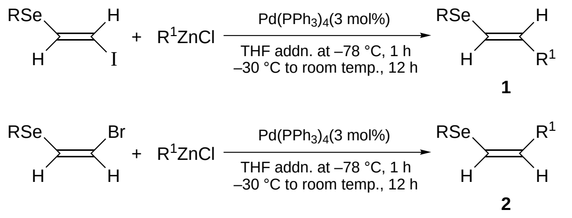
Stereoselective cross-coupling of organozinc reagents with (*E*)-2-iodo- or (*Z*)-2-bromo-1-alkylselanylethenes in the presence of a catalycic amount of $Pd(PPh_3)_4$ is accomplished.

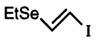
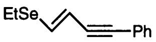
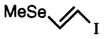
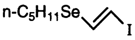
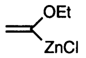
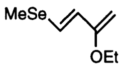
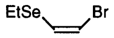
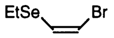
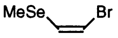
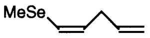
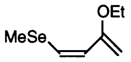
Palladium-catalysed reactions involving organozinc compounds are of rapidly increasing importance in organic synthesis.[1] Carbon–carbon bond formation *via* transition metal catalysed cross-coupling reactions is of primary interest in view of the variety of functionalities which can be used. Transition metal catalysed coupling reactions of organozinc reagents with vinyl halides have been previously reported.[1b] Recently we reported that organozinc reagents stereoselectively coupled with alkenyl diselenides by a Ni-catalysed reaction to afford alkenyl selenides[2] which can be stereospecifically converted to the corresponding alkenes by further Ni-catalysed cross-coupling with Grignard reagents.[3] However, there are no reported studies to date of the stereoselective cross-coupling of organozinc reagents with haloalkylselanylethenes containing difunctionalized groups. Therefore, we now report a stereoselective coupling reaction of organozinc reagents with (*E*)-2-iodo- or (*Z*)-2-bromo-1-alkylselanylethenes by altering the reaction conditions to provide novel alkenyl selenides.

We have recently reported that Pd^0-catalysed hydroboration of terminal alkylselanylacetylenes followed by iodination or bromination under basic conditions produced (*E*)-2-iodo- or (*Z*)-2-bromo-1-alkylselanylethenes,[4] respectively. Originally, we attempted to employ the reaction of phenylethynylmagnesium bromide in THF with (*E*)-2-iodoethylselanylethene in the presence of 3–5 mol% of $NiCl_2(PPh_3)_2$ to afford the expected product **1a**. When the reaction was carried out at room temperature, the yield of the desired product was low because the reaction proceeded with poor stereoselectivity even with low reaction temperatures (Scheme 1). On the other hand, even in the presence of a catalytic amount of $NiCl_2(PPh_3)_2$ and with phenylethynylzinc chloride instead of the Grignard reagent, the reaction failed to afford a satisfactory yield (23% for **1a**). However, after switching the Grignard reagent to phenylethynylzinc chloride, $NiCl_2(PPh_3)_2$ to $Pd(PPh_3)$ (3 mol%) and, when appropriate, altering the reaction temperature, compound **1a** was obtained in 81% yield (Scheme 1). The syntheses of compounds **1b–e** were also examined by coupling organozinc reagents with (*E*)-2-iodo-1-alkylselanylethenes in the presence of 3 mol% of $Pd(PPh_3)$ (Scheme 1). In a similar reaction, (*Z*)-2-bromo-1-alkylselanylethenes gave the corresponding products **2** (Scheme 1). The results are listed in Table 1.



Scheme 1

Table 1 Cross-coupling of organozinc reagents with (*E*)- or (*Z*)-haloalkylselanylethenes

Organozinc reagent[a]	Haloalkylselanylethene	Product	Yield[b] %
$Ph—\equiv—ZnCl$	 iv	 1a	81
 i	 v	 1b	85[c]
$n\text{-}C_4H_9—\equiv—ZnCl$	 vi	 1c	83
$Me_3Si—\equiv—ZnCl$ ii	vi	 1d	81
 iii	v	 1e	78
PhZnCl	 vii	 2a	73
i	 viii	 2b	80
ii	vii	 2c	77
iii	viii	 2d	72

[a]For the preparation of organozinc reagents, see ref. 5. [b]Isolated yield after chromatography. [c]For compound **1b**, see ref. 6

The stereochemistry of compounds **1** was established using the characteristic coupling constants (*J* 14.5–16 Hz) of the *E*-configuration between two olefinic proton signals in the ^1H NMR spectrum (3 MHz). Similarly, the *Z*-configuration of **2** was confirmed by ^1H NMR, with a coupling constant of 9.5 Hz between two olefinic proton signals. The results in Table 1 indicate that the Pd^0-catalysed coupling reaction proceeded with retention of configuration and occurred at the iodine or bromine position.

In conclusion, this synthetic method provides, in high stereoselectivity, novel (*Z*)- or (*E*)-alkenyl selenides, especially those containing organoynyl groups (such as **1a**, **1c**, **1d** and **2c**) that are difficult to prepare by general methods.[7]

Experimental

The ^1H NMR spectra were recorded on an AZ-300 MHz spectrometer with TMS as internal standard. Mass spectra were deter-

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†This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1997, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.

mined by a Finigan 8230 mass spectrometer. IR spectra were obtained in heat capillary cells on a Shimadzu IR-408 spectrometer. Elemental analyses were conducted using a Perkin-Elmer 240B elemental analyser. Silica gel 50 GF_{254} was used for analytical and preparative TLC. Silica gel columns were prepared using silica gel Q/BKUS 3–91 (100–200 Å mesh). The reactions were carried out under a stream of dry nitrogen. All solvents were dried, deoxygenated and redistilled before use.

General Procedure for the Synthesis of (E)- *or* (Z)-1-*Alkylselanyl*-2-*alkylethenes* **1** *or* **2**.—To a stirred mixture of the haloalkylselanylethene (2 mmol) and $Pd(PPh_3)_4$ (0.06 mmol, 3 mol%) at −78 °C in THF (10 ml), the organozinc reagent (2 mmol) in THF (5 ml) was slowly added and the resulting mixture stirred for 1 h. The reaction temperature was warmed to −30 °C and then stirred for a further 3 h, followed by stirring for 9 h at room temperature. The reaction was then quenched by pouring the mixture in to saturated aqueous NH_4Cl (10 ml) in a separatory funnel. Extraction with pentane (2 × 10 ml), washing the combined extracts with saturated aqueous NH_4Cl (10 ml), drying with anhydrous $MgSO_4$ followed by filtration, concentration *in vacuo* and flash chromatography (silica gel, light petroleum (bp 60–90 °C)–EtOAc, 98:2) yielded the pure product **1** or **2** as an oil. (E)-4-*Ethylselanyl*-1-*phenylbut*-3-*en*-1-*yne* **1a**. δ_H ($CDCl_3$) 7.05–7.56 (5 H, m), 6.97 (1 H, d, *J* 16 Hz), 6.35 (1 H, d, *J* 16 Hz), 2.75 (2 H, q, *J* 7.7 Hz) and 1.74 (3 H, t, *J* 7.7 Hz). ν_{max}/cm^{-1} 2230, 1615, 1594, 1560, 1548 and 955. *m*/*z* 236 (M^+ +1, 14), 235 (M^+, 13), 207 (67) and 127 (100). (Found: M^+, 235.1833. $C_{12}H_{12}Se$ requires M_r 235.1868). (E)-1-*Pentylselanyloct*-1-*ene*-3-*yne* **1c**. δ_H ($CDCl_3$) 6.69 (1 H, d, *J* 15 Hz), 6.07 (1 H, d, *J* 15 Hz), 2.77 (2 H, t, *J* 7.5 Hz), 2.44 (2 H, t, *J* 5.8 Hz), 1.68 (2 H, m), 1.05–1.60 (8 H, m), 0.91 (3 H, t, *J* 6.5 Hz) and 0.77 (3 H, t, *J* 6.3 Hz). ν_{max}/cm^{-1} 2217, 1624 and 945. (Found: M^+, 255 and 1149. $C_{13}H_{20}Se$ requires M_r 255.1188). (E)-4-*Pentylselanyl*-1-*trimethylsilylbut*-3-*en*-1-*yne* **1d**. δ_H ($CDCl_3$) 6.78 (1 H, d, *J* 15 Hz), 6.14 (1 H, d, *J* 15 Hz), 2.75 (2 H, t, *J* 7.5 Hz), 1.65 (2 H, m), 1.10–1.49 (4 H, m), 0.93 (3 H, t, *J* 6.6 Hz) and 0.31 (9 H, s). ν_{max}/cm^{-1} 2205, 1613 and 949. (Found: M^+, 273.3551. $C_{12}H_{22}SiSe$ requires M_r, 273.3518). (E)-3-*Ethoxy*-1-*ethylselanylbuta*-1,3-*diene* **1e**. δ_H ($CDCl_3$) 6.37 (1 H, d, *J* 14.5 Hz), 5.75 (1 H, d, *J* 14.5 Hz), 4.85 (2 H, s), 3.36 (2 H, q, *J* 6.7 Hz), 2.21 (3 H, s) and 1.23 (3 H, t, *J* 6.7 Hz). ν_{max}/cm^{-1} 1607, 941 and 901. (Found: M^+, 191,1282. $C_7H_{12}OSe$ requires M_r 191.1312). (Z)-1-*Ethylselanyl*-2-*phenylethene* **2a**. δ_H ($CDCl_3$) 7.0–7.6 (5 H, m), 6.75 (1 H, d, *J* 10 Hz), 6.24 (1 H, d, *J* 10 Hz), 2.95 (2 H, q, *J* 7.9 Hz) and 1.71 (3 H, t, *J* 7.9 Hz). ν_{max}/cm^{-1} 1631, 1591, 1552 and 695. *m*/*z* 212 (M^+ +1, 12), 211 (M^+, 10), 183 (55) and 104 (100). (Found: M^+, 211.1691, $C_{10}H_{12}Se$ requires M_r, 211.1648). (Z)-1-*Methylselanylpenta*-1,4-*diene* **2b**. δ_H ($CDCl_3$) 6.69 (1 H, d, *J* 9.7 Hz), 6.18 (1 H, dt, *J* 9.7, 7.1 Hz), 5.75 (1 H, m), 5.0 (2 H, m), 3.05 (2 H, m), and 2.21 (3 H, s). ν_{max}/cm^{-1} 1607 and 693. (Found: M^+, 161.1017. $C_6H_{10}Se$ requires M_r, 161.1050). (Z)-4-*Ethylselanyl*-1-*trimethylsilylbut*-3-*en*-1-*yne* **2c**. δ_H ($CDCl_3$) 6.71 (1 H, d, *J* 9.5 Hz), 6.06 (1 H, d, *J* 9.5 Hz), 2.78 (2 H, q, *J* 7.7 Hz), 1.70 (3 H, t, *J* 7.7 Hz), 0.31 (9 H, s). ν_{max}/cm^{-1} 2209, 1618 and 705. (Found: M^+, 231.2683. $C_9H_{16}SiSe$ requires M_r, 231.2714). (Z)-3-*Ethoxy*-1-*methylselanylbuta*-1,3-*diene* **2d**. δ_H ($CDCl_3$) 6.41 (1 H, d, *J* 9.5 Hz), 5.81 (1 H, d, *J* 9.5 Hz), 4.6 (2 H, s), 3.41 (2 H, q, *J* 6.5 Hz), 2.20 (3 H, s), 1.25 (3 H, t, *J* 6.5 Hz). ν_{max}/cm^{-1} 1611, 910 and 707. (Found: M^+, 191.1279, $C_7H_{12}OSe$ requires M_r 191.1312).

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