SHORT PAPER

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Stereoselective synthesis of 1,3-enynylselenides via palladium-catalysed cross coupling reactions†

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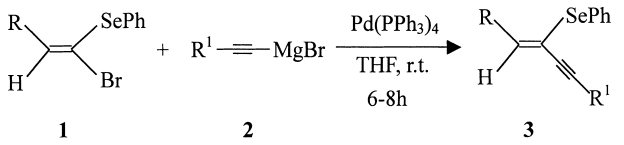
(*E*)-α-Bromovinylselenides undergo a cross coupling reaction with alkynyl Grignard reagents in the presence of tetrakis(triphenylphosphine)palladium(0) in THF at room temperature to afford 1,3-enynylselenides in good yields.

Keywords: 1,3-enynylselenides, palladium, cross coupling reaction

The chemistry of enynes[1] are currently attracting great interest because the conjugated enyne moiety is incorporated in a number of natural products and it can be readily converted in a stereospecific manner into the corresponding diene system.[2,3] The chalcogen-containing enynes will also be useful as building blocks for this purpose, since a lot of useful functional group transformations can be achieved by introduction and removal of chalcogen functions. However, so far, only a few methods for the synthesis of chalcogenoenynes have been reported.[4]

The transition metal-catalysed cross coupling reaction is a highly versatile method for carbon-carbon bond formation and has been widely used as synthetic tool.[5] Recently, Babudri[6] reported that the $NiCl_2$(dppe)-catalyzed cross coupling reaction of (*E*)-1-chloro-2-phenylthioethene with 2-trimethylsilylethynyl Grignard reagent afforded (*E*)-1-phenylthio-4-trimethylsilyl-1-buten-3-yne in good yield. Ma [7] reported the synthesis of 1,3-enynylselenides via palladium-catalysed cross coupling of (*E*)-α-selanylvinylstannanes with haloalkynes. In this paper, we report a novel stereoselective synthesis of 1,3-enynylselenides via cross coupling of (E)-α-bromovinylselenides with alkynyl Grignard reagents in the presence of $Pd(PPh_3)_4$ (Scheme 1).



1 **2** **3**

Scheme 1

We found that when (*E*)-α-bromovinylselenides **1** were allowed to react with alkynyl Grignard reagents **2** in the presence of catalytic amounts of tetrakis(triphenylphosphine)palladium(0) in THF at room temperature for 6–8h, 1,3-enynylselenides **3** were obtained in good yields. Some results are summarised in Table 1.

The products were identified by ^{1}H NMR, IR spectra and elemental analysis. The double bond geometries of the products **3** were determined by the treatment of (*Z*)-1-phenyl-2-phenylseleno-4-phenyl-1-buten-3-yne at –78°C with butyllithium in THF followed by hydrolysis with saturated aqNH_4Cl to produce (*E*)-1,4-diphenyl-1-buten-3-yne **4** (Scheme 2). The stereochemistry of product **4** was easily established, since ^{1}H NMR spectrum of product **4** gives rise to two doublets at δ 6.30 and δ 7.01 with a coupling constant of 16Hz, typical of *trans* positioned protons. The experimental results showed that the palladium-catalysed cross coupling reaction of (*E*)-α-bromovinylselenides with alkynyl Grignard reagents occurred with total retention of configuration. The required starting (*E*)-α-bromovinylselenides **1** were easily prepared in good yields with high stereoselectivity by the addition of hydrogen bromide to alkynyl selenides.[8]

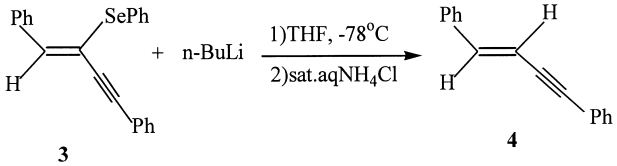
In conclusion, we have developed a novel approach to the stereoselective synthesis of 1,3-enynylselenides by the cross coupling reaction of (*E*)-α-bromovinylselenides and alkynyl Grignard reagents in the presence of a palladium catalyst. The present method has the advantages of readily available starting materials, straightforward and simple procedures, mild reaction conditions and good yields.

Experimental

Tetrahydrofuran(THF) was freshly distilled from sodium-benzophenone prior to its use. IR spectra were obtained on a Shimadzu IR-435 instrument, ^{1}H NMR spectra were recorded on a JEOL FX-90Q(90MHz) instrument with TMS as an internal standard in $CDCl_3$ as solvent and microanalyses were performed on a Vario EL and a Perkin-Elmer CHN2400.

General procedure for the cross coupling reaction of (E)*-a-bromovinylselenides with alkynyl Grignard reagents:* To a 0.67M THF solution of ethylmagnesium bromide (3ml, 2mmol) was added terminal alkyne (2.1mmol) in THF (1ml) at 0°C under nitrogen. After stirring for 30min, the mixture was stirred at 30°C for another 3h. (*E*)-α-bromovinylselenide (1mmol) and $Pd(PPh_3)_4$ (0.02mmol) were then added to the resulting THF solution of alkynyl Grignard reagent and the mixture was stirred at room temperature for 6–8h. Then a saturated aqueous NH_4Cl solution (20ml) was added and the mixture was stirred for 10min, and extracted with diethyl ether (2×30ml). The ethereal solution was washed with distilled water (3×30ml), dried over anhydrous magnesium sulfate and concentrated under reduced pressure. The crude product was purified by column chromatography over silica gel (light petroleum).

Synthesis of (E)*-1,4-diphenyl-1-buten-3-yne*(**4**)*:* To a solution of (*Z*)-1-phenyl-2-phenylseleno-4-phenyl-1-buten-3-yne **3** (0.359g, 1.0mmol) in THF (5.0ml) was added BuLi (1.6M hexane solution, 1.1mmol) at –78°C. After stirring for 1 h, the mixture was hydrolysed with sat. aq NH_4Cl and extracted with Et_2O (2×30ml). The ethereal solution was washed with water (2×15ml), dried ($MgSO_4$) and



3 **4**

Scheme 2

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

Table 1 1,3-Enynylselenides prepared

Entry	*R*	R^1	Yield[a]/%	IR(neat)/cm^{-1}	^{1}H NMR($CDCl_3$), δ(*J*/Hz)	Elemental analysis(calcd.) %C	%H
1	*n*-C_4H_9	CH_3OCH_2	61	3058, 2930, 2212, 1578, 1110	0.87(t,3H,*J*=5.3), 1.06–1.57(m,4H), 2.25–2.40(m,2H), 3.21(s,3H), 4.21(s,2H), 6.40(t,1H,*J*=7.4), 7.23–7.60(m,5H)	62.27(62.54)	6.30(6.51)
2	*n*-C_4H_9	*n*-C_6H_{13}	72	3059, 2928, 2212, 1579, 1438	0.66–1.07(m,6H), 1.10–1.61(m,12H) 2.16–2.34(m,4H), 6.49(t,1H,*J*=6.7), 7.16–7.61(m,5H)	69.31(69.16)	8.23(8.07)
3	*n*-C_4H_9	Ph	91	3058, 2201, 1597, 1490, 1438	0.85(t,3H,*J*=5.4), 1.19-1.45(m,4H), 2.10–2.48(m,2H), 6.38(t,1H,*J*=7.5), 7.06–7.74(m,10H)	70.52(70.80)	5.75(5.90)
4	Ph	CH_3OCH_2	66	3057, 2990, 2928, 2205, 1578, 1090	3.24(s,3H), 4.27(s,2H), 7.19–7.72(m,11H)	65.85(66.06)	4.67(4.89)
5	Ph	*n*-C_6H_{13}	84	3060, 2924, 2199, 1579, 1493, 1456	0.88(t,3H,*J*=5.4), 0.89–1.31(m,8H), 1.94(t,2H,*J*=5.6), 7.04–7.93(m,11H)	71.69(71.93)	6.41(6.54)
6	Ph	Ph	82	3053, 2210, 1594, 1489, 1441	6.90–7.81(m,16H)	73.24(73.54)	4.30(4.46)
7	*n*-C_6H_{13}	CH_3OCH_2	83	3050, 2928, 2213, 1579, 1450	0.88(t,3H,*J*=5.4), 1.08–1.59(m,8H), 2.26–2.43(m,2H), 3.23(s,3H), 4.24(s,2H), 6.37(t,1H,*J*=7.4), 7.18–7.69(m,5H)	64.25(64.48)	7.23(7.16)
8	*n*-C_6H_{13}	*n*-C_6H_{13}	69	3058, 2929, 2211, 1578, 1438	0.66–1.06(m,6H), 1.08–1.59(m,16H), 2.10–2.36(m,4H), 6.47(t,1H,J=7.3), 7.24–7.67(m,5H)	70.23(70.40)	8.31(8.53)
9	*n*-C_6H13	Ph	87	3060, 2926, 2200, 1597, 1490, 1450	0.88(t,3H,*J*=5.4), 1.20–1.58(m,8H), 2.20–2.55(m,2H), 6.34(t,1H,*J*=7.5), 7.10–7.78(m,10H)	71.79(71.93)	6.44(6.54)

[a]Isolated yield based on **1** used.

concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel(light petroleum) and recrystallised(EtOH) to afford enyne **4**(0.173g, 85%); M.p. 96–97°C (lit.[9]96–97°C); δ_H($CDCl_3$) 6.30(d, 1H, *J*=16Hz),7.01(d, 1H,*J*=16Hz), 7.10–7.72(m,10H).

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