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A NOVEL SYNTHESIS OF 1,3-ENYNYLSELENIDES VIA CROSS COUPLING OF (E)-α-SELANYLVINYL-STANNANES WITH HALOALKYNES

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Abstract: Conjugated envines bearing a selanyl group were conveniently obtained under mild conditions *via* cross coupling of the corresponding vinyltines with 1-haloalkynes in the presence of palladium catalysts.

The conjugated enyne moiety is an important unit in organic chenistry. It is incorporated in a number of natural products and it can be readily converted in a stereospecific manner into the corresponding diene system¹⁻³. The synthesis of enynes has been performed using coupling of halloalkynes with vinyl metals like as vinylboron⁴, vinylcopper^{5,6}, vinylzinc^{7,8} vinylaluminum⁹ or vinylmagnesium reagents¹⁰. In this series, the higher compatibility with functional groups is observed with vinylzinc reagents and a convenient way to obtain them is to transmetallate vinylcopper reagents with zinc dichloride⁹.

Stille has reported the use of organotin regents to obtain enynes by cross coupling reaction of vinyl triflates or vinyl iodides with alkynyltins in the presence of palladium catalysts¹¹⁻¹⁴. The interest of the method is a high tolerance for func-

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tional groups such as allylic ether, vinylic thioethers, esters, ketones or trimethylsily ether¹⁵⁻¹⁷. However, the cross coupling reactions of vinyltin with haloalkynes has rarely been reported¹⁸. We have recently prepared (E)- α selanylvinylstannanes by the hydrostannation of 1-selanylalkynes in presence of Pd (PPh₃)₄. (E)- α -Selanylvinylstannanes in which two synthetically versatile groups are linked to same olefinic carbon atom can be considered both as vinylstannanes and vinylselenides. On the basis of the different reactivity of the selanyl group and the stannyl group, sequential transition metal catalyzed crosscoupling reactions can be carried out with aryl halides and Grignard reagents respectively and this provides a convenient method for the stereospecific synthesis of trisubstituted alkenes¹⁹. In connection with our previous research, we decided to explore the possibility of extending this system in order to synthesise 1, 3enynylselenides.

With a convenient route to the (E)- α -selanylvinylstannanes 1, we established the feasibility of using organotin in cross-coupling reactions. Gratifyingly, when the coupling reactions of 1 with a variety of 1-haloalkynes 2 were conducted in DMF at ambient temperature using Pd(PPh₃)₄ and CuI as cocatalyst (scheme 1) fairly rapid reaction occurred affording the desired coupling products 3 in good yields (Table 1).

Scheme 1



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entry	haloalkynes	(E)-α-selanylvinylstannanes	product	yield(%)
8	Ph-≡I	CH ₃ OCH ₂ H SnBu ₃	CH ₃ OCH ₂ SeCH ₃ H	80
b	//I	$\begin{array}{c} CH_3OCH_2 \\ H \\ SnBu_3 \end{array} \\ SePh - Cl - p \\ SnBu_3 \end{array}$	CH ₃ OCH ₂ SePh - Cl -	р 65
c (CH3OCH2−≡−	I NEU3	SeCH ₃ H CH ₂ OCH ₃	73
d	Ph− ≡− Br	SePh H SnBu ₃	SePh H Ph	70
e	Ph-≡-I	$\underbrace{\overset{SePh-Cl-p}{\underset{H}{\overset{SnBu_{3}}{}}}}$	SePh - Cl - p H Ph	65
f	───Br	CH ₃ OCH ₂ SeCH ₃ H SnBu ₃	CH ₃ OCH ₂ H	58
g	Ph−≕-I	CH ₃ OCH _z SePh H SnBu ₃	CH ₂ OCH ₂ SePh H	62
h	Ph-≡-Br	Ph SePh H SnBu ₃	Ph SePh H Ph	56
i	Ph-≡-I	CH ₃ OCH ₂ SePh - Cl - p H SnBu ₃	CH ₃ OCH ₂ SePh - Cl - H	р 62

Table 1 The Synthesis of 1,3-enynylselenides*

a. The product were identified by MS. ¹H NMR and IR sepectroscopy.

In conclusion, we have developed a novel approach to the synthesis of 1, 3enynylselenides by the cross coupling reaction of vinyltins bearing a selanyl group and haloalkynes in the presence of palladium catalyst. The reaction have the advantages of mild conditions, stort reaction time, simple manipulation and good yield.

Experimental

¹H NMR spectra were recorded on a AZ-300 spectrometer with TMS as internal standard. Mass spectra were obtained on Finigan 8230 mass spectrometer. IR spectra were determined on 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 procedure¹⁶.

General procedure for the cross-coupling reactions: Organostannanes 1 (1. 0 mmol) and haloalkynes 2 (1. 0 mmol) were dissolved in DMF (10 ml) under nitrogen at room temperature. 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 with 20% aqueous KF (10%) for 30min before being dried and concentrated. The residue was purified by column chromatography on silica gel, eluting with a mixture of ether and petroleum.

2a: $\delta_{\rm H}$ 7. 42(m,2 H),7. 37(m,3 H),6. 12(t,J=6. 8 Hz,1 H),4. 18(d,J=6. 8 Hz,2 H),3. 30(s,3 H),2. 20(s,3 H). $\nu_{\rm max}$ 3108,3105,2197,1602,1489,1191 cm⁻¹. m/z,266(31.65),171(80.11),141(100.00),77(24.20),45(62.93). **2b**: $\delta_{\rm H}$ 7. 64-7. 24(m,4 H),6. 25(t,J=6. 2 Hz,1 H),4. 20(d,J=6. 2 Hz,2 H),3. 32(s,3 H),2. 12-1. 35(m,6 H),1. 25-0. 80(m,5 H). $\nu_{\rm max}$ 3112, 3108, 2198, 1568, 1481, 1192 cm⁻¹. m/z, 357 (12. 37), 356 (8. 76), 262 (10. 25),261(5.28),155(39.09),45(100.00).

 $2c_{\rm t}$; $\delta_{\rm H}$ 5. 98(t, J = 6. 0 Hz, 1 H), 4. 02(s, 2 H), 3. 30(s, 3 H), 2. 02(s, 3 H),

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1. $20-1.56(m, 8 H), 0.8-1.12(m, 5 H). \nu_{max} 2990, 2195, 1568, 1478, 1180 cm^{-1}. m/z, 276(38, 47), 181(7, 77), 149(50, 72), 110(100, 00), 45(42, 68).$ $2d: <math>\delta_H$ 7. 25-7. 60(m, 10 H), 6. 96(t, J=6.7, 1 H), 2. 15-2. 26(m, 4 H), 1. 4 -1. 20(m, 4 H), 0.8-1.0(m, 2 H). ν_{max} 3109, 3102, 2245, 1578, 1477, 1128, 999 cm⁻¹. m/z, 254(100, 00), 197(12, 13), 157(6, 61), 97(9, 57), 77(7, 79). 2e: δ_H 6. 35(m, 1 H), 7. 6-7. 8(m, 2 H), 7. 10-7. 45(m, 7 H), 2. 10-2. 23 (m, 4 H), 0.9-1. 6(m, 11 H). ν_{max} 3806, 2970, 2201, 1592, 1482, 1138 cm⁻¹. m/z, 402(1, 02), 302(100, 00), 151(31, 46), 77(14, 46).

2f: $\delta_{\rm H}$ 6. 01(t, J=6. 4 Hz, 1 H), 4. 06(d, J=6. 4, 2 H), 3. 30(s, 3 H), 2. 02(s, 3 H), 1. 68–1. 30(m, 6 H), 0. 89–1. 10(m, 5 H). $\nu_{\rm max}$ 2982, 2852, 2215, 1565, 1477, 1120 cm⁻¹. m/z, 260(31. 95), 245(10. 43), 229(100. 00), 165(29. 74), 95(9. 36), 45(51. 99).

2g: $\delta_{\rm H}$ 7. 15-7. 45(m,10 H), 6. 39(t, J=6. 8 Hz,1 H), 4. 10(d, J=6. 8 Hz, 2 H).3. 25(s,3 H). $\nu_{\rm max}$ 3057, 3092, 2925, 2196, 1600, 1579, 1486, 1114 cm⁻¹. m/z, 328(7,70), 171(13. 61), 77(21. 76), 71(100. 00), 45(42. 95).

2h: $\delta_{\rm H}$ 7. 18-7. 65(m,16 H). $\nu_{\rm max}$ 3057,3094,2955,2208,1590,1464,734,689 cm⁻¹. m/z,360(11.82),283(3.29),203(83.87),202(100.00),178(67.79), 77(31.99).

2i: $\delta_{\rm H}$ 7. 53-7. 12(m,9 H), 6. 35(t, J=5. 80 Hz, 1 H), 4. 02(d, J=5. 80 Hz, 2 H), 3. 32(s, 3 H). $\nu_{\rm max}$ 3057, 3024, 2195, 1578, 1494, 1117, 749 cm⁻¹. m/z, 361 (9. 53), 269(87. 68), 191(8. 32), 71(100. 00), 45(19. 28).

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