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A Stereoselective Route to (E)-Vinylic Selenides through the Palladium-Catalyzed Cross-Coupling Reaction of Selenovinylicdialkylboranes with Alkyl Halides

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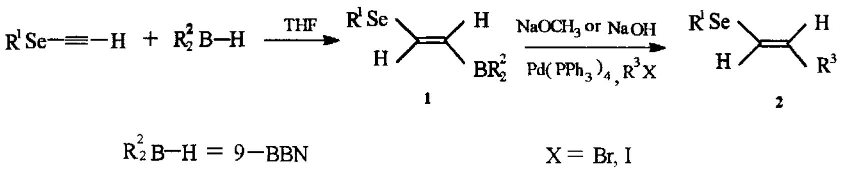
Abstract: The reaction of selenoviylicdialkyboranes with alkyl halides takes place readily in the presence of Pd(PPh_3)$_4$ and sodium methoxide to afford (E)-vinylic selenides in excellent yields

It was previously reported that the palladium-catalyzal cross-coupling reaction of alkenylboronates[1], 9-alky-9-BBN[2] with vinylic bromides containing phenylthio group provided the corresponding vinylic sulfides and (2-ethoxylvinyl) borane[3] reacted with aryl and benzyl halides by palladium-catalyzed cross-coupling. However, to date no report has been published on the cross-coupling of vinylicborane containing selenenyl groups with alkyl halides. We describe here a convenient route to (E)-vinylic selerides **2** from the selenovinylicdialkylboranes **1** , prepared by the hydroboration of terminal selenoacetylene, followed by the reaction with alkyl halides in the presence of catalytic amount of Pd(PPh_3)$_4$ and sodium methoxide. Methylselenovinylicdialkylborane **1a**, derived form the monohydroboration of terminal methylselenoacetylene with 9-borabicyclo [3,3,1] nonane (9-BBN) in THF reacted with benzyl bromide in the presence of 3 mol% of Pd(PPh)$_4$ and 3 equiv of sodium methoxide for 5h under the refluxing condition. It was found that the substitution of the dialkylboryl group occurred readily and gave (E)-1-methylseleno-2-benzyl-ethene **2a** in a yield of 87%, with high isomeric purity (no trace of the other isomers was detected by ^{1}HNMR). The reaction was highly selective to the C-B bond, and the C-Se bond was inert even for longer reaction time in the presence of an excess of benzyl bromide. On the other hand, it should be



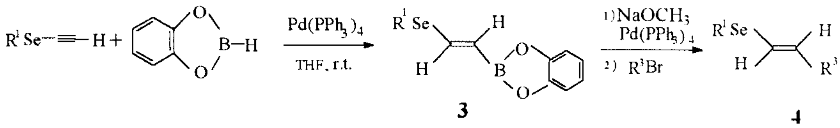
Scheme 1

Table 1. Transformation of selenovonylicdialkyboraned **1** into (E)-vinyle selenides **2**

entry	R^1	R^3X	Base[a]	Yield[b](%)
2a	CH_3	$PhCH_2Br$	A	87
2b	C_2H_5	$CH_2=CH\text{-}CH_2Br$	B	91
2c	C_2H_5	PhI	B	84
2d	n-C_4H_9	p-CH_3PhBr	B	81
2e	n-C_6H_{13}	CH_3I	A	90
2f	n-C_6H_{13}	p-CH_3OPhBr	A	89
2g[c]	Ph	CH_3I	B	88
2h[d]	Ph	n-C_4H_9Br	A	90
2i	Ph	p-CH3OPhBr	A	80

[a] Base is $NaOCH_3$ for A and NaOH for B. [b] Isolated yield. [c] Compound **2g** see ref 4. [d] Compound **2h** see ref. 5

noted that a high yield of the coupling product can be obtained when sodium methoxide is used as base, wherase when an aqueous sodium hydroxide was used, the product yield is only 47%. In a similar manner, (E)-Vinylic selenides **2b-h** were prepared (**Scheme 1**]). The results obtained are listed in **Table 1**. The stereochemistry of product **2** were confirmed by ^1H NMR, with a coupling constant of 14.5 ~ 16Hz between olefinic protons, and a NOE experiment for **2a** showed that irradiations of the methylene protons of benzyl increases the signal for the



4a: $R^1 = CH_3$, $R^3 = CH_2Ph$; **4b**: $R^1 = p-CH_3Ph$, $R^3 = CH_2=CH-CH_2$

Scheme 2

vinylic proton of one position, which indicated that both were on the same side of double bond.

We also tried to carry out the cross-coupling of benzyl or allyl bromides with the catecholesters of alkyselenovinyboranic acids **3** under the same reaction condition[6] (**Scheme 2**), intermidates **3** conveniently prepared by the hydroboration of terminal alkylselenoacetylene with catecholborane in the presence of 3mol% Pd(PPh**3**)**4** in THF (ca. 8h) It was found that the results of **4a** (^{1}H NMR. IR) was corresponding with that of **2a**. **4b**:Oil.^{1}H NMR($CDCl_3$)δ_H(ppm):3.15(m,2H);3.91 (S,3H);5.10(m,2H);5.86(m,H);6.39(m,1H);6.97(d,J=15.1Hz,1H); 7.10-7.65(m,4H). IR υ (cm^{-1}); 1634; 1591; 1561; 1495; 713. MS *m z* (EI): 238(m+1).Yield:83%.

Experimental

Methods. ^{1}H NMR spectra were recorded on an BRUKER AC-P-200 MHz (TMS as internal standard). IR spectra were obtained as neat capillary cells on a shimadzu IR-408 instrument. Elemental analysis were conducted using a Perkin-Elmer 240B elemental anayser. All reactions were carried out in pre-dried glassware (150 ℃, 4h) and cooled under a steam of dry nitrogen.

Material. All solvents were dried, deoxygenated and redistilled before use. Borane[7], 9-BBN[8] and catecholborane[9] were according to literature methods and the borane was standardized by aliquots before use. Commercial sodium borohydride may be used without purification. Boron trifluoride diethyl etherate is treated with anhydrous diethyl ether and distilled from granular calcium hydride. $Pd(PPh_3)_4$[10] was obtained according to the known procedures.

Typical procedure for synthesis of (E)-vinylic selenides (**2a-i**)] — To a freshly prepared suspension of 9-BBN (5mmol) in THF (10ml) at 0 ℃ was add terminal selenoacetylene (5mmol) in THF (2ml) over a period of 5 min. The reaction mixture was stirred until the precipitate completely disappeared (ca. 3h). The solution was poured into a mixture of $NaOCH_3$ or NaOH (15mmol), $Pd(PPh_3)_4$ (0.165g, 0.15mmol) and alkyl halide (5mmol) in THF (3ml), and then the mixture was relfuxed for 5h. After the reaction was completed, the mixture was cooled to room temperature, extracted into pentane (10ml), filtered and concentrated in vacuo. The residue was purified by flash chromatography on 3 ft.X 1 in.Column(100-200 mesh) with light petroleum(bp.30-60 ℃)as elution to give **2a-i.**

(E)-1-methylseleno-3-benzyl-1-propene (**2a**): Oil. IRν(cm^{-1}):1629;1592;1560;947. ^{1}H NMR($CDCl_3$)δ_H(ppm):2.25(s,3H);4.15(d,2H,J=7.3Hz);6.48(m,1H); 6.95(d,1H, J=15.5Hz);7.10-7.62(m,5H).Anal.Calcd.for$C_{10}H_{12}Se$:C%,56.88;H%,5.73.Found: C %,57.05;H%,5.90.

(E)-1-ethylseleno-1,4-pentadiene (**2b**): Oil. IRν(cm^{-1}):1652;1625;993;949;917. ^{1}H NMR($CDCl_3$)δ_H(ppm):1.63(t,3H,J=7.6Hz);2.78(q,2H,J=7.6Hz);3.11(m,2H);5.07(m,2H);5.81(m,2H);6.18(m,1H);6.77(d,1H,J=15.1Hz).Anal.Calcd.for$C_7H_{12}Se$:C%, 48.01;H%,6.91.Found:C%,48.22;H%6.60.

(E)-1-ethylseleno-2-phenyl-ethene(**2c**):Oil.IRν(cm^{-1}):1621;1595;1563;1550;952.^{1}H NMR($CDCl_3$)δ_H(ppm):1.71(t,3H,J=7.5Hz);2.83(q,2H,J=7.5Hz);6.48(d,1H,J=15.7 Hz);7.00(d,1H,J=15.7Hz);7.05-7.06(m,5H).Anal.Calcd.for$C_{10}H_{12}Se$:C%,56.88;H %,6.91.Found:C%,55.94;H%,6.72.

(E)-1-butylseleno-2-(p-methylphenyl)-ethene (**2d**): Oil. IRν(cm^{-1}):1631;1595;1563; 1551;957.^{1}H NMR($CDCl_3$)δ_H(ppm):0.78(t,3H,J=7.0Hz);1.38(m,2H);1.68(m,2H),2. 81(t,2H,J=7.7Hz);3.81(s,3H);6.41(d,1H,J=15.9Hz);6.99(d,1H,J=15.9Hz);7.11-7.6 5(m,4H).Anal.Calcd.for$C_{13}H_{18}Se$:C%,61.66;H%,7.16.Found:C%,61.92;H%,7.00.

(E)-1-hexylseleno-1-propene (**2e**):Oil. IRν(cm^{-1}):1621;950. ^{1}H NMR($CDCl_3$)δ_H(pp m):0.74(t,3H,J=6.9Hz);1.31(m,4H);1.53(m,2H);1.70(m,2H);2.28(d,3H,J=7.2Hz);2. 77(t,2H,J=7.7Hz);6.24(m,1H);6.89(d,1H,J=15.3Hz).Anal.Calad.for$C_9H_{18}Se$:C%,5 2.68;H%,8.84.Found:C%,52.44;H%,8.99.

(E)-1-hexylseleno-2-(p-methoxyphenyl)-ethene(**2f**);Oil.IRν(cm^{-1}):1633;1599; 1564; 1549;957.^{1}HNMR($CDCl_3$)δ_H(ppm):0.87t,3H,J=7.0Hz);.36(m,4H);1.56(m,2H);1.73 (m,2H);2.88(t,2H,J=7.9Hz);1.36(m,4H);1.56(m,2H);1.73(m,2H);2.88(t,2H,J=15.8 Hz);7.10-
7.65(m,4H).Anal.Calad.for$C_{15}H_{22}OSe$:C%,60.60;H%,7.46.Found:C%,60.41;H%,7. 71.

(E)-1-phenylseleno-2-(p-methoxyphenyl)-ethene(**2i**):Oil.IRν(cm^{-1}):1637;1597;156 1,1550,943.^{1}H NMR($CDCl_3$)δ_H(ppm):4.13(s,3H);6.67(d,1H,J=16.0Hz);7.0-7.67(m, 10H).Anal.Calad.for$C_{15}H_{14}OSe$:C%,62.29;H%,4.88.Found:C%,62.45;H%,4.60.

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