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Regio- and Stereoselective Synthesis of (E)-1-Alkylseleno-1,4-Pentadienes by Cross-Coupling of Allyl Bromide with Alkylselenovinylcoppers from Alkylselenovinyldialkylboranes

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Abstract: Alkylselenovinyldialkylborane derivatives, obtained by hydroboration of terminal alkylselenoacetylenes **1** with dialkylboranes **2**, were treated at -15℃ with sodium methoxide and cuprous bromide-methyl sulfide to generate alkylselenovinylcopper intermediates which underwent stereospecific cross-coupling with allyl bromide to yield (E)-1-alkylseleno-1,4-pentadienes **3**. The compounds **3** were formed with retention of configuration predetermined from the stereochemistry of the initial alkylselenovinylboranes.

Methods for the synthesis of symmetric and unsymmetric disubstituted ethenes have been reported.[1] However, the control of stereochemistry for synthesis becomes much more difficult and procedures of various degrees of complexity and validity have been proposed. Although the hydroboration of acetylene has been intensively studied for years,[2] reports on this subject are still appearing.[3,4] This inspires us to enisage that the hydroboration of alkylselenoacetylenes with dialkylboranes would proceeds with proposition and they would provide a straightforward method for synthesis of alkenyl selenides. Such alkenyl selenides are synthetically used as intermediates equivalent to carbonyls and can be stereospecifically converted to alkenes by nickel-catalyzed coupling reactions with Grignard reagents.[5] Since this type of reaction has so far been studied little,[6] it is important to probe the reaction to prepare a species of the novel alkenyl selenides.

Scheme 1

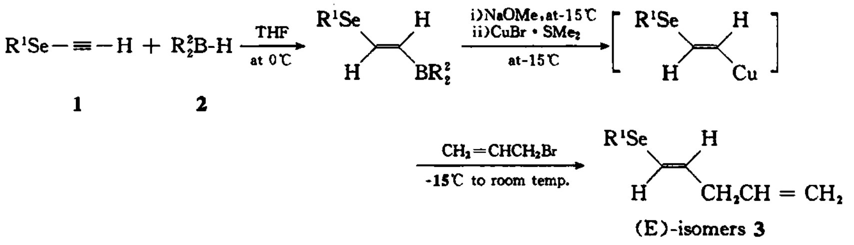

Table 1. Transformation of terminal alkylselenoacetylenes into (E)-1-alkylseleno-1,4-pentadienes

Terminal alkylselenoacetylene	R^1	Hydroborating reagent	R^2_2BH	Yield[a](%)	product[b]
1a	CH_3	**2a**	DCB	73	**3a**
1b	C_2H_5	**2b**	9-BBN	84	**3b**
1c	i-C_3H_7	**2b**	9-BBN	64	**3c**
1d	n-C_4H_9	**2a**	DCB	81	**3d**
1e	n-C_5H_{11}	**2b**	9-BBN	79	**3e**
1f	n-C_6H_{13}	**2b**	9-BBN	87	**3f**
1g	c-C_6H_{11}	**2a**	DCB	68	**3g**
1h	Ph	**2a**	DCB	80	**3h**

a) Isolated yield with isomeric purity of 97-98% by GLC. b) The stereochemistry of products was established by a coupling constant of 15.1-15.3 Hz between olefinic protons in the ^1H NMR spectrum as well as the NOE experiments.

(E)-2-alkylseleno-1-vinyldialkylboranes, derived from the monohydroboration of terminal alkylselenoacetylenes[7] **1** with dicyclohexylborane (DCB) **2a** or 9-borabicyclo[3,3,1]-nonane (9-BBN) **2b**, were treated successively at-15℃ with sodium methoxide and cuprous bromide-methyl sulfide to afford vinyliccopper intermediates, which were conveniently converted into (E)-1-alkylseleno-1,4-pentadienes **3** upon cross-coupling with allyl bromide at the same temperature(**Scheme 1**). The stereochemistry of product **3** were confirmed by ^1H NMR and NOE experiment. No trace of the other isomers was detected by ^1H NMR. The results are listed in **Table 1**. Similarly, we were performed that the **3d** was stereospecifically converted to (4E)-1,4-nonadiene with butylmagnesium bromide according to known procedure,[5] which was consilient with known compound.[8]

To reveal the further scope of cross-coupling, the hydroboration of terminal butylselenoacetylene, followed under the same condition with the cross-coupling of phenyl bromide was also carried out. Yield obtained was low. When the reaction time was added to 5h, the yield would be increased by 63%. In our research, on the other hand, it was found that when the cross-coupling of the c-c bond was formed, the reaction didn't have any influence upon the alkylseleno group.

In summary, we have shown the first exmple of transformation of terminal alkylselenoacetylenes into (E)-1-alkylseleno-1,4-pentadienes **3** by the hydroboration and cross-coupling. The reaction proceeds with regio-and stereospecificity, giving excellent yields of 3 with high isomeric purity. We are currently exploring the synthetic potentialities of the hydroboration of alkylselenoacetylenes.

Experimental

^{1}H NMR spectra were recorded on an AZ-300MHz with TMS as internal standard. Mass spectra were determined by a Finigan 8230 mass spectrometer. IR specta were obtained as neat capillary cells (liquid products) on a shimadzu IR-408 instrument. All synthesis of 3 complexes were carried out under di-nitrogen. Solvents were dried, deoxygenated and distilled before use. The DCB[9] and 9-BBN[10] were prepared according to the literature methods. The borane was made in the laboratory and standardized before use. Commercial sodium borohydride was used without purification.

General procedure for the preparation of (E)-1-alkylseleno-1,4-pentadiene(**3a-h**)

To a freshly prepared suspension of DCB or 9-BBN **2** (5 mmol) in THF at 0℃ was added terminal alkylselenoacetylene **1** (5. 1 mmol) in THF (2 ml) over a period of 5 min. The reaction mixture was stirred until the precipitate of **2** completely disappeared (ca. 3. 5h). The solution was poured into a suspension of $NaOCH_3$(5. 1 mmol) in THF (5 ml) at -15℃. After being stirred for 30 min, addition of this adduct to CuBr • SMe_2(1. 05g, 5. 1 mmol) in THF (3 ml) at -15℃ was followed after 10 min by the addition of 1. 1 equiv of allyl bromide. After being stirred at -15℃ for 1. 5 h, the reaction was allowed to warm slowly to room temperature. The product was extracted into pentane. The extract was dried ($MgSO_4$) and concentrated under a reduced pressure and the residue was purified by flash chromatogarphy on 0. 3 ft x 1 in. Column (100-200 mesh) with light petroleum (bp30-60℃) as elution to give **3**.

(E)-1-methylseleno-1,4-pentadiene (**3a**)

Oil. IR(neat) 1651, 1625, 990, 947, 915 cm^{-1}. ^{1}H NMR($CDCl_3$), δ2. 48(s,3H), 3. 12 (m,2H), 5. 05(m,2H), 5. 82(m,1H), 6. 14(m,1H), 6. 80(d,1H,J=15. 2Hz). Anal. Calcd for $C_6H_{10}Se$: C%, 44. 73; H%, 6. 26. Found: C%, 44. 55; H%, 6. 34.

(E)-1-ethylseleno-1,4-pentadiene (**3b**)

Oil. IR(neat) 1652, 1625, 993, 949, 917 cm^{-1}. ^{1}H NMR($CDCl_3$) δ1. 63(t,J=7. 6Hz, 3H), 2. 78(q,J=7. 6Hz,2H), 3. 11(m,2H), 5. 06(m,2H), 5. 81(m,2H), 6. 18(m, 1H), 6. 77(d,J=15. 1Hz, 1H). Anal. Calcd. for $C_7H_{12}Se$: C, 48. 01%; H,6. 91%. Found: C, 48. 28%; H, 6. 86%.

(E)-1-isopropylseleno-1,4-pentadiene (**3c**)

Oil. IR(neat) 1650, 1621, 1000, 954, 920 cm^{-1}. ^{1}H NMR(CDCl$_3$), δ1.60(d,J=7.5Hz, 6H), 2.65(q,J=7.5Hz,1H), 3.12(m,2H), 5.05(m,2H), 5.78(m,2H), 6.20(m, 1H), 6.74(d,J=15.0Hz,1H). Anal. Calcd. for $C_8H_{14}Se$: C, 51.34%; H, 7.49%. Found: C, 51.52%; H, 7.66%.

(E)-1-butylseleno-1,4-pentadiene (**3d**)

Oil. IR(neat) 1649, 1620, 998, 950, 918 cm^{-1}. ^{1}H NMR(CDCl$_3$) δ0.88(t,J=7.1Hz, 3H), 1.32(m,2H), 1.68(m,2H), 2.68(t,J=7.6Hz,2H), 3.18(m,2H), 5.05(m,2H), 5.85(m,2H), 6.19(m,1H), 6.77(d,J=15.1Hz,1H). Anal. Calcd. for $C_9H_{16}Se$: C, 53.20%; H, 8.02%. Found: C, 52.94%; H, 8.26%.

(E)-1-pentylseleno-1,4-pentadiene (**3e**)

Oil. IR(neat) 1647, 1618, 998, 950, 917 cm^{-1}. ^{1}h NMR(CDCl$_3$) δ0.85(t,J=7.0Hz, 3H), 1.30(m,4H), 1.70(m,2H), 2.6(t,J=7.5Hz, 2H), 3.15(m,2H), 5.05(m,2H), 5.84(m,2H), 6.15(m,1H), 6.78(d,J=15.1Hz, 1H). Anal. Calcd for $C_{10}H_{18}Se$: C, 55.30%; H, 8.35%. Found: C, 55.07%; H, 8.54%.

(E)-1-hexylseleno-1,4-pentadiene (**3f**)

Oil. IR(neat) 1647, 1617, 999, 951, 917 cm^{-1}. ^{1}H NMR(CDCl$_3$) δ0.84(t,J=7.0Hz, 3H), 1.31(m,6H), 1.69(m,2H), 2.65(t,J=7.5Hz,2H), 3.15(m,2H), 5.04(m,2H), 5.80(m,2H), 6.16(m,1H), 6.78(d,J=15.1Hz, 1H). Anal. Calcd for $C_{11}H_{20}Se$: C, 57.14%; H, 8.72%. Found: C, 57.41%; H, 8.95%.

(E)-1-cycloherylseleno-1,4-pentadiene (**3g**)

Oil. IR. 1647, 1621, 990, 945, 915 cm^{-1}. ^{1}H NMR(CDCl$_3$) δ1.10-1.52(m,10H), 2.55 (br,1H), 3.10(m,2H), 5.0(m,2H), 5.88(m,2H), 6.21(m,1H), 6.68(d,J=15.1Hz, 1H). Anal. Calcd. for $C_{11}H_{18}Se$: C, 57.64%; H, 7.91%. Found: C, 57.86%; H, 7.75%.

(E)-1-phenylseleno-1,4-pentadiene (**3h**)

Oil. IR. 1657, 1630, 1000, 955, 920 cm^{-1}. ^{1}H NMR(CDCl$_3$) δ3.20(m,2H), 5.20(m, 2H), 5.92(m,1H), 6.25(m,1H), 6.85(d,J=15.2Hz,1H), 7.05-7.55(m,5H). Anal. Calcd. for $C_{11}H_{12}Se$: C, 59.20%; H, 5.42%. Found: C, 58.94%, H, 5.64%.

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7. A white suspension of ethynlymagenesium bromide intetrahydrofuran (40ml, 20mmol) was added dropwise to a stirread mixture solution of alkylselenium mono-and tribromide at -20℃in tetrahydrofuran (30ml, 20mmol) over 1h, the reaction mixture was stirred at the same temperature for an additional 0. 5h . The mixture was then allowed to warm to room temperature, stirred for 1h. The mixture was treated with sat. aq NH_4Cl(15ml). The phase was separated, dried ($MgSO_4$), and concentrated in vacuo. To the residue was then added pentane (30ml) and $NaBH_4$(0. 11g, 3mmol), respectively. The reaction mixture was stirred at room temperture for 2h. The mixture was treated with sat. aq Na_2CO_3(10ml). The organic phase was separated, dried over $MgSO_4$. Removal of solvent under reduced pressure gave the terminal alkylselenoacetylene **1** which was purified by flash chromatography (light petroleum, bp30-60℃).

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