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Coupling Allylation of Dialkylselenaethenylboranes to give 1,1- and (*Z*)-1,2-Dialkylselenapenta-1,4-dienes†

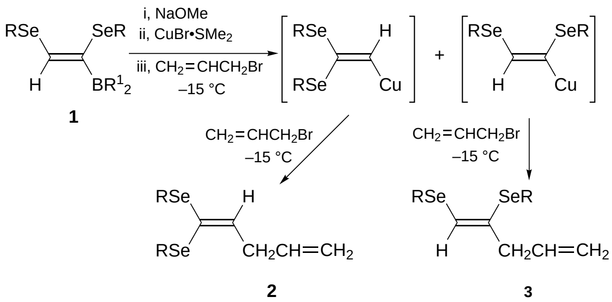
De Yu Yang,*[a] Yi Zhang[b] and Xian Huang[a]

[a]*Department of Chemistry, Hangzhou University, Hangzhou 310028, China*
[b]*Department of Chemistry and Biochemistry, New Mexico State University, Las Cruces, NM 88003, USA*

A new method for the formation of 1,1- and (*Z*)-1,2-dialkylselenapenta-1,4-dienes by coupling allylation of dialkylselenaethenylboranes with allyl bromide in the presence of NaOMe and CuBr·SMe_2 is described; the reaction proceeds *via* the migration of an alkylselenyl group from one olefinic carbon to another.

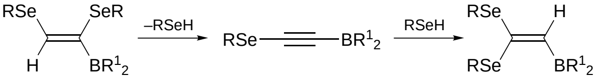
Few syntheses of diselenaalkenes have been reported to date.[1] However, there are still many classes of diselenaalkenes that cannot be synthesised generally, especially dialkylselenaalkenes. Here we report a new method for the synthesis of 1,1- and (*Z*)-1,2-dialkylselenapenta-1,4-dienes, which are obtained by the treatment of (*Z*)-1,2-dialkylselenaethenylboranes with allylic bromide in the presence of sodium methoxide and copper(I) bromide–methyl sulfide. The formation of the 1,1-dialkylselenapenta-1,4-dienes involves a rearrangement of the alkylselenyl group.

We recently reported that the coupling reaction of alkylselenavinylcopper compounds, readily derived by the hydroboration of terminal[2] or internal[3] alkylselenaacetylenes with dialkylboranes followed by treatment with NaOMe and CuBr•SMe_2, with organic halides provides the corresponding alkylselenaalkenes. In the present work, however, dialkylselenaethenylboranes **1**, obtained from the hydroboration of dialkylselenaacetylenes with 9-borabicyclo[3.3.1]nonane (9-BBN), were treated successively with sodium methoxide and cuprous bromide–methyl sulfide, followed by coupling with allylic bromide. It was found that the coupling allylation proceeded smoothly under mild conditions and gave a mixture of the unexpected 1,1-dialkylselenapenta-1,4-dienes **2** and the corresponding (*Z*)-1,2-dialkylselenapenta-1,4-dienes **3** (Scheme 1). The results are presented in Table 1. The stereochemistry of the 1,1-isomer **2a** was confirmed by a triplet of the coupling constant (*J* 7.2 Hz) of one olefinic proton with the methylene related to the same carbon in the double bond in ^{1}H NMR spectrum (300 MHz) and by NOE experiments [irradiation of two allyl methylene protons (δ 3.07), NOE (%)]: H (δ 6.21, olefinic H) (3.7).



Scheme 1

Brown[4] and co-workers previously reported that alkenylcopper intermediates, generated from alkenyldialkylborane derivatives of 9-borabicyclo[3.3.1]nonane, underwent coupling with allylic halides or 1-haloalk-1-ynes to provide stereodefined 1,4-dienes or conjugated enynes. We have also reported that heteroselenium-substituted alkenylboranes are transferred to the corresponding alkenylcoppers followed by coupling with organic halides to yield alkylselenaalkanes.[2,3] These results showed that the reaction proceeded with retention of the alkenylborane configuration. It is not clear why the transformation of the dialkylselenaethenylboranes into the corresponding ethenylcoppers followed by coupling allylation produced the two isomers **2** and **3**. In the present case, an additional consideration is that the possible mechanism according to which 1,1-dialkylselenapenta-1,4-dienes **2** were formed proceeds *via trans*-elimination of HSeR in the presence of base such as NaOMe because the RSe group sterically hinders the approach to boron (a precedent for such an elimination has been reported in the literature),[5] followed by RSeH addition to the alkyne product in the opposite sense to yield $(RSe)_2CCH(BR'_2)$ which would no longer be a hindrance to the attack at boron. The cupration and allylation could thus proceed to give **2** (Scheme 2).



Scheme 2

Experimental

The ^{1}H NMR spectra were recorded on an AZ-300 MHz with TMS as internal standard. Mass spectra were determined using a Finigan 8230 mass spectrometer. IR spectra were obtained in neat capillary cells on a Shimadzu IR-408 instrument. Elemental analyses were conducted using a Perkin-Elmer 240B elemental analyser. Silica gel 60 FC_{254} was used for analytical and preparative TLC. Silica gel columns were prepared using silica gel Q/BKUS 3–91 (100–200 mesh). The reactions were carried out in pre-dried glassware (150 °C, 4 h) and cooled under a stream of dry nitrogen. All solvents were dried, deoxygenated and redistilled before use. The dialkylselenaacetylenes[7] were prepared according to literature methods.

General Procedure for the Synthesis of Dialkylselenapenta-1,4-dienes **2** *and* **3**.—To a freshly prepared suspension of 9-borabicyclo[3.3.1]nonane (5 mmol) in THF (10 ml) at 0 °C was added dialkylselenaacetylene (5.1 mmol) in THF (2 ml) over 5 min. The reaction mixture was stirred until the precipitate completely disappeared (*ca.* 5 h). The solution was then poured into a suspen-

Table 1 Yields and isomeric ratios obtained in the synthesis of 1,1- and (*Z*)-1,2-dialkylselenapenta-1,4-dienes **2a–g** and **3a–g**

Compound	R	Isomeric ratio[a] (**2**:**3**)	Total yield (%)[b]
a	Et	1:3.3	82
b	Bu	1:1.8	81
c	Me	1:8[c]	83
d	pentyl	1:1.5	79
e	hexyl	1:1.2	80
f	cyclohexyl	1:2.8	73
g	Ph	1:1.1[c]	75

[a]Determined by ^{1}H NMR. [b]Isolated yields based on dialkylselenaacetylenes employed. [c]For compounds **3c** and **3g**, see ref. 6.

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*To receive any correspondence.

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sion of NaOMe (5.1 mmol) in THF (5 ml) at -15 °C. After being stirred for 30 min, addition of this adduct to CuBr·SMe$_2$ (1.05 g, 5.1 mmol) in THF (3 ml) at -15 °C was followed, after 10 min, by the addition of 1.1 equiv. of allyl bromide. After further stirring at -15 °C for 1.5 h, the reaction was allowed to warm slowly to room temperature. The product was then extracted into pentane, filtered and concentrated *in vacuo*. The residue was purified by flash chromatography on a 3 ft × 1 inch column with light petroleum (bp 30–60 °C) as eluent to give **2** and **3**.

1,1-*Diethylselanapenta*-1,4-*diene* **2a**. *Oil*. R_f 0.66 (pentane). ν_{max}/cm^{-1} 1637, 819. δ_H 6.21 (1 H, t, *J* 7.2 Hz), 5.67 (1 H, m), 5.0 (2 H, m), 3.07 (2 H, dd, *J* 7.2, 7.5 Hz, 2.91 (2 H, q, *J* 7.9 Hz), 2.88 (2 H, q, *J* 7.8 Hz), 1.75 (3 H, t, *J* 7.9 Hz), 1.69 (3 H, t, *J* 7.8 Hz). *m*/*z* 284 ($M^+ + 2$, 13%), 255 (55), 225 (17), 145 (100) (Found: C, 38.77; H, 6.03. $C_9H_{16}Se_2$ requires C, 38.31; H, 5.72%).

(Z)-1,2-*Diethylselenapenta*-1,4-*diene* **3a**. *Oil*. R_f 0.53 (pentane). ν_{max}/cm^{-1} 1621, 798. δ_H 5.95 (1 H, s), 5.79 (1 H, m), 5.08 (2 H, m), 3.18 (2 H, d, *J* 7.59 Hz), 2.87 (2 H, q, *J* 7.9 Hz), 2.81 (2 H, q, *J* 7.7 Hz), 1.59–1.80 (6 H, m). *m*/*z* 284 ($M^+ + 2$, 17%), 255 (47), 225 (21), 145 (100) (Found: C, 37.91; H, 6.11. $C_9H_{16}Se_2$ requires C, 38.31; H, 5.72%).

1,1-*Dibutylselenapenta*-1,4-*diene* **2b**. *Oil*. R_f 0.69 (pentane). ν_{max}/cm^{-1} 1631, 808. δ_H 6.19 (1 H, t, *J* 7.2 Hz), 5.88 (1 H, m), 5.01 (2 H, m), 3.05 (2 H, dd, *J* 7.2, 7.54 Hz), 2.75–2.97 (4 H, m), 1.56–1.82 (4 H, m), 1.20–1.50 (4 H, m), 0.97 (3 H, t, *J* 6.7 Hz), 0.91 (3 H, t, *J* 6.7 Hz). *m*/*z* 340 (M^+ 2, 9%), 283 (51), 226 (19), 145 (100) (Found: C, 46.52; H, 7.55. $C_{13}H_{24}Se_2$ requires C, 46.16; H, 7.15%).

(Z)-1,2-*Dibutylselenapenta*-1,4-*diene* **3b**. *Oil*. R_f 0.51 (pentane). ν_{max}/cm^{-1} 1619, 795. δ_H 5.97 (1 H, s), 5.81 (1 H, m), 514 (2 H, m), 3.20 (2 H, d, *J* 7.6 Hz), 2.74–2.97 (4 H, m), 1.57–1.79 (4 H, m), 1.24–1.53 (4 H, mn), 0.98 (3 H, t, *J* 6.9 Hz), 0.91 (3 H, t, *J* 6.8 Hz). *m*/*z* 340 (M^+, 12%), 283 (43), 226 (22), 145 (100) (Found: C, 45.72; H, 6.89. $C_{13}H_{24}Se_2$ requires C, 46.16; H, 7.15%).

1,1-*Dimethylselenapenta*-1,4-*diene* **2c**. *Oil*. R_f 0.65 (pentane). ν_{max}/cm^{-1} 1630, 811. δ_H 6.11 (1 H, t, *J* 7.1 Hz), 5.72 (1 H, m), 5.03 (2 H, m), 3.07 (2 H, dd, *J* 7.1, 4 Hz), 2.22 (3 H, s), 2.17 (3 H, s). *m*/*z* 245 (M^+ 2, 14%), 241 (21), 225 (57), 145 (100) (Found: C, 32.75; H, 4.47. $C_7H_{12}Se_2$ requires C, 33.09; H, 7.76%).

1,1-*Dipentylselenapenta*-1,4-*diene* **2d**. *Oil*. R_f 0.68 (pentane). ν_{max}/cm^{-1} 1641, 822. δ_H 6.18 (1 H, t, *J* 7.2 Hz), 5.78 (1 H, m), 5.03 (2 H, m), 3.02 (2 H, dd, *J* 7.2m, 7.6 Hz), 2.81 (2 H, q, *J* 7.8 Hz), 2.79 (2 H, t, *J* 8.1), 1.56–1.80 (4 H, m), 1.15–1.52 (8 H, m), 0.96 (3 H, t, *J* 6.9 Hz), 0.92 (3 H, t, *J* 6.8 Hz). *m*/*z* 368 ($M^+ + 2$, 13%), 313 (3), 297 (48), 225 (16), 191 (4), 163 (4), 145 (100) (Found: C, 49.64; H, 7.38. $C_{15}H_{28}Se_2$ requires C, 49.18; H, 7.70%).

(Z)-1,2-*Dipentylselenapenta*-1,4-*diene* **3d**. *Oil*. R_f 0.55 (pentane). ν_{max}/cm^{-1} 1623, 794. δ_H 5.98 (1 H, s), 5.76 (1 H, m), 5.05 (2 H, m), 3.12 (2 H, d, *J* 7.6 Hz), 2.75–2.91 (4 H, m), 1.53–1.78 (4 H, m), 1.15–1.48 (8 H, m), 0.93 (3 H, t, *J* 6.9 Hz), 0.88 (3 H, t, *J* 6.7 Hz). *m*/*z* 368 ($M^+ + 2$, 16%), 323 (3.6), 297 (60), 256 (5.6), 225 (18), 186 (8), 145 (100) (Found: C, 49.61; H, 7.96. $C_{16}H_{28}Se_2$ requires C, 49.18; H, 7.70%).

1,1-*Dihexylselenapenta*-1,4-*diene* **2e**. *Oil*. R_f 0.66 (pentane). ν_{max}/cm^{-1} 1645. 819. δ_H 6.19 (1 H, t, *J* 7.2 Hz), 5.77 (1 H, m), 5.05 (2 H, m), 3.07 (2 H, dd, *J* 7.2, 7.6 Hz), 2.75–2.92 (4 H, m), 1.55–1.677 (4 H, m), 1.17–1.47 (12 H, m), 0.90 (3 H, t, *J* 6.8 Hz), 0.88 (3 H, t, *J* 6.8 Hz). *m*/*z* 396 ($M^+ + 2$, 9%), 311 (41), 225 (5), 145 (100) (Found: C, 51.32; H, 7.79. $C_{17}H_{32}Se_2$ requires C, 51.78 H, 8.18%).

(Z)-1,2-*Dihexylselenapenta*-1,4-*diene* **3e**. *Oil*. R_f 0.54 (pentane). ν_{max}/cm^{-1} 1628, 798. δ_H 5.59 (1 H, s), 5.71 (1 H, m), 5.07 (2 H, m), 3.15 (2 H, d, *J* 7.7 Hz), 2.73–2.90 (4 H, m), 1.56–1.79 (4 H, m), 1.17–1.48 (12 H, m), 0.93 (3 H, t, *J* 6.8 Hz), 0.88 (3 H, t, *J* 6.7 Hz). *m*/*z* 396 ($M^+ + 2$, 9%), 311 (46), 225 (5), 145 (100) (Found: C, 52.22; H, 8.55. $C_{17}H_{32}Se_2$ requires C, 51.78; H, 8.18%).

1,1-*Dicyclohexylselenapenta*-1,4-*diene* **2f**. *Oil*. R_f 0.66 (pentane). ν_{max}/cm^{-1} 1647, 824. δ_H 6.08 (1 H, t, *J* 7.1 Hz), 5.66 (1 H, m), 5.0 (2 H, m), 3.01 (2 H, dd, *J* 7.1, 7.5 Hz), 2.85–3.05 (2 H, br), 1.10–1.75 (20 H, m). *m*/*z* 392 ($M^+ + 2$, 14%), 309 (48), 225 (19), 145 (100) (Found: C, 52.77; H, 6.88. $C_{17}H_{28}Se_2$ requires C, 52.31; H, 7.23%).

(Z)-1,2-*Dicyclohexylselenapenta*-1,4-*diene* **3f**. *Oil*. R_f 0.56 (pentane). ν_{max}/cm^{-1} 1617, 792. δ_H 5.92 (1 H, s), 5.67 (1 H, m), 4.98 (2 H, m), 3.13 (2 H, d, *J* 7.6 Hz), 2.84–3.08 (2 H, br), 1.12–1.78 (20 H, m). *m*/*z* 392 ($M^+ + 2$, 15%), 309 (58), 225 (16), 145 (100) (Found: C, 51.94; H, 7.01. $C_{17}H_{28}Se_2$ requires C, 51.31; H, 7.23%).

1,1-*Diphenylselenapenta*-1,4-*diene* **2g**. *Oil*. R_f 0.59 (pentane). ν_{max}/cm^{-1} 1637, 1592, 1567, 815. δ_H 7.15–7.65 (10 H, m), 6.31 (1 H, t, *J* 7.0 Hz), 5.96 (1 H, m), 5.08 (2 H, m), 3.11 (2 H, dd, *J* 7.0, 7.4 Hz). *m*/*z* 380 ($M^+ + 2$, 11%), 379 ($M^+ + 1$, 10), 378 (M^+, 9), 303 (55), 225 (20), 145 (100) (Found: C, 54.38; H, 4.61. $C_{17}H_{16}Se_2$ requires C, 53.98; H, 4.26%).

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