The Hydroboration-Iodination of Dialkylselenoacetylenes to Vinylic Diselenides

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Abstract: The hydroboration of dialkylselenoacetylenes **1**, generated from alkylseleno bromides and sodium acetylide in liquid ammonia, with dicycloalkylboranes followed by iodination under basic condition produced (*Z*)/(*E*)-vinylic diselenides (**2**/**3**). The reaction proceeds with a transfer of one cycloalkyl group and smoothly to give major **2** and minor **3** in almost quantitative ratio (**2**:**3**=93:7 to 97:3). The hydroboration-iodination process provides a general method for synthesis of (Z)-vinylic diselenides containing cyclic systems.

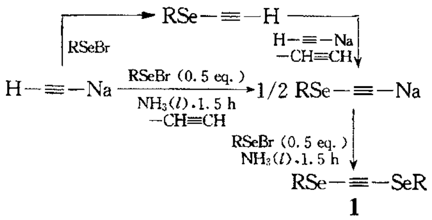
Organoselenium chemistry is of current interest from synthetic and structural point of view[1]. We have recently reported that dialkylselenovinylboranes, derived from the hydroboration of dialkylselenoacetylenes with 9-BBN, reacted with organic halides in the presence of $Pd(PPh_3)_4$ and $NaOCH_3$ to afford the corresponding alkenyl diselenides in good yield[2]. When such method was applied to the synthesis of vinyl diselenides containing cyclic systems, we failed in obtaining the corresponding results. Therefore, we now wish to report that (*Z*)-vinyl diselenides containing cyclic systems could be synthesized by hydroboration of diselenoacetylenes with dicycloalkylboranes, followed by iodination in the presence of a base, which resulted in a transfer of one cycloalkyl group from boron atom to the adjacent carbon.

We found that the reaction of alkylselenyl bromides[3] in benzene in batches with sodium acetylide[4] in liquid ammonia produced at -30 °C dialkylselenoacetylenes[5] **1** in good yields (**Table 1**). Since the reaction failed in affording any terminal alkylselenoacetylenes, the results indicated that there were certainly complete transformations of terminal alkylselenoacetylene into sodium acetylide containing alkylselenyl groups, which further reacted with alkylselenyl bromides to produce compounds **1** (**Scheme 1**).

Table 1. Synthesis of dialkylselenoacetylenes 1a-f

Entry[a]	Dialkylselenoacetylenes	Yield[b] (%)
a	$C_2H_5Se-\equiv-SeC_2H_5$	88[c]
b	$n\text{-}C_4H_9Se-\equiv-SeC_4H_9$	82
c	$n\text{-}C_5H_{11}Se-\equiv-SeC_5H_{11}$	77
d	$n\text{-}C_6H_{13}Se-\equiv-SeC_6H_{13}$	74
e	$c\text{-}C_6H_{11}Se-\equiv-SeC_6H_{11}$	70
f	$PhSe-\equiv-SePh$	85

[a] All products were characterized using ^1H NMR and Elemental analyses. [b] Isolated yields based on dialkylselenides employed. [c] Compound **1a** see ref. 6.



Scheme 1

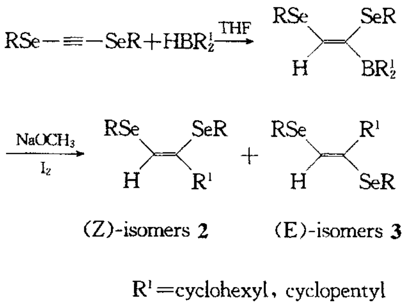
It was previously reported that the iodination of (*E*)-vinylboranes in the presence of base resulted in a transfer of one alkyl group from boron to an adjacent carbon to give the (*Z*)-alkene with high isomeric purity and the reaction proceeded with the inversion of the configuration[7]. We recently have reported the hydroboration-iodination of internal alkylselenoacetylenes with dicycohexylborane, the reaction providing a mixture of major *trans* 1, 2-disubstituted alkenyl selenides (with the inversion of configuration) and minor *cis* 1, 2-disubstituted alkenyl selenides (with the retention of configuration)[8]. However, addition of a solution of dialkylselenoacetylenes **1** prepared above to the dicyclohexylborane gave diselenoethenyldicyclohexylboranes, and successive treatment of these intermediates at -15 °C with a solution of $NaOCH_3$ in $HOCH_3$ and a solution of iodine in THF produced major (*Z*)-1,2-dialkylseleno-1cyclohexylethenes[9] **2a-c** with the retention of configuration and minor (*E*)-1,2-dialkylseleno-1-cyclohexylethenes **3a-c** with the inversion of configuration (**Scheme 2**). Compared with the results of internal alkylselenoacetylenes[8], the ratio of *Z*/*E* isomer (**2a-c**/**3a-c**) obtained here was contrary. To reveal the further scope of the reaction, we also tried to carry out the hydroboration of dialkylselenoacetylenes **1** with dicyclopentylborane[10] that was prepared in situ by treatment of dicyclopentylbromoborane[11] with 0. 25 equiv. of $LiAlH_4$, followed by the iodination under the same condition. Similarly, the reaction afforded major (*Z*)-1,2-dialkylseleno-1-cyclopentylethenes **2d-i** and minor (*E*)-1,2-dialkylseleno-1-cyclopentylethenes **3d-i** (**Scheme 2**). The results are listed in **Table 2**. As shown in **Table 2**, the reaction proceeded with high stereoselectivity and smoothly to give major **2** and minor **3** in almost quantitative ratio (**2**:**3**=93:7 to 97: 3). However, in all cases, highly pure **2** was isolated from the reaction mixtures by simple column chromatography. Thus, the present reaction process provides a method for the synthesis of (*Z*)-1,2-dialkylseleno-1-cyclohexyl or pentylethenes **2**.

Table 2. Synthesis of (Z)-1,2-dialkylseleno-1-cycloalkylethenes **2a**—**i**

Entry[a]	R	R^1	Isolated Yield[b] of **2** %	Ratio/% **2**	**3**	combined Yield[c] of products (**2** and **3**) %
a	Et	$c\text{-}C_6H_{11}$	78	96	4	87
b	$n\text{-}C_4H_9$	$c\text{-}C_6H_{11}$	75	95	5	84
c	$n\text{-}C_6H_{13}$	$c\text{-}C_6H_{11}$	72	94	6	88
d	Et	$c\text{-}C_5H_9$	81	93	7	90
e	$n\text{-}C_4H_9$	$c\text{-}C_5H_9$	71	97	3	81
f	$n\text{-}C_5H_{11}$	$c\text{-}C_5H_9$	69	96	4	80
g	$n\text{-}C_6H_{13}$	$c\text{-}C_5H_9$	70	95	5	85
h	$c\text{-}C_6H_{11}$	$c\text{-}C_5H_9$	60	94	6	77
i	Ph	$c\text{-}C_5H_9$	63	95	5	79

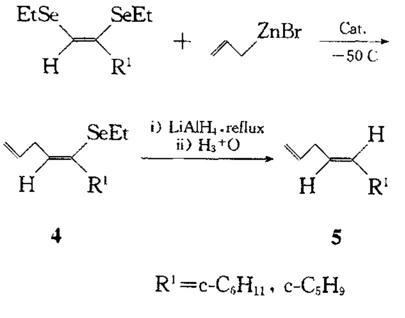
[a] All products were characterized using ^1H NMR, IR, MS or Elemental analyses. [b] Isolated by column chromatography. [c] Determined by GLC and based on dialkylselenoacetylenes **1** employed.

The stereochemistry of the compounds **2** was established by ^{1}HNMR [BRUKER AC-P200 (200 MHz)] according to the steps below: the coupling reaction[2] of **2a** or **2d** at -50 °C with allylzinc bromide in the presence of $NiCl_2(PPh_3)_2$ in THF provided (*Z*)-1-



Scheme 2

ethylseleno-1-cyclohexyl (or cyclopentyl) 1,4-pentadienes **4**, and then metalation of the compounds **4** in reflux with $LiAlH_4$, followed by protonolysis with retention of configuration[8], resulted in (*E*)-1-cyclohexyl (or cyclopentyl)-1,4-pentadienes **5** with a characteristic coupling constant (J=12. 5 or 13 Hz) of (*E*)-isomer in two olefinic protons signals (**Scheme 3**). The configuration of product **3a** or **3d** was then examined according to above method to give (*Z*)-1-cyclohexyl (or cyclopentyl)-1,4-pentadienes with characteristic coupling constant (J=8. 5 or 10 Hz) of (*Z*)-isomer.



Scheme 3

In summary, our results show that the hydroboration-iodination sequence of dialkylselenoacetylenes with dicycloalkylboranes represent a very convenient highly stereoselective synthesis of (*Z*)-1,2-dialkylseleno-1-cycloalkyl-ethenes under mild condition. We are currently exploring the synthetic potentialities of (*Z*)-alkenyl diselenides containing cyclic systems.

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5. General Procedure for the Synthesis of dialkylselenoacetylenes **1a-f**. To 40 mmol sodium acetylide in 50 ml liquid ammonia was slowly added dropwise 20 mmol seleno bromides in 8 ml benzene. After the reaction mixture was stirred for an additional 1. 5 h, to the mixture was slowly added dropwise 20 mmol seleno bromides in 8 ml benzene again. The mixture was stirred for 1. 5 h and warmed up to room temperature. Ammonia was allowed to boil from the reaction mixture, and the residue, having been washed with 30 ml pentane, was filtered and subsequently treated with 20 ml sat. NH_4Cl. The organic layer was separated, dried over $MgSO_4$ and filtered. After removal of the solvent *in vacuo* the residue was purified by flash chromatography (bp 60-90 °C, petroleum) to afford **1** as oil in the yields collected in **Table 1.** For example, for **1b** ^{1}H NMR: δ 2. 82(t,4 H, J=7. 6 Hz, $2xSeCH_2$), 1. 95(m,4 H. 2 x CH_2) . 0. 70-1. 36 (m. 10 H. 2 x CH_2CH_3). Anal. Calc. for $C_{10}H_{18}Se_2$: C,40. 55; H,6. 13. Found C, 40. 87; H,5. 81.
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9. General procedure for synthesis of (*Z*) or (*E*)-vinyl diselenides **2** and **3**. To a 10 mmol solution of cycloalkene in 5 ml THF was added a 5 mmol solution of borane in 1. 25 ml THF at 0 °C with stirring. The precipitate formed dicycloalkylborane was stirred at 0-5 °C for 1 h, and then 5 mmol dialkylselenoacetylene in 5 ml THF was added at 0 °C. After the precipitate had dissolved, the resulting solution was stirred for an additional 30 min at room temperature. To this mixture was then added at -15 °C 3 ml of 6 N NaOMe in HOMe followed by the dropwise addition of a 5 mmol solution of iodine in 3 ml THF over a period of 15 min. After the reaction mixture had been warmed up to room temperature, any excess iodine was decomposed by adding a small amount of aqueous sodium thiosulfate. The products were extracted with hexane and the extracts were dried over anhydrous $MgSO_4$. Solvent was removed in vacuo and the residue was separated by flash chromatography on a 3 ft. x 1 in. column (100-200 mesh) by elusion with petroleum (bp 60-90 °C) to give **2a**—**i** and **3a**—**i** as oil. For example, for **2a**: IR ν(cm^{-1}) : 1636, 801. ^{1}H NMR δ 6.27 (s. 1 H, CH), 3.11 (br, 1 H, CH), 2.88 (q, 2 H, J=7.4 Hz, $SeCH_2$), 2. 85 (q, 2 H, J=7. 2 Hz, $SeCH_2$), 1.58-1.85 (m,6 H, 2 x CH_3), 1. 02-1.57 (m, 10 H, 5 x CH_2). MS *m/z*: 326 (M^+ + 2.15), 324 (M^+, 7.55), 296 (59), 266 (13), 239 (5), 215 (27), 108 (57). Anal. Calc. for $C_{12}H_{22}Se_2$: C, 44.45; H, 6.84. Found : C, 44.83; H, 6.57. for **3b** IR ν(cm^{-1}) : 1641, 815. ^{1}HNMR δ 6.08 (s, 1 H, CH), 3.05 (br, 1 H, CH), 2.85 (t, 2 H, J=7.7 Hz, $SeCH_2$), 2.81 (t, 2 H, J=7.8 Hz, $SeCH_2$), 1.59 -1.83 (m, 4 H, 2 x CH_2), 0.98-1. 54 (m, 10 H, 5 x CH_2). 0.88 (*t*, 3 H, J=6.8 Hz, CH_3), 0.75 (*t*, 3 H, J=6.5 Hz, CH_3). MS *m/z*: 382 (M^+ + 2,19), 380 (M^+, 12), 325 (63), 289 (3.78), 268 (6.7), 134 (80), 108 (33).
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