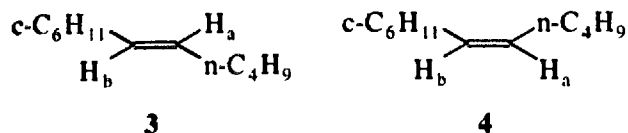
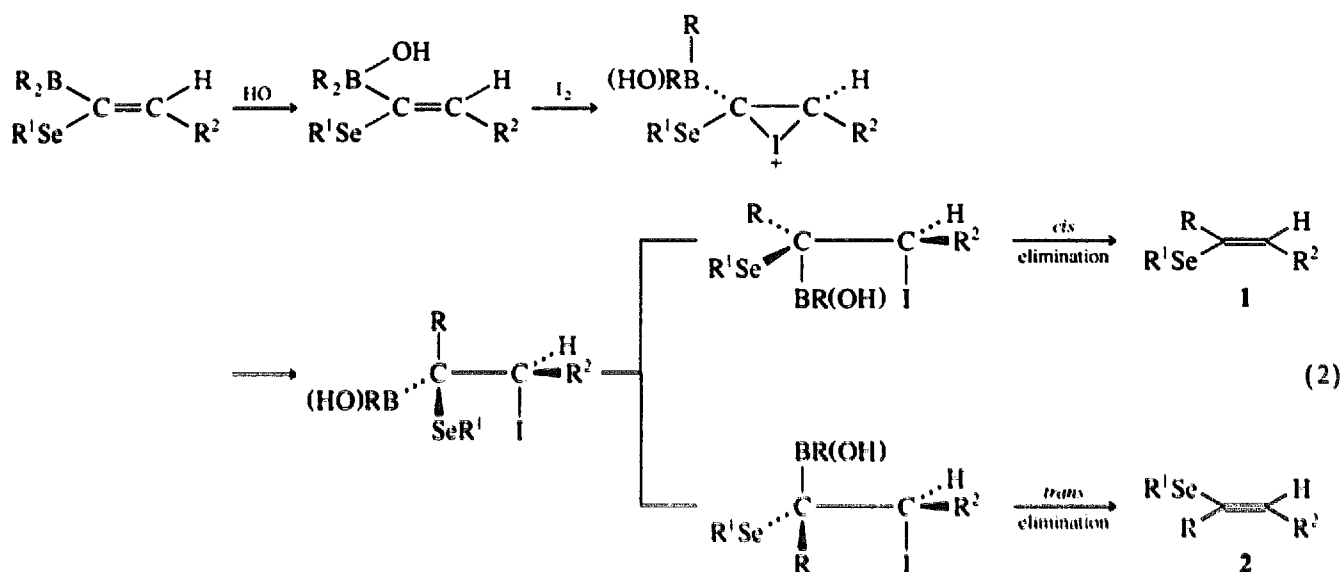


hydroboration of internal alkylselenoacetylenes with dicyclohexylborane proceeds with strong preference for the addition of the boron atom at the carbon adjacent to the alkylseleno group. The *cis/trans* isomers could also be transformed into *trans* **3** and *cis* **4** isomers of 1-cyclohexyl-1-hexene, that are known to have unambiguous stereochemistry [9,10] and could be obtained by treatment of **1a** and **2a**, separated respectively with LiAlH_4 in THF with retention of the configuration [11].



The ratio of isomers **1/2** depends on the size of the R^1 and R^2 of $\text{R}^1\text{Se}-\equiv-\text{R}^2$. The proportion of **1** would



In summary, our results show that the hydroboration-iodination sequence of internal alkylselenoacetylenes with dicyclohexylborane represents a very convenient stereoselective synthesis of *cis/trans* 1,2-disubstituted alkenyl selenides under mild conditions. We are presently exploring the possibilities of extending this procedure for the synthesis of disubstituted alkenyl selenides containing more complex cyclic systems.

3. Experimental section

^1H NMR spectra were recorded on an AZ-300 MHz with TMS as internal standard. Mass spectra were determined by a Finigan 8230 mass spectrometer. IR spectra were obtained as neat capillary cells (liquid products) on a Shimadzu IR-408 instrument. All syntheses of complexes **1** and **2** were carried out under nitrogen using standard techniques [13]. Solvents were dried, deoxygenated and distilled before use. Dicyclohexylbo-

rane and internal alkylselenoacetylene were prepared according to the literature methods, Refs. [13] and [8] respectively. The borane was made in the laboratory and standardized before use. Commercial sodium borohydride was used without purification.

3.1. General synthesis of *cis/trans* disubstituted vinylic selenides (**1** and **2**)

To a solution of cyclohexene (10 mmol) in THF (5 ml) was added a solution of borane (5 mmol) in THF (1.25 ml) at 0°C with stirring. The precipitate formed (R_2BH) was stirred at $0-5^\circ\text{C}$ for 1 h, and then the reaction mixture was diluted with a solution of internal alkylselenoacetylene (5 mmol) in THF (5 ml) added at 10°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 -10°C 6 N sodium hydroxide, followed by the dropwise addition of a solution of iodine (5 mmol) in THF (3 ml) over a period of 15 min. After the reaction mixture had

warmed to room temperature, any excess iodine was decomposed by adding a small amount of aqueous sodium thiosulfate. Solvent was removed in vacuo and the residue was separated by flash chromatography on a 3 ft × 1 in column (100–150 mesh) by elution with pentane to give **1** and **2** respectively.

3.1.1. *cis*-1-Methylseleno-1-cyclohexyl-1-hexene (**1a**)

Oil. $^1\text{H NMR}$ (CDCl_3 , δ ppm): 6.27 (t, 1H, $J = 7$ Hz); 2.47 (s, 3H); 1.9–2.33 (m, 3H); 0.95–1.58 (m, 17H). IR $\nu(\text{cm}^{-1})$: 1630, 807. MS m/z : 258 ($M - 1$). Anal. Found: C, 60.41; H, 9.31. $\text{C}_{13}\text{H}_{24}\text{Se}$ Calc.: C, 60.22; H, 9.33%.

3.1.2. *trans*-1-Methylseleno-1-cyclohexyl-1-hexene (**2a**)

Oil. $^1\text{H NMR}$ (CDCl_3 , δ ppm): 6.81 (t, 1H, $J = 7$ Hz); 2.43 (s, 3H); 1.90–2.31 (m, 3H); 0.95–1.57 (m, 17H). IR $\nu(\text{cm}^{-1})$: 1628, 796. MS m/z : 258 ($M - 1$). Anal. Found: C, 60.31; H, 9.30. $\text{C}_{13}\text{H}_{24}\text{Se}$ Calc.: C, 60.22; H, 9.33%.

3.1.3. *cis*-1-Ethylseleno-1-cyclohexyl-1-hexene (**1b**)

Oil. $^1\text{H NMR}$ (CDCl_3 , δ ppm): 6.25 (t, 1H, $J = 7$ Hz); 2.81 (q, 2H, $J = 7.2$ Hz); 1.93–2.33 (m, 3H); 0.94–1.84 (m, 20H). IR $\nu(\text{cm}^{-1})$: 1631, 805. MS m/z : 272 ($M - 1$). Anal. Found: C, 61.54; H, 9.71. $\text{C}_{14}\text{H}_{26}\text{Se}$ Calc.: C, 61.52; H, 9.59%.

3.1.4. *trans*-1-Ethylseleno-1-cyclohexyl-1-hexene (**2b**)

Oil. $^1\text{H NMR}$ (CDCl_3 , δ ppm): 6.89 (t, 1H, $J = 7$ Hz); 2.80 (q, 2H, $J = 7.2$ Hz); 1.93–2.34 (m, 3H); 0.95–1.85 (m, 20H). IR $\nu(\text{cm}^{-1})$: 1617, 789. MS m/z : 272 ($M - 1$). Anal. Found: C, 61.38; H, 9.74. $\text{C}_{14}\text{H}_{26}\text{Se}$ Calc.: C, 61.52; H, 9.59%.

3.1.5. *cis*-1-Methylseleno-1-cyclohexyl-1-octene (**1c**)

Oil. $^1\text{H NMR}$ (CDCl_3 , δ ppm): 6.21 (t, 1H, $J = 7$ Hz); 2.40 (s, 3H); 1.90–2.30 (m, 3H); 0.63–1.75 (m, 21H). IR $\nu(\text{cm}^{-1})$: 1616, 791. MS m/z : 286 ($M - 1$). Anal. Found: C, 62.57; H, 9.63. $\text{C}_{15}\text{H}_{28}\text{Se}$ Calc.: C, 62.69; H, 9.84%.



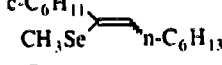
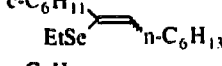
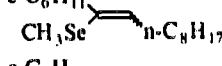
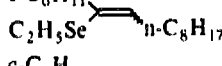

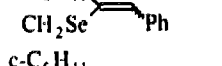
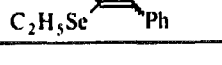
3.1.6. *trans*-1-Methylseleno-1-cyclohexyl-1-octene (**2c**)

Oil. $^1\text{H NMR}$ (CDCl_3 , δ ppm): 6.83 (t, 1H, $J = 7$ Hz); 2.49 (s, 3H); 1.91–2.29 (m, 3H); 0.62–1.74 (m, 21H). IR $\nu(\text{cm}^{-1})$: 1614, 788. MS m/z : 286 ($M - 1$). Anal. Found: C, 62.93; H, 9.41. $\text{C}_{15}\text{H}_{28}\text{Se}$ Calc.: C, 62.69; H, 9.84%.

3.1.7. *cis*-1-Ethylseleno-1-cyclohexyl-1-octene (**1d**)

Oil. $^1\text{H NMR}$ (CDCl_3 , δ ppm): 6.18 (t, 1H, $J = 7$ Hz); 2.76 (q, 2H, $J = 7.3$ Hz); 1.90–2.28 (m, 3H); 0.61–1.84 (m, 24H). IR $\nu(\text{cm}^{-1})$: 1613, 788. MS m/z : 299 ($M - 1$). Anal. Found: C, 63.79; H, 10.19. $\text{C}_{16}\text{H}_{30}\text{Se}$ Calc.: C, 63.97; H, 10.08%.

Table 1
Hydroboration of internal alkylselenoacetylenes with dicyclohexylborane followed by iodination

Entry	Internal alkylselenoacetylene	Disubstituted alkenyl selenide	Yield ^a (%)	<i>cis</i> : <i>trans</i> ^b
a	$\text{CH}_3\text{Se}-\text{C}\equiv\text{C}-\text{n-C}_4\text{H}_9$	$\text{c-C}_6\text{H}_{11}$ CH_3Se 	69	36:64
b	$\text{C}_2\text{H}_5\text{Se}-\text{C}\equiv\text{C}-\text{n-C}_4\text{H}_9$	$\text{c-C}_6\text{H}_{11}$ $\text{C}_2\text{H}_5\text{Se}$ 	72	39:61
c	$\text{CH}_3\text{Se}-\text{C}\equiv\text{C}-\text{n-C}_6\text{H}_{13}$	$\text{c-C}_6\text{H}_{11}$ CH_3Se 	77	31:69
d	$\text{C}_2\text{H}_5\text{Se}-\text{C}\equiv\text{C}-\text{n-C}_6\text{H}_{13}$	$\text{c-C}_6\text{H}_{11}$ EtSe 	68	34:66
e	$\text{CH}_3\text{Se}-\text{C}\equiv\text{C}-\text{n-C}_8\text{H}_{17}$	$\text{c-C}_6\text{H}_{11}$ CH_3Se 	61	29:71
f	$\text{C}_2\text{H}_5\text{Se}-\text{C}\equiv\text{C}-\text{n-C}_8\text{H}_{17}$	$\text{c-C}_6\text{H}_{11}$ $\text{C}_2\text{H}_5\text{Se}$ 	65	30:70
g	$\text{C}_2\text{H}_5\text{Se}-\text{C}\equiv\text{C}-\text{CH}_2\text{OCH}_3$	$\text{c-C}_6\text{H}_{11}$ $\text{C}_2\text{H}_5\text{Se}$ 	57	21:79
h	$\text{CH}_3\text{Se}-\text{C}\equiv\text{C}-\text{Ph}$	$\text{c-C}_6\text{H}_{11}$ CH_2Se 	73	26:74
i	$\text{C}_2\text{H}_5\text{Se}-\text{C}\equiv\text{C}-\text{Ph}$	$\text{c-C}_6\text{H}_{11}$ $\text{C}_2\text{H}_5\text{Se}$ 	75	29:71

^a Isolated yield.

^b Isomer ratio calculated from $^1\text{H NMR}$ data.

3.1.8. trans-1-Ethylseleno-1-cyclohexyl-1-octene (2d)

Oil. $^1\text{H NMR}$ (CDCl_3 , δ ppm): 6.81 (t, 1H, $J = 7$ Hz); 2.75 (q, 2H, $J = 7.3$ Hz); 1.89–2.28 (m, 3H); 0.61–1.85 (m, 24H). IR $\nu(\text{cm}^{-1})$: 1611, 788. MS m/z : 299 ($M - 1$). Anal. Found: C, 64.14; H, 10.22. $\text{C}_{16}\text{H}_{30}\text{Se}$ Calc.: C, 63.97; H, 10.08%.

3.1.9. cis-1-Methylseleno-1-cyclohexyl-1-decene (1e)

Oil. $^1\text{H NMR}$ (CDCl_3 , δ ppm): 6.15 (t, 1H, $J = 7$ Hz); 2.49 (s, 3H); 1.88–2.30 (m, 3H); 0.58–1.77 (m, 25H). IR $\nu(\text{cm}^{-1})$: 1611, 781. MS m/z : 313 ($M - 1$). Anal. Found: C, 64.78; H, 10.42. $\text{C}_{17}\text{H}_{32}\text{Se}$ Calc.: C, 64.94; H, 10.27%.

3.1.10. trans-1-Methylseleno-1-cyclohexyl-1-decene (2e)

Oil. $^1\text{H NMR}$ (CDCl_3 , δ ppm): 6.81 (t, 1H, $J = 7$ Hz); 2.45 (s, 3H); 1.89–2.29 (m, 3H); 0.57–1.78 (m, 25H). IR $\nu(\text{cm}^{-1})$: 1608, 783. MS m/z : 313 ($M - 1$). Anal. Found: C, 65.15; H, 10.01. $\text{C}_{17}\text{H}_{32}\text{Se}$ Calc.: C, 64.94; H, 10.27%.

3.1.11. cis-1-Ethylseleno-1-cyclohexyl-1-decene (1f)

Oil. $^1\text{H NMR}$ (CDCl_3 , δ ppm): 6.14 (t, 1H, $J = 7$ Hz); 2.73 (q, 2H, $J = 7.3$ Hz); 1.87–2.28 (m, 3H); 0.58–1.83 (m, 28H). IR $\nu(\text{cm}^{-1})$: 1609, 780. MS m/z : 327 ($M - 1$). Anal. Found: C, 65.67; H, 10.14. $\text{C}_{18}\text{H}_{34}\text{Se}$ Calc.: C, 65.82; H, 10.45%.

3.1.12. trans-1-Ethylseleno-1-cyclohexyl-1-decene (2f)

Oil. $^1\text{H NMR}$ (CDCl_3 , δ ppm): 6.79 (t, 1H, $J = 7$ Hz); 2.73 (q, 2H, $J = 7.4$ Hz); 1.87–2.25 (m, 3H); 0.55–1.85 (m, 28H). IR $\nu(\text{cm}^{-1})$: 1604, 781. MS m/z : 327 ($M - 1$). Anal. Found: C, 65.94; H, 10.31. $\text{C}_{18}\text{H}_{34}\text{Se}$ Calc.: C, 65.82; H, 10.45%.

3.1.13. cis-1-Ethylseleno-1-cyclohexyl-3-methoxy-1-propene (1g)

Oil. $^1\text{H NMR}$ (CDCl_3 , δ ppm): 7.11 (t, 1H, $J = 6.8$ Hz); 2.88 (q, 2H, $J = 7.1$ Hz); 4.4 (d, 2H, $J = 6.8$ Hz); 3.75 (s, 3H); 2.17 (br, 1H); 1.16–1.66 (m, 10H). IR $\nu(\text{cm}^{-1})$: 1609, 775. MS m/z : 260 ($M - 1$). Anal. Found: C, 54.93; H, 8.66; O, 6.27. $\text{C}_{12}\text{H}_{22}\text{Se}$ Calc.: C, 55.16; H, 8.50; O, 6.12%.

3.1.14. trans-1-Ethylseleno-1-cyclohexyl-3-methoxy-1-propene (2g)

Oil. $^1\text{H NMR}$ (CDCl_3 , δ ppm): 6.54 (t, 1H, $J = 6.8$ Hz); 2.87 (q, 2H, $J = 7.1$ Hz); 4.44 (d, 2H, $J = 6.8$ Hz); 3.70 (s, 3H); 2.14 (br, 1H); 1.18–1.69 (m, 10H). IR $\nu(\text{cm}^{-1})$: 1604, 770. MS m/z : 260 ($M - 1$). Anal. Found: C, 55.22; H, 8.55; O, 6.34. $\text{C}_{12}\text{H}_{22}\text{Se}$ Calc.: C, 55.16; H, 8.50; O, 6.12%.

3.1.15. cis-1-Methylseleno-1-cyclohexyl-1-phenylethylene (1h)

Oil. $^1\text{H NMR}$ (CDCl_3 , δ ppm): 7.10–7.50 (m, 5H); 6.83 (s, 1H); 2.44 (s, 3H); 2.31 (br, 1H); 0.97–1.55 (m,

10H). IR $\nu(\text{cm}^{-1})$: 1654, 1597, 1549, 811. Anal. Found: C, 64.42; H, 7.31. $\text{C}_{15}\text{H}_{20}\text{Se}$ Calc.: C, 64.51; H, 7.22%.

3.1.16. trans-1-Methylseleno-1-cyclohexyl-1-phenylethylene (2h)

Oil. $^1\text{H NMR}$ (CDCl_3 , δ ppm): 7.04–7.50 (m, 5H); 6.75 (s, 1H); 2.41 (s, 3H); 2.28 (br, 1H); 0.95–1.55 (m, 10H). IR $\nu(\text{cm}^{-1})$: 1647, 1588, 1550, 814. Anal. Found: C, 64.37; H, 7.15. $\text{C}_{15}\text{H}_{20}\text{Se}$ Calc.: C, 64.51; H, 7.22%.

3.1.17. cis-1-Ethylseleno-1-cyclohexyl-1-phenylethylene (1i)

Oil. $^1\text{H NMR}$ (CDCl_3 , δ ppm): 7.0–7.55 (m, 5H); 6.81 (s, 1H); 2.69 (q, 2H, $J = 7.1$ Hz); 2.34 (br, 1H); 1.85 (t, 3H, $J = 7.1$ Hz); 0.98–1.60 (m, 10H). IR $\nu(\text{cm}^{-1})$: 1661, 1590, 1544, 805. Anal. Found: C, 65.77; H, 7.66. $\text{C}_{16}\text{H}_{22}\text{Se}$ Calc.: C, 65.52; H, 7.56%.

3.1.18. trans-1-Ethylseleno-1-cyclohexyl-1-phenylethylene (2i)

Oil. $^1\text{H NMR}$ (CDCl_3 , δ ppm): 7.20–7.67 (m, 5H); 6.87 (s, 1H); 2.71 (q, 2H, $J = 7.1$ Hz); 2.25 (br, 1H); 1.81 (t, 3H, $J = 7.1$ Hz); 1.05–1.63 (m, 10H). IR $\nu(\text{cm}^{-1})$: 1663, 1600, 1550, 807. Anal. Found: C, 65.49; H, 7.74. $\text{C}_{16}\text{H}_{22}\text{Se}$ Calc.: C, 65.52; H, 7.56%.

Acknowledgements

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- [11] Preparation of **3** or **4**: a mixture of **1a** or **2a** (1 mmol) and LiAlH_4 (1.5 mmol) in THF (5 ml) was heated at reflux for 3 h. After cooling to room temperature, methanol (1.5 mmol) was added to the mixture. The resulting mixture was stirred for 20 min and filtered. The filtrate was washed with saturated aq. NH_4Cl (2 ml), separated, dried (MgSO_4) and concentrated in vacuum to give a crude product which was purified by flash column chromatography. Eluting with pentane afforded **3** or **4**. The reaction product contained pure *trans* **3** or *cis* **4**, being consistent with the *trans* or *cis* isomers of known 1-cyclohexyl-1-hexene. *trans* Isomer **3**. ^1H NMR (CDCl_3): δ 5.38 (multiplet, 2H); 0.8–2.3 (multiplet, 20H). ^{13}C NMR (CDCl_3): δ 136.58; 127.81; 33.53; 32.55; 32.12; 26.35; 22.34; 14.03 ppm. IR (neat): 2880; 1645; 1450; 970 cm^{-1} . GLC analysis, 98% pure. *cis* Isomer **4**. ^1H NMR (CDCl_3): δ 5.42 (multiplet, 2H); 0.78–2.2 (multiplet, 20H). ^{13}C NMR (CDCl_3): δ 165.67; 126.83; 32.53; 31.79; 31.58; 26.17; 22.29; 14.01 ppm. IR (neat): 3019; 2876; 1640; 1448; 609 cm^{-1} . GLC analysis, 98% pure.
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