# Selenium Transfer Reagent: One-step Alkoxyselenation of Cyclohexene with Bis(2-bromoethyl)selenium Dibromide

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The reaction of bis(2-bromoethyl)selenium dibromide **1** with cyclohexene **2** in alcohol under reduced pressure proceeds smoothly to give bis(2-alkoxycyclohexyl)selenium dibromide (R = Me **4**, R = Et **5**, R = Pr$^i$ **6**) *via* 2-bromocyclohexyl-2′-bromoethylselenium dibromide **3** as an intermediate together with ethene. The diastereoisomers **4a** and **5a** (1*R*,2*R*,1′*S*,2′*S*) and **4b** and **5b** (1*R*,2*R*,1′*R*,2′*R* or 1*S*,2*S*,1′*S*,2′*S*) were separated from **4** and/or **5**. These isomers **4a**/**5a** and **4b**/**5b** were isolated as a *meso* and a racemic mixture, respectively. Although the addition product **6a** (1*R*,2*R*,1′*S*,2′*S*) was only isolated from **6** in the *meso* form, the corresponding diastereoisomer **6b** (1*R*,2*R*,1′*R*,2′*R* or 1*S*,2*S*,1′*S*,2′*S*) was not detected. These results indicated that the Se and Br atoms in the cyclohexane ring of **3**, and the Se and alkoxy groups in the cyclohexane rings of **4**–**6** were in the diequatorial position.

Organoselenium compounds such as benzeneselenenyl halides,[1] *N*-phenylselenophthalimide[2] and dimethyl selenoxide[3] have been used to introduce selenium into alkenes. It is well known[4,5] that the addition of selenium halides to alkenes leads to bis(2-halogenoalkyl) selenide derivatives. Also, the reaction of bis(2-halogenoethyl) selenide with nucleophiles has been investigated.[6] The nucleophile attacks the carbon or the positively charged selenium atom of the episelenonium ion which was formed from bis(2-bromoethyl) selenide **5**. For example, attack by a nucleophile such as benzeneselenolate anion on a carbon gives rise to a normal substitution product. However, episelenurane can be formed when the positively charged selenium atom of the episelenonium ion is attacked by a nucleophile such as the selenocyanate ion, after which the resulting episelenurane decomposes to give ethene and a selenenyl compound. In previous papers, we have reported that in comparison with primary and secondary amides, tertiary amides are reduced highly selectively to their corresponding amines by sodium borohydride–bis(2-bromoethyl)selenium dibromide **1**.[7–9] We also described a convenient one-pot procedure for the synthesis of 2,5-bis(alkoxymethyl)tetrahydroselenophene derivatives using hexa-1,5-diene and the reagent **1**.[10] In connection with the above research, we describe here the alkoxyselenation of **2** *via* an intermediate **3** using the reagent **1**.

The reaction of **1** with cyclohexene **2** (2 equiv.) in methanol at 20 °C for 1 h afforded bis(2-methoxycyclohexyl)selenium dibromide **4** in 11% yield together with ethene. However, the addition product **4** was obtained in higher yield (72%) when the ethene formed was removed under reduced pressure (*ca.* 110 mmHg). Also, the reaction of **1** with **2** in methanol at −50 °C afforded 2-bromocyclohexyl-2′-bromoethylselenium dibromide **3** in 39% yield instead of **4**. The addition product **3** further reacted with **2** in methanol at 20 °C to give **4** in 75% yield together with ethene. The results suggest that the reaction of **1** with **2** gives **4** *via* **3** as an intermediate. In a previous paper, we have reported on the preparation of 2,5-bis(alkoxymethyl)-tetrahydroselenophenes by the cycloaddition of **1** to hexa-1,5-diene. However, the intermediate having a bromoethyl group such as **3** could not be detected.[10] This intermediate **3** was also obtained by the reaction of **1** with **2** in acetic acid. Similar reactions were carried out in various solvents. These results are summarized in Table 1. The reaction of **1** with **2** in ethanol gave bis(2-ethoxycyclohexyl)selenium dibromide **5** under reduced pressure in 61% yield. Furthermore, when propan-2-ol was used as the solvent, the addition product **6** was obtained in 45% yield. Also, the reactions of **1** with **2** were performed using carbon disulfide, acetonitrile and acetic anhydride as the solvent. These reactions gave **3** in 35–65% yield together with ethene. However, the reaction in benzene gave no product and the starting materials were quantitatively recovered. This may be attributed to the low polarity of benzene.

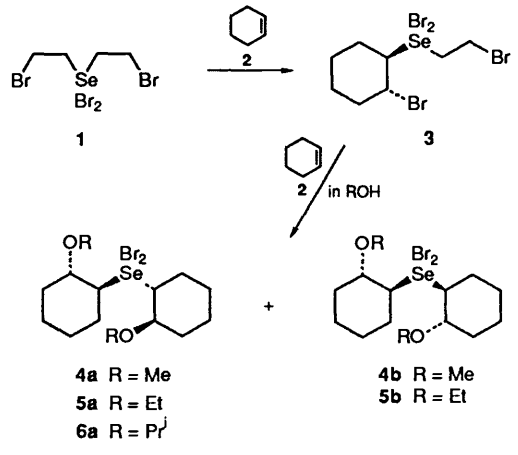



**Table 1** Reaction of **1** or **3** with **2** in various solvent

| Reagent | Solvent | Reaction time (h) | Reaction temp. (°C) | Product | Yield (%) |
|---|---|---|---|---|---|
| **1** | MeOH | 1 | 20 | **4** | 11 |
| **1** | MeOH | 1 | 20 | **4** | 73* |
| **1** | MeOH | 1.5 | −50 | **3** | 39* |
| **1** | AcOH | 4 | 20 | **3** | 70* |
| **3** | MeOH | 1 | 20 | **4** | 75* |
| **1** | EtOH | 7 | 20 | **5** | 61* |
| **1** | $Me_2CHOH$ | 20 | 20 | **6** | 45* |
| **1** | MeCN | 4 | 20 | **3** | 38 |
| **1** | $CS_2$ | 4 | 20 | **3** | 39 |
| **1** | $(MeCO)_2O$ | 4 | 20 | **3** | 48 |
| **1** | $C_6H_6$ | 24 | 20 | No reaction | |

* These reactions were performed under reduced pressure (110 mmHg).

Considering the structures of **4**, **5** and **6**, the four carbon atoms (the 1, 2, 1′, 2′ positions of the cyclohexane rings) which bond to the selenium or oxygen atoms of the alkoxy groups

**Table 2** The ratios of diastereoisomers **4a–6a** and **4b–6b*** and m.p.

| Compound | M.p. (°) | Yield (%) | Ratio (a:b) |
|---|---|---|---|
| **4a** | 135–136 | 52 | 7:3 |
| **4b** | 137–138 | 22 | |
| **5a** | 135.5–136.5 | 43 | 7:3 |
| **5b** | 134–135 | 18 | |
| **6a** | 133–134 | 45 | 10:0 |
| **6b** | | 0 | |

* The configuration at the 1 and 1′ positions in **4a–6a** was *R* and *S*. **4b–6b** were *R* and *R* or *S* and *S*.

**Table 3** Selected bond lengths (Å), and bond and torsion angles (°) for **3**

| 1 | 2 | 3 | 4 | 1–2 | 1–2–3 | 1–2–3–4 |
|---|---|---|---|---|---|---|
| Br(1) | Se | C(1) | C(2) | 2.545(2) | 91.5(3) | 115.8(7) |
| Br(1) | Se | C(1) | C(6) | | | −116.0(6) |
| Br(1) | Se | C(7) | C(8) | | 91.2(3) | 92.9(7) |
| Br(1) | Se | Br(2) | | | 176.94(8) | |
| Br(2) | Se | C(1) | C(2) | 2.561(2) | 91.3(3) | −65.3(7) |
| Br(2) | Se | C(1) | C(6) | | | 62.8(6) |
| Br(2) | Se | C(7) | C(8) | | 89.2(3) | −84.1(7) |
| Br(3) | C(6) | C(1) | Se | 1.965(9) | | 46.2(8) |
| Se | C(1) | C(2) | C(3) | 2.00(1) | 117.0(7) | −175.8(7) |
| Se | C(1) | C(6) | C(5) | | 110.1(7) | 169.8(6) |
| Se | C(7) | C(8) | Br(4) | 1.98(1) | 106.2(7) | |
| C(1) | Se | C(7) | C(8) | | 103.7(4) | −175.2(7) |
| C(2) | C(1) | Se | C(7) | | | 24.2(8) |
| C(6) | C(1) | Se | C(7) | | | 152.4(6) |

**Table 4** Selected bond lengths (Å), and bond and torsion angles (°) for **4a**

| 1 | 2 | 3 | 4 | 1–2 | 1–2–3 | 1–2–3–4 |
|---|---|---|---|---|---|---|
| Br(1) | Se | C(11) | C(12) | 2.585(2) | 91.7(2) | −72.8(6) |
| Br(1) | Se | C(11) | C(16) | | | 51.2(6) |
| Br(1) | Se | C(21) | C(22) | | 88.4(2) | −154.8(7) |
| Br(1) | Se | C(21) | C(26) | | | 82.1(6) |
| Br(1) | Se | Br(2) | | | 172.09(6) | |
| Br(2) | Se | C(11) | C(12) | 2.524(2) | | 102.3(6) |
| Br(2) | Se | C(11) | C(16) | | 94.5(2) | −133.7(6) |
| Br(2) | Se | C(21) | C(22) | | 94.5(2) | 32.6(7) |
| Br(2) | Se | C(21) | C(26) | | | −90.5(6) |
| Se | C(11) | C(12) | O(1) | 2.013(9) | 107.0(7) | −50.2(8) |
| Se | C(11) | C(12) | C(13) | | | −173.4(6) |
| Se | C(11) | C(16) | C(15) | | 116.6(7) | 177.0(6) |
| Se | C(21) | C(22) | O(2) | 2.021(8) | 116.7(6) | 59.0(9) |
| Se | C(21) | C(22) | C(23) | | | 179.5(7) |
| Se | C(21) | C(26) | C(25) | | 105.3(7) | −173.8(7) |
| C(11) | Se | C(21) | C(22) | | 105.9(4) | −63.4(7) |
| C(11) | Se | C(21) | C(26) | | | 173.4(6) |
| C(12) | C(11) | Se | C(21) | | | −161.7(6) |
| C(16) | C(11) | Se | C(21) | | | −37.7(7) |

may be asymmetric carbon atoms. However, the addition of selenium and alkoxy groups to the carbon–carbon double bond proceeded stereospecifically to give *anti*-addition products as described below. That is, the configuration of the 1 and 1′ positions were in agreement with that of the 2 and 2′ positions, respectively. Therefore, two diastereoisomeric isomers (1*R*,1′*S* and 1*R*,1′*R* or 1*S*,1′*S*) may exist with respect to the two carbon atoms which bond to the selenium atom. Accordingly, we attempted the isolation of the diastereoisomeric isomers. These results are summarized in Table 2. The addition products **4** containing two isomers were treated with sodium carbonate to give a colourless oil, which was separated by column chromatography (activated alumina) using hexane–benzene

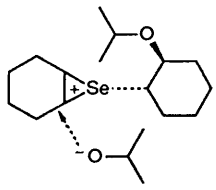



**Fig. 1** Stereoselective addition of isopropoxide

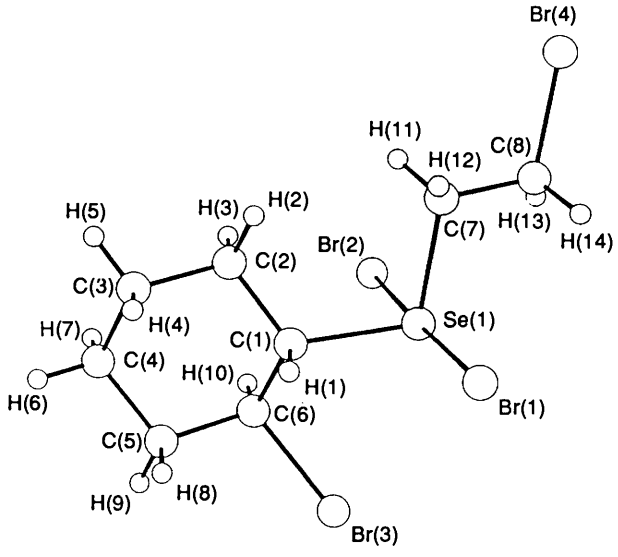



**Fig. 2** A perspective view of compound **3** with the atomic numbering scheme

(1:1) as eluent. The first and second fractions were treated with bromine to give racemic **4b** (1*R*,1′*R* or 1*S*,1′*S*) and *meso*-**4a** (1*R*,1′*S*), respectively; the optical resolution of the latter isomer [(+/−)**4b**] was not, however, carried out. The ratio of **4a** and **4b** was found to be 7:3. After separation of the diastereoisomers of **5** the configuration of **5a** was found to be 1*R*,1′*S* and **5b** 1*R*,1′*R* or 1*S*,1′*S*, respectively. The ratio of **5a** and **5b** was 7:3, similar to that of **4a** and **4b**. In the case of **6**, **6a** (1*R*,1′*S*) was isolated in 45% yield, but **6b** (1*R*,1′*R* or 1*S*,1′*S*) could not be detected. Although formation of **6a** rather than **6b** may arise as a result of stereoselective addition of a 2-propoxy anion to the episelenonium ion **15**, there is, at present, no proof of this. However, since addition of an alkoxy anion to **15** is likely to occur at the position of least steric hindrance as shown in Fig. 1 the reaction of **1** with **2** in propan-2-ol would give **6a** selectively. A similar tendency was observed with **4a** and **4b** and **5a** and **5b**. Namely, the addition products **4a** and **5a**, which assume the 1*R*, 1′*S* configuration, were formed more selectively than **4b** and **5b**, respectively. Consequently, the ratios of **4a** and **4b**, and **5a** and **5b** were 7:3, respectively. The structures were established by 400 MHz $^1$H and $^{13}$C NMR spectroscopy.

To determine the structure in more detail, X-ray analyses of **3** and **4a** were carried out. Selected bond lengths, bond angles and torsion angles for **3** and **4a** are listed in Tables 3 and 4, respectively. The perspective views of **3** and **4a** with an atomic numbering scheme are illustrated in Figs. 2 and 3. The bond lengths, Br(1)–Se and Br(2)–Se of **3** and **4a**, are in the range 2.524(2)–2.561(2) Å. The bond angles, C(1)–Se–C(7) and C(11)–Se–C(21) of **3** and **4a**, are 103.7(4)° and 105.9(4)°, respectively. These values are in agreement with the reported values for the Br–Se bond lengths [2.536(15) Å] in bis(2-bromoethyl)selenium dibromide **1**[9] and C–Se–C bond angles [105(1)°] in 4,4-dibromo-1-thia-4-selenacyclohexane.[11] Also, the Br(1)–Se–Br(2) bond angles are 176.94(8)° and 172.09(6)° in **3** and **4a**, which have a value of almost 180°.[9] Therefore, the selenium atoms of **3** and **4a** have a slightly distorted trigonal-

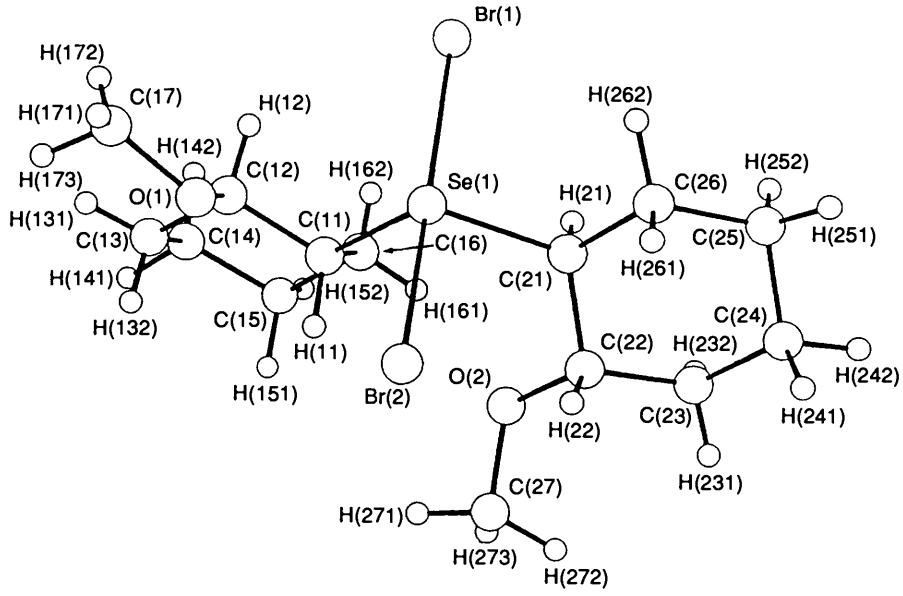



**Fig. 3** A perspective view of compound **4a** with the atomic numbering scheme

bipyramidal geometry with axially coordinated bromine atoms. The torsion angle of Br(3)–C(6)–C(1)–Se in **3** is 46.2(8)°. Therefore, Se and Br(3) in the cyclohexane ring of **3** assumes a diequatorial conformation. Also, similar conformations are observed for each methoxy group and selenium atom in **4a**. These results suggest that the reaction of **1** with **2** proceeds stereospecifically to afford the *anti*-addition products. Also, the torsion angles of Se–C(11)–C(12)–O(1) and Se–C(21)–C(22)–O(2) in **4a** are 50.2(8)° and 59.0(9)°, and the configurations of C(11) and C(21) are *R* and *S*, respectively.

In order to investigate the reaction mechanism, the reactions of diethylselenium dibromide **8** or bis(2-bromoethyl) selenide **9** with cyclohexene **2** in methanol were carried out. The reaction of **9** with **2** gave bis(2-methoxycyclohexyl) selenide **7** (56%) and ethene. Compound **7** reacted with bromine in tetrachloromethane to give **4** in quantitative yield, although the reaction of **8** with **2** gave 1,2-dibromocyclohexane in 38% yield instead of **4**. These findings suggest that the 2-bromoethyl group of **1** plays an important role in the addition. A mechanism for the reaction of $(BrC_2H_4)_2Se$ **9** with a nucleophile such as selenocyanate has already been reported by Lindgren.[6] The first step is the formation of an episelenonium ion **10**, the positively charged selenium of which undergoes nucleophilic attack to produce the episelenurane. Ready decomposition of the latter gives 1-bromo-2-selenocyanatoethane and ethene. In contrast to the above mechanism, the reaction of **1** with **2** may be explained by the following mechanism. Compound **9** formed by the debromination of **1** produces an episelenonium ion **10** which reacts with **2** to afford a episelenonium ion **11** and ethene. Bromine anion attack on **11** then gives **12**, which upon subsequent addition of a bromine atom gives the addition product **3**. The latter undergoes reversible conversion, *via* **12**, into the episelenonium ion **13** which further reacts with **2** to give the episelenonium ion **14** and ethene. Bromine anion and alkoxy anion have the potential to attack **14** competitively; for example addition of bromine anion to **14** would give **15**. Compound **15**, although it was not isolated, could be detected by mass spectroscopy in the reaction of **1** with **2** in propan-2-ol. However, substitution of a 2-bromoalkylseleno group by an alkoxy group *via* an episelenonium ion in alcohol is well established.[6,12] Therefore, compound **15** is converted into **16** *via* **14**. Furthermore, **16** is substituted by an alkoxy group to give **7** *via* the episelenonium ion **17**. Finally, dialkoxy substituted compounds **4**, **5** and **6** are formed by the addition of bromine to **7**. In order to examine the formation of the episelenonium ions as intermediates in this reaction, the $^1H$ NMR spectra of the reaction mixture of **1** and cyclohexene **2** in [$^2H_4$]methanol were recorded. The proton signals of the episelenonium ion were absent, although the proton signals due to the starting materials, ethene and the cyclohexane rings of **4a** were observed. This result suggests that the lifetime of the episelenonium ions as intermediates at room temperature is very short compared on the $^1H$ NMR time scale. However, considering that the reaction of **1** with **2** gave *anti*-addition products and ethene, the episelenonium ions (**10**, **11**, **13** and **17**) would participate in the reaction.

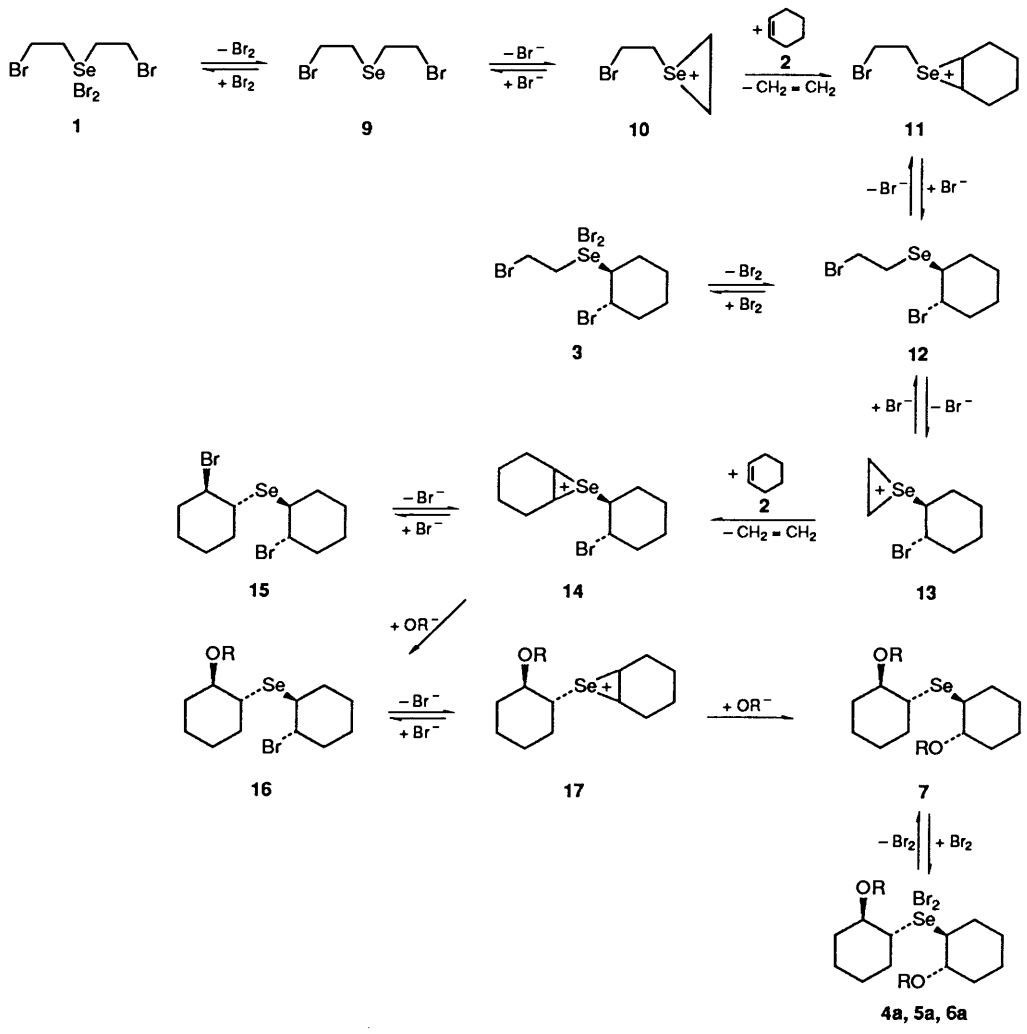
In conclusion, bis(2-bromoethyl)selenium dibromide **1** reacts with cyclohexene **2** to produce *anti*-bis(2-alkoxycyclohexyl)-selenium dibromides, **4**–**6**, together with ethene. Also, *anti*-2-bromocyclohexyl-2′-bromoethylselenium dibromide **3** could be obtained as an intermediate in this reaction. The episelenonium ions **10**, **11**, **13**, **14** and **17** play an important role in this addition.

## Experimental

M.p.s were recorded with a Yazawa micro m.p. apparatus and are uncorrected. $^1H$ NMR spectra were obtained using a JEOL GX 400 spectrometer with $(CH_3)_4$ as the internal standard; *J*-values are recorded in Hz. Gas chromatography was performed on a Shimadzu G.C-8APF gas chromatograph with a PEG 20M (2.0%) 2 m glass column. Elemental analyses were obtained using a Perkin-Elmer 2400. Mass spectra were recorded on a Hitachi M-80 spectrometer.

*Materials.*—Bis(2-bromoethyl) selenium dibromide **1**,[4] bis(2-bromoethyl) selenide **9**[4] and diethylselenium dibromide **8**[13] were prepared according to methods described in the literature. All solvents were purified by distillation in the usual manner.

*Reaction of* **1** *with* **2** *in Acetic Acid.*—A suspension of **1** (4.5 g, 10 mmol) and **2** (3.6 g, 20 mmol) in acetic acid (20 $cm^3$) was stirred at 20 °C for 4 h. The resulting pale yellow solids were filtered off, washed with a little acetic acid and recrystallized from benzene (30 $cm^3$) to give **3** as yellow needles (70%); m.p. 128–129 °C; $\delta_H$(in $CDCl_3$) 1.39–1.64 (m, 2 H), 1.85 (br d, *J* 11.2, 1 H), 1.99–2.13 (m, 2 H), 2.54 (ddd, *J* 1.96, 4.40, 11.2, 1 H), 3.86–4.06 (m, 4 H), 4.67 (td, *J* 4.40, 11.2, 1 H) and 4.86 (td, *J* 4.40, 11.2, 1 H); $\delta_C$(in $CDCl_3$) 80.42 (d), 57.88 (t), 51.20 (d), 38.84




(t), 29.43 (t), 26.06 (t) and 23.39 (t) (Found: C, 19.0; H, 2.3. Calc. for $C_8H_{14}Br_4Se$: C, 18.96; H, 2.39%); *m/z* (20 eV) 506 ($M^+$).

*General Procedure for the Reaction of* **1** *with* **2** *in Methanol under Reduced Pressure.*—A suspension of **1** (4.5 g, 10 mmol) and **2** (3.6 g, 20 mmol) in methanol (30 $cm^3$) was stirred at 20 °C for 1 h under reduced pressure (*ca.* 110 mmHg) with an aspirator. Sodium carbonate (2.1 g, 20 mmol) was added to the reaction mixture, which was then stirred for 2 h and finally evaporated under reduced pressure. Chloroform (30 $cm^3$) was added to the residue and the whole filtered. The chloroform solution was concentrated under reduced pressure and the residue was purified by gel permeation chromatography using THF as an eluent. The main fraction was collected and the solution was evaporated under reduced pressure. The resulting residue was separated and purified by column chromatography (activated alumina) using benzene–hexane (2:1) as eluent. The first fraction was added to a solution of dichloromethane containing bromine (1.6 g, 10 mmol) and the yellow solution was stirred for 10 min at 0 °C; it was then concentrated under reduced pressure. The resulting yellow solid was recrystallized from benzene–hexane (1:1) to give **4b** (1*R*,2*R*,1′*R*,2′*R* or 1*S*,2*S*,1′*S*,2′*S*) in 22% yield. A similar treatment of the second fraction gave **4a** (1*R*,2*R*,1′*S*,2′*S*) in 51% yield; **4a**, m.p. 134–135 °C; $\delta_H(CDCl_3)$ 1.25–1.37 (m, 8 H), 1.81–1.88 (m, 4 H), 2.35 (br d, *J* 10.7, 2 H), 2.71 (br d, *J* 11.2, 2 H), 3.42 (s, 6 H) and 3.92 (br s, 4 H); $\delta_C(CDCl_3)$ 80.87, 56.31, 31.99, 29.30, 27.23 and 23.87 (Found: C, 36.0; H, 5.5. Calc. for $C_{14}H_{26}Br_2O_2Se$: C, 36.15; H, 5.63%); *m/z* (20 eV) 464 ($M^+$); **4b**, m.p. 138–139 °C; $\delta_H(CDCl_3)$ 1.23–1.46 (m, 6 H), 1.80–1.93 (m, 5 H), 2.22 (br d, *J* 11.2, 1 H), 2.36 (br s, 2 H), 2.43 (br d, *J* 10.5, 1 H), 2.73 (br d, *J* 10.5, 1 H), 3.43 (s, 3 H), 3.46 (s, 3 H), 3.83–3.95 (m, 2 H) and 3.95–4.07 (m, 2 H); $\delta_C(CDCl_3)$ 80.78, 79.99, 71.94, 56.93, 56.20, 32.03, 31.90, 30.11, 29.22, 27.19, 26.99, 23.79 and 23.72 (Found: C, 36.2; H, 5.65. Calc. for $C_{14}H_{26}Br_2O_2Se$: C, 36.15; H, 5.63%); *m/z* (20 eV) 464 ($M^+$).

*Compounds* **5a** (1R,2R,1′S,2′S), **5b** (1R,2R,1′R,2′R *or* 1S,2S,1′S,2′S) *and* **6a** (1R,2R,1′S,2′S). These compounds were also prepared using the method described above. **5a**: Yield 43%; m.p. 134–135 °C; $\delta_H(CDCl_3)$ 1.23 (t, *J* 6.7, 6 H), 1.30–1.45 (m, 8 H), 1.77–1.90 (m, 4 H), 2.28–2.38 (m, 2 H), 2.76 (br s, 2 H), 3.46–3.56 (m, 2 H), 3.73 (br s, 2 H) and 4.07 (br s, 4 H); $\delta_C(CDCl_3)$ 79.52, 64.15, 32.61, 29.16, 27.15, 23.96 and 15.49 (Found: C, 38.9; H, 6.2. Calc. for $C_{16}H_{30}Br_2O_2Se$. C, 38.96; H, 6.14%); *m/z* (20 eV) 492 ($M^+$).

**5b**: Yield 18%; m.p. 135.5–136.5 °C; $\delta_H(CDCl_3)$ 1.21–1.26 (m, 6 H), 1.33–1.35 (m, 8 H), 1.79–1.86 (m, 4 H), 2.30–2.33 (m, 2 H), 2.76 (br d, *J* 10.3, 2 H), 3.49–3.55 (m, 2 H), 3.70–3.76 (m, 2 H) and 3.92–4.02 (m, 4 H); $\delta_C(CDCl_3)$ 78.19, 71.49, 64.83, 32.93, 30.01, 29.07, 26.86, 23.73, 15.33 and 15.24 (Found: C, 39.1; H, 6.1%. Calc. for $C_{16}H_{30}Br_2O_2Se$: C, 38.96; H, 6.14%); *m/z* (20 eV) 492 ($M^+$).

**6a**: Yield 45%; m.p. 133–134 °C; $\delta_H(CDCl_3)$ 1.21 (d, *J* 6.3, 6 H), 1.29 (d, *J* 6.3, 6 H), 1.35–1.47 (m, 6 H), 1.78–1.87 (m, 4 H), 2.13 (br d, *J* 11.2, 2 H), 2.23 (br d, *J* 10.7, 2 H), 2.52–2.66 (m, 2 H), 3.81–3.88 (m, 2 H), 3.95 (br d, *J* 10.7, 4 H); $\delta_C(CDCl_3)$ 76.20,

71.60, 34.56, 30.18, 26.74, 23.91, 23.41 and 22.33 (Found: C, 41.6; H, 6.7. Calc. for $C_{18}H_{34}Br_2O_2Se$: C, 41.47; H, 6.59%); *m/z* (20 eV) 520 ($M^+$).

*Reaction of Bis(2-bromoethyl) Selenide* **9** *with* **2** *in Methanol.*—Compound **9** (3.9 g, 10 mmol) was added to a solution of **2** (3.6 g, 20 mmol) in methanol (20 $cm^3$). The solution was stirred for 1 h at 20 °C under reduced pressure (110 mmHg) and then diluted with water (20 $cm^3$). The aqueous solution was extracted with chloroform, and the extract was dried ($MgSO_4$) and concentrated under reduced pressure. The residue was purified by gel permeation chromatography using THF as an eluent. The main fraction was then collected and concentrated under reduced pressure to give a white precipitate and a colourless oil. The solid was recrystallized from diethyl ether to give (1*R*, 2*R*, 1′*S*, 2′*S*)-bis(2-methoxycyclohexyl) selenide **7a** (45%) as white plates; m.p. 78–79 °C. The configuration of **7a** was determined by comparison (m.p. and $^1H$ NMR) of **4a**, derived from **7a** by bromination with an authentic sample of **4a**; $\delta_H(CDCl_3)$ 1.14–1.33 (m, 6 H), 1.49–1.58 (m, 2 H), 1.79–1.90 (m, 4 H), 2.01 (br d, *J* 11.2, 2 H), 2.32 (br d, 10.7, 2 H), 2.85–2.95 (m, 2 H), 3.37 (s, 6 H) and 3.31–3.41 (m, 2 H) (Found: C, 54.8; H, 8.3. Calc. for $C_{14}H_{26}O_2Se$: C, 55.06; H, 8.59%); *m/z* (20 eV) 306 ($M^+$). The colourless oil was added to a solution of bromine (1.6 g, 10 mmol) in dichloromethane (10 $cm^3$) to give a yellow solution which was stirred for 10 min at 0 °C. It was then concentrated under reduced pressure to give a yellow solid which upon recrystallization from benzene–hexane (1:1) afforded (1*R*,1′*R* or 1*S*,1′*S*)-bis(2-methoxycyclohexyl)selenium dibromide **4b** (11%).

*Reaction of* **7a** *with Bromine.*—Bromine (0.8 g, 5 mmol) was added to a solution of **7a** (1.53 g, 5 mmol) in tetrachloromethane (20 $cm^3$) at 0 °C. The mixture was stirred at 0 °C for 10 min and then evaporated under reduced pressure. The resulting residue was recrystallized from hexane–benzene (1:1; 20 $cm^3$) to give **4a** in quantitative yield.

*Reaction of Diethylselenium Dibromide* **8** *with* **2** *in Methanol.*—Compound **8** (2.9 g, 10 mmol) was added to a solution of **2** (3.6 g, 20 mmol) in methanol (20 $cm^3$) and the whole stirred for 1 h at 20 °C. The reaction mixture was then analysed by GLC; the yield of 1,2-dibromocyclohexane was 38%.

*X-Ray Crystallography of* **3** *and* **4a**.—Crystals with dimensions of 0.53 × 0.15 × 0.15 and 0.55 × 0.20 × 0.32 mm for compounds **3** and **4a**, respectively, were used for X-ray crystallography. For **3**: $C_8H_{14}Br_4Se$, *M*, 508.77, triclinic, space group $P\bar{1}$, *a* = 10.649(3) Å, *b* = 11.199(3) Å, *c* = 6.230(2) Å, $\alpha$ = 102.84(3)°, $\beta$ = 97.08(3)°, $\gamma$ = 109.80(2)°, *V* = 665.4(4) $Å^3$, *Z* = 2, $D_c$ = 2.539 g/$cm^3$, $\mu$(Mo-K$\alpha$) = 146.51 $cm^{-1}$; *R* = 0.039, $R_w$ = 0.028 [$\omega = 1/\sigma^2(F_o)$ for 1305 independent reflections with $I > 3\sigma(I)$].

For **4a**: $C_{14}H_{26}Br_2O_2Se$, *M*, 465.13, monoclinic, space group $P2_1/c$, *a* = 15.042(4) Å, *b* = 7.480(4) Å, *c* = 15.793(4) Å, $\beta$ = 91.24(2)°, *V* = 1777(2) $Å^3$, *Z* = 4. $D_c$ = 1.739 g/$cm^3$, $\mu$(Mo-K$\alpha$) = 65.44 $cm^{-1}$. *R* = 0.042, $R_w$ = 0.032, [$\omega = 1/\sigma^2(F_o)$ for 1557 independent reflections with $I > 3\sigma(I)$].

All measurements were performed on a Rigaku AFC5S four-circle automated diffractometer with graphite monochromated Mo-K$\alpha$ radiation. The structures were solved by direct methods (MITHRIL).[14] The non-hydrogen atoms were refined anisotropically. The hydrogen atoms in **3** were calculated at ideal positions with a C–H distance of 0.95 Å and were not refined. The hydrogen atoms in **4a** were located by difference Fourier syntheses (refined only positional parameters). The absorption correction was applied by the $\psi$-scan method. All calculations were performed using the TEXSAN-TEXRAY crystallographic software package from the Molecular Structure Corporation. Tables of fractional atomic coordinates, bond lengths and angles, torsion angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.*

* For details of the deposition scheme, see 'Instructions for Authors,' *J. Chem. Soc., Perkin Trans. 1*, 1993, issue 1.

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