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Bis(2-bromoethyl)selenium dibromide as the selenium-introducing reagent: One-pot preparation of 2,5-bis(alkoxymethyl)tetrahydroselenophenes by the cyclization of 1,5-hexadiene

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Abstract

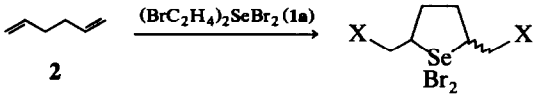
The reaction of bis(2-bromoethyl)selenium dibromide (**1a**) with 1,5-hexadiene (**2**) in methanol or ethanol affords 2,5-bis(alkoxymethyl)tetrahydroselenophene-1,1-dibromides ($R = CH_3$ (**3b**), $R = C_2H_5$ (**3c**)) *via* 2,5-bis(bromomethyl)tetrahydroselenophene-1,1-dibromide (**3a**). The reaction of **1a** with **2** in 1-propanol, 2-methyl-1-propanol or 1-butanol in the presence of sodium carbonate gave 2,5-bis(alkoxymethyl)tetrahydroselenophene ($R = C_3H_7$ (**4a**), $R = (CH_3)_2CHCH_2$ (**4b**) and $R = C_4H_9$ (**4c**)) *via* **3a**. The ratios of the *trans* and *cis* isomers of **3a–3c** are 3:2. In addition, the structure of trans-2,5-bis(methoxymethyl)tetrahydroselenophene-1,1-dibromide (*trans*-**3b**) was determined by X-ray crystallography.

1. Introduction

Organo and inorgano selenium compounds have been used as reagents for introducing selenium as well as various functional groups into unsaturated substrates [1,2]. Nicolaou *et al.* [3,4] have shown that N-phenylselenophthalimide is a useful and effective reagent for organoselenium-induced cyclization in organic synthesis. One of the methods for the synthesis of heterocyclic compounds containing a selenium atom is the cyclization of alkadiene and selenium tetrabromide [5]. In this reaction, the carbon–selenium–carbon (C–Se–C) bond is formed by the cyclization of alkadiene and selenium tetrabromide. However, there has been no report on cycloaddition by the formation of the C–Se–C bond with cleavage of the C–Se bond of the reagent introducing the organoselenium. Recently, we reported a convenient one-pot procedure for the synthesis of symmetric tricalcogena[3]metallocenophanes using **1a** to insert selenium [6]. In previous papers, we described a new procedure for the highly selective reduction of tertiary amide among tertiary, secondary and primary amides to the corresponding amine using dialkylselenium dibromide-$NaBH_4$ in THF [7–9]. In connection with these studies, we report here a convenient one-pot preparation of 2,5-bis(alkoxymethyl)tetrahydroselenophenes by a cyclo-addition of 1,5-hexadiene (**2**) to **1a**.

2. Results and discussion

The reaction of reagent **1a** with **2** in acetic acid at 20°C gave 2,5-bis(bromomethyl)tetrahydroselenophene-1,1-dibromide **3a** in 89% yield together with ethene (entry 1). Similar reactions were carried out in various solvents. These results are summarized in Table 1. Although **1a** reacted easily with **2** in methanol and



2 **3** (**3a**, X = Br; **3b**, X = OCH_3; **3c**, X = OC_2H_5) (1)

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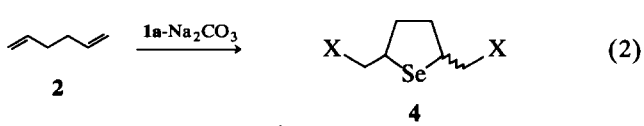
TABLE 1. The preparation of 2,5-disubstituted tetrahydroselenophenes by the reaction of **1** with **2** at 20°C

Entry	Reagent	Solvent	Reaction time (h)	Product	Melting point (°C)	Yield [a] (%)
1	**1a**	AcOH	4	*trans*-**3a**	154–155	53
				cis-**3a**	159–160	36
2	**1a**	MeOH	8	*trans*-**3b**	138–139	45 [b]
				cis-**3b**	140–141	31 [b]
3	**1a**	EtOH	8	*trans*-**3c**	114–115	29 [b]
				cis-**3c**	120–121	19 [b]
4	**1a**	PrOH	14	*trans*-**3a**		48
				cis-**3a**		32
5	**1a**	$(Me)_2CHCH_2OH$	14	*trans*-**3a**		39
				cis-**3a**		26
6	**1a**	BuOH	14	*trans*-**3a**		32
				cis-**3a**		22
7	**1a**	MeOH [c]	2	*trans*-**3a**		26
				cis-**3a**		17
8	**1a**	PrOH [d]	14	**4a** [e]	130/0.05 mmHg [f]	50
9	**1a**	$(Me)_2CHCH_2OH$ [d]	14	**4b** [e]	145/0.05 mmHg [f]	64
10	**1a**	BuOH [d]	14	**4c** [e]	160/0.05 mmHg [f]	70
11	**1b**	MeOH	4	**3b** [e]		8
				3d [e]	131–133	38

[a] Isolated yields. [b] Determined by HPLC. [c] This reaction was carried out at −50°C. [d] These reactions were performed in the presence of sodium carbonate. [e] As the mixture of *trans* and *cis* isomers. [f] Boiling point.

ethanol to give 2,5-bis(alkoxymethyl)tetrahydroselenophene-1,1-dibromide (**3b**) and **3c** in 74 and 48% yields, respectively, the reaction of **1a** with **2** in methanol at −50°C gave **3a** instead of **3b** (entry 7). Also, the reaction of **3a** with **2** in methanol at 20°C gave **3b** in 72% yield. These results suggest that the alkoxyselenation by cycloaddition proceeded *via* **3a** as an intermediate. Furthermore, the reactions of **1a** with **2** in 1-propanol, 2-methyl-1-propanol and 1-butanol at 20°C gave **3a** in 55–80% yields instead of the 2,5-bis(alkoxymethyl) derivatives **4a–4c** (entries 2–6).

In order to obtain **4a–4c**, the reactions of **1a** with **2** in the presence of sodium carbonate were carried out in 1-propanol, 2-methyl-1-propanol and 1-butanol (entries 8–10). These reactions gave 2,5-bis(alkoxymethyl)tetrahydroselenophenes **4a–4c** in 50, 64 and 70% yields, respectively. As Migalina [5] had already reported on the synthesis of **3a** by the reaction of selenium tetrabromide with **2** in diethyl ether, we attempted the reaction of selenium tetrabromide with **2** in methanol. However, the decomposition of selenium tetrabromide occurred at once and this reaction gave no detectable addition product containing selenium and methoxy group. Consequently, one-pot preparation of 2,5-bis(alkoxymethyl)tetrahydroselenophenes (**3b**, **3c** and **4a–4c**) could be performed using reagent **1a** and alcohols (methanol, ethanol, 1-propanol, 2-methyl-1-propanol and 1-butanol) as solvents.

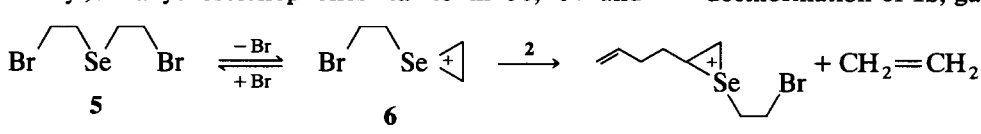


2 **4**

(**4a**, X = OC_3H_7; **4b**, X = $OCH_2CH(CH_3)_2$; **4c**, X = OC_4H_9)

(2)

It is noteworthy that when the reaction of bis(2-bromoethyl)selenium dichloride (**1b**) with **2** was carried out in methanol, cycloaddition gave 2,5-bis(chloromethyl)tetrahydroselenophene-1,1-dibromide (**3d**) and **3b** in 38 and 8% yields, respectively. The reaction of **1b** with **2** to give **3b** may proceed *via* **3d** as an intermediate. Lindgren has reported [10] that the reaction of bis(2-bromoethyl)selenide with a nucleophile such as selenocyanate anion gives ethene and selenenyl compound. As shown in Scheme 1, these findings suggest that bis(2-bromoethyl)selenide (**5**), produced by the dechlorination of **1b**, gave an episelenonium cation (**6**).



5 **6** **7**

Scheme 1.

The resulting **6** when added to the carbon–carbon double bond of **2** gave an episelenonium cation (**7**) as an intermediate together with ethene. Evolution of ethene was thus observed in all reactions.

That the reaction of **1b** with **2** gave **3d** instead of 2,5-bis(bromomethyl)tetrahydroselenophene-1,1-dichloride may be attributed to the bromide ion being more strongly nucleophilic than the chloride ion [11]. Accordingly, the selenium atom was attacked by the former rather than by the latter.

Migalina [5] revealed that the reaction of selenium tetrabromide with **2** in diethyl ether gave **3a**, which with respect to the two bromomethyl groups was a mixture of *trans*:*cis* in the ratio 1:2. In order to determine the ratio of *trans* and *cis* isomers of **3a** obtained by our method, fractional recrystallization of **3a** from chloroform was carried out. The melting point of the first crystals was 154–155°C, which value was in agreement with that already reported for *trans*-**3a**, and the other crystals showed a melting point at 159–160°C. Therefore, the later crystals were *cis*-**3a** [5]. Also, these isomers were given in 53 and 36% yields, respectively. These results showed that the reaction of **1a** with **2** in acetic acid gave a mixture of *trans* and *cis*-**3a** isomers, in the ratio 3:2.

In order to investigate the ratios of the *trans* and *cis* isomers of **3b** and **3c**, the mixtures of isomers were analyzed and identified by HPLC with comparison of the retention times of authentic samples prepared by methoxy or ethoxylation of the corresponding *trans* and *cis* isomers of **3a**. The ratios of *trans* and *cis* isomers were found to be 3:2 for both **3b** and **3c**, and were in agreement with that of **3a**. This result suggested that the alkoxylation proceeded with retention of the configuration *via* **3a** as an intermediate. Therefore, the ratios of *trans* and *cis* isomers of **4a–4c** might also be 3:2, because the reaction of **1a** with **2** in 1-propanol, 2-methyl-1-propanol or 1-butanol afforded *trans*-**3a** and *cis*-**3a** as the intermediate in the ratio of 3:2, respectively.

TABLE 2. Compound *trans*-**3b**: fractional atomic coordinates and thermal parameters (Å^2) with estimated standard deviations in parentheses

Atom	x	y	z	B_{eq}
Br(1)	1.0348(1)	0.2069(2)	0.2144(1)	4.47(6)
Se(1)	3/4	0.1788(2)	1/4	2.33(6)
O(1)	0.8263(7)	0.220(1)	0.5025(6)	4.2(4)
C(1)	0.765(2)	0.312(3)	0.585(1)	7.0(9)
C(2)	0.762(1)	0.013(2)	0.473(1)	3.5(5)
C(3)	0.809(1)	−0.050(1)	0.3651(8)	2.6(4)
C(4)	0.739(1)	−0.256(1)	0.3113(9)	4.2(5)
H(11)	0.80(1)	0.42(2)	0.60(1)	8.6
H(12)	0.68(1)	0.34(2)	0.57(1)	8.6
H(13)	0.79(1)	0.26(2)	0.658(9)	8.6
H(21)	0.646(9)	0.03(1)	0.473(7)	4.0
H(22)	0.790(8)	−0.10(1)	0.534(7)	4.0
H(31)	0.916(8)	−0.05(1)	0.366(7)	2.8
H(41)	0.612(8)	−0.25(1)	0.316(6)	4.3
H(42)	0.77(1)	−0.38(1)	0.344(8)	4.3

To investigate the structures of the cycloaddition products (**3a–3c** and **4a–4c**), mass spectra were measured. The parent peaks of **3a**, **3b** and **3c** appeared at 478, 382 and 410, respectively, at an ionization voltage of 20 eV, although these peaks were not observed at 70 eV. The parent peaks of **4a**, **4b** and **4c** also appeared at 280, 308 and 308, respectively, under the same conditions. Furthermore, the 400 MHz ^{1}H NMR spectra of *trans* and *cis* isomers of the cycloaddition products **3a**, **3b** and **3c** were measured in $CDCl_3$. The chemical shifts due to the two methine protons in *trans*-**3a** appeared at $\delta = 4.65–5.04$ as a complex multiplet. Similarly, the methine proton signals in *cis*-**3a** appeared at $\delta = 4.97–5.02$ as a multiplet. Although these chemical shifts and the pattern of splitting between *trans* and *cis* isomers of **3a** showed no significant difference, the absorption ranges of the multiplets were 0.39 ppm in *trans*-**3a** and 0.05 ppm in *cis*-**3a**.

Similar trends were also shown in the absorption ranges of the multiplets of *trans* and *cis* isomers in **3b** and **3c**. The X-ray analysis of *trans*-**3b** reported below describes how the structure of the five-membered ring in *trans*-**3b** forms a distorted plane, and the torsion angles between the methine protons and methylene protons of axial position in the ring are almost 180°. On the other hand, the structure of the five-membered ring in *cis*-**3b** might not involve a distorted plane in which case the angles between these protons would probably be less than 180°. On account of the angles between these protons in *trans*-**3b** being larger than those in *cis*-**3b**, the coupling constants of the methine protons and methylene protons in the axial position in *trans*-**3b** were large compared with *cis*-**3b**. Therefore, the absorption range of the multiplet of the methine protons in *trans*-**3b** would be expected to be larger than that of *cis*-**3b**. Presumably, a similar explanation would apply to the absorption ranges in *trans* and *cis* isomers of **3a**, **3c**, **4a**, **4b** and **4c**.

In order to investigate the structure in more detail, X-ray analysis of *trans*-**3b** was carried out. The final parameters are given in Table 2. The bond lengths, bond angles and torsion angles are also listed in Table 3. The perspective views of *trans*-**3b** with an atomic numbering scheme are illustrated in Fig. 1. The two methoxymethyl groups assume the same conformation and *trans* geometry. Therefore, the structure has a C_2

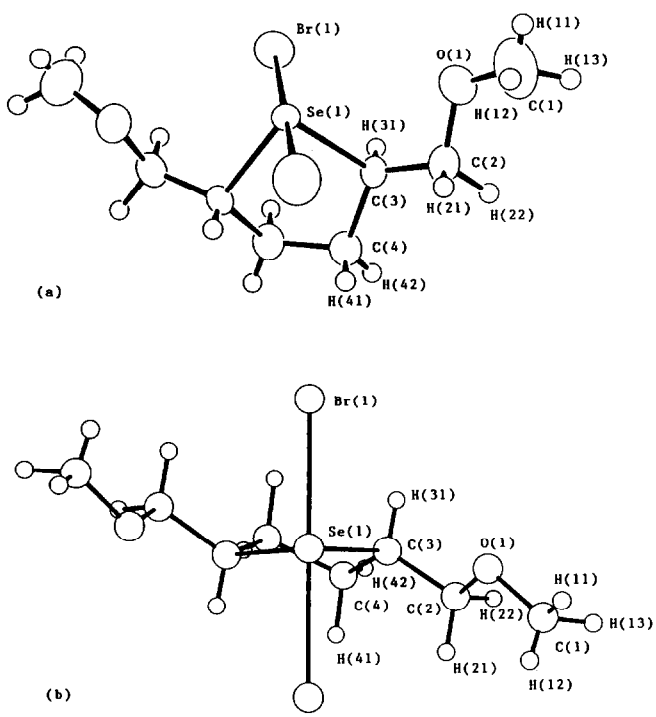


Fig. 1. The perspective views of compound *trans*-**3b** with the atomic numbering scheme; top view (a) and side view (b).

axis passing through the selenium atom from the centre of the dimethylene bridge (C(4)–C(4)) in the ring moiety. The torsion angle between Se(1)–C(3) and C(2)–O(1) is −53.3(9)°. As described above, the conformation of the five-membered ring involved a distorted plane, and the torsion angle (C(3)–C(4)–C(4)–C(3)) was −55(2)°. Therefore, as shown in top view (a) of Fig. 1, the torsion angle of H(31)–C(3)–C(4)–H(41) was almost 180°. The bond angle, Br–Se–Br is 172.16(9)°, *i.e.* almost 180°. This is in agreement with the reported values for the Br–Se–Br bond angle (175.0(6)°) in bis(2-bromoethyl)selenium dibromide (**1a**) [9] and 175.1(1)° in 1-thia-4-selenocyclohexane-4,4-dibromide [12]. Therefore, the selenium atom exists in a slightly distorted trigonal bipyramidal geometry with the two axially coordinated bromine atoms.

3. Experimental section

Melting points were recorded with a Yazawa apparatus and were uncorrected. ^{1}H NMR spectra were determined with a JEOL GX 400 spectrometer and a Hitachi R-1100 in $CDCl_3$ with tetramethylsilane as the internal standard. High-performance liquid chromatography (HPLC) was carried out using a JASCO HPLC system with a Sil, C18-5 column monitored by UV absorption measurements. Mass spectra were obtained with a Hitachi M 80 mass spectrometer. Elemental analyses were obtained with a Perkin Elmer 2400 instrument. Distillation was carried out using a Sibata glass tube oven apparatus, GTO-350RD.

3.1. Materials

Bis(2-bromoethyl)selenium dibromide **1a** [13], bis(2-bromoethyl)selenium dichloride **1b** [14] and selenium tetrabromide [12] were prepared according to the methods described in the literature. All solvents were purified by distillation in the usual manner.

3.2. The reaction of 1a with 2 in acetic acid

A suspension of **1a** (4.5 g, 10 mmol) and **2** (0.82 g, 10 mmol) in acetic acid (20 cm^3) was stirred at 20°C for 4 h. The resulting orange yellow solids were separated and then purified by gel permeation chromatography

TABLE 3. Compound *trans*-**3b**: bond lengths (Å), and bond and torsion angles (°)

1	2	3	4	1–2	1–2–3	1–2–3–4
Br(1)	Se(1)	Br(1)		2.555(1)	172.16(9)	
Br(1)	Se(1)	C(3)	C(2)		91.2(3)	123.8(7)
Br(1)	Se(1)	C(3)	C(4)		91.2(3)	−108.5(7)
Br(1)	Se(1)	C(3)	C(2)		94.4(3)	−50.7(7)
Br(1)	Se(1)	C(3)	C(4)		94.4(3)	77.0(7)
Se(1)	C(3)	C(2)	O(1)	2.004(9)	110.8(7)	−53.3(9)
Se(1)	C(3)	C(4)	C(4)		104.9(6)	40(1)
Se(1)	C(3)	C(2)	O(1)	2.004(9)		−53.3(9)
Se(1)	C(3)	C(4)	C(4)			40(1)
O(1)	C(2)	C(3)	C(4)	1.43(1)	108.4(9)	−173.7(7)
C(1)	O(1)	C(2)	C(3)	1.33(2)	113 (1)	166(1)
C(2)	C(3)	Se(1)	C(3)	1.48(1)		−141.9(9)
C(2)	C(3)	C(4)	C(4)		117.5(9)	163(1)
C(3)	Se(1)	C(3)	C(4)		89.6(6)	−14.1(6)
C(3)	C(4)	C(4)	C(3)	1.52(1)	108.5(8)	−55(2)
C(4)	C(4)	C(3)	Se(1)	1.53(2)		

(Sephadex LH-20) using THF as an eluent. The main fraction was collected and then the solution was concentrated under reduced pressure to give **3a** as a mixture of *trans* and *cis* isomers in 89% yield. Furthermore, the fractional recrystallization of the mixture from chloroform gave *trans*-**3a** and *cis*-**3a** in 53 and 36% yields, respectively. *trans*-**3a**: M.p. 154–155°C. ^{1}H NMR (400 MHz): δ = 2.52–2.62 (m, 2H), 2.90–2.94 (m, 2H), 3.99–4.03 (m, 2H), 4.22–4.28 (m, 2H) and 4.65–5.04 (m, 2H). Found: C, 15.10; H, 2.05. $C_6H_{10}Br_4Se$ calcd.: C, 15.00; H, 2.10%. Mass (20 eV): *m/z* 478 (M^+). *cis*-**3a**: M.p. 159–160°C. ^{1}H NMR (400 MHz): δ = 2.52–2.60 (m, 2H), 2.85–2.96 (m, 2H), 3.96–4.12 (m, 2H), 4.22–4.30 (m, 2H) and 4.97–5.02 (m, 2H). Found: C, 15.04; H, 1.96. Calcd. for $C_6H_{10}Br_4Se$; C, 15.00; H, 2.10%. Mass (20 eV): *m/z* 478 (M^+).

3.3. The preparation of cis-3b from cis-3a in methanol

After a suspension of *cis*-**3a** (0.956 g, 2 mmol) and sodium carbonate (0.212 g, 2 mmol) in methanol (5 cm^3) was stirred at 0°C for 2 h, the resulting solution was concentrated under reduced pressure. The residue was extracted with chloroform (10 cm^3), and then the chloroform solution was concentrated under reduced pressure. The residue was redissolved in tetrachloromethane (20 cm^3). Bromine (0.32 g, 4 mmol) was added to the solution at 0°C, and then the solution was stirred for 30 min. The solution was concentrated under reduced pressure. The resulting orange crystals were collected by filtration and washed with small amounts of hexane. The crystals were recrystallized from benzene to give *cis*-**3b** in 30% yield. M.p. 140–141°C. ^{1}H NMR (400 MHz): δ = 2.32–2.40 (m, 2H), 2.58–2.66 (m, 2H), 3.44 (s, 6H), 3.91–3.95 (m, 2H), 4.27–4.33 (m, 2H) and 4.72–4.80 (m, 2H). Found: C, 25.16; H, 4.06. Calcd. for $C_8H_{16}Br_2O_2Se$: C, 25.07; H, 4.22%. Mass (20 eV): *m/z* 382 (M^+).

3.4. Cis-3a, trans-3b and trans-3c

These were prepared using the same method as described above.

Cis-**3c**. Yield 22%. M.p. 120–121°C. ^{1}H NMR (400 MHz): δ = 1.23 (t, J = 7.0 Hz, 6H), 2.29–2.40 (m, 2H), 2.58–2.64 (m, 2H), 3.55–3.67 (m, 4H), 3.96–4.00 (m, 2H), 4.30–4.35 (m, 2H) and 4.73–4.80 (m, 2H). Found: C, 29.28; H, 4.79. Calcd. for $C_{10}H_{20}Br_2O_2Se$; C, 29.22; H. 4.91%. Mass (20 eV): 410 (M^+).

Trans-**3b**. Yield 86%. M.p. 138–139°C. ^{1}H NMR (400 MHz): δ = 2.30–2.38 (m, 2H), 2.59–2.63 (m, 2H), 3.45 (s, 6H), 3.90–3.95 (m, 2H), 4.27–4.34 (m, 2H) and 4.70–4.81 (m, 2H). Found: C, 25.29; H, 4.31. Calcd. for $C_8H_{16}Br_2O_2Se$: C, 25.07; H, 4.22%. Mass (20 eV): 382 (M^+).

Trans-**3c**. Yield 56%. M.p. 114–115°C. ^{1}H NMR (400 MHz): δ = 1.25 (t, J = 7.0 Hz, 6H), 2.25–2.40 (m, 2H), 2.55–3.10 (m, 2H), 3.32–3.75 (m, 4H), 3.96–4.05 (m, 2H), 4.27–4.35 (m, 2H) and 4.70–4.85 (m, 2H). Found: C, 29.12; H, 4.69. Calcd. for $C_{10}H_{20}Br_2O_2Se$: C, 29.22; H, 4.91%. Mass (20 eV): 410 (M^+).

3.5. The reaction of 1a with 2 in methanol

A suspension of **1a** (4.5 g, 10 mmol) and **2** (1.8 g, 10 mmol) in methanol (20 cm^3) was stirred at 20°C for 8 h. The resulting orange solids were collected by filtration and washed with small amounts of methanol. The solids were recrystallized from benzene to give **3b** as a mixture of *trans* and *cis* isomers in 73% yield, whose ratio was determined by comparison with authentic samples in HPLC analysis. HPLC was carried out using methanol : water = 3 : 1 as an eluent, and the flow rate was 0.5 cm^3 min^{-1}. The retention times of *trans*-**3b** and *cis*-**3b** were 3.89 and 6.63 min, respectively. The ratio of *trans*-**3b** and *cis*-**3b** was found to be 3 : 2.

3.6. The reaction of 1a with 2 in ethanol

A suspension of **1a** (4.5 g, 10 mmol) and **2** (1.8 g, 10 mmol) in ethanol (20 cm^3) was stirred at 20°C for 8 h. The resulting orange solids were collected by filtration and washed with small amounts of ethanol. The solids were recrystallized from benzene and hexane (2 : 1) to give **3c** as a mixture of *trans* and *cis* isomers in 48% yield. The ratio of *trans* and *cis* isomers was determined as *trans* : *cis* = 3 : 2 by the same method as described above. The retention times of *trans*-**3c** and *cis*-**3c** were 4.68 and 6.71 min, respectively.

3.7. The reaction of 1a with 2 in 1-propanol

A suspension of **1a** and **2** in 1-propanol was stirred at 20°C for 14 h. The resulting solids were collected by filtration and washed with small amounts of 1-propanol. The solids were purified by gel permeation chromatography using THF as an eluent. The main fraction was concentrated under reduced pressure to give a mixture of *trans*-**3a** and *cis*-**3a** in 80% yield. The fractional recrystallization of a mixture from chloroform gave *trans*-**3a** and *cis*-**3a** in 48 and 32% yields, respectively.

3.8. The reaction of 1a with 2 in 1-propanol in the presence of sodium carbonate

A suspension of **1a** (5.4 g, 12 mmol), **2** (1.0 g, 12 mmol) and sodium carbonate (0.63 g, 6 mmol) in 1-propanol (30 cm^3) was stirred at 20°C for 14 h. The resulting colourless solution was concentrated under reduced pressure. The residue was extracted with chloroform, and the solution concentrated again. The residue was chromatographed on alumina using chloro-

form as an eluent. The main fraction was concentrated, and the residue distilled under reduced pressure in a glass tube oven to give 2,5-bis(propoxymethyl)tetrahydroselenophene (**4a**) as a mixture of *trans* and *cis* isomers. Yield 50%. B.p. 130°C/0.05 mmHg. ^{1}H NMR (60 MHz): $\delta = 0.98$ (t, $J = 7.2$ Hz, 6H), 1.57 (six, $J = 7.2$ Hz, 4H), 1.92–2.50 (m, 4H), 2.60–3.60 (m, 2H), 3.50 (t, $J = 7.2$ Hz, 4H), 3.56–3.62 (m, 2H) and 3.65–3.92 (m, 2H). Found: C, 51.37; H, 8.91. Calcd. for $C_{12}H_{24}O_2Se$: C, 51.60; H, 8.68%. Mass (20 eV): 280 (M^+).

3.9. 2,5-bis(2-methyl-1-propoxymethyl)tetrahydroselenophene (4b) and 2,5-bis(butoxymethyl)tetrahydroselenophene (4c)

Compounds **4b** and **4c** were prepared by the same method as above.

4b. Yield 64%. B.p. 145°C/0.05 mmHg. ^{1}H NMR (60 MHz): $\delta = 0.98$ (d, $J = 7.6$ Hz, 12H), 1.60–2.28 (m, 2H), 2.56–3.05 (m, 4H), 3.12–3.70 (m, 8H) and 3.65–3.95 (m, 2H). Found: C, 54.59; H, 9.39. Calcd. for $C_{14}H_{28}O_2Se$: C, 54.70; H, 9.20%. Mass (20 eV): 308 (M^+).

4c. Yield 70%. B.p. 160°C/0.05 mmHg. ^{1}H NMR (60 MHz): $\delta = 0.72$–1.20 (m, 6H), 1.20–1.85 (m, 8H), 2.50–2.95 (m, 4H), 3.25–3.60 (m, 8H), 3.60–3.75 (m, 2H). Found: C, 54.50; H, 9.32. Calcd. for $C_{14}H_{28}O_2Se$: C, 54.70; H, 9.20%. Mass (20 eV): 308 (M^+).

3.10. The reaction of 1b with 2 in methanol

A suspension of **1b** (1.83 g, 5 mmol) and **2** (0.41 g, 5 mmol) in methanol was stirred at 20°C for 4 h. The precipitates were collected by filtration and washed with small amounts of methanol. The solids were recrystallized from benzene to give **3b** and 2,5-bis(chloromethyl)tetrahydroselenophene-1,1-dibromide (**3d**) in 8 and 38% yields, respectively. **3d**. Yield 38%. ^{1}H NMR (60 MHz): $\delta = 2.20$–2.56 (m, 2H), 2.60–3.10 (m, 2H), 3.80–4.39 (m, 2H), 4.45–4.65 (m, 2H) and 4.65–5.40 (m, 2H). Found: C, 18.62; H, 2.45. Calcd. for $C_6H_{10}Br_2Cl_2Se$: C, 18.39; H, 2.58%. Mass (20 eV): 391 (M^+). Furthermore, the reaction of **3d** (0.782 g, 2 mmol) with sodium carbonate (0.212 g, 2 mmol) in methanol (5 cm^3) gave *trans*-**3b** and *cis*-**3b** in 23 and 18% yields, respectively.

3.11. X-Ray crystallography of trans-3a

A yellow prismatic crystal of $C_8H_{16}O_2Br_2Se$ having approximate dimensions of $0.500 \times 0.320 \times 0.320$ mm was mounted in a glass capillary. All measurements were made on a Rigaku AFC5S diffractometer with graphite monochromated Mo Kα radiation and a 12 KW rotating anode generator. Crystal data: F.W. = 382.98, monoclinic, space group $P2/n$, $a = 8.592(2)$ Å, $b = 6.218(3)$ Å, $c = 12.146(3)$ Å, $\beta = 98.74(2)°$, $V = 641.4(4)$ Å^3, $Z = 2$, $D_c = 1.983$ g cm^{-3}, μ(Mo Kα) = 90.42 cm^{-1}. The structure was solved by direct methods. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located by difference Fourier synthesis. The absorption correction was performed by ψ-scan method. All calculations were performed using the TEXSAN [15] crystallographic software package from the Molecular Structure Corporation.

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